Vibrational Analyses of Carbonyl Isocyanates and Isothiocyanates

by

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We accept this thesis as conforming to the required standard

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Abstract

A series of seven carbonyl isocyanates and three carbonyl isothiocyanates of the general formula R-CO-NCE (where E represents either oxygen in the carbonyl isocyanates or sulfur in the carbonyl isothiocyanates) were synthesized based on reported literature methods. The substituents of the carbonyl isocyanates were CH_3, $CH_2C\ell$, $CHC\ell_2$, $CC\ell_3$, OCH_3, SCH_3, and NCO. The three carbonyl isothiocyanates studied had fluoro, chloro, and acetyl groups as the substituents (F, $C\ell$, and CH_3 respectively).

The vapour phase, and in some cases the liquid phase, infrared spectra and liquid phase Raman spectra were recorded for these families of carbonyl iso(thio)cyanates at room temperature. The molecules' fundamental group frequencies were assigned via a vibrational analysis of each spectrum. Although the characteristic group frequencies diagnostic of the iso(thio)cyanato group appeared relatively insensitive to the nature of the substituent, a slight correlation between increasing electronegativity of the substituent and increasing frequency of the bands was noticeable.

In some of the spectra, certain features were observed to possess what appeared to be peak pairs. This offered evidence that more than one conformer was present in the spectra at room temperature. Assignments of these observed pairs were based on the assumption that the two planar conformations of the molecules, a result of rotation of the iso(thio)cyanato group about the C-N bond, are the more

stable isomers. Distinction between the *cisoid* and *transoid* isomers was made on the basis of force-field calculations, MNDO/AM1 calculations, band contour analyses, and variable-temperature spectral data. Structural preferences of the isomers are dependent upon the nature of the substituent. The variable-temperature spectral information was utilized to qualitatively analyze the stability of the different conformers in relation to their observed peak positions and relative intensities.

Assignment of the bands belonging to the carbonyl isothiocyanate molecules is relatively easy when they are compared to the carbonyl isocyanates. The bands diagnostic of the substituent in the isocyanates and isothiocyanates are more or less unaffected by the sulfur/oxygen exchange in the NCE group. However, the bands associated with the iso(thio)cyanate group are mass sensitive and the isothiocyanate stretching fundamentals appear at lower frequencies than their carbonyl isocyanate counterparts (~250-300 cm^{-1} lower). The bending motions are also mass-dependent but do not differ in frequency by as great an amount in carbonyl isothiocyanates compared to carbonyl isocyanates. Distinguishing between the possible conformations in carbonyl isothiocyanates is more difficult than in their isocyanate counterparts. The separation between observed features in the C=O region of the spectra in NCS molecules is only 15-20 cm^{-1} as compared to 25-35 cm^{-1} in carbonyl isocyanates indicating a closeness in energy between the isomers. With the data obtained from AM1/MNDO calculations, the relative stabilities of the isothiocyanate conformers were predicted. The *cisoid* isomer is predicted to be more stable in the fluoro- and acetyl compounds whereas the *transoid* conformer was predicted to be more stable for the chloro- compound. These observations parallel those of the corresponding carbonyl isocyanates.

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I would like to dedicate this thesis to my family, especially to my mother and father and late grandmother, Beatrice Landry. Also to a dear friend, the late Myra Filion. Her life was something to be admired..... I will never forget you.

Chapter 1
Introduction

1.1 Some General Statements about Carbonyl Iso(thio)cyanates

Carbonyl isocyanates were first discovered in the 1860's and carbonyl isothiocyanates some twenty years later (1). It has been almost one hundred years after the discovery of the above family of compounds that modern, simplified, synthetic methods were employed to readily prepare acyl iso(thio)cyanates. The general structural framework of a carbonyl iso(thio)cyanate is shown in Figure 1.1. The molecular skeleton consists of an NCE group adjacent to the carbonyl group (E= O or S) with another substituent (R) also positioned adjacent to the carbonyl group.

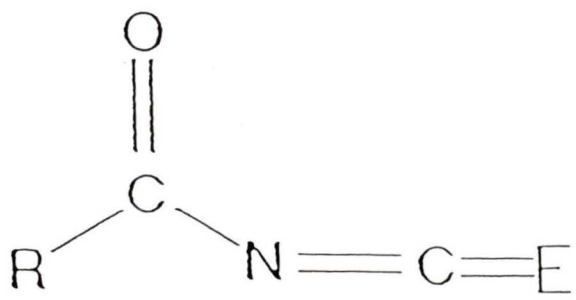


Fig. 1.1. The general structural formula for carbonyl iso(thio)cyanates.

A molecule with this structural skeleton is quite valuable in organic chemistry. By the end of the 1950's, a vast interest in acyl isocyanates and isothiocyanates came

about because of their ability to react with other organic reagents. Such reactivity would enable carbonyl iso(thio)cyanates to become important starting materials and reagents in organic syntheses. The first isothiocyanates, although synthesized in the laboratory, also appear freely in nature in some higher order plant forms. Some low-boiling point isothiocyanates were isolated by various organic techniques to yield what are known as "mustard oils" since the isothiocyanates were isolated from mustard seeds (2). It was because of this interest, and the role that these compounds played in organic chemistry, that a series of review articles concerning the syntheses, reactivity, and applications of acyl iso(thio)cyanates was published at the end of the 1960's and early 1970's (1-3). A German chemist, by the name of Hagemann, patented several reactions involving chlorocarbonyl isocyanate (CCI) and published a separate review dealing solely with CCI pertaining to the compound's versatility (4).

Carbonyl isocyanates and isothiocyanates have found many applications in chemistry and other scientific areas. It is most probably because of these applications that there is a variety of cyanates and isocyanates commercially available today. Many carbonyl iso(thio)cyanates are used in a wide range of synthetic chemistry as starting materials or reagents (1-4). Chlorocarbonyl isocyanate, for example, is a starting reagent in the preparation of many other carbonyl isocyanates studied in this thesis (see reaction schemes of chapter 2). Trichloroacetyl isocyanate (TCAI) is a standard derivatization agent used in nuclear magnetic resonance spectroscopy (nmr) for the identification of alcohols and thiols (5). Both acyl isocyanates and isothiocyanates have found usefulness in the fields of medicine and biology. There are several references in current and past literature review articles on patented

acyl iso(thio)cyanates (1,3) that pertain to these fields. These are just a few of many examples of the applicability of carbonyl isocyanates and isothiocyanates.

The methods used to prepare carbonyl iso(thio)cyanates have only been recently developed (last 25 years) despite having been discovered over one hundred years ago. There are numerous procedures reported in the literature regarding various synthetic methods pertaining to carbonyl iso(thio)-cyanate (1-4). Many methods have been modified from their original schemes to simplify procedures and, more importantly, to maximize product yields. Some of the simplest preparative methods of carbonyl isocyanates and isothiocyanates involve the reaction of an acid halide with a (thio)cyanate salt in an appropriate solvent (1). It was with this general scheme that acetyl isocyanate (AI) and acetyl isothiocyanate (AIT) were prepared. Details of synthetic methods used for the compounds studied in this project are outlined in chapter two. Carbonyl isocyanates and isothiocyanates are synthesized from reagents that contain the NCE group in the starting materials\reagents or are formed during the reaction. The above examples (AI and AIT) are examples where the iso(thio)cyanate group is present in the reactants. The synthesis of dichloroacetyl isocyanate (DCAI) from oxalyl chloride and dichloroacetamide is an example of the latter synthetic scheme.

Carbonyl isothiocyanate syntheses are very similar to carbonyl isocyanate synthetic methods and have progressed in a similar fashion. Preparation of the isothiocyanates is somewhat more complicated than the synthetic procedures used to prepare their isocyanate counterparts. These complications stem from the fact that carbonyl isothiocyanates are, thermally, less stable than their isocyanate counterparts. Choice of a proper solvent,

preferably one with a low boiling point, and thiocyanate salt derivative, is essential. This obviously complicates the synthetic procedure in that low temperatures are required to prevent decomposition of the compound and to inhibit the evaporation of the solvent. Jochims and Bunnenburg (6) used liquid sulfur dioxide (bp -10°C) as the solvent in their synthesis of chlorocarbonyl isothiocyanate (CCIT). Sulfur dioxide was chosen because of its ability to dissolve thiocyanate salts whereas the ammonium chloride by-product is insoluble in the liquid. This synthetic procedure, although difficult, was highly successful because of the high product yield (>70 %) and the ease with which the solvent was discarded, a tradeoff which is quite acceptable. As the importance of carbonyl iso(thio)cyanate chemistry grew and diversified, so did means for their preparation, some examples, of which, are covered in numerous literature articles (1-4).

It was not the scope of this project to look into the reactions involving carbonyl isocyanates and isothiocyanates but brief mention should be made of their importance in organic chemistry because of their reactivity. The presence of two carbonyl groups (2 C=E groups) in these compounds increases the reactivity of the R-CO-NCE since there are two positions that are susceptible to nucleophilic attack which may result in subsequent addition or substitution. The nucleophile utilized and the substituent (R) are the prominent factors in determining which C=E site is attacked. Carbonyl iso(thio)cyanate reactivity is well documented in various literature reviews (1-4).

1.2 Infrared Spectroscopy

1.2a. Theory of Infrared Spectroscopy

The infrared region of the electromagnetic spectrum ranges from 12,800 cm^{-1} to 10 cm^{-1} (7). The most familiar area, in relation of spectral analysis of the ir region, is known as the middle region which is located between 4000 and 200 cm^{-1}.

Infrared spectroscopy is one of the best spectroscopic tools for qualitative and/or quantitative analyses of chemical compounds. One of the most important functions ir spectroscopy serves is that of identification of compounds whose spectra are often quite complex. Each compound has its own individual ir spectrum serving as a fingerprint which distinguishes one particular compound from another.

In order for a molecule to absorb radiation, it must undergo a magnetic or electrical change which interacts with the magnetic or electric field of the incident radiation. To absorb infrared radiation, a molecule must undergo a net change in dipole moment as it vibrates. When a molecule vibrates, fluctuation in dipole moment in a bond of a molecule may occur which interacts with the infrared radiation to cause a change in amplitude in vibration and absorption of radiation results. In other words, ir radiation causes excitation of molecular vibrations in a molecule.

A vibration can be looked upon as an oscillation of an elastic body from its equilibrium position. Vibrations result from the relative motion between bonded atoms in a molecule that are not quite fixed in space but instead fluctuate continuously as a result of interactions between the atoms and bonds. Vibrational motions can be classified

as being either the stretching or bending of the bonds in a molecule. A stretching vibration can be defined as a change in interatomic distance along the axis of the bonded atoms (8) whereas a bending vibration involves a change in angle between two bonds. The number of vibrations that a molecule has depends upon the number of atoms in the molecule. In the case of the non-linear carbonyl iso(thio)cyanate family, there are *3N-6* vibrations characteristic to the molecule. These *3N-6* vibrations are referred to as fundamental or normal modes of vibration. The carbonyl iso(thio)cyanate skeletal framework (CO-NCE) accounts for nine fundamental vibrations: four stretches and five bends. There are additional vibrations associated with the molecule but the number is dependent on the number of atoms in the substituent group.

1.2b. The Mechanical Model of a Simple Vibration

A vibration involves displacement of a bond(s) from its(their) equilibrium position as a result of a change in bond distance or bond angle in a molecule. There is a force required to return the atoms to its equilibrium position and it can be represented by Hooke's law (9):

$$\frac{dV(x)}{dx} = -k\Delta x \qquad (1)$$

where V is the potential energy of the bond, k is the restoring force required to return the bond to its equilibrium position and Δx is the displacement of the bond from its equilibrium position. There is an increase in energy proportional to the force required to return the bond to its equilibrium position as the bond vibrates. Integration of equation (1), in relation to the displacement

of the bond, yields the potential energy of this oscillation:

$$\int dE = k\int x dx \qquad (2)$$

$$E = \tfrac{1}{2}kx^2 \qquad (3)$$

A bond has a characteristic vibrational frequency which depends on the mass of the atoms involved and the restoring force to counteract the bond's displacement but independent of the energy of the system. The energy, hence frequency of the oscillation is directly proportional to the square root of the force constant and inversely proportional to square root of the mass of the system. The vibrational frequency is described by equation (4):

$$\nu_m = (2\pi c)^{-1}(k/m)^{1/2} \qquad (4)$$

Since vibrational energies are quantized, the allowed vibrational energies (E_υ) are calculated from the Schrodinger equation (10). The vibrational wavefunctions (ψ_υ) are given by the product of what is known as the Hermite polynomials and a Gaussian function

$$\psi_\upsilon = N_v H_v(\epsilon)\exp(-\epsilon^2/2) \qquad (5).$$

The normalization factor (N_v) is given by:

$$N_v = [(\alpha/\pi)^{1/2}(2^v v!)^{-1}]^{1/2}$$

where $\epsilon = \alpha^{1/2}x$ and $\alpha = \frac{2\pi\nu_i}{h}$

and $H_v(\epsilon)$ represents the Hermite polynomials. For a simple harmonic oscillator the solution to the vibrational energy problem is given by:

$$\epsilon_\upsilon = (\upsilon+\tfrac{1}{2})h\nu_m \qquad (6)$$

where υ is the vibrational quantum number and ν_m is the frequency of oscillation. Energy added to the system, if it matches the frequency of a vibration, increases the amplitude of the vibration. This simple model is only an approximation but is expected to be analogous to molecular vibrations since the lower energy portion of the potential well is expected to be very similar to that of the diatomic example. When $\upsilon=0$ it can be seen that the energy is non-zero so there is still some potential energy shared between the atoms of the bond or, in other words, the atoms are not completely at rest.

1.2c. Vibrational Selection Rules

In order for a vibrational transition to take place, whether it be via absorption or emission, the vibration must give rise to a change in dipole moment such that

$$(\partial\mu/\partial x) \neq 0. \qquad (7)$$

The transition moment ($R_{v'v''}$) relates the interacting states of a molecule to the incident radiation. The transition moment is a vector quantity which represents the probability of a transition taking place:

$$R_{v'v''} = \int \psi_{v'} \mu \psi_{v''} dx \qquad (8)$$

where dx is the change in internuclear distance from its equilibrium position and μ is the dipole moment induced by the vibration. The vibration in a heteronuclear diatomic molecule has $\mu\neq0$ and changes as the internuclear distance changes. The variation with distance can be expressed as a Taylor series (11) which transforms the transition moment to:

$$R_{v',v''} = \mu\int\psi_{v'}\psi_{v''}dx + (\partial\mu/\partial x)\int\psi_{v'}x\psi_{v''}dx + \ldots\ldots \quad (9)$$

The wavefunctions $\psi_{v'}$ and $\psi_{v''}$ are eigenfunctions of the same Hamiltonian making them orthogonal such that the first term in equation (9) is equal to zero so the transition moment becomes:

$$R_{v',v''} = (\partial\mu/\partial x)\int\psi_{v'}x\psi_{v''}dx + \ldots\ldots \quad (10)$$

The first term of this expression is non-zero if $\Delta\upsilon = \pm 1$ (9).

In any bond, there is a distance at which, if stretched far enough, the bond cannot be restored to its equilibrium position. At this point the bond breaks. This affects the potential energy curve in such a manner that the curve flattens out as a particular x value is reached. This value occurs at a distance greater than the equilibrium position of the bond (x_e). This distance correlates to a particular energy value which is known as the dissociation energy of the bond. The force constant of the bond gets weaker (i.e. $k\rightarrow 0$) when $x > x_e$, thus flattening the curve of the potential giving it an asymmetric profile. The vibrations of the nuclei are not perfectly elastic so the stretching of the oscillator is not perfectly elastic. This phenomenon is known as anharmonicity. With the vibrations not being perfectly elastic, the vibrational energy levels are not equally spaced. These levels gradually crowd together as υ increases. The change in υ ($\Delta\upsilon$) may, in fact, be greater than one. Anharmonicity modifies the vibrational selection rules for both infrared and Raman spectroscopy to include transitions from $\upsilon=0$ to $\upsilon=1,2,3\ldots$. ($\Delta\upsilon = \pm 1,2,3\ldots$).

1.2d. Overtone and Combination bands

Features that arise in the infrared and Raman spectra are not only a result of fundamental transitions. Transitions that take place involving upper vibrational states where $\Delta\upsilon = \pm 2,3..$ result in bands that are called overtone bands. Overtones usually appear at approximately twice or three times the vibrational frequency of the $\Delta\upsilon = 1$ transition but are much less intense.

There are particular bands that appear in the vibrational spectra of molecules that are a result of the combination of two or more fundamental modes. These bands are called combination bands and they arise from transitions to vibrationally excited states of more than one normal vibration which results in the addition of frequencies . Combination bands are useful even though they add to the complexity of the spectrum. These bands may help evaluate fundamentals that appear at lower frequencies which are not always seen in the vibrational spectrum. Figure 1.2 presents a schematic of the three types of vibrational energy levels.

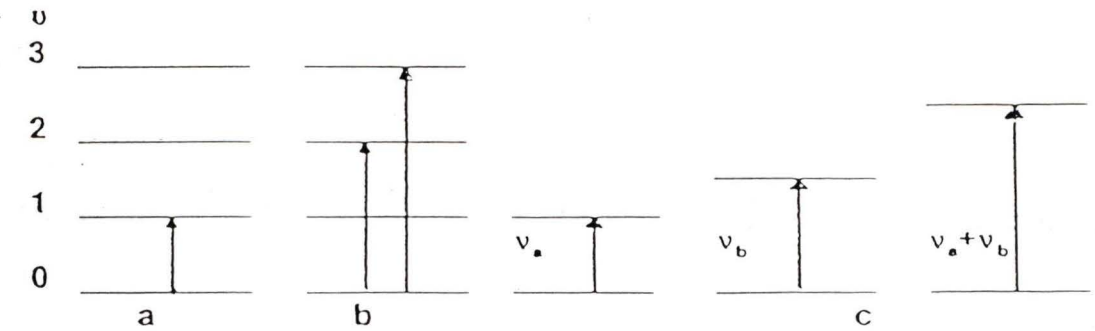


Fig 1.2 Schematic showing transitions that occur in vibrational spectroscopy: (a) normal transition, (b) vibrational overtones and (c) combination bands.

1.2e. Vibrational Coupling

Although designation of a particular observed feature as a certain fundamental is the common practice among spectroscopists, it should be mentioned that the molecular motions of the atoms in a polyatomic molecule are often complex and involve the motions of all the atoms in the molecule contributing to a particular feature. The fundamental can be looked at as the sum of all the displacements of the atoms in a molecule pertaining to that fundamental. The characterization of a fundamental stems from the dominant motion of one bond as the molecule is excited. The fundamental of the carbonyl bond is an extreme case. During the excitation of the carbonyl bond, all the atoms in the molecule are displaced but it is the carbon-oxygen bond that goes through the largest displacement so the observed feature is characterized a carbonyl stretch.

Vibrational transitions, whether they appear as fundamental, combination, or overtone bands, can complicate a spectrum of a larger polyatomic molecule. The energy of one vibration may be influenced by that of another. This phenomenon is known as vibrational coupling. Coupling of vibrations may cause a particular vibrational band to appear at one frequency in the spectrum of one molecule whereas the same band may appear at a quite different frequency in another molecule. It is hard to state that a particular bond will appear at a particular frequency in every molecule where that bond is present. It is better said that the vibrational frequency of a particular bond will appear in a certain frequency range. The C-N stretching fundamental is a good illustration of how a vibration of a bond can appear over a range of frequencies. Coupling between the motions of the C-N stretch and the N=C=E symmetric stretch result in the C-N stretch appearing in the range 650- 1050 cm^{-1}.

This tends to complicate the assignment of the C-N stretch especially if it is observed in the same region as another fundamental.

The principle behind the idea of vibrational coupling is the same as that involved in the phenomenon known as Fermi resonance. Fermi resonance, however, involves the coupling of a fundamental with a combination or overtone band. The possibility exists that an energy level resulting from a vibrational overtone or combination sum or difference may lie very close in energy to an energy level of a fundamental mode. An accidental degeneracy may develop between the two levels causing them to exchange energy and, in a sense, resonate. The combination or overtone band may gain intensity from this energy exchange at the fundamental's expense. The resonance between these two levels would cause the two features to separate from each other causing their appearance at lower and higher frequencies than their expected frequencies complicating the assignment of the two features.

1.2f. Band Contours

As molecular vibrations become excited, the corresponding molecular rotations also become excited. These rotational excitations lead to a rotational fine structure in each band. The shapes of each of these bands are known as band contours. Individual rotational lines of a given band may be observed if the resolution of the instrument is sufficient. Usually, only a band envelope is observed in most spectra. The shape of the band is determined by the axes of inertia in the system. The orientation of the axes depends upon the type of molecule under study. Planar molecules, such as the carbonyl iso(thio)cyanates in this study, are classified as

asymmetric rotors. This particular classification molecule has its moments of inertia (I_n) unequal to each other. The principal moment of inertia about any axis in a system through the center of mass is given by:

$$I = \sum m_i r_i^2 \qquad (11).$$

There is an axis about which I has its maximum value for the molecule and this is known as the c-axis (11). In carbonyl ios(thio)cyanates, the c-axis protrudes out of the plane of the molecule whereas the axis containing the molecule's smallest moment of inertia is called the a-axis and is perpendicular to the c-axis. Perpendicular to these two axes is a third axis called the b-axis and the moment of inertia along this axis lies between the values of the c and a axes. Figure 1.3. shows how these axes are situated about a carbonyl isocyanate.

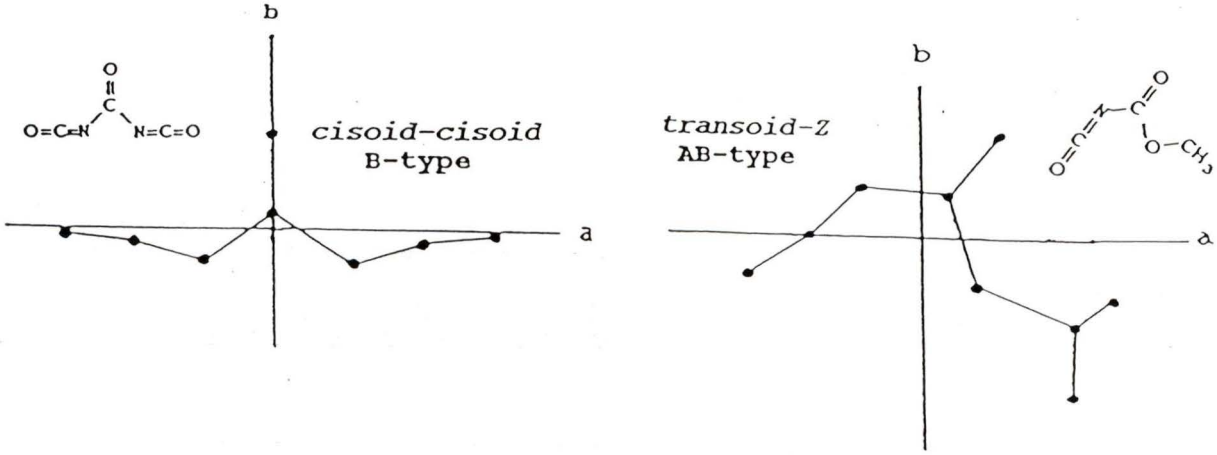


Fig. 1.3. The orientation of the principal axes about a carbonyl isocyanate. The c-axis is out of the plane of the paper.

It can be seen that a vibration out of the plane of the molecule will cause a change in dipole moment along the c-axis. Such a vibrational transition along this axis will result in an absorption band that is called a C-type band. In-plane vibrations that cause changes in dipole moments along the a and b-axes will give rise to A- and B-type band profiles respectively. It is also possible to have an in-plane vibration that has components of change in dipole moment along the a and b-axes. These absorptions result in vibrations that are AB hybrids and the contour is known as an AB-type band. The profiles of these bands are shown in Figure 1.4.(12).

Band profiles are useful tools in spectroscopic analyses. In the carbonyl iso(thio)cyanates with C_s geometry studied here, all of the out-of-plane vibrations will possess a C-type band contour which is easily distinguishable from the other band types. Band profiles are also useful in differentiating the different isomers present. If the axes of one isomer are oriented in a manner different from its geometric counterpart, some bands representing the same vibration will be expected to exhibit different band profiles. This enables easier assignment of a particular band to its proper isomer.

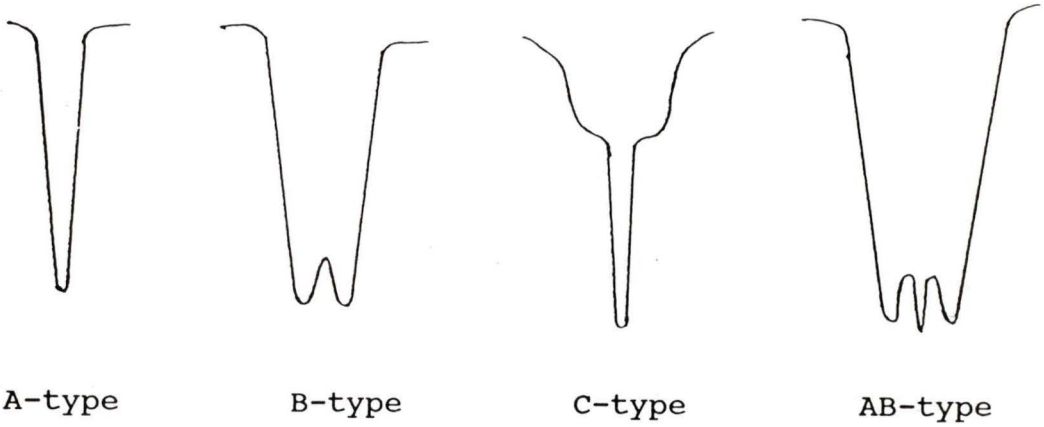


Fig. 1.4. Infrared band profiles.

1.3 Theory behind Raman Spectroscopy

In the previous section, it was explained that molecular vibrations that involved a change in dipole moment may be investigated by means of infrared spectroscopy. Those vibrations that do not exhibit this change in dipole moment during a vibration are infrared inactive. It is possible, however, to study these vibrations as well as other molecular vibrations by way of a light scattering process known as Raman scattering. Raman scattering is based on the phenomenon that when radiation passes through a transparent medium, small amounts of radiation are scattered in all directions (8). When a monochromatic source is employed, the scattered energy will consist of radiation with the same frequency as the incident radiation (Rayleigh scattering) as well as scattered light with frequencies higher and lower than that of the incident radiation (Raman scattering).

A Raman vibrational transition can be considered as a two-photon process. When a sample absorbs an incident photon at a frequency ν_1 equal to that of the excitation source the molecule gets excited from the ground state to a virtual state (V). A second photon, with a frequency ν_2, is emitted upon transition from the virtual state back to the ground electronic state . If ν_2 is equal to ν_1, then the emitted photon will wind up in the same vibrational state from which it originated. If the molecule and photon exchange energy during the absorption process, the energy of the emitted photon can be either greater or less than the energy of the incident photon. If the molecule gains energy, the photon will be "scattered" with an energy $h\nu+\Delta E$ ($\nu_2>\nu_1$) whereas if the molecule undergoes an energy loss, the scattered frequency will be $h\nu-\Delta E$ ($\nu_2<\nu_1$). The net result of this process is that the scattered radiation

(Raman shift) is shifted in frequency from the incident radiation by an amount ΔE, which corresponds to energies in the mid-infrared region. Figure 1.5 illustrates these scattering processes. In this case ΔE corresponds to the energy difference between the ground vibrational state and the first excited vibrational level of the ground electronic state. This is why Raman spectroscopy is considered as a complementary process to infrared spectroscopy.

The Raman shifts toward higher frequency are called anti-Stokes shifts whereas Stokes shifts are Raman shifts toward lower frequencies. Stokes shifts are more intense than anti-Stokes shifts because at room temperature the majority of the molecular population is in the ground vibrational state.

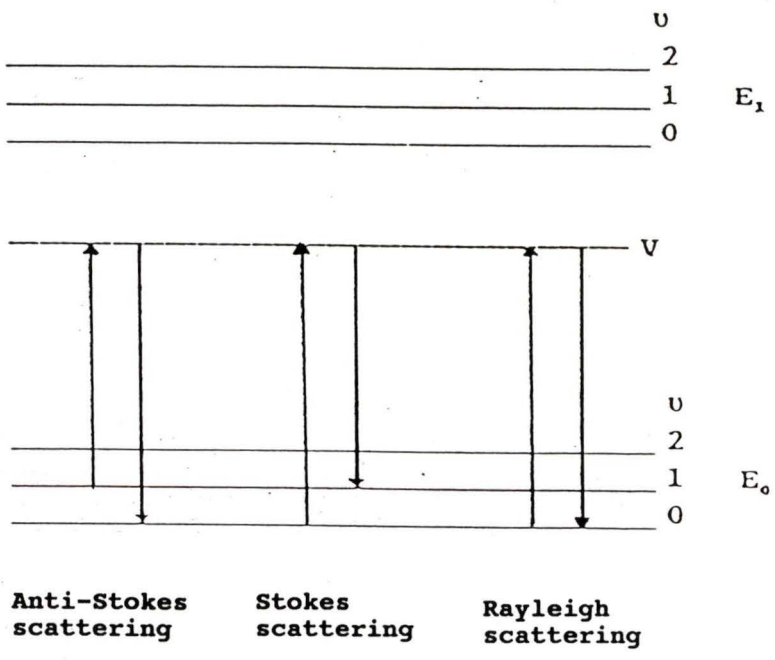


Figure 1.5. Raman scattering processes.

1.3b. Mechanical Model behind Raman Scattering

To be ir active, molecules must undergo a change in dipole moment during a vibration. Raman scattering involves a slightly different mechanism. The irradiated molecule's electron cloud must undergo a distortion. This distortion causes a molecule to become temporarily polarized (i.e. develop an induced dipole). The degree of scattering depends on how easily the electron cloud is distorted. A Raman shift, therefore, depends on a change of polarizability rather than a change in dipole moment. This is why a vibration-rotation band is observed in the Raman spectrum and not in the ir spectrum of a homonuclear diatomic. The molecule's net dipole moment does not change during vibration but the polarizability does as the bond is stretched and compressed therefore making the stretch Raman active.

The change in polarizability or induced dipole moment must be non-zero such that:

$$(\partial\alpha/\partial x) \neq 0 \qquad (12).$$

for a vibration to be Raman active. The size of the induced dipole (μ) depends on the polarizability and the change in energy of the incident radiation (11).

$$\mu = \alpha E \qquad (13).$$

During molecular vibrations, the polarizability fluctuates periodically at a rate given by the partial derivative of the polarizability function as a function of distance ($\partial\alpha/\partial x$). When a sample is irradiated with a beam of frequency ν, the electric field of the molecule varies as:

$$E = E_o \cos(2\pi\nu t) \qquad (14)$$

where E_o is the maximum amplitude of the wave. Substituting into equation (13) gives

$$\mu = \alpha[E_o\cos(2\pi\nu t)] \qquad (15).$$

The polarizability of a molecule at any point is:

$$\alpha = \alpha_o + (\partial\alpha/\partial x)E_o\cos(2\pi\nu_m t) \qquad (16).$$

where ν_m is the frequency of the internal motion. Mathematical manipulation yields

$$\mu = \alpha_o[E_o\sin(2\pi\nu t)] + 1/2\ (\partial\alpha/\partial x)E_o\cos(2\pi\nu t)(\nu+\nu_m) + 1/2\ (\partial\alpha/\partial x)E_o\cos(2\pi\nu t)(\nu-\nu_m) \qquad (17)$$

as the expression for the induced moment. The first term of equation (15) represents the Rayleigh scattering while the second and third terms represent the anti-Stokes and Stokes scattering processes.

The change in polarizability can be expressed as a Taylor series in the same manner as the dipole moment. The expression for the transition moment becomes

$$R_{v'v''} = (\partial\alpha/\partial x)\int\psi_{v'}x\psi_{v''}dx + \ldots\ldots \qquad (18)$$

and is non-zero only if $\Delta\upsilon = \pm 1$ (9). Anharmonicity (section 1.2d) modifies this rule to include transitions $\Delta\upsilon = \pm 1,2,3\ldots$ Vibrational overtones and combination bands can also be present in Raman spectra and are explained in section 1.2d.

1.3c. Depolarization Ratio

Most assignments of infrared and Raman bands are based

on assignments of other related molecules or by looking at various tables that list vibrational group frequencies. These tools as well as other information present in the spectrum such as intensity of the bands and peak position are important in determining the structure of a molecule. In Raman spectroscopy, there is an additional technique that can be utilized in band assignments. The technique is based on the plane of polarization of the incident radiation and the plane of the vibration responsible for the scattering. This method is used to determine the depolarization ratio of the band.

The depolarization ratio is defined as

$$\rho = I_{\perp}/I_{\parallel} \qquad (19)$$

where $I_{\perp}$ and $I_{\parallel}$ are the measured intensities of the scattered radiation perpendicular and parallel, respectively, to the direction of polarized, incident radiation. The degree of polarization (ρ) is the measure of polarization in terms of light transmitted parallel and perpendicular to the plane of the polarized light.

Depolarization experiments were carried out by placing a quarter-wave plate between the excitation source and the sample which serves to rotate the plane of polarized light. When molecules are excited by plane-polarized radiation, the scattered radiation is polarized to various degrees depending on the type of vibration responsible for scattering. Orientation of the plate with respect to the xz and xy planes (Figure 1.6) will show the degree to which the incident light is polarized. Figure 1.6 shows that the incident radiation is polarized in the yz plane. Part of the scattered radiation is polarized parallel to the incident beam (xz plane). Light polarized in this direction

is called parallel polarized light ($I_{\parallel}$). The remainder of the scattered radiation is in the xy plane which is perpendicular to the radiation and is therefore called perpendicularly polarized light ($I_{\perp}$). When $I_{\perp}$ is zero, the light is completely polarized and therefore ρ is equal to zero. For unpolarized light, $I_{\perp}$ is equal to $I_{\parallel}$ so $\rho = 1$. Polarization experiments will result in values of ρ between zero and one (i.e. $1>\rho>0$).

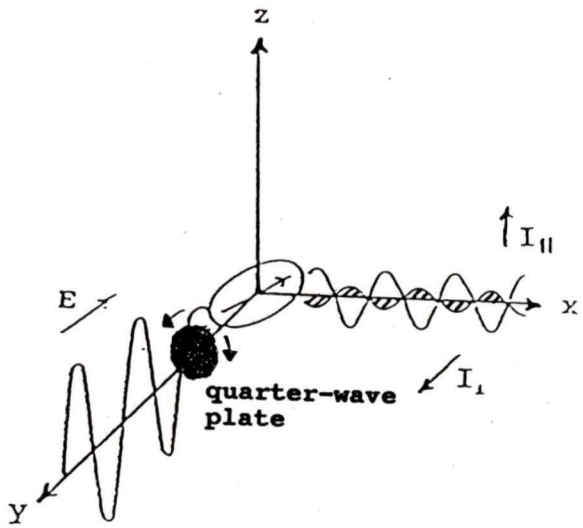


Fig. 1.6. Raman depolarization experiment.

Raman active vibrations will be plane-polarized to a different extent depending on the geometry of the molecule. Values of ρ that are less than 0.75 (8) describe bands that are polarized and therefore symmetric in nature whereas values of $\rho > 0.75$ represent vibrations that are depolarized and the vibration is believed to be non-symmetric. These measurements are not always conclusive since some bands may appear to be depolarized where, in fact, they are only weakly plane-polarized. By looking at the intensities of (de)polarized bands, either qualitatively or quantitatively, assignments of various vibrational modes can be facilitated.

1.4 Force Field Calculations

Vibrational assignments are made with the use of infrared and Raman spectra. The difficulty in assigning various features in the spectra varies depending on the molecule being studied. Molecules that contain only two or three atoms have four or fewer normal modes of vibration depending on the molecule's geometry. However, in larger molecules where there is an increased number of atoms, there is an increased number of vibrations associated with the molecule. The more vibrations that are present, the more complicated the spectrum of the molecule is. In assigning spectra, the distinction between fundamental modes and combination bands and overtones has to be made. Once this distinction is made, assignment of a fundamental to a particular vibration has to be made. Most assignments of fundamental vibrations are made by analogy to structurally related compounds. There are, however, other tools which can aid in peak assignment. The use of band contours, looking at peak intensities in both the ir and Raman spectra, as well as depolarization ratios help in band characterization. Another method that can be utilized to provide useful information for assigning features in the vibrational spectrum is the use of theoretical calculations.

Earlier discussion of infrared spectroscopy established that there is a direct relationship between the restoring force of a bond displaced from its equilibrium position and the bond's vibrational frequency. Knowing what either the force constant is or what the vibrational frequency for a bond is, the other can be calculated. The calculated vibrational frequencies are compared to experimentally obtained values. The procedure of calculating these variables can be used in a circular manner in order to

refine calculated values to obtain a more exact correlation between experimental and calculated values.

The force constant of a bond can be expressed in terms of a potential energy function by utilizing equation 1. This is a simple model employed for homonuclear diatomic molecules. Polyatomic molecules are obviously more complicated because of the increased number of bonds present. The more bonds present in a molecule, the larger the number of force constants needed to describe the system. For a polyatomic molecule, equation 1 would transform into

$$V = \tfrac{1}{2}\{f_1x_1^2 + f_2x_2^2... + f_nx_n^2 + f_{12}x_1x_2 + ...f_{nm}x_nx_m\} \quad (20).$$

where f_1 and f_2 are force constants for a particular motion whether it be a bend or stretch and the f_{nm}'s are the interaction force constants between two motions and x is the displacement of the various atoms in these motions. The problem with calculating the vibrational frequencies for a given polyatomic molecule is that there are more force constants needed than there are fundamental modes to be calculated. The calculations can be simplified by using a model that best fits the type of calculation required. A couple of these models will be discussed later in this chapter.

It is already known that there are 3N-6 vibrational degrees of freedom but it is sometimes more convenient to work in a more general case (i.e. using 3N coordinates). The secular equations that are obtained in these calculations will have 3N solutions with 3 solutions a result of translation, 3 solutions contributed by rotation and the remainder of the solutions indicative of vibrations.

To determine the resulting motions of a vibration, the

forces acting on each atom have to be evaluated based on Hooke's Law (9):

$$F(x) = (\partial V/\partial x_i) = -k_i(\Delta x_i) \qquad (21)$$

where x_i-x_j is the change in bond length during the course of a vibration. After the values of F_i are evaluated, a set of secular equations pertaining to the motion of the molecule is constructed. The roots of these equations correspond to a specific motion of a normal mode. The frequency (ν_i) of this mode is determined from the root of the secular equations (13) using the equation

$$\frac{\lambda_i^{1/2}}{2\pi} = \nu_i \qquad (22).$$

In complicated systems each atom is described by a set of Cartesian coordinates such that

$$x_1y_1z_1,\ x_2y_2z_2,\ldots\ldots\ldots x_Ny_Nz_N$$

or in general terms, ξ_{3N} where

$$\xi_1 = x_1, y_1, z_1 \quad \xi_2 = x_2, y_2, z_2.$$

In the Gwinn program used in this thesis research, kinetic and potential energy matrices are set up in terms of a Cartesian coordinate system (14). These matrices are based on 3N degrees of freedom. The kinetic energy equation is represented by the equation

$$T = \tfrac{1}{2}\sum m_i q_i^2 \qquad (23)$$

with q_i representing any generalized coordinates (14) while the potential energy is expressed as a Taylor series:

$$V = V_o + \sum_i (\partial V/\partial \xi_i)_o \xi_i + \tfrac{1}{2}\sum_{ij}(\partial V^2/\partial \xi_i \partial \xi_j)_o + \ldots\ldots \quad (24).$$

Since V_o is the potential with all atoms in the system at their equilibrium positions. V_o can be set equal to zero because it is the reference point where we measure the relative change in potential. The $(\partial V/\partial \xi_i)_o$ term is also zero because in a stable molecule the equilibrium position is of minimum energy. The coordinate system used is variable depending on the calculation program used. The coordinates can be expressed as mass-weighted coordinates by replacing $\sqrt{m_i}q_i$ with ζ_i (13). This replacement causes equation (23) and (24) to be transformed to

$$T = \tfrac{1}{2}\sum \zeta^2 \quad (25)$$

$$V = \tfrac{1}{2}\sum_{ij}(\partial V^2/\partial \zeta_i \partial \zeta_j) = \tfrac{1}{2}\sum_{ij} b_i \zeta_i \zeta_j \quad (26)$$

respectively. Substitution of the above expressions for T and V in the Lagrangian (L = T - V) yields a set of 3N second-order differential equations represented by equation (27).

$$\ddot{\zeta}_i + \sum b_{ij}\zeta_j = 0 \quad (27).$$

with the solution to the equation written as

$$\zeta_i = B_i \sin(\lambda_i^{1/2} t + \beta) \quad (28).$$

A vibration that satisfies equation (28) is a normal vibration. There should be *3N-6* solutions to the equation (28) which correspond to the normal vibrational modes characteristic of that molecule.

Another alternative is to use what is known as the *normal coordinate* system (15) which is a coordinate system where the kinetic and potential energies are contained in the diagonal elements of their respective matrices. Using normal coordinates allows for a 3N-dimensional problem to be reduced to 3N one-dimensional problems. Nevertheless, in a polyatomic molecule, each of these coordinate systems will have 3N roots as the solutions to their respective secular equations with six roots being equal to zero for the translational and rotational components. The remaining 3N-6 roots represent the fundamental modes of vibration in the molecule.

The Gwinn program (15) incorporates the kinetic energy matrix (called the G-matrix) into its program but, through a series of transformations, the G-matrix is transformed into a unit matrix and is not directly involved in the calculation of the vibrational frequencies. This leaves a potential energy matrix involving secular equations that are based on force constants and mass-weighted coordinates. The degree of complexity of the potential field matrix (called an F-matrix) varies depending on how detailed the user wants to set up the matrix.

An F-matrix with dimensions of (3N-6) x (3N-6) is constructed with the elements of the diagonal representing the force constants of bond and the off-diagonal elements are force constants that pertain to interactions between different bonds. There are various models which describe the complexity of the F-matrix with each model varying in the degree of interaction between bonds.

The *Valence force field* (VFF) model employs only force constants that represent the restoring forces that are along valence bonds and resist changes in angles between the

valence bonds such that

$$V = \tfrac{1}{2}\{k_{ri}[(\Delta r_1)^2 + (\Delta r_2)^2 + \ldots.(\Delta r_n)^2] + k_{\delta i}[(\delta_{12})^2 + (\delta_{23})^2 + \ldots.+ (\delta_{nm})^2]\} \quad (29).$$

This model incorporates only diagonal elements (i.e. no interaction constants).

A second, more detailed model is the *Generalized Valence force field* (GVFF). The approach that this model takes is basically the same as that described in the VFF model but also included are the interactions between stretching and bending motions. The matrix becomes more complicated as off-diagonal elements are now included. The potential can be calculated according to

$$V = \tfrac{1}{2}(\sum K_i(\Delta r_i)^2 + \sum H_i(\Delta \alpha_i)^2 + \sum K'_{ij}(\Delta r_i)(\Delta r_j) + \sum H'_{ij}(\Delta \alpha_i)(\Delta \alpha_j) + \sum E'_{ij}(\Delta r_i)(\Delta \alpha_j)\} \quad (30)$$

with K, H, and E being force constants for the stretching, bending and stretching-bending interactions respectively.

In the third model, the *Urey-Bradley force field* model (UBFF), a mixed potential is employed such that interactions between non-bonded atoms are included in the calculation of the molecule's fundamental frequencies. This adds more non-zero elements to the F-matrix therefore adding more detail to the secular equations which, in turn, increases the complexity of the model. The F-matrix can be set up according to one of the above models. The more refined the matrix, the more detailed the calculations will be. For detailed calculations of vibrational frequencies, a UBFF model can be employed whereas the other two models can be utilized for a general survey of calculated frequencies.

Once the force field matrix is constructed, the program diagonalizes the matrix and the vibrational frequencies are calculated from the roots of the secular equations (eigenvalues). The Gwinn program (15) also calculates the eigenvectors from the eigenvalues. These eigenvectors are the normal coordinates of the molecule in terms of mass weighted coordinates. These eigenvectors show the displacement of the atoms during the vibration.

The Gwinn program calculates the vibrational frequencies associated with a particular molecule based on the principles discussed in this section. The calculated frequencies provide the user with an idea of where the fundamental frequencies of the molecule should appear in the spectrum. The calculated frequencies also include the eigenvectors associated with each atom which correspond to the displacement of the atoms during the vibration and, therefore, indicating the motion of the molecule associated with the fundamental. The F-matrices employed in the study of carbonyl isocyanates (16) were based on the UBFF model but not all elements of the matrix were considered non-zero. The only interaction force constants that were included were those involving the bonds directly adjacent to each other.

The results of the force field calculations were useful in distinguishing between bands that belong to the different possible isomers. The eigenvectors were also useful in that they illustrated the particular motion of the molecule involved in the fundamental vibration as well as qualitatively showing the vibrational coupling that goes on between the different vibrations.

1.5 Purpose of the Project

In section 1.1, the uses and applications of carbonyl iso(thio)cyanates in chemistry and other scientific fields were outlined briefly with reference to several review articles concerning the applications of carbonyl isocyanates in science (1-4). There is, however, a severe lack of rapport between their reactions and syntheses and their physical and structural characteristics. Studies concerning the structure of carbonyl iso(thio)cyanates are sparse at best even though these compounds have been synthesized for years.

There are several possible reasons why spectroscopists have avoided analyses of carbonyl iso(thio)cyanates in the past. The existence of these compounds dates back over one hundred years but since there were considerable time gaps between the discoveries of these carbonyl iso(thio)cyanates, a proper spectroscopic survey, encompassing various related groups of these compounds (i.e. acetyl isocyanate and its chloacetyl derivatives), has not been attempted. It is only now that spectroscopists are getting involved in the analyses of iso(thio)cyanates.

The instability of the carbonyl iso(thio)cyanates is another important factor why spectroscopists have ignored study of these compounds. In the past, the ready decomposition, high reactivity as well as the odorous nature of these compounds has discouraged spectroscopic study. Only with the advancements in spectroscopic techniques and commercial availability of some carbonyl isocyanates has the analysis of carbonyl isocyanates and isothiocyanates been simplified.

The goal of this project is to characterize several of

these compounds in an attempt to achieve a better understanding of their structure which may hopefully lead to a better understanding of their chemical behaviour. With an increased understanding of the structure of carbonyl iso(thio)cyanates, organic chemists may, perhaps, use the information to advance the usage of carbonyl iso(thio)-cyanates in synthetic chemistry.

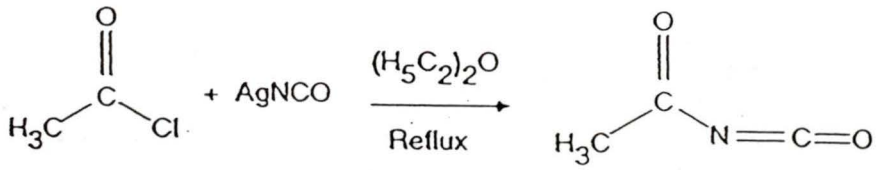
There is the possibility that carbonyl iso(thio)cyanates can have more than one geometrical comformation. The preference for a particular geometry depends on the substituent attached to the CO-NCE framework. It would be of interest to synthetic chemists to know which conformation is favoured in order to predict the outcome of synthetic reactions. If a particular conformation of an carbonyl iso(thio)cyanate is required for a reaction, a stable carbonyl isocyanate known to have that conformation could be utilized. A survey of the conformational preferences of substituted carbonyl isocyanates is in the preparative stages by a collaborating group (17).

With the use of the experimental and theoretical techniques described in this chapter, we attempt to analyze and assign the bands in the vibrational spectra of a group of carbonyl isocyanates and isothiocyanates.

Chapter 2
Experimental

2.1 Preparation and Purification of Carbonyl Isocyanates

2.1a Synthesis of Acetyl Isocyanate (AI)



In order to carry out the synthesis of acetyl isocyanate (1), a fresh sample of silver isocyanate (reactant) had to be prepared. Silver isocyanate was prepared by dissolving 40.50 g of potassium cyanate (FW = 81.11 g/mol, 499.3 mmol) in 300 mL of water. This mixture was added slowly (1 hour) to a 1 L round bottom flask containing 84.52 g of silver nitrate (FW = 169.89 g/mol, 497.6 mmol) in 200 mL of water. Upon addition of the $KOCN/H_2O$ mixture to the flask, the solution in the flask took on a creamy-white colour as more precipitate formed. This mixture was stirred vigorously with a mechanical stirrer for a period of two hours. The white precipitate was suction-filtered and collected on a watch glass where it was stored in an oven at 100°C for a period of twenty-four hours. Before use the silver isocyanate was dried on a vacuum line for six hours.

In a 250 mL 2-neck round-bottom flask, 20.05 g of dried silver isocyanate (FW= 149.89 g/mol, 133.8 mmol) was

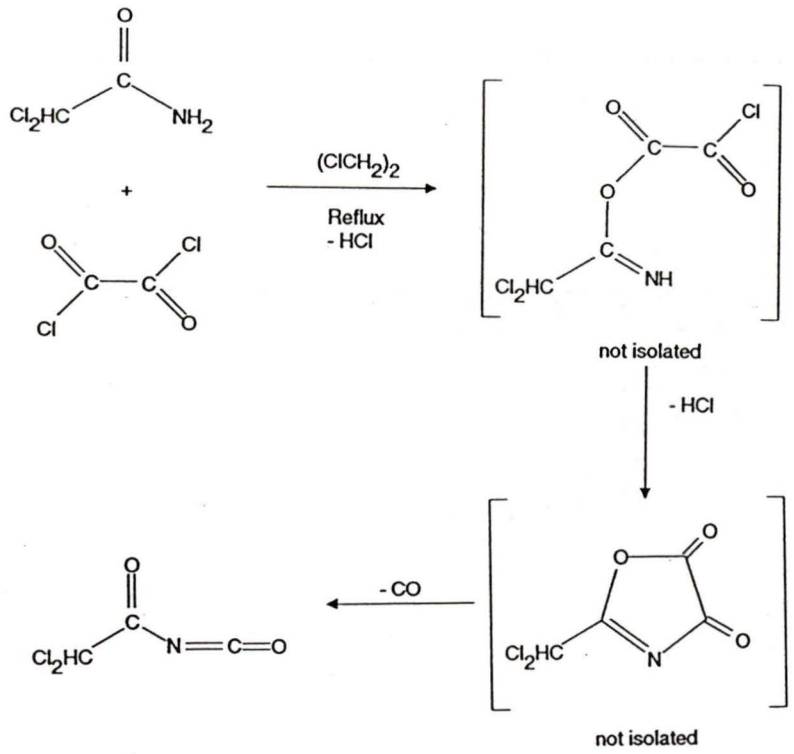
suspended in 100 mL of diethyl ether (bp 35°C). This mixture was stirred while sitting in an ice bath. To this mixture, 9.0 mL of acetyl chloride (FW= 78.50 g/mol, 126.6 mmol) in 30 mL of diethyl ether were added slowly (30 minutes) via a dropping funnel. The reaction was quite exothermic so an ice bath was used to keep the flask cool. After all the acetyl chloride was added, the ice bath was removed and the reaction was allowed to reflux for a period of two hours. During this time, it was noticed that the suspension went from a slight greyish colour to an off-white colour with a slight tint of purple throughout. The solution mixture was suction-filtered through a small frit and washed with a 30 mL portion of diethyl ether.

The diethyl ether was removed on a rotary evaporator with the water bath set at a temperature of 5°C. The solution that remained had a slight orange colour indicative of crude acyl isocyanates. This clear, orange solution was then fractionally distilled. The first fraction collected (<75°C) contained 2.20g (~20 %) of a clear, colourless and very lachrymatory liquid which proved to be acetyl isocyanate (AI). This sample of AI was recondensed into a glass storage tube where it was degassed on a vacuum line and then sealed until ready for spectroscopic study.

2.1b. Purification of Chloroacetyl Isocyanate (CAI)

Our sample of Chloroacetyl isocyanate (CAI) was purchased from the Aldrich Chemical Company (Milwaukee, Wi). The sample was distilled in order to rid the compound of impurities that result upon standing in air for a prolonged period of time. A 1.0 ml sample was recondensed into a sealable glass tube where it was stored prior to spectroscopic study.

2.1c. Preparation and Purification of Dichloroacetyl Isocyanate (DCAI)



The preparation of dichloroacetyl isocyanate (DCAI) first involved the preparation of α,α- dichloroacetamide (FW= 128.0 g/mol). Synthesis (17) was carried out according to the reaction:

$$CC\ell_3\text{-}CH(OH)_2 + 2NH_4OH \text{ --------> } C\ell_2HC\text{-}CO\text{-}NH_2 + NH_4C\ell + H_2O$$

A solution of 134 g of chloral hydrate (FW = 165.40 g/mol, 810.1 mmol) in 400 mL of diethyl ether was stirred mechanically in a 2-litre, 2-neck flask. A second solution of 12 g of potassium cyanide (FW = 65.12 g/mol, 184.3 mmol) in 220 mL of concentrated ammonium hydroxide was added slowly via a dropping funnel (30 minutes). A condenser was attached to the second neck upon addition of the KCN\NH_4OH solution because the reaction began to reflux vigorously. The stirring continued for 30 minutes then the two layers that were formed during the reaction were separated. The ether layer was

washed with 75 mL of water then with 75 mL of 10 % aqueous sulfuric acid. The aqueous layer was extracted with three 75 mL portions of ether. These extracts were then combined and dried with 40 g of sodium sulfate and the ether was removed by distillation. The residue was cooled and the walls of the flask were scratched to initiate crystal growth. The solid (pure white crystals) was then suction-filtered and washed with cold benzene (25 mL). A melting point determination was carried out and it was determined to be 98°C which corresponds to the literature value of 97.5 - 99.5°C (17). After drying, the yield was determined to be 56.0 g.

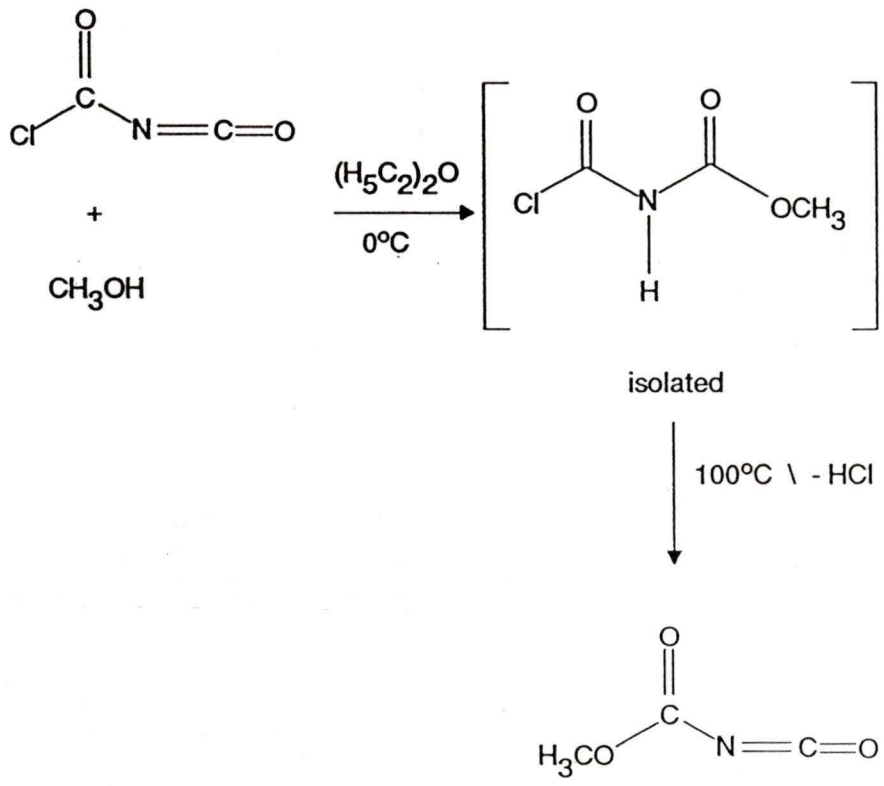
The method followed in the preparation of dichloroacetyl isocyanate was based on the procedure of Speziale and Smith (18,19). A solution of 10.0 g of α,α-dichloroacetamide and 25 mL of freshly distilled 1,2-dichloroethane was stirred in an ice bath for ten minutes. An 8.0 mL sample of oxalyl chloride (FW = 126.9 g/mol, 91.7 mmol) was added all at once to the α,α-dichloroacetamide/1,2-dichloroethane mixture by syringe. While being stirred (over the period of 1 hour), the mixture became cloudy and white. It was then heated to reflux for four hours in an oil bath. The mixture was distilled under reduced pressure on a rotovapor to remove the solvent and excess oxalyl chloride (bp 63°C).

The remaining solution, dark orange in colour, was then distilled fractionally at 22 torr. The three fractions collected were clear and colourless. A total yield of 6.4 g (~53 %) of DCAI (bp 30-32°C/22 torr, lit. bp 135°C/35 torr) was collected. The product was then transferred to a glass storage tube, degassed and stored until used for spectroscopic identification.

2.1d. Purification of Trichloroacetyl Isocyanate (TCAI)

TCAI is available commercially from the Aldrich Chemical Company (Milwaukee, Wi) in high purity so no further purification was needed (nmr data). A 1.0 mL sample of the colourless, lachrymatory liquid was recondensed into a glass storage tube, degassed and sealed until used for spectroscopic study.

2.1e. Synthesis of Methoxycarbonyl Isocyanate (MCI)

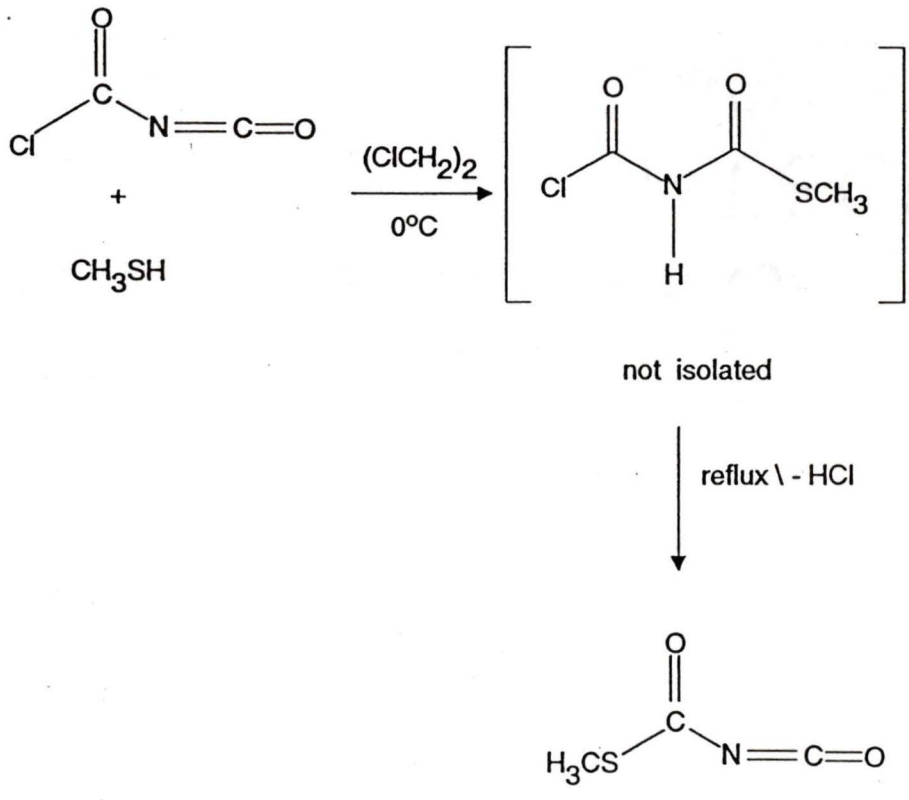


The preparation of methoxycarbonyl isocyanate was reported by Hagemann in 1977 (4). The method involves combining methanol and chlorocarbonyl isocyanate (CCI) in a solvent. This was the procedure followed here. A 5.0 g sample of purified CCI (FW = 105.5 g/mol, 47.4 mmol) was dissolved in 30 mL of distilled diethyl ether while the flask was immersed in an ice bath. A mixture of 2.0 mL of methanol in 10 mL of diethyl ether was added slowly through a dropping funnel. After complete addition, the mixture was stirred for thirty minutes at 0°C. During this time, a white precipitate (iminodicarboxylic acid chloride methyl ester) formed. The solvent was removed under slight vacuum.

The white crystalline solid was dried and then placed in a flask which was attached to a reflux apparatus. The flask was heated to 100°C. The solid melted and began to reflux and this was allowed to continue for a two hour period at which no more HCℓ evolved (tested with pH strips). Distillation yielded 2.0 g of MCI (FW = 101.1 g/mol, bp 97°C) as a clear, colourless and very lachrymatory liquid. The liquid was then recondensed into a glass tube and sealed until needed.

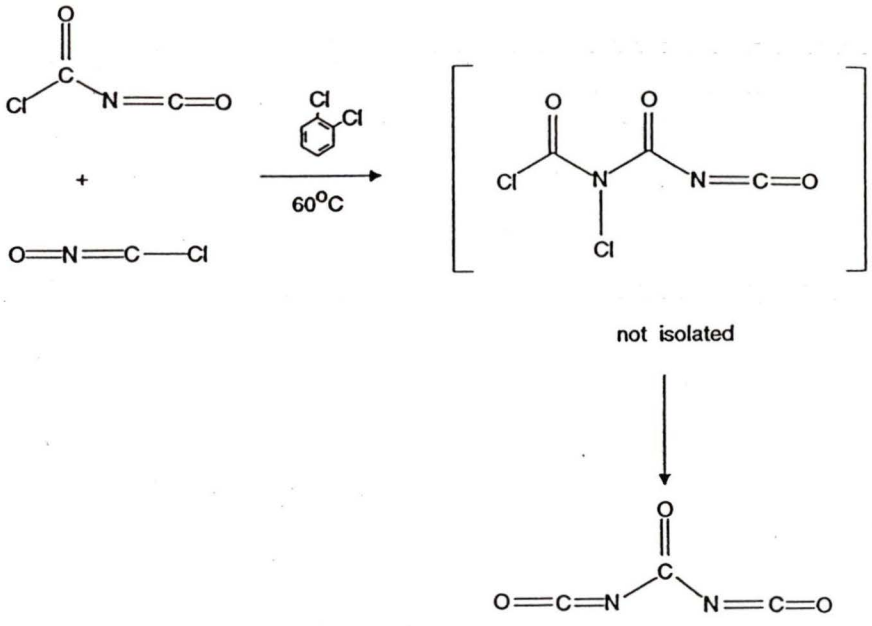
2.1f. Preparation of Thiomethoxycarbonyl Isocyanate (TMCI)

The method proposed by Hagemann (4) in the preparation of methoxycarbonyl isocyanate was also followed in the preparation of thiomethoxycarbonyl isocyanate. Methanethiol (FW = 48.1 g/mol) was purchased from the Kodak Chemical Company. A 2.3 g (48 mmol) sample was recondensed into an ice-cooled glass storage tube. Chlorocarbonyl isocyanate (4.9 g/47 mmol) was dissolved in 20 mL of 1,2-dichloroethane at 0°C. The methanethiol was then allowed to condense into the ice-cooled solution while being stirred.



After all the methanethiol was condensed into the reaction vessel, a condenser and drying tube were attached. Stirring of the solution continued as the reaction temperature was allowed to rise to room temperature. The reaction remained clear and colourless. The contents of the flask were then brought to reflux until no further HCℓ gas evolved. The 1,2- dichloroethane was then removed by distillation. The liquid that remained was colourless and had a very strong odour. The lachrymatory liquid, TMCI (FW = 117.1 g/mol, bp 125°C), was stored in a sealable tube.

2.1g. Synthesis of Carbonyl Diisocyanate (CDI)



Carbonyl diisocyanate was prepared by following Hagemann's method (20). In a 2-necked 100 mL round bottom flask, 4.9 g of trichloroisocyanuric acid (TCICA, FW= 232.4 g/mol, 21.1 mmol), an off-white powder, were suspended in 20 ml of 1,2-dichlorobenzene (bp 180°C). This mixture was heated to 60°C in an oil bath in order to dissolve the TCICA. A 5.0 g quantity of chlorocarbonyl isocyanate (FW= 105.5 g/mol, 47.4 mmol) was added very slowly to the TCICA/1,2-dichlorobenzene mixture with stirring. The mixture turned yellow upon mixing and the reaction bubbled vigorously. The yellow-green gas ($C\ell_2$) could be noticed moving up the condenser. The reaction was brought up to 180°C (reflux temperature) over a period of two hours after the addition of CCI was completed. The reflux was halted but left stirring for two hours after the yellow colour in the condenser disappeared.

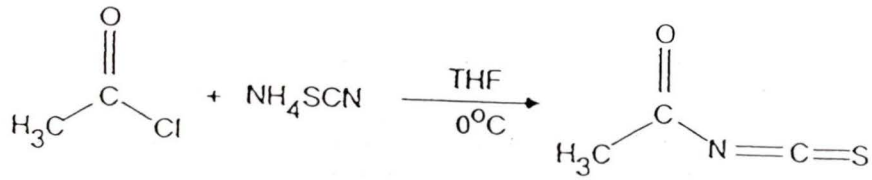
The mixture was then fractionally distilled over a small Vigreux column into three 5 ml round bottom flasks.

The three samples collected (<100°C, 100-105°C, and >105°C) were all clear and colourless. Infrared data showed that the first fraction contained unreacted starting material (CCI). The infrared spectra of the remaining two fractions were identical so they were combined. The total mass collected for the CDI (FW = 112.0 g/mol, bp. 100-103°C) sample was 2.2g (~41 %).

Over short periods of time, the sample of CDI turned slightly yellow. The impurities were removed on a vacuum line. The sample was condensed into a glass storage tube as a clear, colourless liquid until spectroscopic analysis was carried out. CDI trimerizes to a white solid over a prolonged period of time so spectroscopic analysis of the monomer was carried out immediately after purification. Klapstein and Nau (21) melted the solid to regain the monomer after trimerization but this did not occur when tried in our laboratory. The solid, however, did melt to give a viscous liquid whose infrared spectrum did not match that of the desired compound.

2.2 Preparation of Carbonyl Isothiocyanates

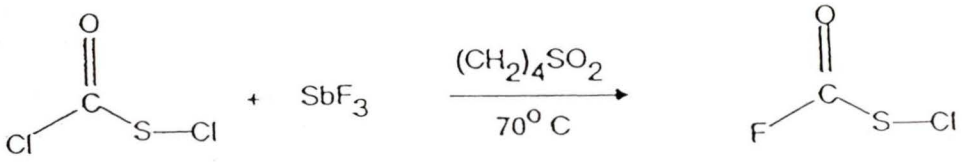
2.2a. Preparation of Acetyl Isothiocyanate (AIT)

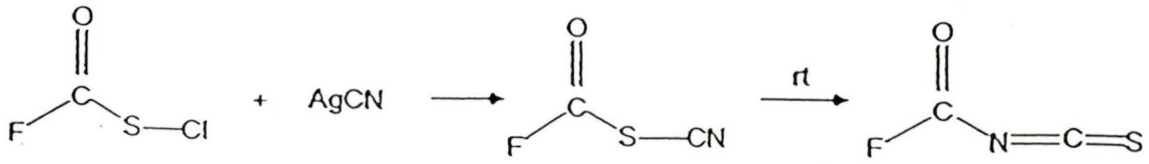


An amount of ammonium thiocyanate (FW= 76.12 g/mol), exceeding that required stoichiometrically for the reaction, was dried on a vacuum line for four hours. From this quantity, 8.62 g (113.2 mmol) was dissolved in 70 mL of dry tetrahydrofuran (THF). A solution of 8.8 g of acetyl chloride (FW= 78.5 g/mol, 113 mmol) in 30 mL THF was cooled in an ice bath. The ammonium thiocyanate/THF solution was added slowly to the acetyl chloride mixture by means of a dropping funnel. Each drop of the ammonium thiocyanate/THF solution caused the reaction mixture to turn a pinkish-violet colour and then to a creamy whitish-pink colour. This could be evidence of a reaction intermediate but it was not proven. After complete addition, the reaction mixture was stirred at 0°C for two hours. The mixture was then suction-filtered through a microfrit and the precipitate was washed with 20 mL of THF. The solvent was then removed by a rotovapor and the remaining solution was distilled over a small Vigreux column. The distilled product was clear and colourless but upon standing in air for a very short time, the product took on a slight yellow colour. The impurities were removed by hooking the sample to the vacuum line at a slightly reduced pressure. Spectroscopic analyses were performed immediately, before decomposition occurred.

2.2b. Synthesis of Fluorocarbonyl Isothiocyanate (FCIT)

i- Preparation of Fluorocarbonylsulfenyl Chloride (FCSC)





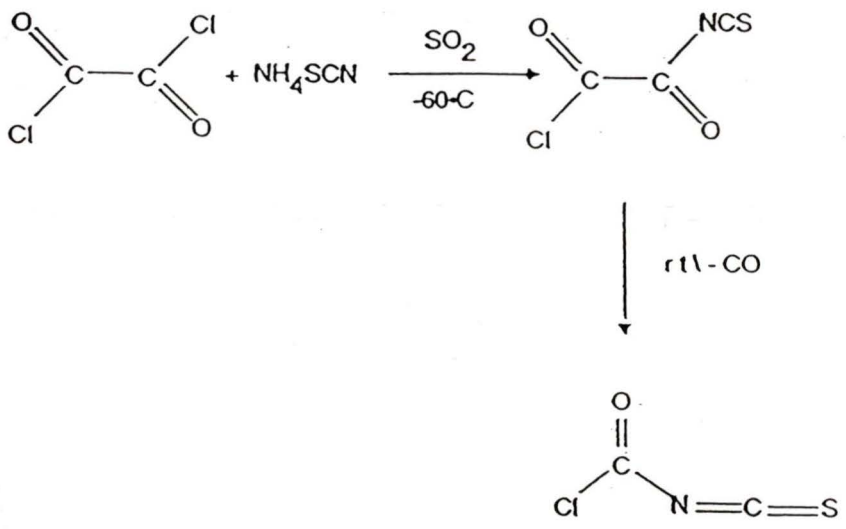
The preparation of fluorocarbonyl isothiocyanate (FCIT) first involved the preparation of fluorocarbonylsulfenyl chloride (FCSC) via a procedure taken from the literature as reported by Haas and Reinke (22). This procedure involved synthesizing the fluoro compound from the corresponding chloride as shown in the scheme above. A 50 g sample of antimony trifluoride (FW= 178.75 g/mol, 279 mmol) was suspended in 75 mL of tetramethylene sulfone (bp 285°C) while being stirred in an oil bath at 100°C. The addition of reactant was performed in this manner since the solvent has a melting point of 27°C (solid at room temperature). The whitish-grey suspension was stirred for about two hours. At the end of this period, 25.0 g of chlorocarbonylsulfenyl chloride was added to the stirred suspension slowly (thirty minutes) via a dropping funnel. The reaction mixture was then brought to a temperature of 200°C. A clear, yellow coloured liquid with a very foul odour began to distil over into an ice-cooled flask. The yellow liquid was fractionally distilled yielding a total mass of 10.08 g of fluoro-carbonylsulfenyl chloride (FW = 114.52 g/mol, bp 45°C). The last two fractions were combined since ^{13}C, ^{19}F and ir data matched that of pure FCSC reported by earlier workers.

2.2b.ii.- Preparation of Fluorocarbonyl Isothiocyanate

A 4.75 g (41.5 mmol) quantity of FCSC was condensed into a very well secured 100 ml 2-neck round bottom flask that contained 8.3 g of dried silver cyanide (FW= 133.89 g/mol, 62.0 mmol). The mixture was cooled to (-70°C) and allowed to warm up very slowly. As the reaction is highly exothermic, care had to be taken to ensure that the adapters were clamped tightly to the flask to prevent leaks and subsequent loss of product. The exothermic reaction began when the mixture warmed up to 10°C and lasted approximately two minutes. The suspension was stirred for an additional fifteen minutes.

The yellow suspension did not appear to contain any liquid product but reducing the pressure caused a clear, colourless liquid to recondense into the liquid-nitrogen cooled storage tube. Approximately 1 mL of the liquid was collected. ^{19}F nmr data agreed with that of earlier reported literature (22) but there was also evidence of a decomposition product, most likely F-CO-S-CO-F. Also present in the ^{19}F spectrum was a peak that matched that of fluorocarbonyl thiocyanate. This result was not found by Nau (23) but reported in previous literature on FCIT (22). This other product was however not isolated (see reaction scheme). The product was purified on the vacuum line and recondensation of the product yielded only about 0.5 ml of product. After a few hours, the FCIT took on a slightly yellow colour so recondensation was carried out prior to spectroscopic study.

2.2c. Synthesis of Chlorocarbonyl Isothiocyanate (CCIT)



The procedure followed in the preparation of chlorocarbonyl isothiocyanate (see above reaction scheme) was taken from the method of Bunnenberg and Jochims (6). Before the reaction could be started the solvent, sulfur dioxide, had to be dried. This was achieved by passing the sulfur dioxide through concentrated sulfuric acid and then through a column of drierite. Approximately 150 mL of the gas was condensed into a 2-necked round-bottom flask (graduated) which was submerged in a dry ice and salt\ethanol mixture.

A 11.4 g (150 mmol) sample of dried (on a vacuum line) ammonium thiocyanate (FW = 76.12 g/mol) was weighed into a 250 mL flask. The flask was cooled in a dry ice and salt\ethanol bath that contained a cryostat coil to maintain the temperature at (-60°C). Once the flask (wrapped in aluminum foil for insulation) was cooled, the 150 mL of SO_2 was transferred to the flask via a vacuum inlet system. As the mixture was stirred, the inorganic salt dissolved in the

solvent. Argon was pumped through the flask in order to exclude moisture from the system. The liquid mixture turned a orange-yellow colour at this time.

The solvent mixture was transferred into a 200 mL dropping funnel that was pressure compensated to avoid loss of sulfur dioxide. A low-temperature condenser was attached atop the funnel to prevent loss of solvent from the system. As the solution was transferred to the funnel it boiled vigorously.

While being cooled, 13.1 mL (d= 1.455 g/mL) of oxalyl chloride (FW = 126.93 g/mol, 150 mmol) were injected into a two-necked flask through a serum cap. The solution mixture of ammonium thiocyanate in sulfur dioxide was added dropwise to the magnetically stirred oxalyl chloride over a two hour period. Upon addition, a white precipitate was noticed in the reaction flask (ammonium chloride). After complete addition, the dropping funnel was replaced by a condenser and the reaction was allowed to reflux overnight at (-10°C) in a cryostat cooled solution of dry ice and salt\ethanol mixture.

The resultant reaction mixture was yellow in colour. This mixture was filtered through a small microfrit into a 500 mL flask to get rid of the ammonium chloride salt. The solvent was removed from the clear, yellow filtrate at (-10°C) under slight vacuum. The solid that remained was crystalline and had a dark yellow colour. The solid (lachrymatory and odorous) was transferred to a 100 mL flask and dried for a couple of hours at a pressure of 15 torr. The weight of the product, oxalyl chloride isothiocyanate, (FW = 149.54 g/mol) was determined to be 18 g (~80 %).

An 8.0 g amount of oxalyl chloride isothiocyanate was transferred into a 50 mL flask along with approximately 0.2 g of activated charcoal. The flask was connected to a condenser with a drying tube attached and the mixture was heated up to 85°C for four hours. The yellow solid melted quickly as it was heated. A balloon was attached to the free end of the drying tube to monitor CO gas which evolves upon heating the mixture. The yellow liquid (crude chlorocarbonyl isothiocyanate) was fractionally distilled to yield 3.6 g (~55 %) of chlorocarbonyl isothiocyanate. The clear, colourless distillate possessed a very strong lachrymatory odour. Upon storing the sample, the liquid acquired a slightly yellow tint.

2.3 Instruments Utilized for Spectroscopic Analyses

The instruments used in the spectroscopic analyses and the conditions at which they were operated are described below.

FT-IR Bruker IFS-25

All gas phase infrared spectra were recorded on this instrument. A 10 cm quartz glass cell with potassium bromide (KBr) windows was used to hold the sample. The sample was condensed into the cell at various pressures. The spectra were recorded between 4000-400 cm^{-1} with an evacuated cell used as a reference. Thirty-two scans were run in each spectrum (instrument standard). The resolution of the recorded spectra was 2 cm^{-1}. The spectra were plotted on a Hewlett-Packard 7475A plotter.

IR Bruker 1320

Liquid infrared spectra were recorded on this table-top

Bruker model which ran in the range 4000-400 cm^{-1}. The spectra were obtained by placing a drop of liquid between two cesium iodide (CsI) plates which were then mounted in the cell holder. Various continuous scans were run in three or twelve minute intervals depending upon how stable the compound was in liquid form. KBr plates were also employed if the compounds showed evidence of reacting with the CsI plates. Resolution of the peaks was estimated to be 3 cm^{-1}.

Raman Measurements

All Raman measurements were recorded on a Jobin-Yvon Ramanor HG2S monochromator perpendicular to the incident laser beam which used 500 mW (focussed) power. The laser beam (excitation λ of 514.5 nm) originated from a Spectra Physics 2020 Argon Ion laser. The spectra were measured in the range 3500-100 cm^{-1}. Raman experiments performed involved having the acyl iso(thio)cyanate samples in the liquid phase. The samples were sealed in glass nmr-style tubes (diameter 5 mm). Calibration of the spectra were achieved using known argon ion plasma lines as well as with reference to chloroform. The resolution of the sharp features in the Raman spectra was estimated to be ± 3 cm^{-1}. The spectra were measured at a continuous scan rate of 20 cm^{-1}\ minute.

^{1}H- NMR

The ^{1}H proton spectra were measured on a 360 MHz Bruker AMX 360 instrument. Various amounts of sample (depending upon availability) were pipetted in 5 mm glass tubes with deuterated chloroform ($CDCl_3$) as solvent. Tetramethylsilane (TMS) was used as a reference point for the measurements (Chemical shift, δ= 0.00 ppm).

^{13}C- NMR

The ^{13}C nmr data were obtained on a 360 MHz Bruker AMX 360 instrument. The sample preparation involved was identical to that of the ^{1}H nmr samples with the exception that tetramethylsilane was excluded from the sample and $CDCl_3$ served as both the reference (δ= 77.0 ppm) and the solvent.

Variable-temperature measurements

The variable-temperature infrared spectra were recorded in the same manner as the room temperature ir spectra. The data were obtained between the range 400-4000 cm^{-1} at various pressures. Variable temperature spectra were performed with an in-house heating apparatus recording temperatures between 0 and 60°C.

Raman Dye-laser experiments

The instability of the acyl isothiocyanates in the 514.5 nm argon ion laser beam led to the trial of utilizing a dye laser to possibly minimize photodecomposition of the sample of the less stable CCIT. A 652 nm excitation with an output of 100mW focussed power from a rhodamine 640 argon ion-pumped Coherent 590 dye laser was employed to perform these experiments. The spectra were calibrated using chloroform and toluene as external standards. With these sharp features, the resolution of the bands is expected to be ±3 cm^{-1}. Spectra were obtained for CCIT but of inferior quality to those obtained with the argon ion laser employing the 514.5 nm line as its excitation wavelength.

Chapter 3
Acetyl Isocyanate and its α-Chloro Derivatives

3.1 Introduction

This chapter deals with the assignment of the experimentally observed frequencies of the infrared and Raman spectra recorded for on acetyl isocyanate and its mono-, di-, and trichloro-substituted counterparts. The general structure of acetyl isocyanate is shown in Figure 3.1. The different molecules in the family result from increasing chlorine substitution on the carbon atom α to the carbonyl group.

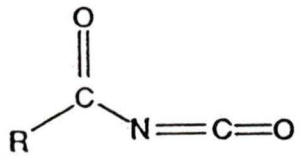


Fig. 3.1. The general structure of AI and its chloro derivatives.

The geometry of acetyl isocyanate has been determined via other experimental techniques such as gas phase electron diffraction (24) and microwave spectroscopy (24,25) as well as theoretically by *ab initio* calculations (24). There have been no other experimental data offered in the literature pertaining to structural analyses of these compounds apart from brief mention of the Raman spectrum (900- 200 cm^{-1}) of the parent molecule, acetyl isocyanate (26), and mention of some ir data (νNCO and νCO) by a Russian group in 1986 (27).

Acetyl isocyanate (AI) and its α-chloro-substituted derivatives (CAI, DCAI, and TCAI) can be characterized as belonging to the C_s point group based on the assumption that the *cisoid* and *transoid* configurations (i.e. planar geometry) are the more stable conformers. These nine-atom molecules have twenty-one normal modes of vibration. Of these twenty-one normal modes, fourteen are considered to be in-plane (a′) and seven are out of the plane (a") of the molecule. According to the C_s point group selection rules, all of these modes are infrared and Raman active (Appendix 1).

Acyl isocyanates are able to adopt one of three conformations two of which are planar and the third non-planar *gauche*. The planar structures may be *cisoid* or *transoid* with respect to the orientation of the carbonyl and the isocyanato bonds that are contained in the structure of the compounds. These three conformational structures result from rotation of the isocyanato (-NCO) group about the C-N bond. The conformers, while similar in structure, have slightly different energies thus resulting in minor differences in their vibrational spectra. Evidence for this is found in the infrared and Raman spectra of acetyl isocyanate and its α-chloro-substituted derivatives.

For the partially α-chloro-substituted acetyl isocyanates, there exists the further possibility of different rotomers from rotation about the C-C bond. There has been no conclusive evidence to confirm this possibility in our research or in experimental work carried out by Yarkova and her research group (27) in their brief infrared study of chloro-substituted acetyl isocyanates. Evidence from our research on acetyl isocyanate and its α-chloro derivatives as well as other acyl isocyanates (26,28-35) suggests that the different confomations that are found are a result of rotation of the isocyanato group about the C-N bond linking

the NCO group to the C=O group. This evidence stems from the investigation of the peaks assigned to the NCO symmetric stretch. The changes that occur in the liquid Raman spectra for this NCO peak are characteristic for all of the compounds of this group whereas were it a result of rotation of the methyl group about the C-C bond, the change in the NCO symmetric stretch would appear only in the mono- and dichloro-substituted species. This evidence tends to favour the idea of the conformers arising from rotation about the C-N bond.

The gas phase infrared and liquid Raman spectra of AI and its family of α-chloro derivatives are presented in Figures 3.2 and 3.3. The experimental conditions used to obtain these spectra are discussed in section 2.4. The assignments of the observed frequencies for the respective spectra are listed in Tables 3.1 through 3.4. Assignments have been based on studies, both experimental as well as theoretical, of similarly structured compounds.

3.2 Results and Discussion

3.2a. The region between 3400- 1300 cm^{-1}.

The fundamental stretching frequencies for acyl isocyanates (νNCO, νCO) lie in this higher energy region of the vibrational spectra. The stretching fundamentals for the methyl group (νCH_n) are also found in this region around 3000 cm^{-1}. In this series of molecules (AI, CAI, DCAI, and TCAI), the carbonyl and isocyanate stretching vibrations contribute three very prominent infrared absorption bands. These features are also intense in the Raman spectra with the exception of the isocyanate asymmetric stretch. This fundamental appears as a very weak peak in the spectra.

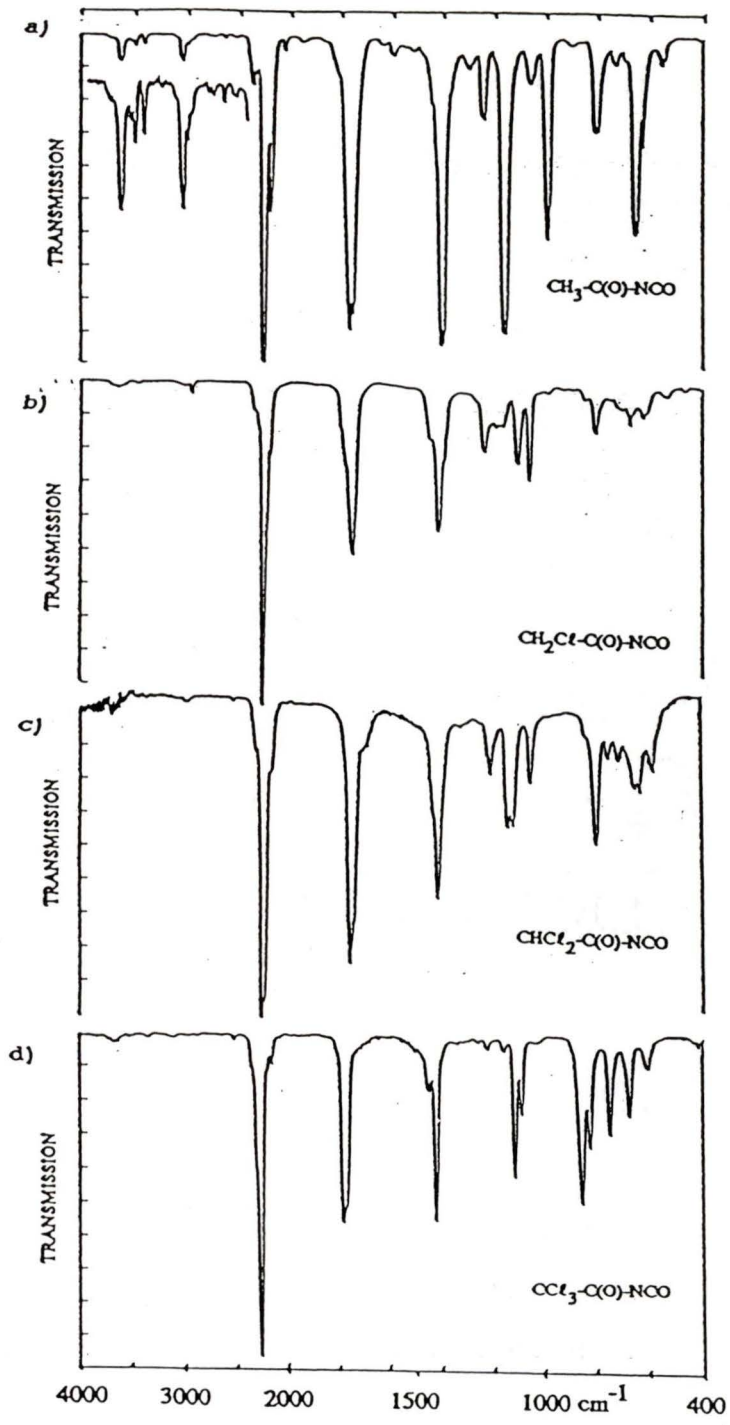


Fig. 3.2. The vapour-phase infrared spectra of acetyl and choroacetyl isocyanates: (a) p= 4 torr (insert, p= 20 torr); (b) p= 1 torr; (c) p= 2 torr; (d) p= 1 torr. The wavenumber scale is linear between 4000 and 2000 cm^{-1}, and between 2000 and 400 cm^{-1}.

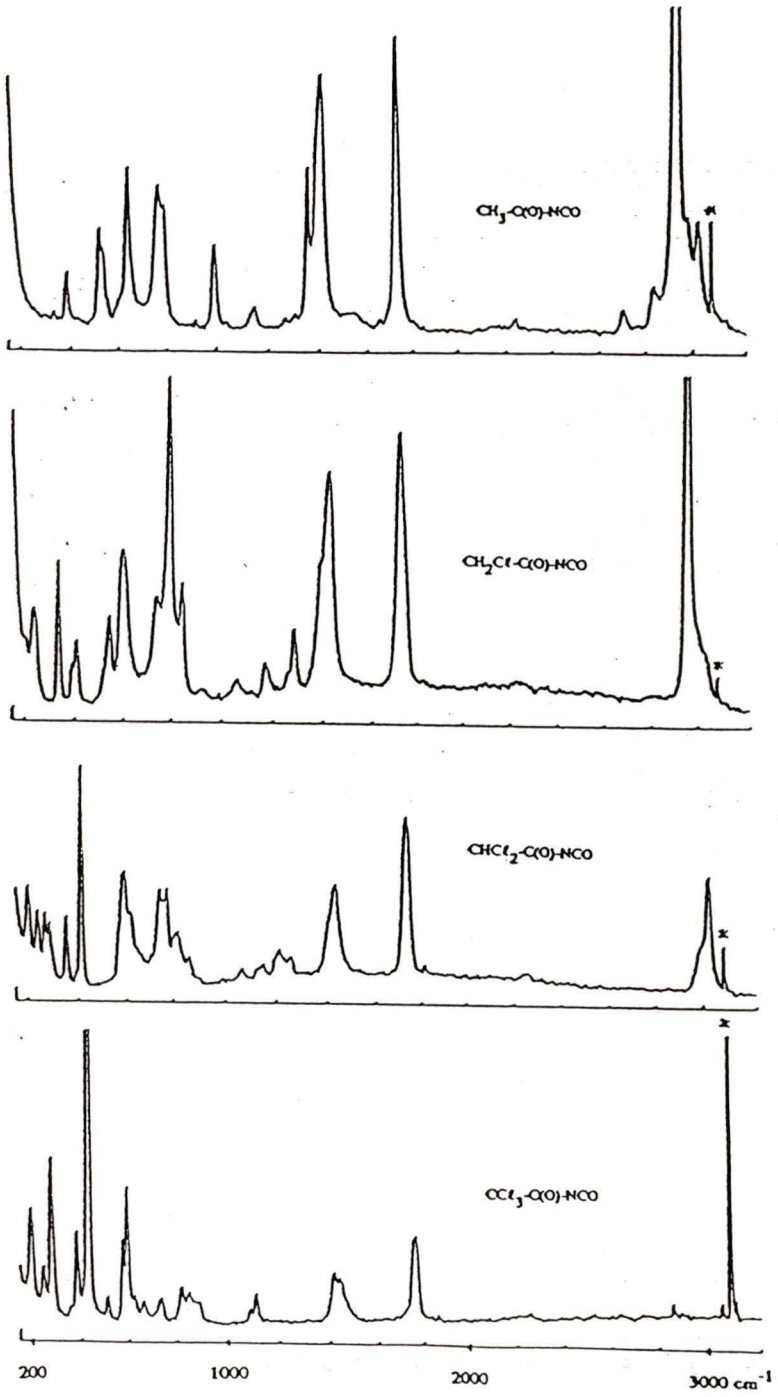


Fig. 3.3. The unpolarized liquid Raman spectra of acetyl isocyanate and chloroacetyl isocyanates using 514.5 nm excitation. The sharp peak identified with an asterisk at a displacement of 3082 cm^{-1} is an Ar^{+} plasma line from the laser, as are the weak features at 2858, 3052, and 3016 cm^{-1} in the $C\ell_3CONCO$ spectrum.

The vibrational frequencies attributed to the methyl group have been well studied in such molecules as acetaldehyde and acetone (36). Assignments of the methyl features in these α-chloro-substituted acyl isocyanates were based on assignments made from the closely related α-chloroacetamides (37) and α-chloroacetaldehydes (38). In the methyl component of AIC, the CH stretching vibration accounts for three peaks (one symmetric and two asymmetric). The weaker, higher energy peaks are associated with the asymmetric stretching (Raman: 3030/2985 cm^{-1}) while the more intense, lower energy feature is the symmetric stretch (ir: 2949 cm^{-1}). The assignment is made easy by looking at the respective intensities of the Raman peaks. Raman intensity is governed by the change in polarizabilty involved in the excitation of a fundamental. The symmetric stretch for the CH component is expected to give rise to the most intense peak of the three stretching components of the methyl group.

In looking at the methyl group in its equilibrium position as compared to when it undergoes a stretching motion, we observe that there is some displacement of the bond when the motion takes place. If we picture the displacement in relation to a coordinate axis, we can observe the change in polarizability with the displacement. In an asymmetric stretch, the negative displacement (to one side of the group) is equal to that of the positive displacement (the opposite side) therefore resulting in no net change in polarizability ($d\alpha/dQ$) with respect to changes in the normal coordinates of the atoms in the bond. However, in the case of the symmetric stretch, the polarizabilty decreases as the bond stretches and increases as the bond contracts so near the equilibrium polarizability value, the net polarizability ($d\alpha/dQ$) is non-zero. Therefore, since Raman intensity is dependent upon change in polarizability, the symmetric stretch would be more intense.

Where the three substituents of the α-carbon are equivalent, MNDO calculations (39) predict that the O-cis structure (X cis to carbonyl O) to be the most stable. These calculations also predict that the calculated energies of formation for the possible conformers of the acetyl species and the trichloro-substituted molecule are so similar that their expected vibrational frequencies would not differ enough to allow distinction between the different rotomers. Experimental studies show no evidence to support the presence of these different rotomers about the C-C bond in terms of band splitting or band broadening for ν(C-H) in AI or ν(C-Cℓ) in TCAI.

Recording the spectra in the liquid phase as opposed to the gas phase did not lend support to the possibility of different rotomers in that the band profile remained the same for the stretching peaks in question. If such rotomers were present, one would expect the profile to change somewhat, upon going to the condensed phase or by performing variable temperature studies, as one species would become more populated thus resulting in a lowering in intensity of the more stable species and an increase of another peak (or shoulder?) pertaining to a population gain of the other higher energy species. This idea is supported by the liquid ir work carried out by a Russian group on trichloroacetyl isocyanate (27) and also by Mido et al. who looked at the rotational isomerism of ethyl trichloroacetate (40).

In the case where the α-carbon is heterogeneously substituted (CAI and DCAI), there is a further possibility of isomerism which is based on rotation about the C-C bond. There are three rotomers that can result; O-cis, N-cis, and gauche. These structures are shown in Figure 3.4. The

possibility of having different isomers based on this rotation about the C-C bond has been discussed in detail for the corresponding acetaldehydes (38) and acetamides (37). This, perhaps, may explain the complexity of the spectra of the chloro and dichloro- species where shoulders appear associated with the CH_2 deformation modes (1200-1000 cm^{-1}) and the $C\ell_2$ and $C\ell$ stretching modes (800-600 cm-1).

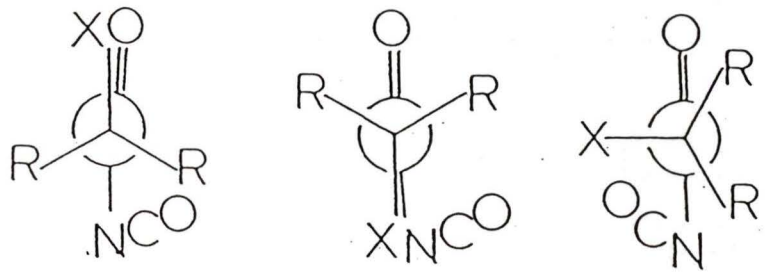


Fig. 3.4. Possible rotomers of AI that are a result of rotation of the methyl group about the C-C bond.

The cases of CAI and DCAI are slightly different from those of AI and TCAI. In the former pair the substituents on the methyl group are no longer equivalent thus making the relative location of the substituent with respect to the system different from AI and TCAI. This is suspected to have a larger effect on the vibrational frequencies pertaining to the fundamentals of the methyl and chloro-substitued groups in CAI and DCAI because the difference in calculated heats of formation spans a larger energy difference between the possible isomers than in the cases of AI and TCAI. MNDO calculations (39) predict the gauche isomer to be the most stable in the monochloro species (α $C\ell$-C bond oriented 90° to the C=O bond). This is a reasonable prediction in that one would expect the heavier, bulkier chlorine atom to be out of the plane in order to minimize steric repulsive forces. Yarkova et al. (27) state that the N-cis conformation (where $C\ell$ is cis with respect to

the N atom) is favoured in the liquid phase along with the gauche conformer. For the $CH_2C\ell$ deformation mode they assigned the peaks to the following conformers:

O-cis	855 and 1083 cm^{-1}
N-cis	842 and 1100 cm^{-1}
gauche	825 and 1070 cm^{-1}

We could not confirm the assignments that were given in this reference since our experimental data did not coincide with theirs. Our liquid ir data showed peaks at 1111, 1066, and 841 cm^{-1}. The peaks located at 1111 and 841 cm^{-1} in our experimental data might possibly belong to that of the N-cis rotomer. The remaining feature at 1066 cm^{-1} is tentatively assigned to the gauche conformer. There was however, no sign of a peak at 825 cm^{-1} to coincide with the data for the gauche conformer. The gas phase spectrum for chloroacetyl isocyanate is more complex in that there are a number of peaks that fall in the range of the rotomers. These data lend support to the theory that no conformer can be excluded in the gas phase.

Dichloroacetyl isocyanate gives a slightly different result. The N-cis conformer (the H-C-C=O dihedral angle = 180°) is energetically favoured over its O-cis (H-C-C=O dihedral angle = 0°) counterpart in MNDO calculations by about 0.2 kcal/mole. Sterically, this is a logical assumption since the two chlorine atoms would be out of plane. This may explain the experimental results observed in the liquid Raman spectrum for this molecule. There are two peaks in the ν(C-H) region where in the absence of such rotational isomerism only one is expected. One can tentatively assign the peak at 3021 cm^{-1} to the O-cis conformer and the shoulder at 2983 cm^{-1} to the N-cis conformer. The broad peak that occurs at 1215 cm^{-1} is

assigned to the CH bending mode but may actually be the unresolved conformers.

3.2b. Carbonyl Stretching Region.

The carbonyl stretching frequency can be assigned without argument. The infrared peaks for this stretch ranged from 1752 to 1777 cm^{-1} in this series of α-chloro-substituted acetyl isocyanates. There is a slight increase in frequency with increasing chloro-substitution on the α-carbon. This trend is noticed in other related molecules such as α-chloroacetamides (37) and α-chloroacetaldehydes (38). There was no clear evidence in the carbonyl peaks to support the presence of different conformers even though there is evidence for this in other modes.

3.2c. NCO Stretching Fundamentals.

The features that appear between 2255-2275 cm^{-1} and 1400- 1425 cm^{-1} are characteristic of organic isocyanates and have been studied in a variety of molecules (26,28-32,41-43). The two stretches are a result of the interaction between the N=C bond and the C=O bond of the isocyanato group. The degree to which they interact is seen in the separation of the two peaks. The higher energy peak is associated with the asymmetric stretch and is very prominent in the infrared while being very weak in Raman spectra. The symmetric stretch appears to be prominent in both the Raman and infrared spectra. Table 3.1 gives a comparison of the NCO stretching frequencies. The slight increase in frequency correlates with an increase in electronegativity. The NCO asymmetric stretch presents no clear evidence to support the possibility of the existence

of two conformers in the liquid Raman spectra but one should remember the peak is very weak and somewhat broad so the lack of resolution and intensity may account for this.

The NCO symmetric stretch in the vapour phase infrared spectra did not prove any more useful in proving the existence of the second isomer but this is understandable since the cisoid geometry is the only isomer favoured in the gas phase. The liquid Raman spectra, however, did show some interesting results in the symmetric stretching region for the isocyanato group. The Raman peak that is associated with the NCO stretch in each of the molecules was unsymmetrical. In particular, there is a shoulder that appears on the higher energy side of the main feature. And in the case of trichloroacetyl isocyanate, there are two distinct peaks separated by approximately 30 cm^{-1} (1453/1426 cm^{-1}). The higher energy shoulders (peak in the case of TCAI) are attributable to the higher energy transoid conformer which tends to gain population upon going to the condensed phase. The two peaks in TCAI were of equal intensity in the Raman spectra in the liquid phase. Cooling the sample provided us with some valuable information. Upon cooling, the intensities of the peaks changed; the higher energy peak lost intensity . Heating the Raman cell slightly caused an increase in intensity for this same peak. This information has persuaded us to assign the higher energy peak to the transoid isomer.

Our results mimic other variable temperature data of related carbonyl isocyanates (28) in that the results present evidence that appreciable amounts of the less stable conformer are found in liquid phase and in some cases, there is evidence to support the idea of different conformers in both the vapour and liquid phase. It is then natural to assume that additional features that arise, elsewhere in the

spectra, on going from the gas phase to the liquid phase (or vice versa) are a result of an increase (decrease) in population for the less stable conformer.

Table 3.1. Comparison of Observed NCO Stretching Frequencies (cm^{-1}) for Acetyl and α-Chloroacetyl Isocyanates.

	Mode	H_3C- species	$H_2C\ell C$- species	$C\ell_2HC$- species	$C\ell_3C$- species
Vapour	ν NCO_{as}	2255	2264	2273	2258
	ν NCO_s	1466	1415	1425	1422
	ν_{ave} NCO	1860	1840	1849	1840
Liquid	ν NCO_{as}	2240	2246	2258	2259
	ν NCO_s	1406	1408	1431	1426
	ν_{ave} NCO	1823	1827	1844	1843

There are other prominent features in the spectrum of acetyl isocyanate near the region of the isocyanato symmetric stretch. Since they do not occur in the spectra of trichloro-acetyl isocyanate, these bands are attributed to the methyl component (CH_n) of the molecules. In the Raman spectrum of AI, the strong band that appears at 1364 cm^{-1} is assigned as the symmetric methyl deformation mode. The peak is observed in the ir spectrum as a medium-weak feature. This intensity relation in the two spectra is indicative of symmetric modes. The deformation's asymmetric counterpart lies somewhat higher in energy in both spectra. The fundamental appears as a shoulder on the NCO symmetric stretch of the infrared spectrum at a frequency of 1442 cm^{-1}. Similar arguments are used to assign the CH_2

deformation modes in the Raman spectra of CAI as well as the CH deformation mode in DCAI.

The other peak in the vibrational spectra of this series of molecules relative to the methyl substituent is the CH_n rocking motion. This motion usually lies in the region of the spectrum between 800 cm^{-1} and 1000 cm^{-1}. In acetyl isocyanate this feature appears around 990 cm^{-1} while in chloroacetyl isocyanate the peak occurs at a lower frequency (~850 cm^{-1}). This is consistent with that observed by Durig et al. in their brief mention of acetyl isocyanate (26).

The fundamental modes that describe the motions of the methyl group will be analogous in nature to those in $CC\ell_3$ since all the substituents on the methyl carbon atom are equivalent. The same logic can be applied to CH_n and $CC\ell_n$ in the monochloro- and dichloro-substituted acetyl isocyanates where the motions of the C-Cℓ bond in CAI and C-H bond in DCAI will be the same but located at different frequencies. This is understandable since the chloro species are heavier than the methyl compound causing their fundamentals to appear at lower frequencies. In-depth analyses on α-chloroacetaldehydes and acetamides (38,37) have made assignments pertaining to the carbon-chlorine bond in α-chloroacetyl isocyanates relatively unambiguous. Table 3.2 shows the comparison of these modes in the three sets of molecules.

3.2d. Other Notable Fundamentals.

The other fundamentals left to be assigned are the C-C and C-N stretching modes. Although we designate particular peaks as either C-C or C-N, in essence, an actual peak is of

mixed character because of the interaction (coupling) between these two stretches. The C-C stretching frequencies for these α-chloro-substituted acetyl isocyanates would be similar to acetyl halides since the isocyanato group is considered a pseudohalogen. Assignments have been made on this assumption and the features that appear for the C-C stretch are found in the region between 1060 and 1160 cm^{-1}. If this designation is correct, then there appears to be a slight increase in frequency with increased electronegativity. The C-N stretching mode couples with the C-C stretch and also couples with the NCO stretch. It can be concluded from this that the C-N stretch is affected by its environment. This is seen in the force field calculations of carbonyl diisocyanate which shows that the fundamentals associated with the NCO symmetric stretch and the C-N stretch are of mixed character (30). The predominently C-N stretching mode is observed between 750 and 850 cm^{-1} and this is consistent with other C-NCO systems (26,41-43).

3.3 Cisoid/ Transoid Isomerism

Since all species of the α-chloro-substituted acetyl isocyanates show the same spectral changes for the NCO symmetric stretch, it can be concluded that the isomerism that occurs is a result of the rotation of the isocyanato group about the C-N bond and not a consequence of rotation of the acyl group about the C-C bond. The gas-phase infrared spectra of the acetyl isocyanates can be adequately assigned if the assumption of the presence of only one isomer is valid. In this family of molecules, the *cisoid* conformer is believed to be more stable than its *transoid* counterpart. This is believed to be the case for a number of reasons. Semi-empirical AM1\MNDO calculations show the

cisoid conformer to be more stable in each of the chloro-substituted isocyanates (39). Secondly, the gas phase microwave spectral analysis of acetyl isocyanate reached the same conclusion, namely that the more intense lines found in the microwave spectrum were that of the *cisoid* conformer (25). Sterically, one would theorize that the isocyanato group would prefer being as far away as possible from the bigger chlorine atoms. The *cisoid* geometry accommodates this argument.

Table 3.2. Observed Frequencies (cm^{-1}) seen in α-chloroacetyl isocyanates, α-chloroacetaldehydes and α-chloroacetamides. Uncertainties are- ir: ±2 cm^{-1}, R: ±3 cm^{-1}.

	Fundamental	R-CO-H (38)	R-CO-NH_2 (37)	R-CO-NCO this work
$CC\ell_3$- species	ν $CC\ell_3$ symmetric	850	834	848
	asymmetric	733	826	738
	δ $CC\ell_3$ in-plane	269	313	286
	out-of-plane	244	289	251
	ρ $CC\ell_3$	204	-	202
$CHC\ell_2$- species	ν $CC\ell_2$ symmetric	437	-	424
	asymmetric	800	828/773	807
	δ $CC\ell_2$	399	292	363
	ρ $CC\ell_2$	228	-	202
$CH_2C\ell$- species	ν C-Cℓ	619	777	608
	δ C-Cℓ	335/220 (277)	268	341/240 (290)

There are examples of related carbonyl isocyanates in which the presence of both conformers are detected in appreciable amounts (28-32) in both the vapour and liquid phase. Our work on trichloroacetyl isocyanate and other variable temperature analyses of related carbonyl isocyanates have shown that the more stable conformer is indeed the *cisoid* conformer. One conclusion that can be reached is that there are appreciable amounts of both the *cisoid* and *transoid* isomer present in the liquid phase at room temperature for acetyl isocyanate and its chloro-derivatives. The additional spectral features arise from the higher energy conformer that gains population for the condensed phase.

Table 3.3 **Observed Frequencies (cm^{-1}) and Assignments in Acetyl Isocyanate.**

Infrared vapour	Raman liquid	Assignment
3634 w		2255 + 1406 = 3661
3500 vw		2x1758 = 3516
3406 vw		2255 + 1146 = 3401
3042 w	3030 ms	$\nu_{as}(CH_3)$
2989 vw	2985 ms	$\nu_{as}(CH_3)$
2949 vw	2941 vvs	$\nu_{s}(CH_3)$
2869 vw	2845 mw	2x1419 = 2838
	2715 w	2x1364 = 2728
2360 w		1363 + 991 = 2354
2273 vvs	2258 vw	$\nu_{as}(NCO)$
2194 ms		1159 + 1057 = 2216
2049 vw		1057 + 991 = 2048
1951 vvw		1159 + 798 = 1957

1758 vs	1745 vs	ν(CO)
1596 w		2x798 = 1596
1442 w		$\delta_{as}(CH_3)$
	1419 vs	ν_s(NCO) *transoid*
1406 s	1406 m,sh	ν_s(NCO) *cisoid*
1363 mw	1364 s	$\delta_s(CH_3)$
1294 vw	1310 vw	2x649 = 1298
1241 mw	1267 vw	
1159 s	1154 w	ν(CC)
1057 w		
991 ms	993 m	$\rho(CH_3)$
798 m	791 ms	ν(CN) *cisoid*
	771 s	ν(CN) *transoid*
649 ms	653 s	δ(NCO) *cisoid; a'*
621 m	618 w,sh	δ(NCO) *cisoid*; a"
	566 w,sh	
551 w	548 m	δ(CCO) *cisoid*
	533 m	δ(CCO) *transoid*
	398 mw	δ(CCN)
	344 vw	

Table 3.4 Observed Frequencies (cm^{-1}) and Assignments in Chloroacetyl Isocyanate.

Infrared vapour	Infrared liquid	Raman liquid	Assignment
	3022 w,sh		1731 + 1299 = 3030
	2999 mw	3005	$\nu_{as}(CH_2)$
2964 vw	2953 m	2958 vvs	$\nu_s(CH_2)$
		2856 vw	2x1439 = 2878
	~2544 vw,br		2x1270 = 2540
	2341 m,sh		1731 + 602 = 2333
2264 vvs	2246 vvs	2246 vvw	ν_{as}(NCO)
2226 ms,sh			1163 + 1066 = 2229
2196 mw,sh			2x1110 = 2220
			1415 + 804 = 2219
	2079 vvw,sh		1731 + 340 = 2071

1788 mw,sh			1415 + 401 = 1816 ?
1752 vs	1731 vvs	1737 vs	ν(CO) *cisoid*
	1584 vw		2x792 = 1584
1448 mw,sh			$\delta(CH_2)$
		1439 s	ν_s(NCO) *transoid*
1415 s	1425 vs	1408 m,sh	ν_s(NCO) *cisoid*
	1328 vw		792 + 528 = 1230
1274 mw	1299 w	1300 mw	$\delta(CH_2)$ *cisoid*
	1270 mw	1278 w	$\delta(CH_2)$ *transoid*
1237 w		1218 vw	2x608 = 1216
1196 w	1193 m	1186	(CH_2) twist
1163 w			
1110 m	1111 m		ν(CC) *transoid ?*
1066 ms	1066 vs	1069 w	ν(CC) *cisoid*
	918 m	~925 w,br	608 + 341 = 949
849 vvw	841 m,sh	848 m	$\rho(CH_2)$
804 ms	792 s	799 vs	ν(CN) *cisoid*
	745 w,sh	747 m	ν(CN) *transoid*
	699 m		
667 vw			CO_2 impurity
607 vw	602 ms	608 ms,br	δ(NCO)/ν(CCℓ)
534 w	528 m	555 m	δ(CCO)
418 vvw	414 vw	416 mw	δ(CCN) *cisoid*
	402 vw	401 w	δ(CCN) *transoid*
	340 vw	341 m	δ(C-Cℓ)
		240 m	δ(C-Cℓ)
		204 vw	

Table 3.5 Observed Frequencies (cm^{-1}) and Assignments in Dichloroacetyl Isocyanate.

Infrared vapour	Raman liquid	Assignment
3692 vvw		2273 +1425 = 3698
	3021 ms	ν(CH) *O-cis?*

2990 vw	2983 m,sh	ν(CH) N-*cis?*
2273 vvs	2258 vw	ν_{as}(NCO)
2246 ms,sh		1425 + 815 = 2240
2195 mw		1134 + 1068 = 2202
1764 vs	1746 vs	ν(CO)
	1717 w,sh	1076 + 629 = 1705
1443 m,sh	1446 s	ν_{s}(NCO) *transoid*
1425 s	1431 mw,sh	ν_{s}(NCO) *cisoid*
1262 vvw	1253 w	651 + 600 = 1251
1234 w,sh		815 + 424 = 1239
1222 mw	1215 w	δ(CH)
1197 vw	1198 w	777 + 424 = 1201
	1177 vw	749 + 424 = 1173
1156 ms	1159 vw	815 + (363) = 1178
1134 ms		774 + (363) =1137
1068 mw	1076 vw	ν(CC)
858 vw,sh	863 mw	600 + 251 = 851
		2x424 = 848
815 s	807 m	$\nu_{as}(CC\ell_2)$
774 mw	777 s	ν(CN) *cisoid*
	749 s	ν(CN) *transoid*
731 m		2x(363) = 726
	714 w	424 + 288 = 712
675 m		(363) + (288) = 671
		(424) + (251) = 675
	629 ms	δ(NCO); a'
600 mw	600 s	δ(NCO); a"
	424 vvs	$\nu_{s}(CC\ell_2)$
	363 m	$\delta(CC\ell_2)$
	288 m	
	272 m	
	251 m	$\omega(CC\ell_2)$
	202 ms	$\rho(CC\ell_2)$

Table 3.6. Observed Frequencies (cm^{-1}) and Assignments in Trichloroacetyl Isocyanate.

Infrared vapour	Infrared liquid	Raman liquid	Assignment
2559 vw			1448 + 1110 = 2558
2307 vw,sh			
2258 vvs	2254 vvs	2259 vw	ν_{as}(NCO)
2199 w	2195 w,sh		1110 + 1087 = 2197
	2153		1421 + 725 = 2156
	1802 w		1421 + 388 = 1819
1777 vs	1764 vs	1762 ms	ν(CO)
	1725 m,sh		
	1693 w,sh		2x843 = 1686
	1609 vw		1421 + (202) = 1621
	1584 vw		843 + 735 = 1578
	1445 s,sh	1453 m	ν_s(NCO) *transoid*
1422 vs	1421 vs	1426 m	ν_s(NCO) *cisoid*
	1357 vvw		735 + 622 = 1354
	1280 w		843 + 440 = 1283
1262 vw	1273 w		669 + 600 = 1269
1220 w	1204 w		814 + (392) = 1206
1153 w	1152 w		2x579 = 1158
1110 s	1110 s	1117 s	ν(CC) *cisoid*
1087 m	1086 ms	1094 w	ν(CC) *transoid*
1020 w	1022 vvw		742 + 286 = 1028
	888 w,sh	888 w	2x443 = 886
		870 w	584 + 286 = 870
851 s	843 vs	848 mw	$\nu_{as}(CC\ell_3)$
814 ms	815 s	820 mw	$\nu_{as}(CC\ell_3)$
742 ms	735 ms	738 mw	ν(CN)
669 m	662 ms	665 mw	δ(NCO) *cisoid*; a'
	622 vw	633 w	δ(NCO) *transoid*; a'
600 mw	596 m	602 s	δ(NCO) *cisoid*; a"
	579 w,sh	584 ms	δ(NCO) *transoid*; a"
		522 mw	δ(CCO)
434 vw	440 vw	443 vvs	$\nu_s(CC\ell_3)$

414 w		
388 vw		
	392 ms	δ(CCN)
	368 vw	
293 vw		
282 w	286 s	$\delta(CC\ell_3)$
	251 m	$\delta(CC\ell_3)$
	202 ms	$\rho(CC\ell_3)$

3.4 Conclusion

We have presented the gas-phase infrared (and liquid-phase data where possible) and liquid-phase Raman spectra for a family of compounds with the structure R-CO-NCO, where R= CH_3, $CH_2C\ell$, $CHC\ell_2$, and $CC\ell_3$. Assignment of the observed bands in the spectra has been tabulated for each of these molecules. From the observations, there are two planar isomers present which are a result of rotation of the isocyanato group about the C-N bond. All evidence supports the *cisoid* isomer as the more stable conformer in the gas phase whereas there are appreciable amounts of both the *cisoid* and *transoid* isomers in the liquid phase.

Chapter 4
Methoxycarbonyl and Thiomethoxycarbonyl Isocyanate

4.1 Introduction

This chapter involves the presentation and analyses of the liquid and vapour phase infrared spectra as well as the liquid Raman spectra of methoxycarbonyl isocyanate (MCI) and thiomethoxycarbonyl isocyanate (TMCI). Details pertaining to the synthetic procedures followed during the course of preparation of these compounds are found in Chapter 2. MCI and TMCI differ from its precursor, chlorocarbonyl isocyanate, in relation to the substituent attached to the carbonyl isocyanate. In the reaction, the chlorine is replaced by a (thio)methoxy group (H_3C-E- where E= S or O). The spectra for these chlorocarbonyl derivatives (MCI and TMCI) are quite complex. This complexity offers evidence for the presence of more than one rotational conformer in both the liquid and gas phases. In looking at the possible conformations for these compounds, one can see that the possibility of *cisoid\transoid* isomerism exists based on rotation of the isocyanato group about the C-N bond. Further consideration shows that there is also the possibility of rotation of the methoxy group about the C(O)-O bond. Assuming that the molecule has a planar framework and that the rotation about the methyl-oxygen bond can be neglected, as heavy atoms would favour, there is the possibility of E\Z orientations of the methyl group relative to the carbonyl group. These isomeric forms are shown in Figure 4.1.

All of these conformations for MCI and TMCI can be characterized as belonging to the C_s point group each of which has twenty-four normal modes of vibration. The

twenty-four modes can be divided into 16 a′ (in-plane) and 8 a" (out of plane) representations. Under the C_s point group, all of these modes are infrared and Raman active. The twenty-four normal modes that each molecule possesses combined with the possibility of four distinct conformations, presents what could be a very complicated spectrum. If each isomer was present in the sample then there might possibly be ninety-six modes present in the vibrational spectra along with the vibrational overtones and combination bands producing a very congested spectrum.

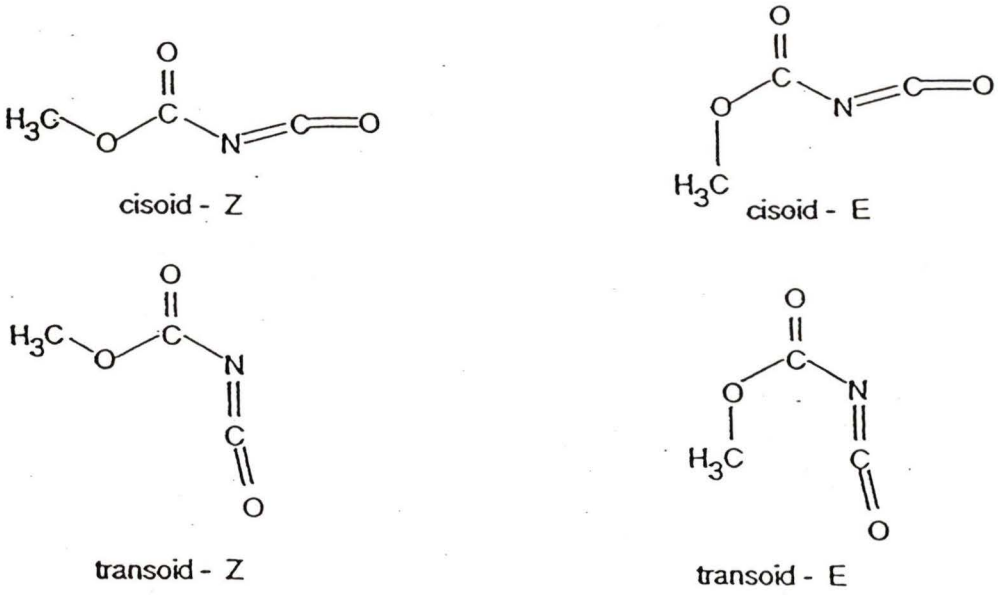


Fig. 4.1. The possible planar orientations of (thio)methoxy carbonyl isocyanate.

4.2 Results and Discussion

4.2a. Fundamentals of the Methyl Group.

Distinguishing between the conformers presents a challenge in the interpretation of the spectra. At first glance, it can be surmised that three of the four possible isomers have an equal probability of existence and therefore

make for the possibility of each being present in the spectrum. The fourth structure, the *transoid-E* geometry (Fig.4.1), is highly improbable for steric reasons. Examining the features in the spectra does allow for assignment of certain bands to its particular conformer. The distinction between the conformers will be discussed as a survey of the spectra is completed.

The stretching vibrations of the methyl group are indifferent to whether the methyl fragment is attached to an oxygen or sulfur atom. These vibrations appear in the region 3050 - 2900 cm^{-1} (Figures 4.3 and 4.4). There are three vibrations expected to appear in this region characteristic of this group: two asymmetric stretching modes and one symmetric stretch. Over time, literature precedents on molecules containing methyl groups have placed the asymmetric stretches at slightly higher frequencies than that of the corresponding symmetric stretch. Assignments of these fundamentals can be verified by looking at the Raman spectrum for either MCI or TMCI. The most intense line in this region should belong to the symmetric stretch. This is the case in these examples. The Raman spectrum shows a very strong peak at 2969 cm^{-1} for MCI and two weaker features at slightly higher energy (3019/3042 cm^{-1}). This is also evident in the Raman spectrum of TMCI with the exception that one of the asymmetric modes is not evident. This absence is the probable result of a lack of intensity for the fundamental, stemming from a very weak motion in the methyl group but, nevertheless, the motion is a characteristic mode of the molecule.

The deformation modes of the methyl group are very similar to those of methyl esters and have been looked at extensively. The deformation mode for the methyl group of MCI can be compared to that of methyl carbamate (44) so

assignment of this mode has been made simpler. This mode is typically located near 1450 cm^{-1} and so the feature at 1453 cm^{-1} in the ir spectrum (1456 cm^{-1} R) of MCI is assigned to the methyl deformation. In methyl carbamate, the deformation has an asymmetric and symmetric component and they can both be visible in the vibrational spectra. A second feature is not found in the spectrum of MCI. One must assume that the asymmetric and symmetric deformations are fairly similar in frequency so only one peak appears for this degeneracy.

Studies on thiocarbamate esters place these deformation modes at somewhat lower frequencies than their carbamate ester counterparts. The symmetric deformation of the methyl group in TMCI, in agreement with such a prediction, appears in the vicinity of 1320 cm^{-1} in the Raman and infrared spectra. The asymmetric deformation, however, is not seen in our spectrum whereas it is located around 1420 cm^{-1} in thiocarbamate (45). This motion, if it follows the trend of thiocarbamate esters, is expected to give rise to a band in the same region as the isocyanato symmetric stretch. It is more than likely that the asymmetric methyl deformation is masked by the more intense feature that is designated as the symmetric stretch.

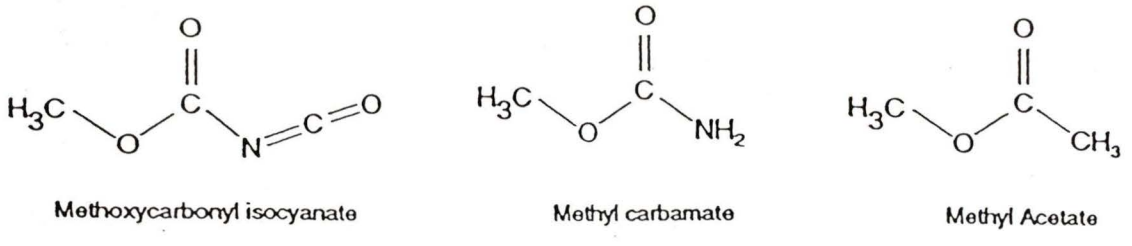


Fig.4.2. Methoxycarbonyl isocyanate and structurally related compounds.

The rocking motion of the methoxy group consists of an in-plane and out-of-plane vibration. In methyl acetate (46), the rocking motions are observed at 1194 (a′) and 1160 cm^{-1} (a") respectively. In the infrared spectrum of MCI, there are two peaks of equal intensity that appear in this vicinity. They are the only two peaks found in this region so it is logical to conclude that the features at 1194 cm^{-1} and 1180 cm^{-1} are those of the methyl in-plane and out-of-plane vibrations respectively. The rocking mode for the corresponding thiomethoxy mode is expected to be at a lower frequency due to the mass sensitivity of the mode. For example, in S-methylthiocarbamate (45), the rocking motion appears at 968 cm^{-1}. The feature is not seen in the spectra of TMCI. The fundamental is most likely masqued by the more intense C-N stretch.

There is a peak which appears at ~200 cm^{-1} on the shoulder of the Rayleigh line in the Raman spectra of MCI and TMCI. Peaks also appear as very weak features in the low frequency region of the ir spectrum (~210 cm^{-1}). These features are characteristic of methyl torsional modes and have been tentatively assigned as such.

4.2b. Vibrations of the Isocyanato Group.

The appearance of a strong infrared absorption in the region 2280-2250 cm^{-1} for both methoxy-carbonyl isocyanate and its thio derivative is expected according to the previous studies of other organic isocyanates studied by our group (31,32,48) and with those studied by others (26-29,32,41-43). This asymmetric stretching fundamental, however, as in the examples referenced above, displays only a weak Raman signal. Mass sensitivity does not seem to exhibit as much influence on the observed band with this

fundamental mode as it does with the other fundamentals. The difference in position of the stretch in the infrared spectra of the two molecules, MCI and TMCI, is less than 10 cm^{-1} (2262 and 2257 cm^{-1} respectively). This is expected upon examination of the structures of the molecules. The NCO group is not directly attached to the oxygen or sulfur atom so the substituent is far enough removed from the isocyanato group to cause any significant changes in its absorption frequency. In such a case the asymmetric vibration is fairly independent of structural change.

In contrast to the lack of intensity of the asymmetric peak, the symmetric NCO stretch gives rise to a rather intense Raman feature; in the ir spectrum the isocyanato symmetric stretch is much weaker than its asymmetric counterpart. This is not out of character for symmetric and asymmetric stretches of the isocyanato group as observed in the spectra of other carbonyl isocyanates (26-35,41-43,47). As in the asymmetric case the distance of the isocyanate group from the sulfur atom does not appear to be an influence in peak displacement. Whether the substituent is the methoxy or thiomethoxy group, the location of the symmetric stretch does not vary considerably. The frequency assigned to the NCO symmetric stretch in both MCI and TMCI does not differ greatly for the two molecules. The stretch for MCI appears at 1420 cm^{-1} while in TMCI, it appears at 1404 cm^{-1}. The isolation of the isocyanato group from the rest of the molecule is evident in our results.

There are two peaks (1420\1413 cm^{-1}) of equal intensity in the infrared vapour spectrum of MCI. These have been assigned to the *cisoid\transoid* geometries respectively. These bands appear at 1404\1384 cm^{-1} for the same phase in the spectrum of TMCI. This further supports the assignment of the methyl deformation at 1453 cm^{-1} in MCI as well as the

assignment of the NCO symmetric stretch. If the peak at 1453 cm^{-1} were the NCO symmetric stretch, one would expect to see a similar peak in TMCI since the motion appears to be essentially mass independent. Since there is no peak in this region of the spectra of TMCI the band at this frequency is not characteristic of the NCO symmetric stretch. The methyl bending motion, however, is mass-dependent and appears at a much lower frequency in the spectra of TMCI than its methoxy counterpart. As in thiocarbamate esters, this bend was found to appear around 1320 cm^{-1} (too low for a NCO symmetric stretch) thus leaving the two peaks at 1404 and 1384 cm^{-1} to be undoubtedly the NCO symmetric stretches.

Since there are two features present in the vapour-phase infrared spectrum for this fundamental, it can be concluded that appreciable amounts of both isomers are present in the vapour and liquid phases. Distinction between the possible isomers was made on the basis of AM1/MNDO calculations (39). In both compounds, the *cisoid* isomer was calculated to have the higher frequency. Also, since the lower frequency peak gains intensity on going to the condensed phase for MCI, it can be assigned to the higher energy *transoid* isomer since upon going to the liquid phase, the less stable isomer gains intensity. This reasoning correlates with the explanation offered by Durig et al. in their explanation of the presence of two isomers in the liquid vibrational spectra of chlorocarbonyl isocyanate (28).

Deformations of the NCO group are found in the region 600- 660 cm^{-1} as they are in other acyl isocyanates (28,30,47). This vibration can take place in the plane as well as out of the plane of the molecule therefore there are two peaks found in the spectra for this motion. The in-plane deformation appears at a slightly higher frequency

than the out of plane bend. This occurs in both MCI and TMCI where the motions are separated by approximately 40- 50 cm^{-1}.

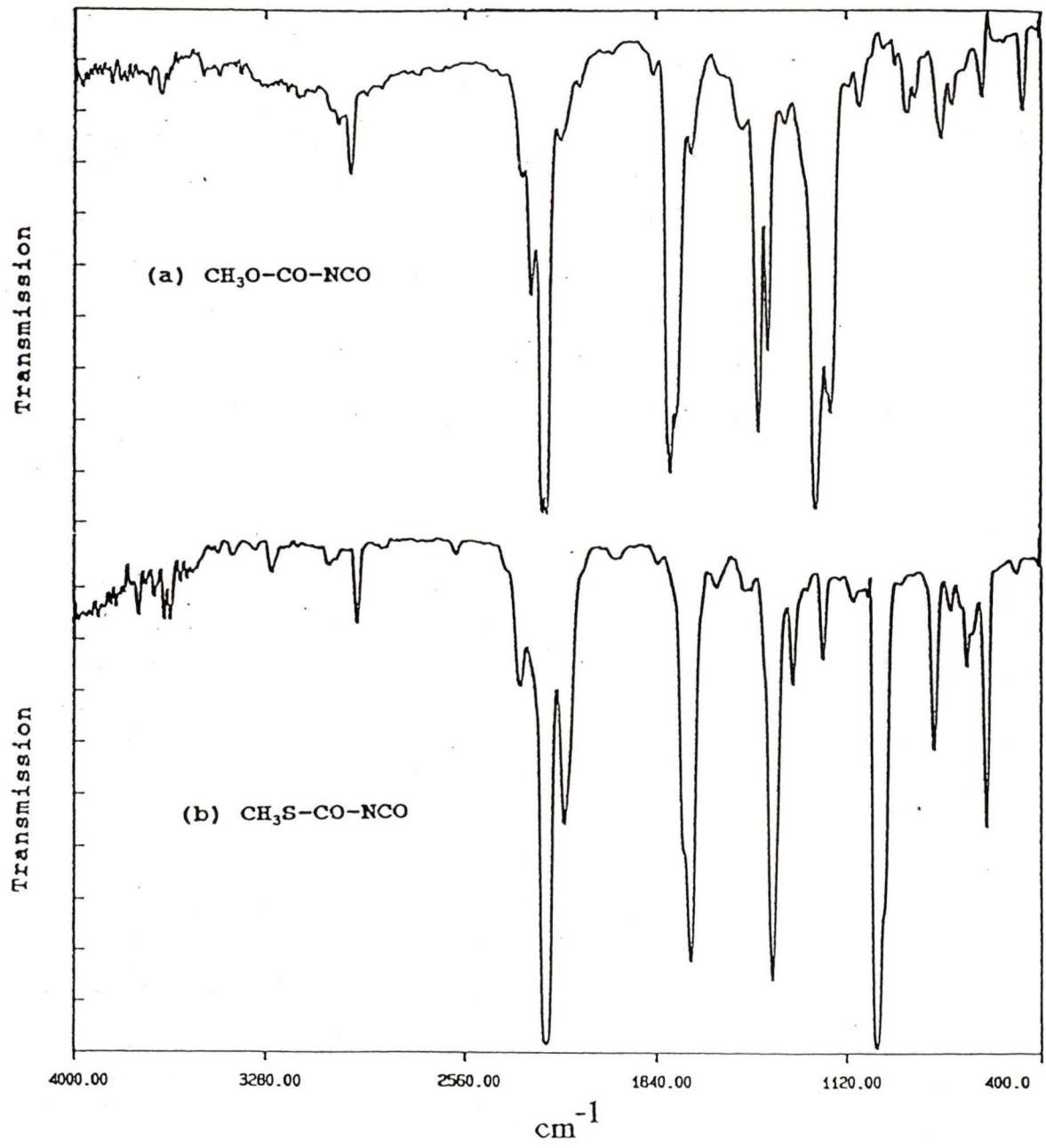


Fig.4.3. The vapour phase infrared spectra of: (a) MCI, P = 5 Torr; and (b) TMCI, P = 3 Torr.

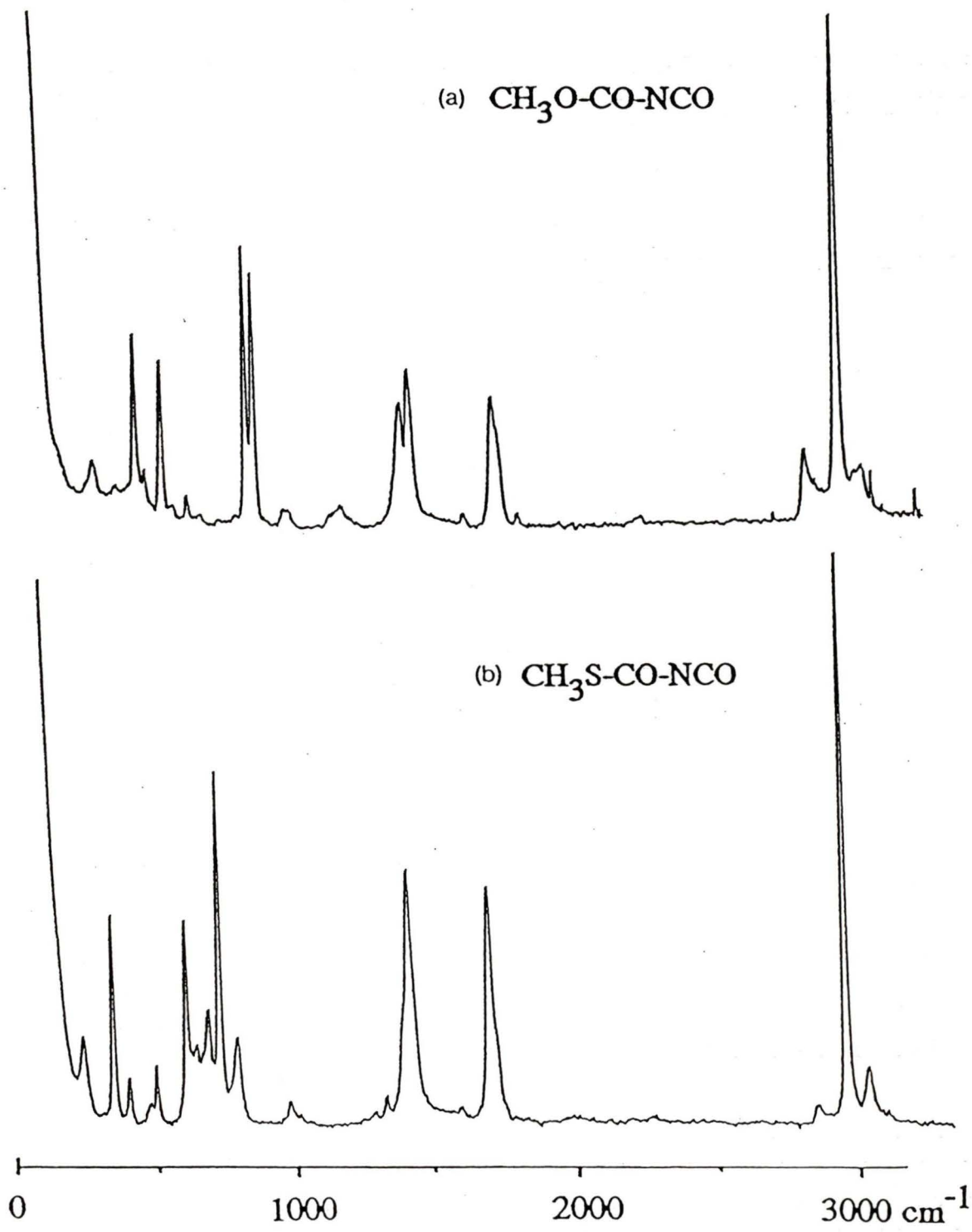


Figure 4.4. The liquid Raman spectra of (a) MCI and (b) TMCI.

4.2c. The Carbonyl Region.

The liquid and vapour phase spectra of MCI and TMCI, unlike the spectra of their acetyl and chloroacetyl carbonyl isocyanate relatives, do show evidence of different conformers being present in their respective carbonyl stretches. Examination of Figures 4.3 and 4.4 shows that there are indeed two absorptions present in the infrared spectra. There is still some question though as to which conformer is which. The *transoid-E* conformer can be excluded because of steric reasons but there remain three possible isomers and only two bands present in the spectra. The higher frequency stretch (1795 cm^{-1}) in MCI exhibits an AB hybrid contour which, based on predicted moments of inertia, is expected only for the *transoid-Z* isomer. The lower frequency stretch (1764 cm^{-1}) has a B- type band contour which is expected for both cisoid conformations. Also in support of the *transoid-Z* assignment are the results of semi-empirical (AM1) calculations which predict this isomer to have the highest frequency of the three (39).

No differentiation of the two cisoid isomers can be made based on ν(CO) band contours since both the *Z* and *E* conformers should exhibit B-type character. This then makes it impossible for further assignment of the peak at 1764 cm^{-1} without having more information available. Calculated frequencies (16,39) do not allow for a reasonable assessment either since the carbonyl stretches for the two isomers are calculated to differ by only 1 cm^{-1}. To distinguish between the two cisoid geometries, in order to assign the peak at 1764 cm^{-1}, we had to look at another fundamental.

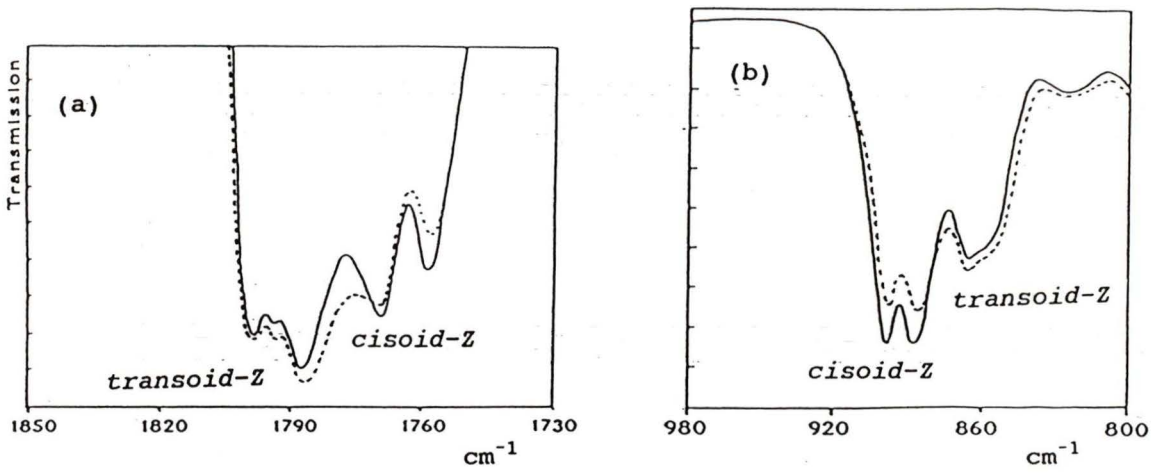


Fig. 4.5. Variable-temperature results for (a) the carbonyl stretching region and (b) the C-N stretching region of MCI: 20°C (solid line); 50°C (dashed line).

4.2d. C-N Stretching Mode.

Comparison of the C-N stretches in the acetyl and chloro-substituted acetyl isocyanates to the same stretch in MCI\TMCI gives a good example of how mechanical coupling of the R- substituent with the C-N bond varies the frequency of the C-N stretch dramatically. From the scan of the frequencies assigned to the C-N stretch in other reported acyl isocyanates, one can see that the nature of the substituent affects the position of the C-N stretch greatly. For example, in our analysis of the acetyl isocyanate and its chloro-derivatives, the C-N stretch was located in the region 770-800 cm^{-1} whereas in MCI and TMCI the C-N stretch appears almost 100 cm^{-1} greater in frequency (896 and 1001 cm^{-1} respectively) than that of acetyl isocyanate.

It is with reference to the C-N stretch that we can differentiate between the two cisoid conformers, *cisoid-E* and *cisoid-Z*. Although the frequency of the C-N stretch is reported over a fairly diverse range of frequencies, and no

general conclusions can be made on its location with respect to substituent, this fundamental does play a vital role in the distinction between the different isomers present in the phases studied here. The two isomers that contribute to the C-N region of the infrared spectra are well resolved ($\Delta\nu$= 30 cm^{-1}). Variable temperature experiments revealed that the lower frequency peak at 862 cm^{-1} gains intensity upon heating while its counterpart at 892 cm^{-1} loses intensity upon heating. This supports the assignment of the lower energy peak to the *transoid-Z* conformer and correlates with the (AM1) calculated C-N stretching frequency for the conformer which places the mode at 867 cm^{-1} (39). Determination of the *transoid-Z* isomer has simplified the task of distinguishing between the cisoid conformers. Since the experimental value for the cisoid feature is 892 cm^{-1}, it can be assigned to the *cisoid-Z* isomer. This conclusion was reached by comparing the experimentally obtained value with the calculated values for the *cisoid-Z* and *cisoid-E* conformers. The calculated value for the *cisoid-Z* value is 888 cm^{-1} whereas the *cisoid-E* geometry has an expected C-N stretching frequency of 852 cm^{-1}. The difference in frequency between the two geometries enables easy assignment. This calculated value for the *cisoid-E* conformer is lower than that of the *transoid-Z* isomer. Experimentally, the order of peak appearance is reversed. It can therefore be concluded that the feature at 892 cm^{-1} is the *cisoid-Z* isomer.

This assignment to the respective conformers can be further supported by the knowledge that in esters, Z-isomers are favoured over E-isomers (48,49). An analogy is drawn between the methoxycarbonyl isocyanate and esters since both share the basic RO-CO-R structure (shown in Figure 4.2). In these types of molecules, the Z-isomer is favoured because of the interaction between the oxygen lone electron pair and

the antibonding σ-orbital of the carbonyl bond. This interaction tends to stabilize the Z-isomer through resonance. If the molecule was oriented in the E-geometry, the alignment of orbitals would not favour this stabilization because of misalignment of the contributing orbitals.

Another factor favouring the Z-preference is that the ester C-O bond dipole in the Z-rotomer is in opposition to the carbonyl bond dipole thus reducing the overall dipole moment of the molecule and resulting in increased bond strength. The E-rotomer has these bond dipoles aligned such that the overall effect is additive making the overall dipole moment larger resulting in a decreased bond strength. Since stabilization favours the reduction of this overall molecular dipole, the Z-isomer is preferred over its E-rotomer counterpart. This has been shown in molecules such as methyl formate, formic acid and methyl acetate (49,50).

Thiomethoxycarbonyl isocyanate is expected to exhibit the same trends as MCI. The isomeric possibilities are equally as probable in TMCI as in MCI even though the orbitals on the sulfur atom may not have as effective an overlap due to a greater separation between the sulfur atom and carbonyl carbon atom. Distinguishing between the *cisoid-Z* and *cisoid-E* isomers in TMCI presented the same problems as in MCI. In this instance VT-IR spectroscopy did not prove as beneficial as it did in MCI because both of the C-N stretching vibrations in question have similar calculated values. However, one can argue by analogy that the *cisoid-Z* isomer would be the more stable conformer based on the assumption that the Z-ester preference holds true. This has been shown for carbonyl sulfenyl compounds such as H-CO-SH and F-CO-SCH_3 (48). It should be noted, though, that the effects that favour the Z-isomer are weaker for thiomethoxy compounds than for methoxy compounds. This

perhaps could explain why the C-N stretching frequencies for both cisoid conformers are very similar in TMCI.

4.2e. Vibrations Involving the C-O and C-S Bonds.

In the region between 900 and 1180 cm^{-1} where the methoxy C-O stretch is expected to appear, there is only one peak appearing in the liquid infrared spectrum of MCI. There is also a peak of weak intensity in the Raman spectrum at 1006 cm^{-1}. These peaks are assigned to the C-O stretch. The thiomethoxy C-S stretch in TMCI appears as a medium feature in the Raman spectrum at 684 cm^{-1}. This feature is analogous to the S-methyl thiocarbamate (45) and to dimethyl thioether (51) whose H_3C-S frequencies are reported at 696 and 692 cm^{-1} respectively. This same feature is observed in the infrared spectrum of TMCI but only very weakly.

The carbonyl carbon-oxygen (sulfur) vibration, is observed at a higher frequency than the (thio)methoxy C-O(S) vibration. The S-C stretch is found at 725 cm^{-1} and the O-C stretch is located at 1236 cm^{-1}. The reason that the carbonyl carbon-oxygen bond is stronger than the methyl carbon- oxygen bond can be explained by resonance. The C-O bond of the O-C=O fragment can acquire partial double bond character through resonance thus increasing the bond order of the O-C bond making it more stable and this is seen through the higher frequency of the O-C bond in relation to the methyl carbon-oxygen bond. With the bond being more stable, it will take more energy to cause the bond to vibrate.

The only other fundamentals that remain to be assigned are the skeletal bending vibrations such as the C-O-C and C-S-C deformations. These deformations appear in the low energy region of their respective spectra. The COC bend in

MCI was located at 320 cm^{-1} and 321 cm^{-1} in the liquid ir and Raman spectra respectively and almost 80 cm^{-1} lower in its TMCI derivative (235 cm^{-1} ir\ 240 cm^{-1} R). This is consistent with the results found in methyl carbamate (44) and S-methyl carbamate (45). The (S\O)-C-N bonds also show the same mass dependence relationship. The O-C-N deformation appears at 474 cm^{-1} in methoxycarbonyl isocyanate while for thiomethoxy-carbonyl isocyanate the deformation appears at 346 cm^{-1}. Assignments for the observed features for both of these molecules are listed in Tables 4.1 and 4.2.

Table 4.1. Observed Frequencies (cm^{-1}) and Assignments for Methoxycarbonyl Isocyanate.

Infrared vapour	Infrared liquid	Raman liquid	Assignment
3666 vw	3674		2253 + 1423 = 3676
3504 vvw	3482		2262 + 1235 = 3497
	3293 mw		2253 + 1027 = 3280
3154 vvw			2262 + 892 = 3154
	3137 vw		2253 + 888 = 3141
3036 vvw	3040 w,sh	3042	$\nu_{as}(CH_3)$; a'
3014 vvw	3016 mw	3019 mw	$\nu_{as}(CH_3)$; a"
2969 w	2963 ms	2969 vvs	$\nu_{s}(CH_3)$; a
2918	2894		2x1454 = 2908
2877 vvw			2262 + 612 = 2874
2856 vvw	2850 vw	2852 mw	2x1420 = 2840
2730 vvw			2262 + 466 = 2728
2652 vvw	2648 vw		1764 + 892 = 2656
			1423 + 1236 = 2659
2346 w	2340 ms,sh		1453 + 892 = 2345
2312 mw			1453 + 862 = 2315
2262 vvs	2253 vs	2250 vw	ν_{as}(NCO)
2201 w			1453 + 763 = 2216

	2194 m,sh		1423 + 760 = 2183
2130 vw	2124 w,sh		1235 + 892 = 2127
	1846 vw	1834w	1236 + 604 = 1840
1795 s	1800 vs	1764 ms,sh	ν(C=O) *transoid*
1764 s	1746 vs	1750 ms	ν(C=O) *cisoid*
	1638 ms		1423 + (215) = 1638
			1177 + 468 = 1645
	1523 m		
1453 mw	1448 m,sh	1456 ms	$\delta_{as}(CH_3)$; $\delta_s(CH_3)$
1420 ms	1423 s	1424 m	ν_s(NCO) *cisoid*
1413 ms			ν_s(NCO) *transoid*
	1315 m		
1235 vs	1236 ms	1236 vw	ν(CO)
1194 s	1190 m,sh	1196 w	$\rho(CH_3)$; a'
1180 s	1177 s	1171 w	$\rho(CH_3)$; a"
	1027 m		
		1006 w	$\rho(CH_3\text{-}O)$
	992 w	993 w	Cℓ-CO-NCO impurity
892 w	888 ms	896 s	ν(CN) *cisoid*
862 w	861 ms	867 s	ν(CN) *transoid*
	823 mw	821 vw	
763 w	760 w	764 vw	δ(OCO); a"
724 w			
		696 vw	
	654 vw	658 w	δ(NCO); a'
612 w	600 w	604 vw	δ(NCO); a"
572 vw	566 w	567 ms	δ(OCO); a'
	501 vw	507 w	321 + 190 = 511
466 w	468 ms	474 ms	δ(OCN)
	395 w	397 vw	2x190 = 380
	320 w	320 vw	δ(COC)
	~215 w,sh	~190 vw,sh	$\tau(CH_3)$

Table 4.2. Observed Frequencies (cm^{-1}) and Assignments for Thiomethoxycarbonyl Isocyanate.

Infrared vapour	Infrared liquid	Raman liquid	Assignment
	3756 vvw		
3653 vw			2257 + 1404 = 3661
3635 vw			2257 + 1384 = 3641
	3620 vw		
3462 vvw	3477 vvw		2257 + 1208 = 3465
3394 vvw			2x1709 = 3418
3233 vvw	3255 vvw		2257 + 1004 = 3261
3046 vvw			$\nu_{as}(CH_3)$; a'
3023 vvw	3029 vvw	3021 m	$\nu_{as}(CH_3)$; a"
2945 w	2938 w	2940 vvs	$\nu_{s}(CH_3)$; a'
2850 vvw	2832 vvw	2835 mw	
2360 mw			
2257 vvs	2241 vvs	2241 vvw	ν_{as}(NCO)
2187 w			1404 + 787 = 2191
2177 vw,sh	2174 w,sh		1384 + 787 = 2171
1836 vvw	1811 vvw		
1740 ms	1710 ms	1711 ms,sh	ν(C=O) *transoid*
1709 s	1686 s	1689 s	ν(C=O) *cisoid*
	1588 w	1585 w	2x786 = 1572
	1504 vvw		996 + 495 = 1491
1404 s	1405 s	1407 s	ν_{s}(NCO) *cisoid*
1384 m,sh	1380 m,sh	1385 ms, sh	ν_{s}(NCO) *transoid*
1323 w	1319 w	1319 mw	$\delta(CH_3)$
1270 vvw	1283 vvw	1265 w	2x637 = 1274
	1246 vvw	1231 vvw	637 + 604 = 1241
1208 w			
	1194		2x595 = 1190
1004 vs	996 vs	1001 vvw	ν(CN) *cisoid*
973 s,sh	971 s,sh	965 vw	ν(CN) *transoid*
787 m	782 mw	786 m	
727 mw	731 w	725 vs	ν(CS)

689 m	678 vw	684 m	$\nu(CH_3-S)$
639 vvw	638 mw	637 mw	δ(NCO); a'
606 mw	595 mw	604 ms	δ(NCO); a"
490 vvw	495 mw	498 w	δ(OCS)
		470 vw	2x240 = 480
	410 w	403 w	2x202 = 404
	340 w	346 ms	δ(SCN)
	235 vw	240 mw	δ(CSC)
	213 vw,sh	~202 w,sh	$\tau(CH_3)$

4.3. Conclusion

With the information gathered from the infrared and Raman spectra of (thio)methoxycarbonyl isocyanate, vibrational analyses of the two compounds was achieved. It was determined from evidence in the vibrational spectra that two conformations of a possible four isomers were present, in both the liquid and vapour phases of the samples, for methoxycarbonyl isocyanate as well as two conformations for its thio derivative. With the aid of analyses of other acyl isocyanates and methyl esters as well as variable-temperature infrared spectroscopy, the two isomers present in the vibrational spectra were determined to be the *transoid-Z* and *cisoid-Z* isomers. It can also be concluded that the stretching fundamentals of the isocyanato group were not affected by the substitution of a sulfur atom in place of an oxygen atom (i.e. methoxy group vs. thiomethoxy group).

Chapter 5
Carbonyl Diisocyanate (CDI)

5.1 Introduction

In the previous two chapters, acyl isocyanates were analyzed in regards to various substituents and their effect on the vibrations of the carbonyl isocyanate skeleton. This chapter will continue this study. The infrared and Raman spectral data will be presented for the unique acyl isocyanate that has, as a substituent, another isocyanate group. This molecule is known as carbonyl diisocyanate (CDI) and its general structure is shown in Figure 5.1.

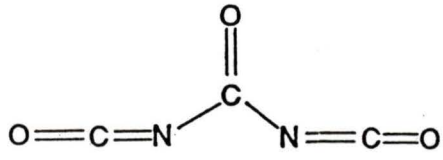


Fig. 5.1. General Structure of CDI.

As one can conclude from the figure, CDI has the general structural formula X_2CO where both X-substituents are identical. The vibrational spectra of X_2CO molecules where X = H, halogens (i.e. Cℓ, F), or pseudohalogens (i.e. -C≡CH, -C≡N) have been studied extensively. Since the isocyanato group may be considered a pseudohalogen, a good analogy can be drawn between carbonyl diisocyanate and diethynyl ketone [CO-$(C{\equiv}CH)_2$] and carbonyl cyanide [CO-$(C{\equiv}N)_2$]. Vibrational analyses of the latter molecules were carried out by Harney, Miller and Tyrrell in the early 1970's (52). CDI, however, unlike its other acyl isocyanate counterparts, has come to the forefront of vibrational study only recently so a study

of the disubstituted carbonyl isocyanate is timely.

This group of molecules [CO-$(C\equiv CH)_2$, CO-$(C\equiv N)_2$, and CO-$(NCO)_2$] are quite similar in structure. These molecules are also similar, being isoelectronic. However, in one respect, CDI is different from the other two examples.

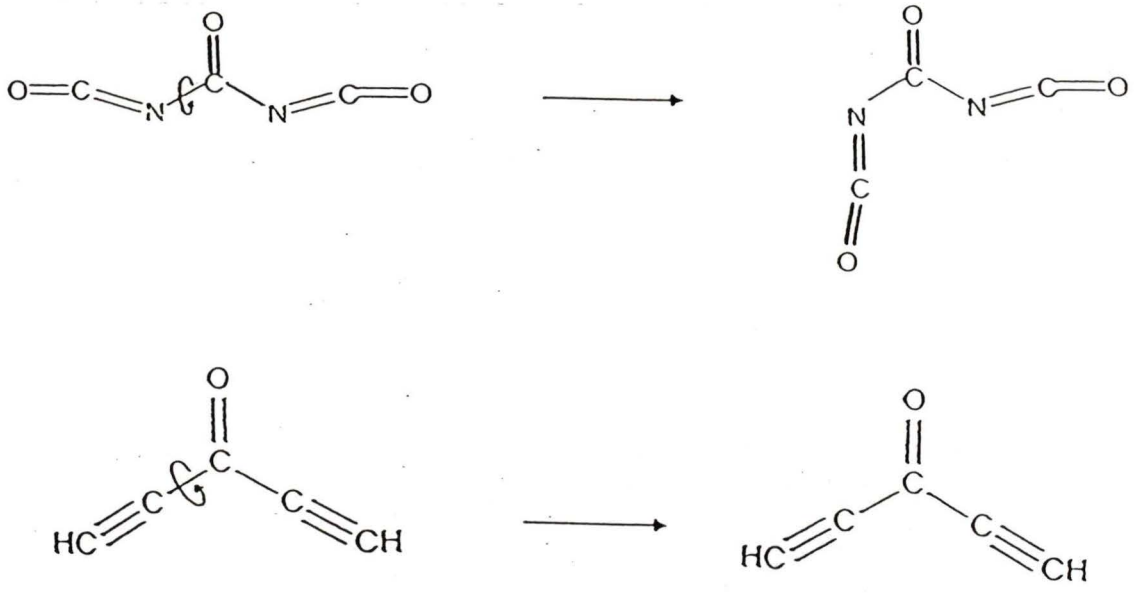


Fig. 5.2. Rotation of the NCO group about the C-N bond showing one of the possible orientations of CDI in comparison to the rotation of the HC≡C- group about the C-C bond.

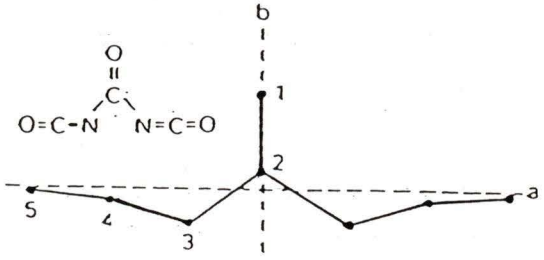
Both the cyano and ethynyl substituents are nearly linearly attached to the carbonyl carbon atom so they exhibit only one conformation. However the isocyanate group of disubstituted carbonyl isocyanate is not linearly attached to the carbonyl carbon atom so it can exhibit more than one conformation. Internal rotation about the C-N bond allows different geometric structures whereas rotation about the C-C bonds in carbonyl cyanide and diethynyl ketone leads to the same geometric structure.

Carbonyl diisocyanate can exist in a number of different conformations since each isocyanato group can independently adopt a *cisoid*, *transoid* or *gauche* orientation with respect to the carbonyl group although conjugation tends to eliminate the possibility of a gauche geometry. Regarding the planar geometry of CDI, three isomers have to be considered as being viable: *cisoid-cisoid, cisoid-transoid,* and *transoid-transoid*. These conformations are shown in Figure 5.3. The *transoid-transoid* rotomer, as in the case of *transoid*-E conformation of MCI and TMCI, is sterically unfavourable. MNDO/AM1 calculated heats of formation (39) lend support to this conclusion. There is also evidence in the analysis of the carbonyl stretching fundamental (discussed later in section 5.2c) which also confirms that the *transoid-transoid* species is not present in the vibrational spectra of CDI. Comparison with other carbonyl isocyanates and variable-temperature spectral data confirm the presence of two conformers in the vapour-phase ir spectrum of CDI. Both the liquid Raman and liquid ir spectra also show evidence of the presence of two isomers. Evidence will be presented later in the discussion that the mixture of the two isomers present in the spectra consist of the planar *cisoid-cisoid* and *cisoid-transoid* conformers.

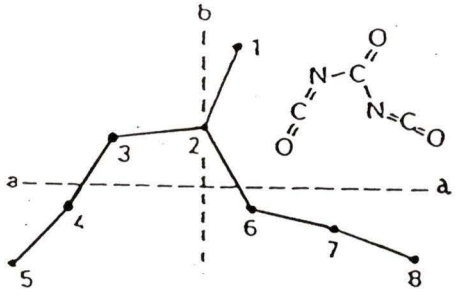
5.2 Results and Discussion

5.2a. CDI

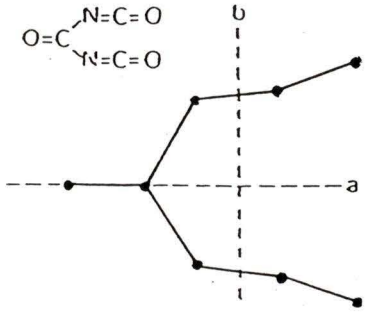
Carbonyl diisocyanate has an interesting feature pertaining to its planar geometry. With the possible geometric configurations that the molecule can adopt, the isomers can be characterized under a different point group.



Cisoid-Cisoid



Cisoid-Transoid



Transoid-Transoid

Fig. 5.3. The planar conformations of CDI. Geometrical parameters are listed in Table 5.2. The dotted lines locate the a and b inertial axes.

If the two isocyanate groups are oriented in the same fashion, as in the case of the *cisoid-cisoid* geometry (or *transoid-transoid* if sterically favourable), then the molecule can be classified under the C_{2v} point group. However, if the molecule has its isocyanato substituents aligned in different orientations, as in the *cisoid-transoid*

geometry, the molecule has only one plane of reflection and therefore is characterized under the C_s point group. In either case, there are eighteen fundamental vibrations indicative of the six atom system. The vibrations span the various symmetry groups as follows:

$$C_{2v}: \quad 7a_1 + 2a_2 + 6b_1 + 3b_2$$

$$C_s: \quad 13a' + 5a''$$

All the modes of CDI are ir and Raman active if the molecule is characterized under the C_s point group. All the modes of CDI under the C_{2v} point group are Raman active while only sixteen of the eighteen are infrared active. Two out-of-plane normal modes ($2a_2$) are infrared inactive.

5.2b. NCO fundamentals

The isocyanato antisymmetric stretching modes show two features in both the ir (2275\2241 cm^{-1})and Raman spectra (2273\2218 cm^{-1}). These two features could arise as a result of two possibilities: the first explanation is that the two features are characteristic of the two isomers present and the second is that the peak pairs are a result of vibrational coupling between the two isocyanate groups. The former is less likely to be the case since, for the considerable number of acyl isocyanates now reported, there has been no mention of two peaks for the NCO asymmetric stretch. In other words, there has been no measurable distinction made between the possible geometric conformers for ν_{as}(NCO). The second explanation involving the coupling between the two isocyanate groups resulting in in-phase and out-of-phase combinations, is deemed more probable. Evidence, both experimental and theoretical, supports the

coupling theory rather than the idea of rotational isomerism. In the ir and Raman spectra the splittings corresponding to the asymmetric NCO feature are of equal intensity. This was not the case where there was evidence of the presence of two conformers being observed.

Variable-temperature infrared studies support this theory in that the relative intensities of the peaks did not change by any substantial amount upon heating the sample, a result not expected if the peaks belonged to different isomers. If the peaks were representative of the possible conformers, then one would expect to see a difference in comparative intensities in the two peaks. These results therefore reject the possibility that the two features belong to different molecules.

Force field calculations performed by our group as well as MNDO/AM1 calculations (39) predict two infrared bands for each isomer. The calculations also show that the two features are separated by roughly 40 cm-1. Comparing the calculated frequencies for the two isomers showed that the two bands predicted for the isocyanato asymmetric stretches are virtually overlapped (2272 cm^{-1}). If any distinction could be made between the isomers, then it would be more likely that the observer would see four features in this region of the spectrum: two in-phase and two out-of-phase features with an in-phase\out-of-phase combination characteristic to each isomer. Calculations coincide with literature precedents and predict the out-of-phase stretch to be the higher of the two.

A further possible explanation should be mentioned. The second strong ir feature in the region of asymmetric NCO stretching could arise as a result of Fermi resonance, a term used to describe the phenomenon that two molecular

vibrational frequencies that lie very close in energy are in resonance with each other and exchange energy. The resultant peaks are said to interfere with each other causing the higher energy vibrational fundamental to show a rise in frequency while the lower energy vibration decreases in frequency. In this particular case, the resonance might arise from a fundamental mode (ν_{as}NCO) that lies close in energy to that of a combination band (i.e. ν_{s}NCO + νC-N) with the combination band gaining intensity at the expense of the fundamental since the combination band is expected to be much weaker than the fundamental. This possible explanation for the observations is deemed less probable because in the thirteen other acyl isocyanates (R-CO-NCO) reported only one such feature is present in the region (2250-2275 cm^{-1}).

The isocyanato symmetric stretch appears as a strong feature in both the infrared and Raman spectra. As in the case of the NCO asymmetric stretching fundamental, there are two features associated with this peak and they have been assigned as in-phase and out-of-phase vibrations (1426/1403 cm^{-1} respectively) based on the same arguments used to assign the asymmetric NCO stretching vibration. Experimentally, evidence of different isomers is not observed. This is in contrast to the calculated results which indicate that the two symmetric NCO stretching fundamentals differ by an amount significant enough that the two fundamentals for both isomers should be observed. The observation of only two peaks in the spectra suggests that the fundamentals for the conformers are closer in frequency than the program predicts.

There is the possibility of four deformations associated with the NCO group since the substituents are

identical. Two of these are in-plane while two are out-of-plane. These vibrations are quite similar in energy and lie in a narrow frequency range (600-650 cm^{-1}). The in-plane deformations are generally located at higher frequencies than their out-of-plane counterparts. Both the ir and Raman spectra of CDI show four distinct features in this region. The two higher energy peaks at 687/657 cm^{-1} in the ir spectrum (685/660 cm^{-1} R) are most likely the in-plane modes and the features at 615/609 cm^{-1} (ir) are the out-of-plane NCO deformations. There is some uncertainty as to whether the separations between peaks (687/657 cm^{-1}) are a result of vibrational coupling with the peaks of the other isomer unresolved from them or whether the peaks are a result of rotational isomerism. Experimental evidence seems to support the latter explanation. Vibrational coupling between the two bends of the peak pairs is not expected to be very large. Also since two of the out-of-plane modes are infrared forbidden ($2a_2$), one would expect one of the two NCO deformations to be absent in the ir spectrum of CDI. Variable temperature-IR studies indicate a variation of intensity upon heating in the peak pair at 615/609 cm^{-1} (the weaker feature gains intensity upon heating). These experimental results support the idea that the features are, indeed, a result of two different isomers with any vibrational coupling unresolved in the band.

5.2c. Carbonyl Stretching and Deformation Modes

There are two distinct features found in the carbonyl region of the ir spectrum of carbonyl diisocyanate. Only one peak is found in the Raman spectrum but its asymmetric profile suggests that there are, in reality, two overlapping peaks. The higher frequency feature (liquid:1756 cm^{-1} ir/ 1763 cm^{-1} R) is the weaker peak of the two. Both of these

bands show B-type band contours which is consistent with what is predicted for the *cisoid-cisoid* and *cisoid-transoid* isomers. It is a result of these band contour observations that the *transoid-transoid* isomer was excluded from possibly being present in the vibrational spectra for CDI. The *transoid-transoid* geometry is expected to exhibit a predominantly A-type carbonyl stretching band profile but this band shape is not observed in any of the infrared spectra (liquid or vapour-phase). The lower carbonyl frequency (1735 cm^{-1} ir-liquid) is predicted to be that of the *cisoid-cisoid* isomer based on force field calculations (30) as well as results of MNDO/AM1 calculations (39). The higher frequency is thus assigned to the *cisoid-transoid* rotomer.

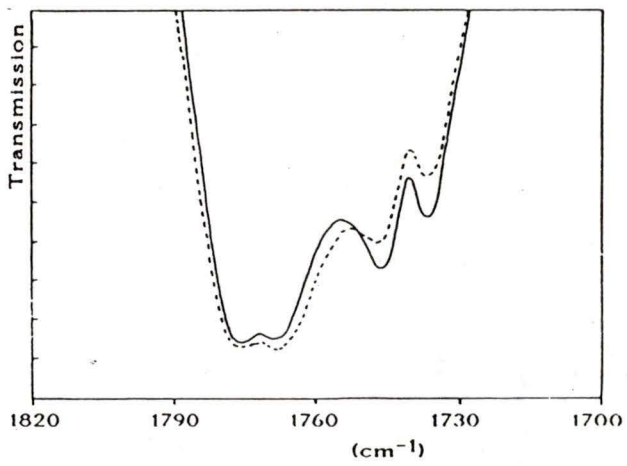


Fig. 5.4. Variable-temperature results for the carbonyl stretching region for CDI: 22°C (solid line); 55°C (dashed line). Also illustrated are the band contours for the carbonyl peak.

Calculations of B-type P-R branch separations by the method of Seth-Paul and Dijkstra (53) for the *cisoid-cisoid* and *cisoid-transoid* isomers of CDI were predicted to be 7.4 and 7.8 cm^{-1} respectively. The experimental values were consistent with these predicted results for the B-type contour. Unfortunately, the resolution of our spectra does not allow us to distinguish between the isomers with such

calculations. The reasoning behind performing such calculations was for comparison purposes only between our experimental values with other typical carbonyl molecules that exhibit B-type bands.

A molecule that houses a carbonyl bond and has at least one plane of symmetry will have two deformations associated with that plane: one that is in-plane (δ CO) and another that is out-of-plane (γ CO). Seth-Paul (54) has given a simple empirical method for estimating the carbonyl out-of-plane deformation frequencies in R'R"CO molecules. The product of the two parameters γ(R') and γ(R"), where R'and R" maybe be any given substituent, yields a value for the deformation mode. Data obtained from various carbonyl

isocyanates {R'=NCO; R"= F (26), Cℓ (28), OCH_3 (34), and SCH_3 (34)} give an average value of γ(R'=NCO) of $27cm^{-1/2}$. In CDI, R'= R" so the product of $\gamma(R')\times\gamma(R")$ is actually $(27cm^{-1/2})^2$. This product (729 cm^{-1}) gives an estimate of γCO that is consistent with that found experimentally for CDI. The lower frequency infrared band located at 726 cm^{-1} is assigned to the *cisoid-transoid* isomer and the peak at 737 cm^{-1} is assigned as belonging to the *cisoid-cisoid* isomer.

Infrared bands observed at 542 cm^{-1} and 522 cm^{-1} are attributed to the in-plane carbonyl deformations for the *cisoid-cisoid* and *cisoid-transoid* rotomers respectively. The observation of a lower frequency for this in-plane motion is consistent with that reported for other acyl isocyanates (31,47) and other structurally related symmetrical (C_{2v}) keto type compounds such as diethynyl ketone and carbonyl cyanide (52). The carbonyl deformations for the latter molecules are observed at 688/548 cm^{-1} (in-plane) and 712/550 cm^{-1} (out-of-plane) respectively. The separation between the in-plane and out-

of-plane carbonyl deformation modes is in good agreement to the molecules just referenced.

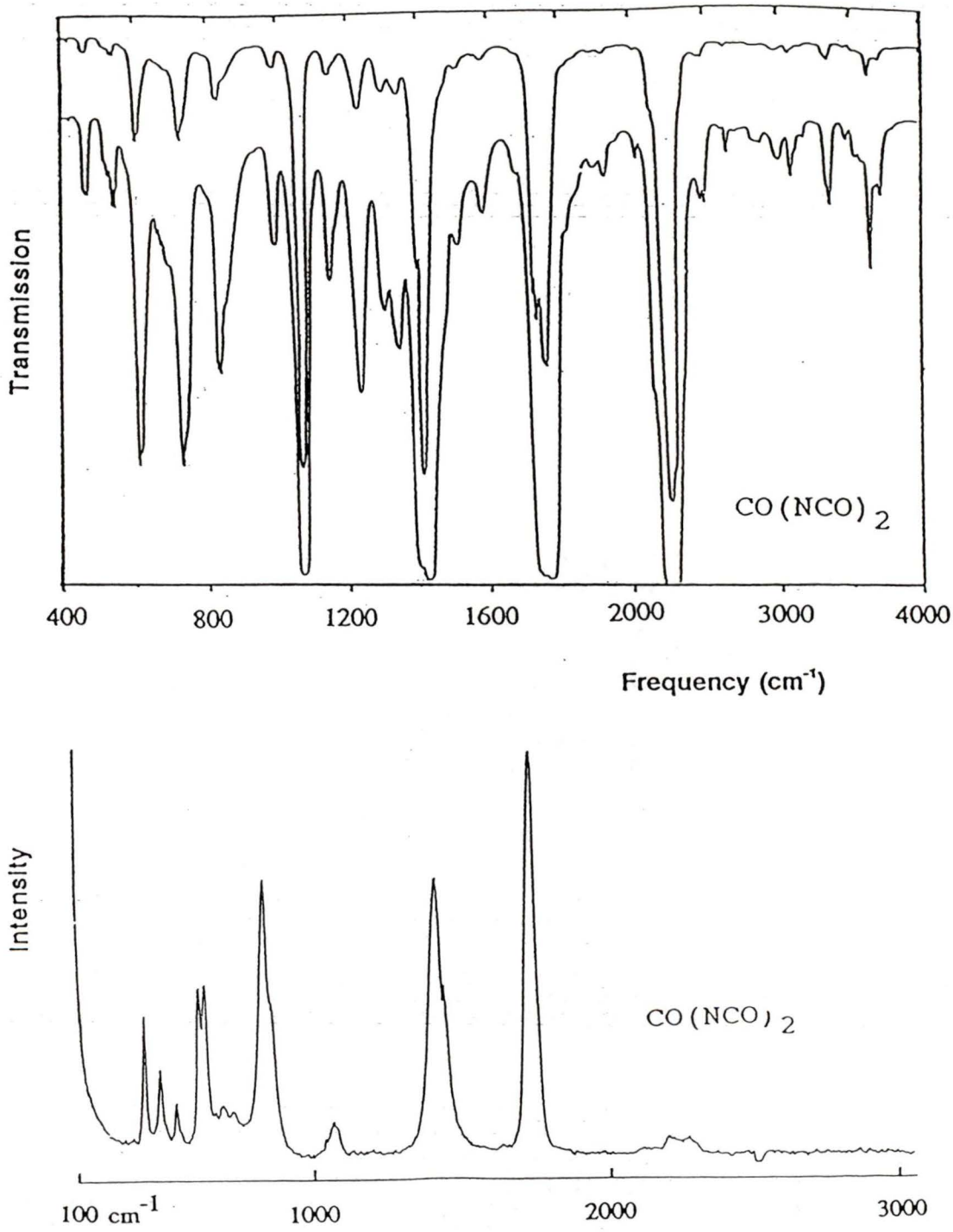


Fig.5.5. Upper: the vapour phase infrared (P= 25 torr; insert: P= 3 torr) and, lower: liquid Raman Spectra of CDI.

5.2d. NCN Vibrations

The stretching vibrations associated with the C-N bonds can be described in similar fashion to the NCO stretching vibrations. There are two C-N stretches characteristic of CDI (see Figure 5.6). The stretches are best described as in-phase and out-of-phase stretching motions or symmetric or asymmetric stretches. The resulting two peaks for the C-N stretching fundamentals are caused by interaction between the two C-N bonds. The interaction allows for the vibrations to be moving in the same motion (asymmetric) or opposed to each other (symmetric). There are also NCN deformations that are fundamental vibrations for the molecule. The in-plane deformation is called the scissoring motion while the out-of-plane bend is called a rocking motion.

Urea is probably the typical "simple" example used to describe the NCN vibrations. In urea (55), the asymmetric and symmetric stretches are reported at 1468 and 1005 cm^{-1} respectively. The corresponding motions in CDI are expected to appear at lower frequencies because of mass sensitivity of the substituent (NH_2 versus NCO). The out of phase NCN stretch is assigned to the features observed at 1075 cm^{-1} and 1068 cm^{-1} respectively for the *cisoid-cisoid* and *cisoid-transoid* conformers while the in-phase stretch for the former appears at 855 cm^{-1} while the stretch for the latter appears at 831 cm^{-1}. The separation between the in-phase and out-of-phase stretches is not as great in CDI as it is in urea. The lack of coupling between the two stretches is most likely, again, a result of mass sensitivity. Urea-d_4 (56) has the same structure as urea except that deuterium atoms have replaced hydrogen atoms. The observed frequencies for the NCN stretching modes also decrease slightly with the increased mass of the substituents as well

as the separation between the peaks reflecting the mass sensitivity of the coupling interaction.

Conformational analysis distinguishing the two isomers was based on variable temperature studies. The features at 1068/831 cm^{-1} gained intensity relative to the other pairing (1075/855 cm^{-1}) upon heating and therefore assigned as the out-of-phase and in-phase NCN stretching modes for the *cisoid-transoid* isomer.

The NCN scissoring fundamental appears as two medium intensity Raman lines at 469 cm^{-1} and 413 cm^{-1} for the *cisoid-cisoid* and *cisoid-transoid* isomers respectively. Progressive decreases in frequency for the NCN scissoring fundamental occur as the mass of the substituent increases. This is apparent in comparing urea (55) to urea-d_4 (56). The NCN scissoring motion appears at 558 cm^{-1} in urea whereas the equivalent motion in urea-d_4 is approximately 75 cm^{-1} lower in frequency.

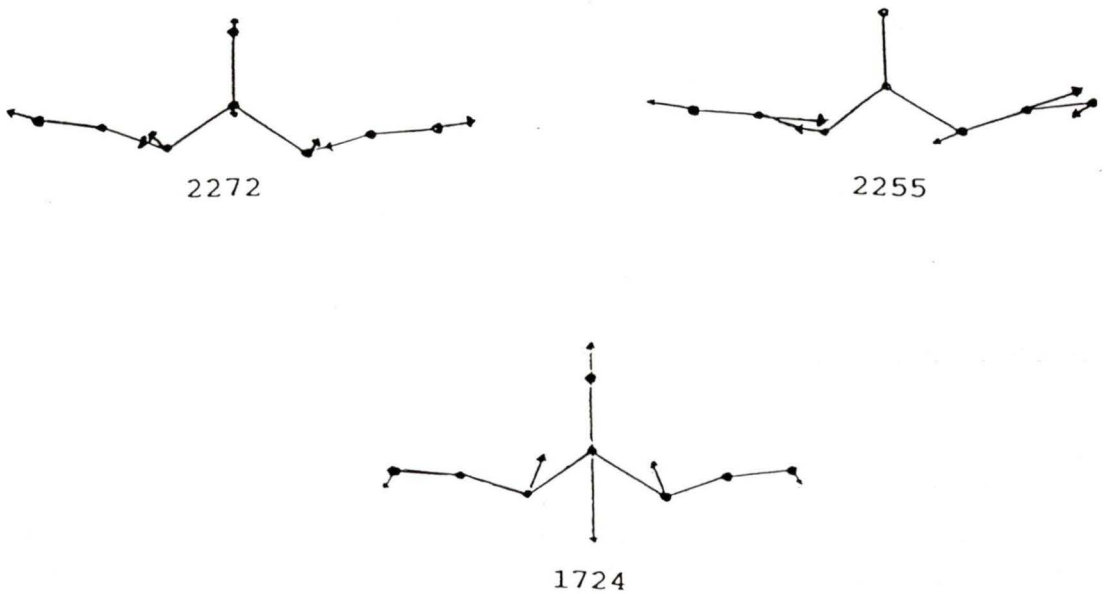
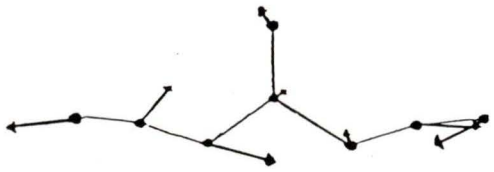
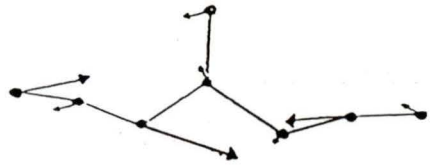


Fig. 5.6. Calculated frequencies (cm^{-1}) and predicted motions (exaggerated) for the in-plane fundamentals of CDI.



1451



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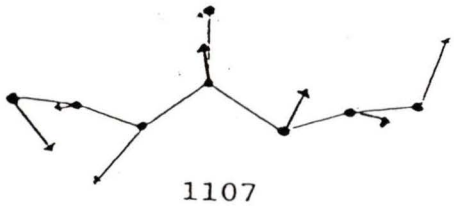

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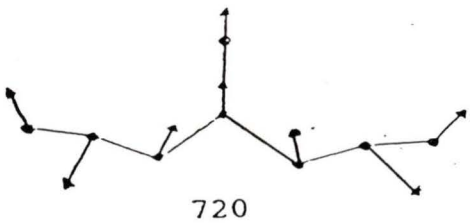

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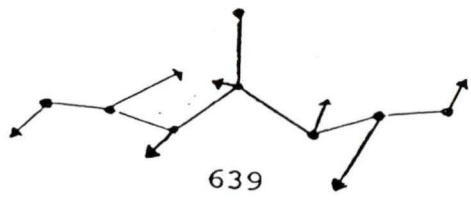

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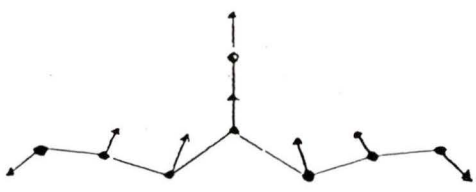

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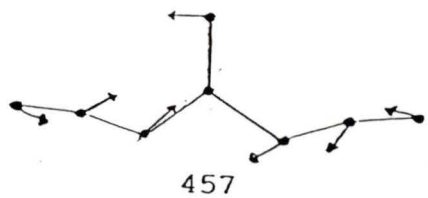

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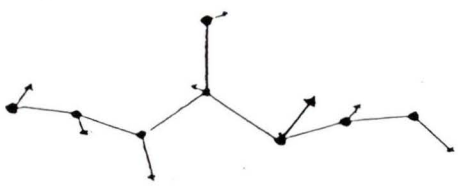

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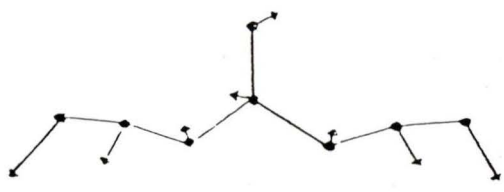

94

Fig. 5.6 continued. Calculated motions for CDI (exaggerated).

The other bending fundamental expected in the vibrational spectrum of CDI is that of the C-N=C bend. This bend is expected to be quite low in energy and may well be below 200 cm^{-1} as force field calculations predict (170 cm^{-1} and 94 cm^{-1} respectively for in-plane and out-of-plane motions). We do not observe any such feature in the Raman spectrum except for a rather ill-defined shoulder appearing at approximately 155 cm^{-1} arising out of the background of the Rayleigh line. This feature is tentatively assigned to one of the C-N=C bending fundamentals. Assignments for the vibrational spectra of carbonyl diisocyanate are listed in Table 5.1.

Table 5.1. Observed Frequencies (cm^{-1}) and Assignments in Carbonyl Diisocyanate

Infrared vapour	Infrared liquid	Raman liquid	Assignment
3713 w			2275 + 1426 = 3701
3677 vw			2275 + 1403 = 3678
3638 mw			2241 + 1403 = 3644
3583 vvw			
3535 vvw			2×1772 = 3544
3468 vvw			2×1741 = 3482
3350 w			2275 + 1068 = 3343
3326 vw,sh			2241 + 1068 = 3309
3169 vvw			1741 + 1426 = 3167
3081 vw	3071 mw		2241 + 855 = 3096
2993 vvw			2275 + 726 = 3001
2835 vvw			1772 + 1068 = 2840
2814 vvw	2808 vw		1741 + 1075 = 2816

2641 vvw			
2488 vw			1426 + 1068 = 2494
2462 vw	2461 vw		1403 + 1068 = 2471
2275 vvs	2272 vs	2273 vw,b	ν_{as}(NCO)
2241 vvs	2219 vvs	2218 vw,b	ν_{as}(NCO)
2139 w,sh			2×1068 = 2136
1927 vvw			1075 + 855 = 1930
1894 vvw			1068 + 831 = 1899
1777 vvs,R 1772 min 1768 vvs,P	1756 vvs,b	1763 s,sh	ν(C=O) *cisoid-transoid*
1748 vs,R 1741 min 1737 vs,P	1735 vs	1736 vvs	ν(C=O) *cisoid-cisoid*
1676 vvw			2×835 = 1670
		1638 vvw	
1584 vw			855 + 726 = 1581
1512 vw,b			855 + 657 = 1512
1426 vs	1424 vs,b	1444 s	ν_{s}(NCO)
1403 s		1413 vs	ν_{s}(NCO)
1342 mw			726 + 615 = 1341
1232 m			2×615 = 1230
1145 w			615 + 538 = 1153
1075 vs,sh	1066 vs	1065 w	ν(NCN) out of phase *cisoid-cisoid*
1068 vs		1034 vw	ν(NCN) out of phase *cisoid-transoid*
995 w 991 min 986 w			522 + 465 = 987

862 mw 855 min 848 mw	853 mw	855 ms,sh	ν(NCN) in phase *cisoid-cisoid*
835 ms 831 min 827 ms	824 ms	835 vs	ν(NCN) in phase *cisoid-transoid*
737 m,sh			γ(CO) o.o.p. *cisoid-cisoid*
728 s 726 min 724 s	726 s	722 w	γ(CO) o.o.p. *cisoid-transoid*
687 vw	687 m	685 w	δ(NCO), in plane
657 vvw,sh	662 w	660 w	δ(NCO), in plane
615 s		628 ms	δ(NCO), o.o.p
609 s	604 s	604 ms	δ(NCO), o.o.p
546 w 538 w	540 mw	536 vw,sh	δ(CO) in plane, *cisoid-cisoid*
526 vw 522 min 517 vw	526 w	523 w	δ(CO) in plane, *cisoid-transoid*
471 vw 465 vw 461 vw	469 mw	469 mw	δ(NCN) *cisoid-cisoid*
	420 vvw	413 m	δ(NCN) *cisoid-transoid*
		375 vvw	1444 - 1065 = 379
		349 vvw	1413 - 1065 = 348

5.3 Force Field Calculations

To complement the proposed vibrational assignments in Table 5.1, a simple normal coordinate analysis program developed by Gwinn (15) was employed to calculate the frequencies of the in-plane vibrational fundamental modes for the *cisoid-cisoid* and *cisoid-transoid* geometries of carbonyl diisocyanate. In addition to the calculated frequencies, the program also provides the location of the inertial axes and hence information pertaining to the band contours of the fundamental vibrations. The program also yields information about the molecular motions involved in each calculated frequency which can be then related to vibrational coupling between bonds.

Explanation of the aspects of the program and force field theory are discussed in Section 1.4. Initially a generalized valence force field was created for the *cisoid-cisoid* conformer with values for the force constants of the carbonyl isocyanate skeleton transferred from ab initio, harmonic calculations on *cis*-chlorocarbonyl isocyanate (28,29) and from urea (57). The geometrical parameters used to calculate the normal coordinates for both isomers are shown in Table 5.2. As mentioned in section 1.4, the generalized force field theory involves only interactions between bonds of adjacent atoms. The F-matrix (Table 5.3) was constructed on this basis and the off-diagonal interaction constants were included for only structurally adjacent motions. Small refinements were made to six parameters in order to obtain an optimum fit after the original calculation was performed. This procedure was used to obtain values for the *cisoid-transoid* moiety with virtually no change in the F-matrix (force field) other than substitution of the *trans*-chlorocarbonyl isocyanate values for the *transoid* skeleton of the molecule. Table 5.4

presents a comparison of calculated and observed frequencies for CDI.

A number of observations were made with the aid of these calculations. First, and foremost, the in-plane vibrational frequencies were calculated giving the position of these in-plane modes in a simulated spectrum and this was used to draw a comparison to experimentally observed values. Using the NCO asymmetric stretch as an example, the program predicts that this mode appears at a frequency of 2272 cm^{-1} which is very close to the observed value of 2275 cm^{-1}. Secondly, by studying the inertial axes, it was determined that the carbonyl bond of the *cisoid-cisoid* isomer is of 100% B-type character and that the *transoid-transoid* isomer is 100 % of A-type character. The "hybrid" isomer, the *cisoid-transoid* conformer, was also predicted to have its carbonyl bond peak to be predominantly of B-type character.

Table 5.2. Geometrical parameters used in calculating the normal coordinates of CDI.

Geometrical parameters: cisoid-cisoid

r(C=O_1) carbonyl	1.173Å	∠(O_1CN)	120.5°
r(C-N)	1.382Å	∠(CNC)	124.6°
r(N=C)	1.218Å	∠(NCO_5)	173.8°
r(O_5=C) isocyanate	1.133Å	∠(NCN)	119.0°

Geometrical parameters: cisoid-transoid

r(C=O_1) carbonyl	1.169Å	∠($O_1C_2N_6$)	120.5°
r(C_2-N_6)	1.382Å	∠($O_1C_2N_3$)	121.5°
r(C_2-N_3)	1.375Å	∠($C_2N_6C_7$)	124.6°
r(N_6=C_7)	1.218Å	∠($C_2N_3C_4$)	132.3°
r(N_3=C_4)	1.209Å	∠(NCO_8)	173.8°
r(O_8=C_7) isocyanate	1.133Å	∠(NCO_5)	174.2°
r(O_5=C_4) isocyanate	1.136Å	∠(NCN)	118.0°

Table 5.3. F-Matrix for the in-plane vibrations of CDI. Entries for the *cisoid-transoid* isomer, where different from those of the *cisoid-cisoid* isomer, are in parentheses. Entries transferred from Refs [28], [29], and [56] are in italics. Units are mdyn $Å^{-1} = 10^2$ Nm^{-1}.

	S_{12}	S_{23}	S_{34}	S_{45}	S_{26}	S_{67}	S_{78}	S_{123}	S_{234}	S_{345}	S_{126}	S_{267}	S_{678}	S_{326}
S_{12}	10.00 (10.20)	1.135	0	0	1.135	0	0	0.345	0	0	0.345 (0.295)	0	0	-0.088
S_{23}		6.20	0.402	0	4.19	0	0	0.222	0.108	0	0	0	0	0.170
S_{34}			12.82	1.971	0	0	0	0	1.059	0.365	0	0	0	0
S_{45}				16.97	0	0	0	0	0	0.032	0	0	0	0
S_{26}					6.20	0.402 (0.414)	0	0	0	0.222 (0.348)	0.108 (0.450)	0	0	0.170
S_{67}						12.82	1.971 (2.042)	0	0	0	1.059 (1.055)	0.365 (0.376)	0	0
S_{78}							16.97	0	0	0	0	0.032 (0.015)	0	0
S_{123}								0.926	-0.003	0	0	0	0	0
S_{234}									0.178	0.072	0	0	0	0.050
S_{345}										0.800	0	0	0	0
S_{126}											0.926 (0.899)	-0.003 (-0.022)	0	0
S_{267}												0.178 (0.160)	0.072 (0.016)	0.050
S_{678}													0.800	0
S_{326}														2.202

The internal coordinates S are labelled as follows: s_{ij}, stretching of bond between atoms i and j; s_{ijk} bending of angle formed by atoms i,j and k.

Table 5.4. Calculated and observed in-plane vibrational frequencies (cm^{-1}) for *cisoid-cisoid* and *cisoid-transoid* CDI. C_{2v} symmetries refer to the *cisoid-cisoid* isomer.

Approximate mode description	*cisoid-cisoid*		*cisoid-transoid*	
	ν_{calc}	ν_{obs}	ν_{calc}	ν_{obs}
NCO antisymmetric stretch (a_1)	2272	2275	2272	2275
NCO antisymmetric stretch (b_1)	2255	2241	2255	2241
C=O stretch (a_1)	1724	1741	1763	1772
NCO symmetric stretch (a_1)	1451	1426	1444	1426
NCO symmetric stretch (b_1)	1366	1403	1403	1403
CN stretch (a_1)	1107	1075	1007	1068
CN stretch (b_1)	872	855	846	831
NCO bend (a_1)	720	687	767	687
NCO bend (b_1)	639	657	669	657
CO bend (b_1)	461	536	526	523
NCN bend (a_1)	457	436	434	413
CNC bend (a_1)	170	---	157	---
CNC bend (b_1)	94	---	87	---

Comparison between band contours of the carbonyl bands observed in the ir gas-phase spectrum and those predicted by the Gwinn program has helped exclude the *transoid-transoid* molecule from being present in the spectrum of CDI. The force field calculations also helped distinguish whether a pair of peaks was a result of rotational isomerism or due to in-phase/ out-of-phase peak combinations. The calculations revealed that there are two motions expected for the asymmetric and symmetric stretching fundamentals in relation to the equivalent substituents: the motions being in-phase and out-of-phase. The force field calculations helped confirm that the two peaks observed in the region of the NCO asymmetric stretch were indeed a result of vibrational interaction of the two isocyanate groups rather than

evidence of the two expected rotational isomers. Calculations predicted that the frequencies for both isomers were virtually overlapped and that a pair of peaks was predicted for each isomer in that region. Also analysis of the molecular motions of the predicted pair of features did show that the motions of the pair were, indeed, in-phase and out-of-phase combinations.

Some aspects of the molecular motions of the bands were presented to us in looking at the calculated vibrational frequencies. Figure 5.6 shows the predicted motion for each of the calculated frequencies for the *cisoid-cisoid* conformation of carbonyl diisocyanate. Analysis of the frequencies calculated by the program for CDI shows the expected coupling between the vibrational modes of the molecule, in particular, the coupling between the C-N stretch and the NCO stretch. This coupling is illustrated in Figure 5.5. by showing the contribution of each vibration to the two fundamentals.

5.4. Conclusion

An infrared and Raman vibrational analysis for carbonyl diisocyanate was performed and assignments for its fundamental modes were carried out using structurally related molecules of the general formulas X_2CO and R-CO-NCO. A simple force field calculation was performed to help assign some of the more difficult fundamental modes. Calculations have shown that the interactions between the equivalently substituted carbonyl isocyanate are unique in comparison to the other carbonyl isocyanates studied in that the interaction between the C-NCO bonds produces two motions, one in-phase and the other out-of-phase, and that

the fundamental stretches for the C-NCO fragment appear as peak pairs.

Comparison between experimental and calculated values for the fundamental vibrational modes of CDI are in good agreement. It should be noted that the fit is not perfect and that these force field calculations were performed using a simple model for comparison purposes only and not for a detailed theoretical analysis. It was not the scope of this project to partake in such a task but only to draw support for the vibrational assignments made for carbonyl diisocyanate.

Chapter 6
Carbonyl Isothiocyanates

6.1 Introduction

Carbonyl isothiocyanates have the same structural skeleton as carbonyl isocyanates with the exception that sulfur replaces oxygen in the NCE framework. The general structure of carbonyl isothiocyanates is shown in Figure 6.1. Like their carbonyl isocyanato counterparts, carbonyl isothiocyanates have been known for years but have been more or less ignored spectroscopically, most probably because of their very strong lachrymatory odour. While there is some general spectroscopic information reported on alkyl isothiocyanates, such as methyl isothiocyanate (58), there is nothing in present and past literature on carbonyl isothiocyanates with the exception of infrared and dipole moment analyses on substituted benzoyl isothiocyanates (59).

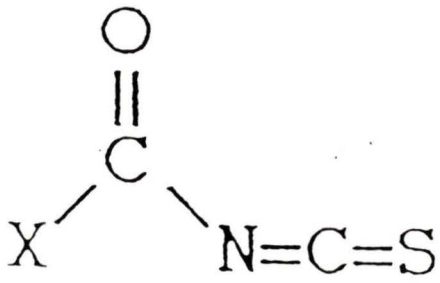

Fig. 6.1. The carbonyl isothiocyanate framework.

The object of this chapter is to look at a few examples of carbonyl isothiocyanates (X= F-, Cℓ-, and CH_3) comparing them to their carbonyl isocyanate counterparts. These examples of carbonyl isothiocyanates can adopt one of three conformations: two planar and one non-planar *gauche*

geometry. Of the two planar conformations, one of the geometries is *cisoid* where the NCS group is cis to the carbonyl group while the second is *transoid* which has the NCS group located trans to the carbonyl group. The different conformations are a result of rotation of the NCS group about the C-N bond just as it is in carbonyl isocyanates. Slightly displaced vibrational frequencies are expected for each conformer since each isomer is expected to have a slightly different energy.

The fundamental vibrations of the isothiocyanato group will be the same types as those of the isocyanato group but the vibrational frequencies involving the NCS group are expected to be lower than that of the NCO group because of the heavier sulfur atom. Although there have been no geometric data reported on carbonyl isothiocyanates, the geometries of the fluoro- (FCIT), chloro- (CCIT), and acetyl isothiocyanates (AIT) are expected to be analogous to their carbonyl isocyanate counterparts.

The isothiocyanate examples studied in this chapter can be characterized under the C_s point group. Fluoro- and chlorocarbonyl isothiocyanate are six-atom molecules and will have 12 normal modes of vibration which can be further divided into nine in-plane fundamental modes (a′) and three out-of-plane modes (a"), all of which are ir and Raman active. Of these twelve vibrational fundamentals, five modes are characterized as stretches, while the remaining seven are bends. Acetyl isothiocyanate is a nine-atom molecule that has twenty-one normal modes of vibration. The twenty-one fundamentals of AIT subdivide in the C_s point group into 14 in-plane modes and seven out-of-plane modes. All three carbonyl isothiocyanates studied here will have the same number of fundamentals characteristic to the carbonyl isothiocyanate framework. There will be nine

fundamentals characteristic of the CO-NCS framework: four stretches and five bends (3a′ and 2a").

The gas and liquid phase spectra of the CCIT and FCIT show features that appear to belong to different geometric conformations whereas the gas phase spectrum of AIT shows only one conformer. However, there is a hint in the liquid spectra that there may be more than one isomer present. As in acetyl isocyanate the cisoid conformer of AIT is the isomer present in the gas phase.

6.2. Problems with Isothiocyanates

The carbonyl isothiocyanates studied in this chapter were much more difficult to work with in relation to synthesis and spectroscopy than their carbonyl isocyanate counterparts. It is quite probable that these difficulties have inhibited spectroscopists from performing vibrational analyses of these compounds.

The carbonyl isothiocyanates are even more lachrymatory than the carbonyl isocyanates and are more difficult to handle because of this. Synthesis was much more difficult in that solvents such as liquid sulfur dioxide in the synthesis of CCIT were used. Using liquid sulfur dioxide requires that low temperatures (<-10 °C) be used to prevent evaporation. Other solvents were utilized in preparation of the halo-derivatives but were unsuccessful. One example was using THF (tetrahydrofuran) as the solvent in the preparation of CCIT just as in the synthesis of AIT. It was hoped that using THF would simplify the reaction greatly and the use of SO_2 as a solvent would not be needed. The reaction did occur according to nmr and ir data but isolation of the product was unsuccessful. The THF could

not be removed by distillation, evaporation or vacuum distillation. This unfortunate result made the synthesis of CCIT much more troublesome.

Isothiocyanates appear to be thermally more unstable than isocyanates. Whereas CO_2 was an impurity commonly seen as decomposition of carbonyl isocyanates occurred, CO_2, CS_2, and COS are commonly observed as decomposition products in isothiocyanates. Carbon dioxide is very volatile and can be easily removed whereas the latter decomposition products are less volatile and more troublesome to get rid of. It is fortunate that the decomposition products are easily identified and that they do not overlap with group frequencies.

Carbonyl isothiocyanates turn yellow almost immediately upon being exposed to air so the liquid products collected had to be degassed and sealed in air-tight containers. The degree of decomposition seemed to vary with the colour of the liquid ranging from colourless (pure product) to a slight yellow to a deep orange-red colour. In Raman experiments, excitation with the 488 nm (blue) or 514.5 nm (green) line caused the sample to turn to a dark orange gelatinous substance after prolonged exposure to the beam indicating that photodecomposition had occurred. There are three possible explanations for this decomposition. First: probable explanation is that the minute quantity of impurities present in the sample absorb the energy of the incident excitation source causing the impurities to be electronically excited. The excited impurities partake in a series of intramolecular vibrational relaxations which give off energy in the form of heat. It is this heat that in turn heats the sample sufficiently to cause thermal decomposition. This process would be a photochemical\ thermal decomposition mechanism. Second: the excitation

source possesses enough energy to excite the molecules of the sample to an excited electronic state. This excited state, however, overlaps another continuous (unstable) electronic state. If an electronic transition occurs in a region where its vibrational levels overlap, then there is the possibility that the molecule will 'cross over' to the continuous state and the molecule will dissociate. Third, and most probable, is that the molecules of the sample are electronically excited (as in the previous explanation) to some upper state. Once in the excited state, the molecule then goes through a series of vibrational relaxations which, as in the first case, produces sufficient heat to decompose the sample.

There are ways to circumvent this problem. One possibility is to have a light source that has a lower excitation energy. A Nd:YAG laser which has a excitation energy of 1064 nm (9398 cm^{-1}), which is considerably lower than the 514.5 nm of the argon-ion laser used in our experiments. Using a Fourier-transform Raman instrument would also be advantageous in this case where a series of scans can be recorded in a short period of time and averaged giving a reliable spectra. Another experimental technique to solve the problem of decomposition is to use a dye laser with an appropriate dye (in this case a red dye). The excitation line would then be of lower energy and may not excite the sample to an upper electronic state.

Of these possibilities, using a Fourier transform apparatus would probably yield the best results because of the short amount of time needed to record a spectrum. The shorter the time the sample is in the beam, the less the chance of decomposition. We were fortunate to get access to such an apparatus and FT-Raman spectra were recorded for CCIT and FCIT. There was some doubt as to how good these

spectra were due to the time between synthesis of the compounds and recording of the spectra. The Raman spectrum of FCIT was recorded in our lab using the 514.5 nm line of the argon ion laser as the excitation source as a confirmation of the FT results. Because the sample decomposed over a relatively short period of time, only portions of the spectrum could be run with any given sample. This is quite time consuming because the reproducibility of the peaks must be checked and also a fair amount of sample is needed since once decomposition occurs, the sample can no longer be used. The peaks that were observed in the FT-Raman spectrum were also observed in the spectrum recorded in our lab. Nearing the end of the project, a functional dye laser was made available which enabled a Raman analysis of CCIT (unfortunately there was no samples of AIT and FCIT left to try this experiment). Details and experimental conditions for this experiment are found in section 2.3. A number of peaks that appeared in the FT-Raman spectrum were confirmed using the dye laser apparatus. These additional experimental data provided sufficient information to carry out a complete vibrational analysis on this series of carbonyl isothiocyanates.

6.3 Results and Discussion

6.3a. Fundamentals of the Isothiocyanate Group

The isothiocyanate group is responsible for two principal stretching vibrations: one symmetric and the other asymmetric, both fundamentals being separate and distinguishable.

The asymmetric stretch behaves spectroscopically in an identical manner to isocyanates. The band for this stretch

is the most prominent feature in the infrared spectrum while in the Raman spectrum, the peak is very weak. The asymmetric and symmetric isothiocyanato stretches show a mass dependence in comparison to their isocyanate counterparts. The asymmetric NCS stretch occurs approximately 300 cm^{-1} lower than ν_{as}(NCO) while the symmetric NCS stretch is also decreased by an equivalent amount. The degree of interaction between the stretches in both cases is very similar in that the separation between the asymmetric and symmetric stretches in both examples is very similar ($\Delta\nu$ 800-900 cm^{-1}). The separation between the asymmetric and symmetric stretches depends upon the degree of interaction between the two fundamentals. Measuring such an interaction is almost impossible since there is also coupling between the symmetric isothiocyanato stretch and other features that appear in the same vibrational region of the spectrum (i.e. the interaction between ν_s(NCS) and ν(C-F) which will be discussed later). This is because the symmetric NCS stretch is observed in a region that is more congested and will therefore be involved in more mechanical coupling whereas the isocyanato symmetric stretch is located in a region where other group frequencies are less likely to be found in molecules with the carbonyl iso(thio)cyanate framework.

The asymmetric stretch in carbonyl isothiocyanates can be assigned without argument even though it is located some 300 cm^{-1} lower that its isocyanate counterpart. In the three carbonyl isothiocyanates analyzed in this study (FCIT, CCIT and AIT) this vibrational feature is observed between 1945 and 1990 cm^{-1}. Like their carbonyl isocyanate counterparts, there is no evidence of rotational isomerism evident in either spectrum. The ir band is so intense and broad that no information can be gathered in regards to band contour and subsequent conformational analysis. There are several

shoulders that appear with this band but they can be explained as overtones and combination bands that are enhanced as a result of Fermi resonances.

The order of appearance of ν_{as}(NCS) is somewhat surprising. In the equivalent carbonyl isocyanates FCI (60), CCI (28,29) and AI (47) the increase in observed frequency corresponds with increasing electronegativity. The ordering for the carbonyl isothiocyanates in this analysis has the methyl substituent showing the highest frequency for ν_{as}(NCS) followed by the fluoro then chloro compounds. The mixed ordering might possibly be explained as a slight coupling between the carbonyl band and the asymmetric isothiocyanato stretch. The two fundamentals are much closer in frequency than the two corresponding fundamentals in carbonyl isocyanates so the likelihood of coupling between the two fundamentals is more prominent in carbonyl isothiocyanates.

The isothiocyanato symmetric stretch, as stated earlier, appears about 300-400 cm^{-1} less than its equivalent isocyanato stretch. The NCS symmetric stretching fundamental, since it appears in the region between 1000-1200 cm^{-1}, is more susceptible to coupling with the C-X stretch [ν(C-F) and ν(C-C)] and ν(C-N). As shown in the previous chapters, coupling with ν(C-N) is present in all the carbonyl isocyanates studied and the motions associated with ν_s(NCO) and ν(C-N) are undoubtedly of mixed character. Coupling between ν(C-X) and ν_s(NCS) will be greater when the peaks are closer in energy. When the levels are energetically similar, they will become accidentally degenerate and an exchange of energy occurs. This in turn will cause the peaks to be displaced from their 'usual' observed frequencies with one increasing in frequency while the other decreases in frequency. The symmetric NCS stretch

in FCIT undergoes such a displacement. The band appears at approximately 130 cm^{-1} lower than the corresponding stretches in CCIT (1147 cm^{-1}) and AIT (1194 cm^{-1}). The lower frequency observed for ν_s(NCS) (1028/1018 cm^{-1}) is a result of coupling with the C-F stretch (1242/1213 cm^{-1}). In other carbonyl halides such as propiolyl fluoride (61) and cyanoformal fluoride (62) the C-F stretch is reported at 1157 cm^{-1} and 1175 cm^{-1} respectively. Studies on fluorocarbonyl isocyanate (60) place this fundamental at 1163 cm^{-1}. These C-F frequencies are very comparable to the less coupled isothiocyanato symmetric stretch in CCIT and AIT. In our spectra of FCIT there are two features located at 1028 cm^{-1} and 1242 cm^{-1}. These observed peaks are a mixture of the ν(C-F) and ν_s(NCS) fundamentals. To remain consistent with the literature we have assigned the higher frequency to the C-F stretch and the lower frequency to the symmetric isothio-cyanate stretch. A physical representation of this coupling is shown in Figure 6.2. It is difficult to assign a relationship between the electronegativity of the substituent and vibrational frequency for symmetric isothiocyanate stretch since the region is quite congested and undoubtedly susceptible to vibrational coupling.

The NCS bending vibrations are expected to be observed at lower frequencies than their NCO counterparts as in the case of the other NCS fundamentals because of the heavier NCS group compared to the NCO group. These modes should lie in the range 450-600 cm^{-1} in accordance to the assignments of Kniseley et al. (58) in their analysis of methyl isothiocyanate. Thus the Raman lines at 555 and 451 cm^{-1} are assigned to the out-of-plane and in-plane bending modes respectively in FCIT and at 614/481 cm^{-1} respectively for AIT. In the case of CCIT, only the assignment of the NCS in-plane bending motion is assigned to the ir feature at 523 cm^{-1}. The out-of-plane is not found in the vibrational

spectra of CCIT. It is probably not observed due to the intensity of the ir and Raman features of the COCℓ bending motions which appear in the region 580-715 cm^{-1}.

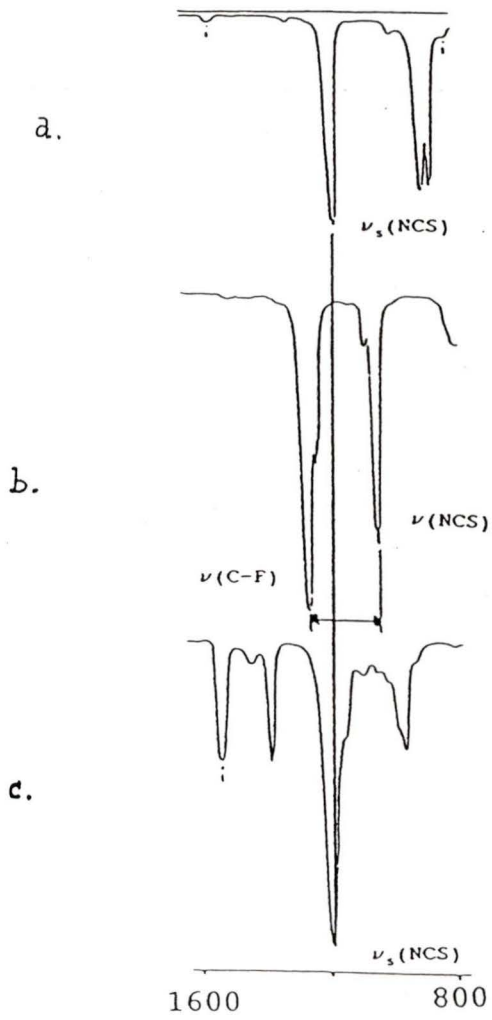

Fig. 6.2. Schematic illustrating the coupling between the C-F and NCS symmetric stretches in FCIT: a-CCIT;b-FCIT;and c-AIT.

6.3b. The Carbonyl Region.

The effects upon the carbonyl frequency resulting from the exchange of oxygen with the heavier sulfur atom are for the most part nonexistent. There is a slight reduction in ν(C=O) as compared to the equivalent isocyanates. The increase in observed vibrational frequency of the carbonyl stretch with increasing electronegativity of the substituent is also evident. The observed frequencies for the carbonyl isothiocyanates presented in this chapter are shown in Tables 6.1-6.3.

Evidence of conformational isomerism in analysis of the carbonyl stretch is not as complimentary as it was in the carbonyl isocyanates. In carbonyl isocyanates, the band envelope was a pertinent tool in distinguishing between isomeric conformations. The separation between the isomers in carbonyl isothiocyanates is reduced indicating that the isomers present (*cisoid* and *transoid*) are closer in vibrational energy than they are in carbonyl isocyanates. The reduced separation makes band contour analysis more difficult or even impossible depending upon how distinguishable the two bands are. The reduced separation may also be caused by the coupling of the asymmetric isocyanato stretch with the *transoid* isomer which would force its carbonyl stretch to appear closer to the *cisoid* carbonyl stretch. The features are usually overlapping thus making analysis impossible.

With sulfur/oxygen exchange, the molecule is now much heavier thus reducing the P-R splitting in the carbonyl band because of the increased rotational constant of the molecule. This reduced splitting makes the band more difficult to analyze in relation to its band envelope.

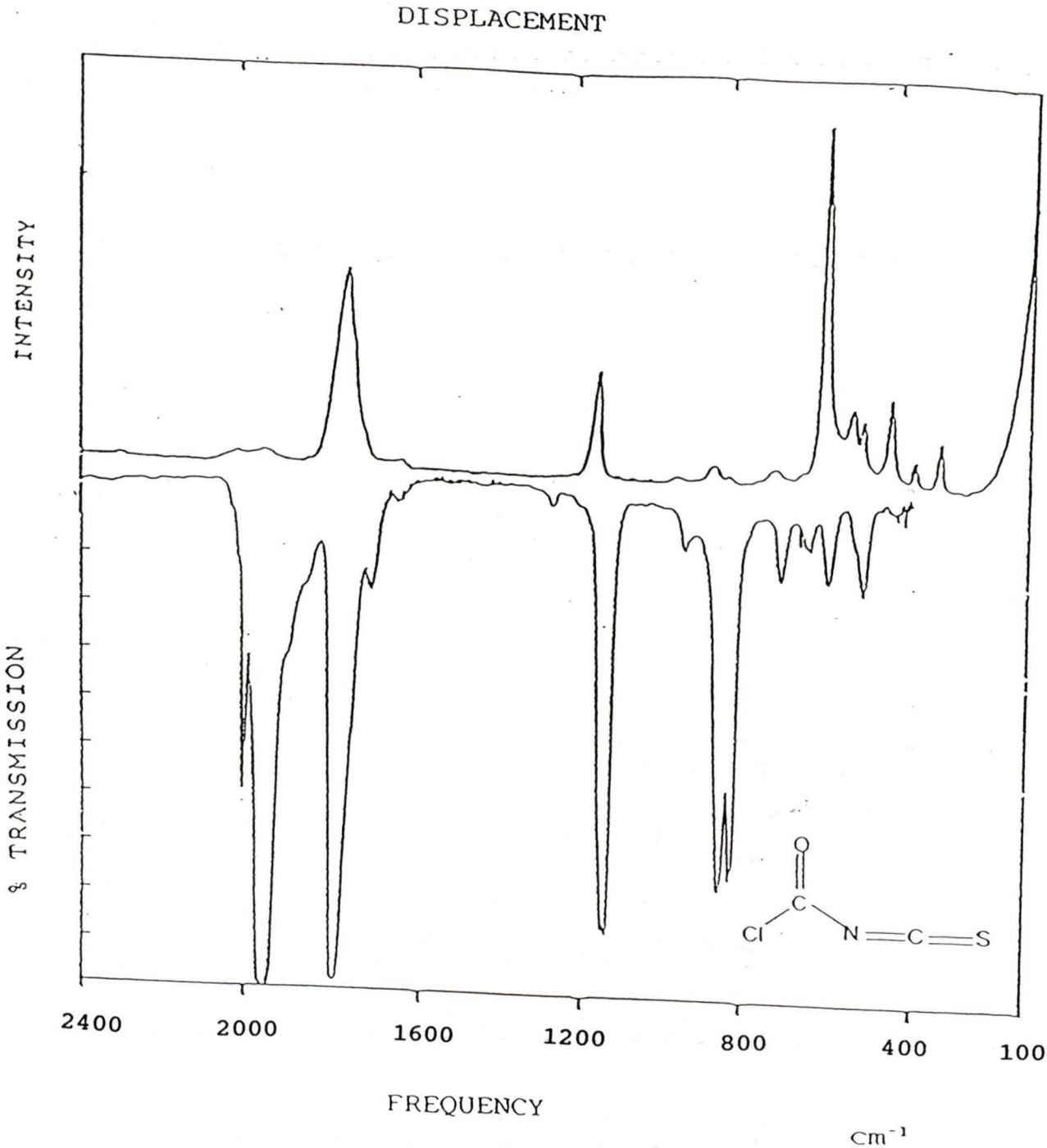

Fig. 6.3. Upper: The liquid Raman spectra and lower: the vapour-phase infrared (P= 30 Torr) of CCIT.

Table 2. Observed Frequencies (cm^{-1}) and Assignments for Chlorocarbonyl Isothiocyanate.

Infrared vapour	Infrared liquid	Raman liquid	Assignment
3904 vw			2x1963 = 3926
2941 vvw			1804 + 1147 = 2951
	2923 vvw		1958 + 955 = 2913
2825 w			1958 + 865 = 2823
	2789 vvw		
2682 vw			1804 + 865 = 2669
	2645 vvw		1772 + 859 = 2631
2560 mw			1958 + 599 = 2557
			2x1276 = 2552
	2529 vw		1772 + 735 = 2507
2389 vw			
	2358 vvw,sh		1770 + 598 = 2368
2284 m	2297 vw		2x1147 = 2294
2074 w,sh			
2037 s	2012 sh		1154 + 859 = 2013
1963 vvs	1959 vvs		
1959 min	1947 min	1945 vw,b	ν_{as}(NCS)
1956 vvs	1935 vvs		
1914 w,sh			
1808 vvs			
1805 min	1772 vvs	1770 s	ν(CO) *transoid*
1801 vvs			
1774 sh	1745 sh	1750 m,sh	ν(CO) *cisoid*
1724 mw			2x865 = 1730
1663 vvw			1147 + 516 = 1663
1536 vw			2x763 = 1526
1449 vw			2x715 = 1430
1363 w			763 + 599 = 1362
1276 mw			
1260 mw	1264 w		

1255 sh			644 + 599 = 1243
		1205 vvw,b	2x598 = 1196
1147 vvs	1154 s	1154 m	ν_s(NCS)
955 w	948 w	954 vw	598 + 379 = 977
865 vvs	859 s	859 vw	ν(CN) *transoid*
834 vvs	823 vvs	822 vw	ν(CN) *cisoid*
	735 w		
	715 w	708 vw	ρ(COCℓ) a' *cisoid*
644 w	642 w	644 vvw	δ(COCℓ) a" *transoid*
599 mw	597 mw	598 s	ρ(COCℓ) a' *transoid*
516 mw	523 m	527 mw	δ(NCS) a' *transoid*
		502 w	δ(NCS) a' *cisoid*
	473 vw		ν(CCℓ) *cisoid*
439 vw	439 vw	437 mw	ν(CCℓ) *transoid*
		402 vvw,sh	
		379 w	δ(COCℓ) *transoid*
		323 w	δ(COCℓ) *cisoid*

The gas phase ir spectrum of AIT, as in AI, indicates the presence of only one isomer. MNDO/AM1 calculations (63) predict the *cisoid* isomer to be the more stable isomer. This is consistent with what was predicted for acetyl isocyanate. The liquid vibrational spectra recorded for AIT do not confirm the presence of a second isomer in analysis of the carbonyl peak. This is not surprising as a second feature was not noticed in the liquid spectra of AI.

The halo-derivatives (F,Cℓ) of carbonyl isocyanates, however, do show signs of isomerism in their gas phase spectra as well as liquid spectra. In FCIT, there appear to be two overlapping peaks in the carbonyl region of the

infrared spectrum. The higher energy peak is observed at 1863/1852 cm^{-1} and the lower energy feature is located at 1843/1833 cm^{-1}. It is impossible to determine the contour of the bands since they are so close in frequency and therefore the contours are useless in determining which band belongs to which isomer. Assuming the same relation holds true for FCIT as it does in FCI, the higher energy peak is assigned to the *transoid* conformer leaving the lower energy band as the *cisoid* conformer. This assignment is confirmed by variable temperature results which show that the higher energy, less stable isomer gains intensity upon heating whereas the more stable, lower energy isomer loses intensity. This is expected as the energy provided by heating the sample is enough to overcome the energy barrier to convert one isomer to the other (rotation of the NCS group about the C-N bond is made easier through heating).

The chloro compound has its carbonyl frequency at 1805 cm^{-1} with a shoulder appearing at 1770 cm^{-1}. The *transoid* conformer is assumed to be the more stable isomer based on results of MNDO calculations (63) and the results obtained from chlorocarbonyl isocyanate. Variable-temperature studies, however, did not produce any significant changes in peak intensity in either of the peaks. Although the peaks are well separated (35 cm^{-1}), the stronger band at 1805 cm^{-1} (*transoid*) is rather ill-defined in terms of its band envelope. There is no way that we can confirm that it is of its predicted AB-type contour as compared to the predominantly B-type contour predicted for the *cisoid* isomer.

6.3c. The C-N Stretch

The C-N stretch in isothiocyanates is located in the

general region 690-1000 cm^{-1}. It is hard to pinpoint any general trend in the assignment of ν(C-N) in these families of molecules (both NCO and NCS) because of the mixed character of the observed peaks. The C-N stretch and iso(thio)cyanato symmetric stretch appear to be synchronous where any motion along the C-NCE bonds involves a mixture of motions of the carbonyl carbon and nitrogen atom with the NCE group. The degree of coupling is impossible to predict since there are usually other fundamentals involved in the coupling (e.g. C-X). Force-field calculations (16) do show that ν(C-N) and ν_s(NCS) are greatly mixed as in the case of CDI. Figure 6.4 shows an example of the mixed character of the C-N stretch in CCIT.

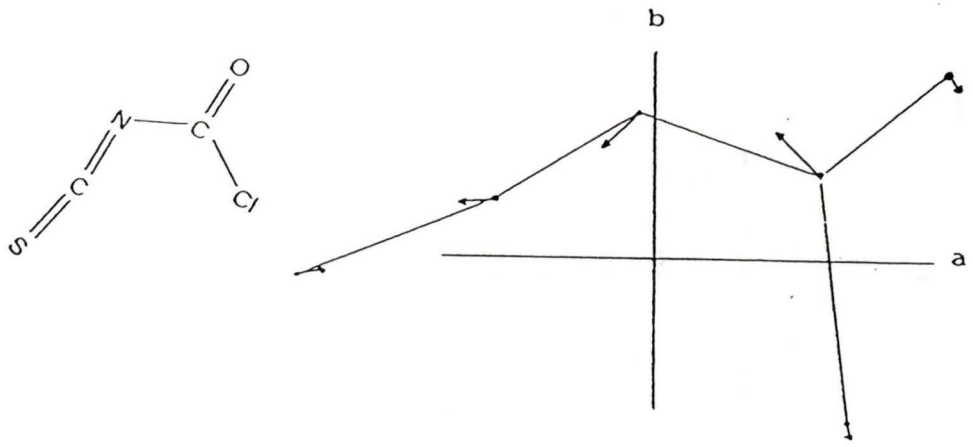

Fig. 6.4. The mixed character of the C-N stretch.

Reported literature on alkyl isothiocyanates has mixed views on the assignment of ν(C-N) and ν_s(NCS). A series of papers in the late 1960's debated the assignment of these two fundamentals. The debate, obviously, was over what feature in the corresponding regions belonged to what fundamental. Both

Ham and Willis (64) and Costoulas and Werner (65) assign the C-N stretch as the higher frequency (~1090 cm^{-1}) and the

symmetric NCS stretch as the lower frequency in question (~655 cm^{-1}). Ham and Willis based their assignment on normal coordinate calculations for the isolated NCS group and their results predicted ν_s(NCS) to be the lower calculated frequency. Costoulas and Werner argued that ν(C-N) was the higher frequency on the basis of methyl amine whose C-N stretch appeared at 1045 cm^{-1}. Both assignments were later proved invalid by Kniseley et al. (58). They showed that Ham and Willis used data (bond lengths) that were inaccurate. Also Kniseley stated that Ham and Willis did not account for interaction with the rest of the molecule. Costoulas and Werner's assignments were also discredited by Kniseley (58) in that methyl amine was a poor choice for an analogy because the amine group and isothiocyanate group do not have very much in common except for the nitrogen atom. He continued by reporting that a better structural analogy could be drawn between methyl isocyanate or methyl azide since these molecules had more in common with methyl isothiocyanate. However, when these frequencies in question were studied in these molecules, Kniseley found that there was no support for the assignment because ν(C-N) appears at a much lower frequency (910 cm^{-1}). With the heavier sulfur atom replacing oxygen, the expected C-N nitrogen fundamental would be expected to appear at a lower frequency.

Kniseley et al. (58) assigned the lower frequency to the C-N stretch. He used the idea of restricted rotation about the C_α-N bond to prove his theory with heavier alkyl substituents. Kniseley used variable-temperature studies (cooling) to show that one of the two bands located in the region 640-690 cm^{-1} disappears upon cooling. In the higher frequency region, there was only one broad peak observed and no significant change was observed upon cooling. They used this to assign the 644 cm^{-1} band in methyl isothiocyanate to ν(C-N) and therefore the peak observed at 1088 cm^{-1} to the

NCS symmetric stretch. He argued that the energy difference between conformers would be more noticeable in the C-N bond since the rotation occurs about this bond.

It is with this idea that we have confirmed the observed frequencies in the region 690-865 cm^{-1} to ν(C-N) rather than ν_s(NCS). Variable-temperature ir spectroscopy proved a most useful tool in distinguishing between the isomers present in the spectrum. Regarding the two regions in question, there are two distinct bands present in the FCIT and CCIT spectra in the lower energy region and one broader peak observed in the higher energy region. This is a similar observation to what Kniseley made (58). Recorded ir spectra at 10°C, 22°C, and 55°C ± 2°C show changes in relative intensities of the observed lower energy features whereas the higher energy peak did not change significantly. This has enabled us to confirm Kniseley's results. The basis for this assignment is as follows: the rotation of the NCS group about the C-N bond should show the greatest vibrational energy difference between conformers in the C-N stretch and C-N=C bend since this is the pivot point of the molecule. This is seen in the spectrum of CCIT where there are two distinct bands separated by 30 cm^{-1} (865 and 834 cm^{-1}). As mentioned earlier, there is no evidence of two distinct bands present in the higher energy region but there seems to be a shoulder on the higher energy side of the peak which could be evidence for the other isomer. If this feature was the major component of the C-N fundamental there should be two separate and distinguishable features. Since there is no evidence of this, it is logical to conclude the lower frequency region, where there are two features present, is the region where the C-N fundamental is located. The NCS symmetric stretch will be affected but should not show a huge energy difference between conformers. In the recorded spectra there was no evidence of intensity loss or gain in the main feature or shoulder of the NCS symmetric

mode. It is not disputed , however, that the bands are of mixed character but this information provides evidence that the lower band is of greater C-N stretching character than the NCS symmetric stretch.

The assignment of which ν(C-N) stretch belongs to which isomer is another task. Figure 6.5 shows the changes in relative intensities of the two C-N stretches for CCIT. Analogous to Cℓ-CO-NCO (28,29) and MNDO calculations (63), the *transoid* conformer is expected to be the more stable isomer. The information gathered from the VT-spectra shows that the peak at 865 cm^{-1} belongs to the *transoid* isomer and the peak at 834 cm^{-1} to the *cisoid* conformer. Upon heating, the lower frequency band gains intensity while the higher frequency feature loses intensity. This is expected as the energy provided by the heating is sufficient to convert the *transoid* isomer to the *cisoid* resulting in a population gain for the less stable conformer and therefore an increased intensity in its observed frequency. The energy provided by the heating is ample enough to overcome the barrier to rotation that results from restricted rotation about the C-N bond. The opposite is the case for cooling. In cooling the sample there is even less energy for the rotation of the NCS group about the C-N bond so there molecules will tend to favour the less energetic, more stable *transoid* isomer. The resulting cooled ir spectrum will show a decrease in the less stable isomer as the barrier to rotation is even harder to overcome.

The same arguments can be used to distinguish between the two isomers in the analysis of the C-N stretch in FCIT. The *cisoid* isomer is predicted to be more stable in the fluoro compound according to MNDO calculations (63). In FCIT the observed peak pair at 774 cm^{-1} (ir) and 788 cm^{-1} (R) are assigned to the *cisoid* isomer while the lower frequency at 778 cm^{-1} (R) is assigned to the *transoid* conformation.

The trend that the higher frequency belongs to the more stable conformer in carbonyl isothiocyanates is consistent with the conformational assignments of ν(C-N) in the corresponding chloro and fluorocarbonyl isocyanates (28,29,60).

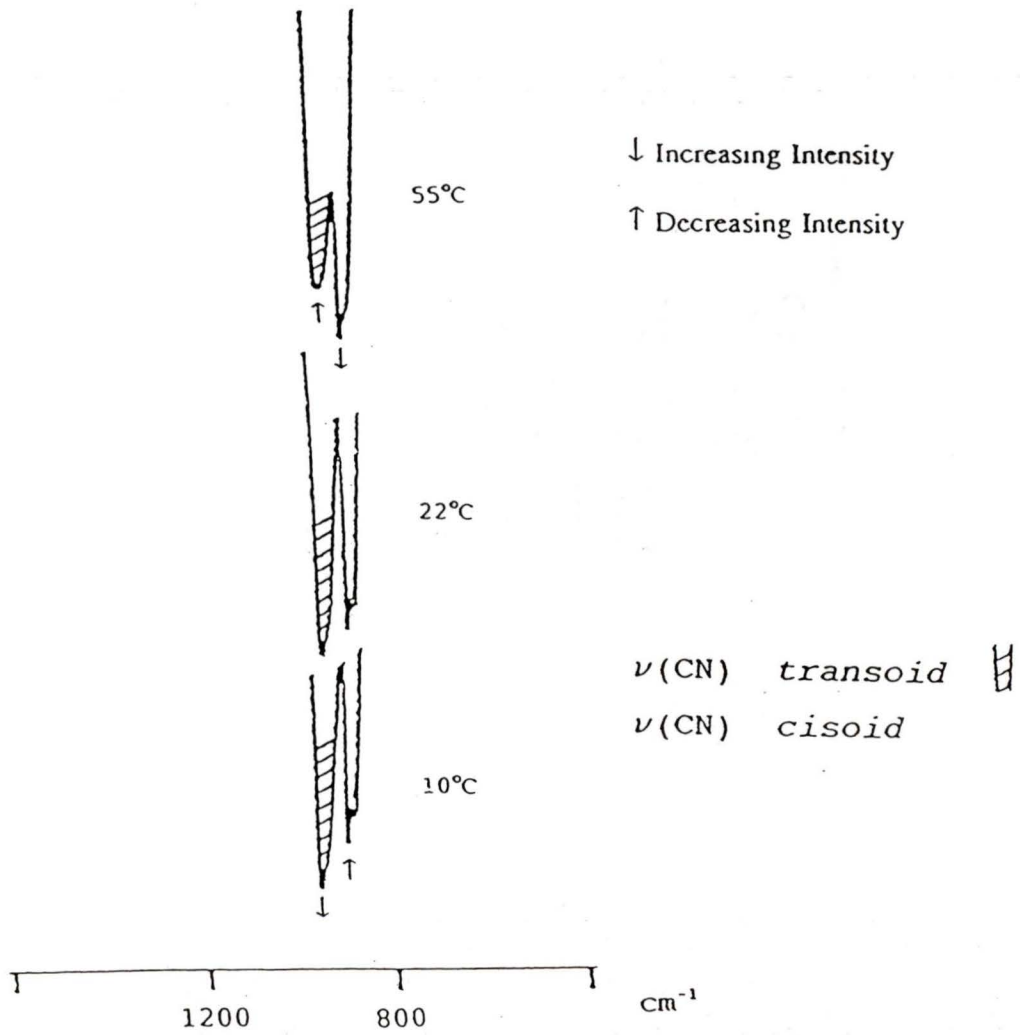

Fig. 6.5. Variable-temperature infrared spectra of CCIT.

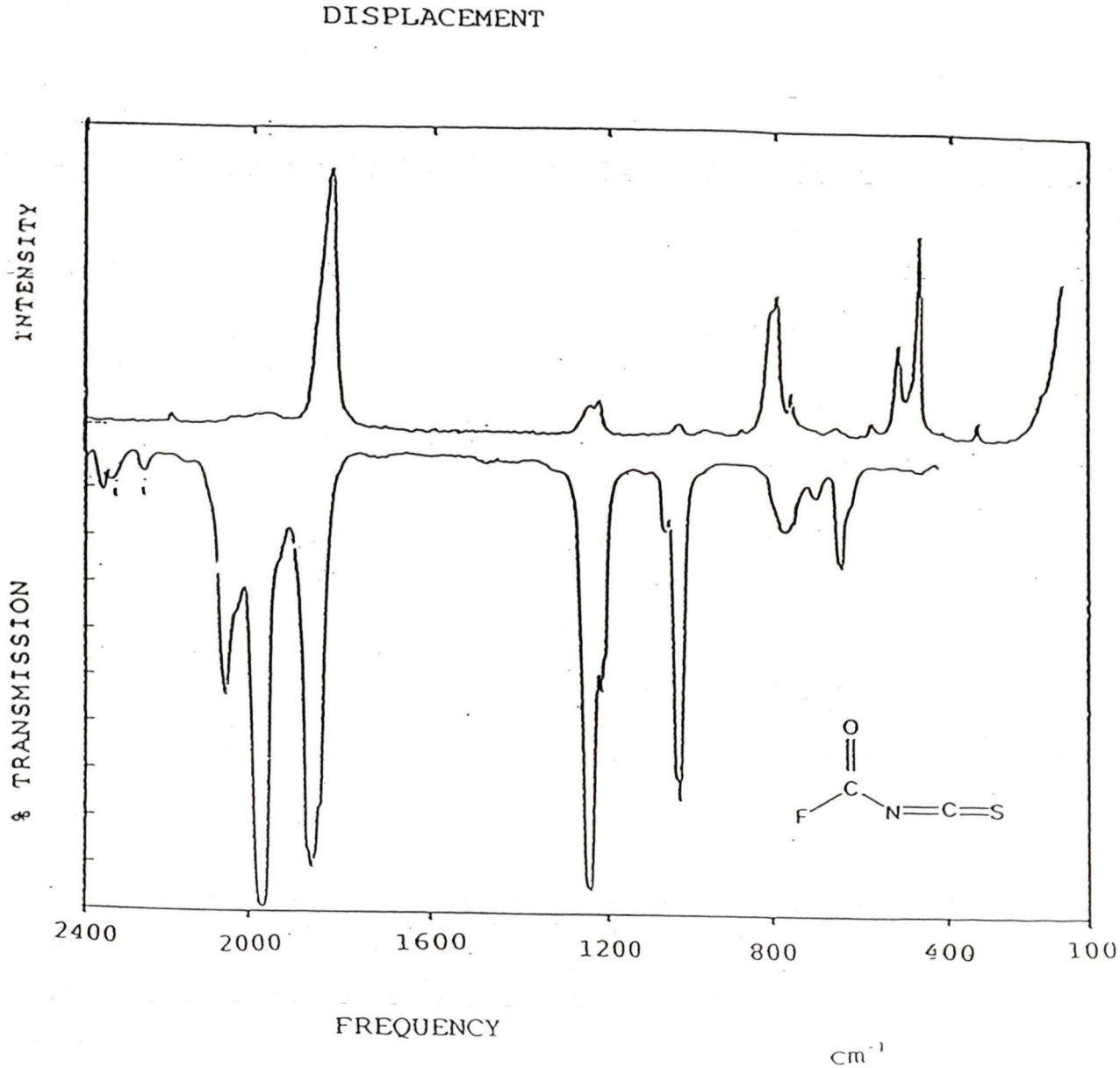

Fig. 6.6. Upper: The liquid Raman spectrum and lower: the vapour-phase infrared spectrum (P= 1 Torr) of FCIT.

Table 6.2. Observed Frequencies (cm^{-1}) and Assignments in Fluorocarbonyl Isothiocyanate.

Infrared vapour	Raman liquid	Assignment
3903 w		2x1969 = 3938
3695 vvw		2x1859 = 3718
3657 vvw		2x1838 = 3666
3198 vvw		1969 + 1213 = 3182
3073 vvw		1859 + 1213 = 3072
2973 w		1969 + 1018 = 2987
2748 vw		
2607 vvw		1838 + 774 = 2612
	2190 vvw	
2027 ms		2x1018 = 2036
1969 vvs	1955 vvw,b	ν_{as}(NCS)
1863 vs		
1859 min	1819 sh	ν(CO) *transoid*
1852 vs		
1843 vs		
1838 min	1808 s	ν(CO) *cisoid*
1833 vs		
1242 vs	1233 w	ν(C-F) *cisoid*
1213 ms	1214 w	ν(C-F) *transoid*
1052 vw		
1026 s	1017 sh	ν_s(NCS) *cisoid*
1018 s	1010 vw	ν_s(NCS) *transoid*
958 vw	952 vw	496 + 451 = 947
	792 sh	ν(CN) cisoid
774 vw	778 ms	ν(CN) *transoid*
763 vw		451 + 319 = 770
743 vw	744 w	δ(COF) a"
739 sh		
692 vvw,b	687 vvw	δ(COF) a'
640 vw,sh	639 vvw	2x319 = 638
617 vvw,sh		
608 vvw,sh		
	555 vw	δ(NCS) a"
	496 m	ρ(COF)

	496 m	ρ(COF)
449 vw	451 ms	δ(NCS) a'
	393 vvw	
	319 vw	δ(FCN)
	179 sh	δ(CNC)

6.3d. Fundamentals involving the C-X groups

While it is convenient to label bands in the carbonyl isothiocyanate tables as C-X stretches, they are, without a doubt, coupled to some extent to the C-N stretch and the bands are of mixed character. Assignment of these C-X fundamentals is made much easier if we employ the help of previously studied acid pseudohalides (61,62), acetyl halide (46) and the corresponding carbonyl isocyanates (26,28-35,60).

The C_α-CH_3 stretching and bending fundamentals are identical to those observed in acetyl isocyanate and have been studied extensively in such molecules as acetamide (38) and acetaldehyde (36). The three fundamentals used to describe the C-H stretching modes appear at almost the same frequencies as they do in AI. The slightly lowered frequencies in AIT appear in the same manner as observed in AI, with the symmetric C-H stretching mode being the most intense feature in the spectrum while the two asymmetric stretches are much weaker and appear at slightly higher frequencies than their symmetric counterparts. Assignments for AIT are listed in Table 6.3 while Table 6.4 illustrates the fundamentals of the methyl group in AIT and AI. The assignment of $\delta(CH_3)$ is made much easier in isothiocyanates than in isocyanates. The region where these fundamentals are expected to appear (1360-1450 cm^{-1}) is uncongested unlike the case in the spectra of AI where the fundamental

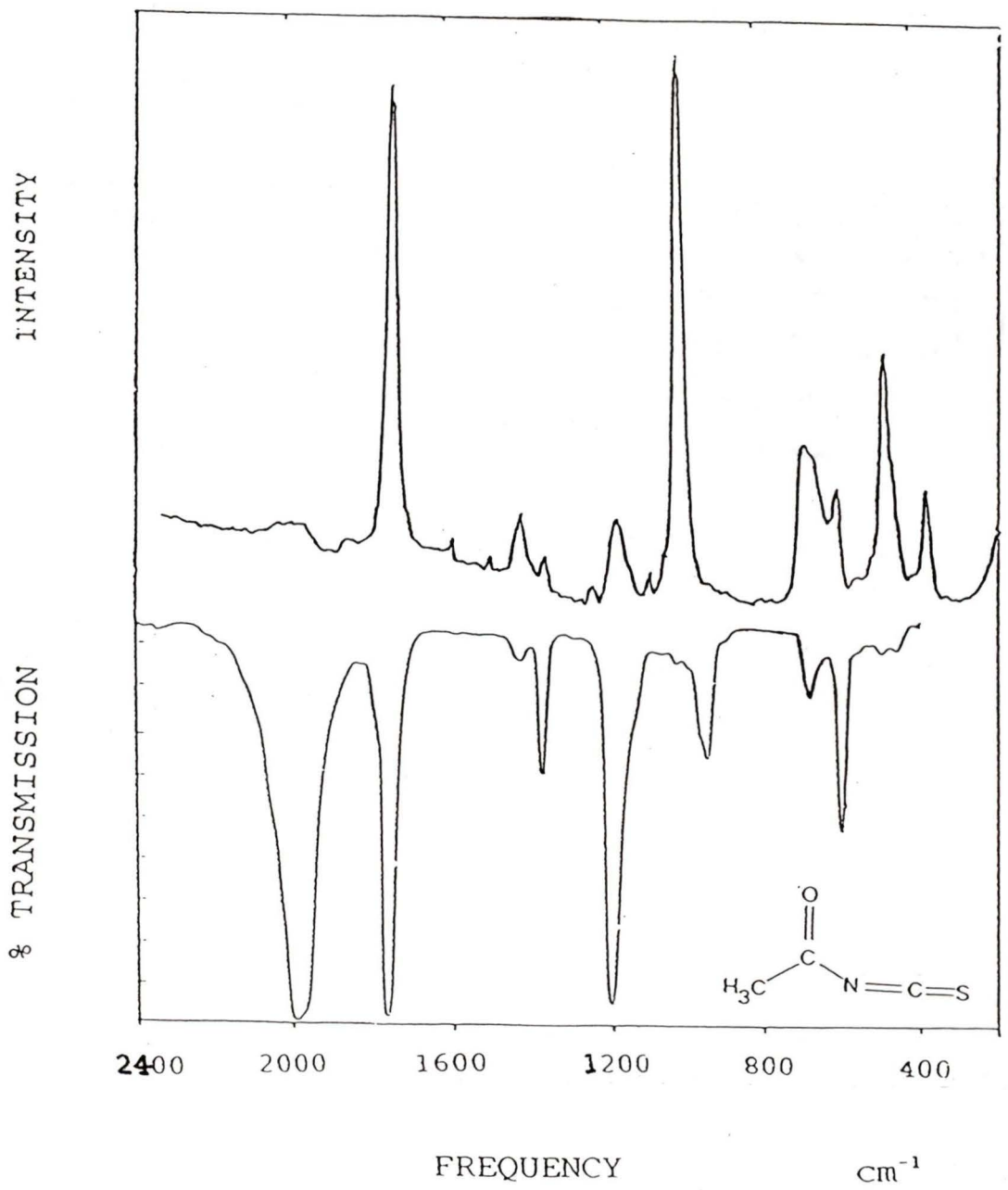

Fig. 6.7. Upper: The liquid Raman spectrum and lower: the vapour-phase infrared spectrum (P= 20 Torr) and of AIT.

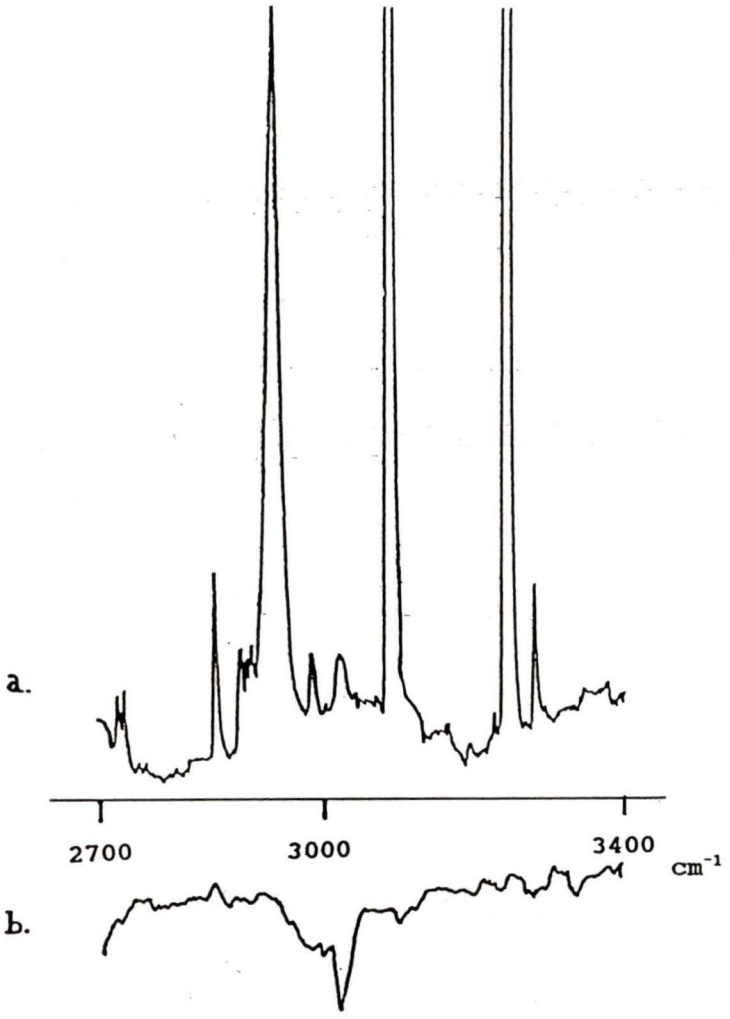

Fig. 6.8. a: The liquid Raman spectrum and b: the vapour-phase infrared spectrum (P= 35 Torr) of the methyl stretching region of AIT.

Table 3. Observed Frequencies (cm^{-1}) and Assignments for Acetyl Isothiocyanate.

Infrared vapour	Infrared liquid	Raman liquid	Assignment
3502 vw			2x1763 = 3526
	3437		2x1736 = 3472
3000 sh	3010 w	3017 w	$\nu_{as}(CH_3)$
2963 sh	2948 sh	2976 w	$\nu_{as}(CH_3)$
	2920	2929 vs	$\nu_{s}(CH_3)$
2865 vvw		2835	2x1428 = 2856
2665w	2640 w		

2557 vw			1374 + 1194 = 2568
2361 w			2x1194 = 2388
2338 sh			1736 + 603 = 2339
		2020 vw	2x1018 = 2036
1987 vvs	1986 vvs,b	1991 vw,b	ν_{as}(NCS)
1963 sh		1960 vw	
1831 vvw	1818 mw		1368 + 461 = 1829
1798 sh			1194 + 603 = 1797
1763 vvs	1736 vvs	1731 vvs	ν(CO) *cisoid*
		1597 vvw	1018 + 565 = 1583
1531 vvw			CS_2 impurity
		1438 sh	
1428 w		1428 mw	$\delta_{as}(CH_3)$
	1414 m		
1374 m	1368 s	1363 w	$\delta_{s}(CH_3)$
1294 w			
		1241 w	
1194 vvs	1185 vs,b	1184 mw,b	ν_{s}(NCS)
1139 mw,sh	1121 mw,sh	1150 w,sh	ν(CC)
		1095 w	614 + 481 = 1095
1079 w			
		1063 vw,sh	603 + 461 = 1064
1030 w,sh	1030 w	1018 vvs	ρ(CH3)
998 sh	988 w		603 + 373 = 976
949 m	954 mw		
790 vvw	790 vvw	787 vvw	456 + 230 = 786
686 mw	692 w	693 m	ν(CN) *cisoid*
	662 sh	677 sh	ν(CN) *transoid*
		629 vw,sh	δ(NCS) a" *transoid*
603 ms	603 s	614 m	δ(NCS) a" *cisoid*
566 vw	559 vw	565 vw	δ(CCO) a"
489 vvw,b	484 w	481 ms	δ(NCS) a' *cisoid*
461 vvw	461 sh	456 mw,sh	δ(NCS) a' *transoid*
	373 w	376 m	δ(CCN)
	362 vvw		

Table 6.4. Observed frequencies (cm^{-1}) of the methyl group in acetyl isocyanate and acetyl isothiocyanate.

Fundamental	CH_3-CO-NCO		CH_3-CO-NCS	
	ir (± 2 cm^{-1})	Raman (± 3 cm^{-1})	ir (± 2 cm^{-1})	Raman (± 3 cm^{-1})
$\nu_{as}CH_3$	3042	3030	3000	3017
$\nu_{as}CH_3$	2989	2985	2963	2976
$\nu_{s}CH_3$	2949	2941	-	2929
$\delta_{as}CH_3$	1442	-	1428	1428
$\delta_{s}CH_3$	1363	1364	1374	1363
ρCH_3	991	993	1030	1018
νC-C	1159	1154	1139	1150

The fundamentals that result from the vibrations of the COX bonds are expected to be observed at very similar frequencies to their isocyanate counterparts since the sulfur\oxygen substitution in the NCE group is too far away to influence where these vibrations will occur.

Besides the C-X stretch, the COX bonds are responsible for an in-plane and out-of-plane bend as well as a rocking motion. There are two bands of fairly weak intensity in the 685-750 cm^{-1} region of the FCIT ir spectra where the in-plane and out-of-plane COF bending fundamentals are expected. The bands are fairly weak and are rather ill-defined for classification as to which band is characteristic of which fundamental. The band centred at 739 cm^{-1} has a profile that suggests a C-type band contour which is characteristic of an out of plane bend in a planar

molecule. The assignments are made easy by comparison with assignments of related molecules such as fluorocarbonyl isocyanate (60) and cyanoformyl fluoride (62). The C-F stretch, as mentioned earlier, is coupled with symmetric NCS stretching fundamental. The two features that appear are of mixed character. The coupling increases the frequency of what is assigned as the C-F stretch to 1213 cm^{-1}. This is slightly higher than what is reported as the C-F stretch in fluorocarbonyl isocyanate (1157 cm^{-1}) and cyanoformyl fluoride (1175 cm^{-1}).

The COCℓ bends are harder to assign because the region in which they are expected to appear (430-650 cm^{-1}) is also the region where the C-Cℓ stretch is anticipated to appear as well as the isothiocyanato bending fundamentals. The observed frequencies for the COCℓ bending motions of CCIT do not deviate significantly from those observed in CCI. Since the C-Cℓ stretch is also expected to appear in this region of the spectra, it is logical to infer that this stretch will couple to the in-plane COCℓ bends to produce bands of mixed character. The COCℓ rocking motion is the most probable candidate for mode-mixing based on what is observed in force field calculations (16). The idea of these motions being of mixed character is also supported in the analyses of CCI (28,29). The COCℓ out-of-plane bend appears as a weak infrared feature at 644 cm^{-1}. The band has a C-type of the band profile which confirms that it is an out-of-plane feature. This evidence is in agreement with the 635 cm^{-1} assignment for δCOCℓ a" in chlorocarbonyl isocyanate (28). The in-plane bend appears at a frequency of 440 cm^{-1}.

The CCO bending fundamentals in acetyl isothiocyanate are also complicated to assign because these fundamentals are also expected to appear in the same region as δ(NCS). The CCO in-plane and out-of-plane bends can be expected to

appear in close proximity to the equivalent motions in acetyl isocyanate. By analogy, this leads to the assignment of the CCO out-of-plane bend at 565 cm^{-1} (R) with its in-plane counterpart at 461 cm^{-1}. The out-of-plane assignment is consistent with what is calculated for the CO out-of-plane deformation by the method of Seth-Paul (54). Using the values obtained for the fluoro (60) and chlorocarbonyl isocyanate (28) compounds and what is assigned as γ(C=O), we obtain a value of 26.76 $cm^{-1/2}$ for γ(NCS). Using the value obtained for the methyl group [$\gamma(CH_3)$= 21.5 $cm^{-1/2}$ (54)], γ(C=O) is calculated to be 575 cm^{-1}. This value is reasonable for the assigned value of 565 cm^{-1} in AIT as is and the assigned value of 548 cm^{-1} in acetyl isocyanate. Raman polarization experiments would also aid in distinguishing between the in-plane and out-of-plane bends and could confirm these tentative assignments.

Tables 6.1-6.3 list the observed frequencies and assignments for CCIT, FCIT, and AIT respectively.

Chapter 7
Summary and Conclusion

7.1 Summary and Conclusion

This chapter will present a summary of the results and conclusions obtained in each of the chapters. The work reported in this thesis involves the preparation, characterization, and complete vibrational analyses of the infrared and Raman spectra of a group of selected carbonyl iso(thio)cyanates and in some cases, normal coordinate calculations.

The acyl isocyanates and isothiocyanates were prepared according to literature methods with slight modifications in certain examples. Although most of these compounds have been prepared previously, detailed vibrational analyses of these compounds had not been performed. It is for this reason that these carbonyl iso(thio)cyanates form the basis of this work.

The isocyanato asymmetric stretch appears in the region 2250-2275 cm^{-1}. The features observed for the NCO asymmetric stretch are very intense and fairly broad in the infrared spectra while the features are very weak and broad in the Raman spectra. This stretch is rather insensitive to the nature of the substituent but the data suggest that there is an inductive effect present. There appears to be a slight increase in frequency of ν_{as}(NCO) with increasing electronegativity of the substituent.

In all the vibrational spectra recorded for carbonyl isocyanates, there was no observable evidence of geometric conformations being present in the region of the isocyanate

asymmetric stretch. The most likely reason for there not being any evidence of different conformers is that ν_{as}(NCO) for each conformer is so close in energy that the two features are superimposable and therefore indistinguishable. This reasoning is supported by looking at the calculated values of ν_{as}(NCO) for the *cisoid-cisoid* and *cisoid-transoid* isomers of CDI. Both calculated values of ν_{as}(NCO) for the two isomers are 2272 cm^{-1}, making them indistinguishable in any spectra. Even if the two were distinguishable, the ν_{as}(NCO) ir band is so intense and broad that the band's profile is poorly resolved. If both isomers were present in the spectra they may not be observed because of the poor resolution. The same can be said for the Raman bands indicative of the NCO asymmetric stretch but, here, instead of being too intense, it is the lack of intensity that may hinder the observation of two isomers.

The carbonyl stretching region yielded nothing spectacular in relation to observed results. The feature appeared in the range 1705-1780 cm^{-1}. The order of appearance of the carbonyl frequencies roughly parallels the electronegativity of the group attached to the carbonyl group:

$$CC\ell_3 > CH_3O \approx CHC\ell_2 > CH_3 > CH_2C\ell > NCO > CH_3S$$
$$1777 > 1764\ 1764 > 1758 > 1752 > 1741 > 1709\ cm^{-1}$$

The NCO symmetric stretching frequencies appeared as medium to strong bands in both the infrared and Raman spectra in the range 1400-1425 cm^{-1}. Increases in electronegativity of the substituent caused a corresponding increase in frequency of the isocyanato symmetric stretch. Table 7.1 gives a comparison of the observed stretching fundamentals for the isocyanate group of the seven isocyanates studied in this work.

The NCO bending mode can be divided into two modes based on the molecules' planar geometry. One of the bends occurs in the plane of the molecule while the other is out of the plane. These bends are typically found in the region between 600-690 cm^{-1} and are usually of medium or weak intensities. The NCO bending fundamentals are coupled to the R-C(O) bending modes to a lesser extent than the corresponding stretching motions. As in the case of the NCO symmetric stretching fundamental, there appears to be a relation between increasing frequency of the observed feature and increasing electronegativity of the substituent.

Table 7.1. Observed stretching fundamentals (cm^{-1} ± 2 cm^{-1}) for the isocyanate group.

	$CHCl_2$	CCl_3	CH_3O	NCO	CH_2Cl	CH_3	CH_3S
ν_{as}NCO	2273	2258	2262	2258	2264	2255	2257
ν_{s}NCO	1425	1422	1420	1418	1415	1406	1404
ν_{AVE}NCO	1849	1840	1841	1838	1840	1831	1831

The C-N stretch is very hard to characterize in relation to the substituent associated with the molecule in question. The spectral data acquired in the spectra offer no evidence of any trends between substituent and frequency of the C-N stretch. The coupling present in each example of the iso(thio)cyanates studied is the main factor behind this lack of trend. The feature that is assigned as the C-N stretch is undoubtedly of mixed character. There is

coupling between the R-C(O)-N bonds which complicates the assignment of ν(C-N). Besides being coupled to the R-C(O)- bond, the C-N stretch is also coupled to the NCE symmetric stretch. The amount of coupling between the stretches mentioned above varies with each substituent. To date there is no clear relation on how the substituents interact with the C-N stretch and the NCO symmetric stretch. This topic alone could possibly be the subject of a separate project.

In some examples of the vibrational spectra of the carbonyl isocyanates and isothiocyanates studied, there was evidence of more than one isomer being present in the recorded spectra. Where there was evidence for more than one isomer, detailed assignments for both isomers were made. The assignments were based on variable-temperature spectra as well as comparison with calculated values for the fundamental in question. Isomerism in the carbonyl iso(thio)cyanates occurs as a result of rotation of the NCE group about the C-N bond. It was evident in almost all the vibrational spectra recorded that there were two very separate and distinct C-N stretching bands present. These two bands showed the greatest separation between isomers in comparison to other fundamentals (e.g. ν(C=O)). This is not surprising as the greatest energy difference between the identical motions of the different isomers present would occur in this band since the isomerism is a result of rotation about this C-N bond.

There possibility of isomerism as a result of rotation of the R- group about the O=C-R bond also exists in some examples of the carbonyl isocyanates studied (e.g. acetyl isocyanate and it chloro-derivatives). This possibility can be ruled out because of the observations of the C-N and symmetric NCO stretches in the spectra of CX_3-CO-NCO molecules (X= H or Cℓ). All the species of that group show

the same changes in the C-N and symmetric NCO stretching regions, therefore indicating that the isomerism is a result of rotation about the C-N bond and not the C-R bond.

In the cases of methoxy- and thiomethoxycarbonyl isocyanates, there were four possible planar conformations that the molecules could possess. The spectra recorded indicated that two of the four isomers were present in both the liquid and vapour phase spectra. By analogy to other methyl esters and with the use of variable-temperature spectral data the isomers present in the ir and Raman spectra of (thio)methoxycarbonyl isocyanate were deduced to be the *transoid-Z* and *cisoid-Z* isomers. The sulfur/oxygen exchange that differentiates these molecules had very little effect on the carbonyl isocyanate framework. The slightly lowered frequencies for the thio compound can be attributed to the heavier sulfur atom.

The vibrational analyses performed on CDI indicated that interaction between the two C-NCO fragments produces two motions: one in-phase and one out-of-phase for each fundamental. These motions result in several peak pairs for the C-NCO fundamentals. Simple force field calculations helped assign some of the more difficult bands where there was significant congestion in the spectrum.

The substitution of sulfur for oxygen on going from isocyanates to isothiocyanates produces no change in the fundamentals present for the CO-NCE framework. The position of the bands associated with the NCE group, however, are expected to appear at lower frequencies for the NCS group fundamentals because of the mass-sensitivity of the group. The symmetric and asymmetric stretches appear approximately 300 cm^{-1} lower than their isocyanate counterparts. The relation between increasing electronegativity and increasing

frequency is not evident in the asymmetric NCS stretch and the carbonyl stretch. The possible reason for this is that the mechanical coupling that occurs between the two fundamentals as a result of the lower NCE frequency outweighs the electronegative substituent effects. The symmetric stretch was also harder to assign because of its lowered frequency. This fundamental was more susceptible to vibrational coupling with the C-C and C-F stretches in acetyl and fluorocarbonyl isothiocyanates.

The carbonyl peak is virtually unaffected by the replacement of oxygen with the heavier sulfur atom. Only a very slight reduction in frequency could be noticed in comparison to their isocyanate counterparts. Distinction between isomers of the isothiocyanates was more difficult than in the case of the isocyanates when looking at the carbonyl bands. The band contours which were important in distinguishing between different isomers in isocyanate compounds were rather ill-defined in the carbonyl isothiocyanates. This is a result of a reduced band separation between isomers as well as the reduced P-R separation because of the presence of the heavier sulfur atom.

As mentioned in chapter 6, there were several difficulties in recording the Raman spectra of the carbonyl isothiocyanates because of their thermal and photochemical instabilities. Analyses of these carbonyl isothiocyanates were performed using the infrared spectral data and with the limited Raman data that were recorded.

7.2 Future Work

There is the possibility of future work concerning the spectroscopy of carbonyl isocyanates and isothiocyanates

pertaining to the characteristics of these molecules and their structures.

An in-depth analysis of the substituent effects on the carbonyl isocyanate framework could be undertaken. A survey of the substituent effects could be furthered with emphasis on the coupling effects of the C-N stretch with the C-R and the NCO symmetric stretches in hopes that some sort of rapport can be discovered in relation to the mechanical coupling that occurs in these molecules. Comparison of these coupling analyses with the inductive effects of the substituents may yield some interesting results.

Another interesting analysis would be the study of the barrier of the rotation of the NCE group about the C-N bond. This could be achieved through accurate, quantitative variable-temperature infrared measurements. This would also further probe the *cisoid-transoid* conformation problem confirming which isomer is more stable in each example by experimentally determining the molecules' ΔH values and looking at the enthalpy differences for the *cisoid* and *transoid* conformers. More detailed theoretical calculations concerning these barriers to rotation will also accommodate the variable-temperature ir experiments. These results would provide a better picture of why certain conformations are preferred in certain carbonyl iso(thio)cyanates. The results may further clarify the *cisoid\transoid* preference in terms of polarizability of the substituents as well as steric effects.

Further work on the recording of the Raman spectra of the carbonyl isothiocyanates could be performed by using a different excitation source or perhaps a different Raman apparatus. Collection of better Raman spectra or faster Raman spectra before decomposition occurs may enable depolarization experiments to be performed which would help

clarify assignments in the lower energy region of the spectra.

A more detailed look at the instability of the carbonyl isothiocyanates studied in this survey could be initiated. This would enable the molecules to be studied at the electronic level and would clarify what mechanism is causing the molecule to decompose.

An interesting extension of the force field calculations carried out in this work would involve a more in-depth theoretical analysis accounting for the coupling effects that occur between the NCO and C-R stretches with the C-N stretch. This could be done in conjunction with the experimental work on the coupling analyses and would provide a better calculated spectrum for the examples used in this work.

The study of carbonyl iso(thio)cyanates could be extended to include molecules that are closely related to the molecules studied here. Such an example would be to try to synthesize the molecules HC≡C-CO-NCO, NC-CO-NCO, $CO-(NCS)_2$ and OCN-CO-NCO in order to compare their vibrational spectra to that of carbonyl diisocyanate. The parent molecules to the carbonyl iso(thio)cyanates have yet to be synthesized and characterized vibrationally.

Appendix 1

List of Acronyms for Carbonyl Isocyanates

AI	- Acetyl isocyanate	- CH_3-CO-NCO
AIT	- Acetyl isothiocyanate	- CH_3-CO-NCS
CAI	- Chloroacetyl isocyanate	- $C\ell H_2C$-CO-NCO
CCI	- Chlorocarbonyl isocyanate	- $C\ell$-CO-NCO
CDI	- Carbonyl Diisocyanate	- OCN-CO-NCO
CCIT	- Chlorocarbonyl isothiocyanate	- $C\ell$-CO-NCS
CCSC	- Chlorocarbonylsulfenyl chloride	- $C\ell$-CO-$SC\ell$
DCAI	- Dichloroacetyl isocyanate	- $C\ell_2HC$-CO-NCO
FCI	- Fluorocarbonyl isocyanate	- F-CO-NCO
FCIT	- Fluorocarbonyl isothiocyanate	- F-CO-NCS
FCSC	- Fluorocarbonylsulfenyl chloride	- F-CO-$SC\ell$
MCI	- Methoxycarbonyl isocyanate	- CH_3O-CO-NCO
TCAI	- Trichloroacetyl isocyanate	- $C\ell_3C$-CO-NCO
TCICA	- Trichloroisocyanuric acid	- 3 $C\ell$-NCO
THF	- Tetrahydrofuran	
TMCI	- Thiomethoxycarbonyl isocyanate	- CH_3S-CO-NCO
TMS	- Tetramethyl silane	

Appendix 2

The C_s point group table.

C_s	E	$\sigma_h(xy)$	
A'	1	1	T_x, T_y, R_z
A"	1	-1	T_z, R_x, R_y

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