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University of South Carolina, Columbia, South Carolina 29208)

Principal Investigator - James R. Durig, Chaired Professor of Chemistry

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SUMMARY OF PROGRESS

We have been studying the vibrational spectra from 4000 to 33 cm^{-1} of several molecules which may be present in the atmosphere of the Jovian planets. These studies have been made to provide vibrational frequencies which can be used to: (1) determine the compositions of the cloud covers of several of the planets; (2) provide structural information under favorable circumstances; (3) provide necessary data from which accurate thermodynamic data can be calculated; (4) and furnish information as to the nature of the potential energy function of the molecules and forces acting within them.

Gerard P. Kuiper¹ has pointed out that the Jovian atmospheres are expected to contain H_2 , He, N_2 , H_2O , NH_3 , CH_4 , Ar and possibly SiH_4 . He had also listed a number of other gases that should be considered because they are composed of fairly abundant atomic species and have boiling points below 120°C [see Table 8, pg. 349-350 of reference (1)]. He has also pointed out that until more is known about the atmospheres of the planets it is useful to keep a fairly large number of possible constituents in mind in planning further spectroscopic work.

Some of the molecules which we have studied can be produced photochemically from methane, ammonia, and hydrogen sulfide which are thought to be constituents of the planets with reducing atmospheres. Some of the compounds will polymerize under ultraviolet radiation and drop out of the atmospheres. However, planets with a hot base, like that of Jupiter, may rebuild molecules destroyed photochemically. Therefore, we have used these criteria in selecting the compounds which we have studied. In our initial work on the vibrational spectra of molecules of astrophysical interest we studied hydrazine² and methylamine.³ However, there are several other small molecules which contain hydrogen, carbon and nitrogen which also should be possible constituents of the reducing

atmospheres and we previously selected methyl hydrazine⁴, unsymmetrical dimethyl hydrazine⁵, symmetrical dimethyldrazine⁶, propylene imine⁷, and 1-pyrazoline⁸ for our studies. In addition a vibrational study of HNCS and DNCS has been completed⁹ and the results reported in the previous progress report.

Closely related to our studies of these nitrogen containing compounds has been our work on the carbonyl containing molecules. We have previously reported work on carbon trioxide¹⁰, trifluoromethyl peroxide¹¹, ethylene carbonate¹², γ -butyrolactone¹², cyclopentanone¹², oxalyl chloride¹³, glyoxal¹⁴, oxalyl bromide¹⁵, and oxalyl fluoride¹⁶. In a continuing study of oxalyl compounds, we have completed investigations of 2,3-butanedione (biacetyl), thiooxamide and oxamide and copies of the two papers which were submitted to the Journals of Physical Chemistry and Molecular Crystals and Liquid Crystals can be found in Appendices I and II, respectively.

We have recently recorded the vibrational spectra of several molecules of chemical formula, $[\text{COX}]_2$, where X = F, Cl, Br and H and determined their molecular symmetries in the solid and fluid states.¹³⁻¹⁶ For the halogen containing molecules, the spectra for the fluid states showed the presence of two geometric isomers and the data have been shown to be consistent for that expected for the cis and trans isomers. In these studies it has been shown that structural conclusions can only be correctly made if the infrared and Raman spectra are obtained for these compounds in at least two different physical states with one of them being the solid. Closely related to these studies is our investigation of the infrared and Raman spectra of 2,3-butanedione which is commonly called biacetyl.

There have been several previous vibrational studies¹⁷⁻²⁰ of biacetyl with the more recent one by K. Noack and R. N. Jones¹⁹ being the most complete. However, there are some inconsistencies in the work of Noack and Jones which cannot be readily explained. For example, they have assigned the Raman lines

at 240 and 538 cm^{-1} to out-of-plane bending modes of b_g symmetry whereas there should be only one mode of such symmetry unless one gives the methyl torsional mode such a description. However 240 cm^{-1} is too high a frequency for the methyl torsional mode for this type of molecule. Noack and Jones¹⁹ as well as Harris and Witkowski²⁰ have assigned the strong Raman line at 685 cm^{-1} as the skeletal bending mode of a_g symmetry but such an assignment leaves no reasonable explanation for the Raman line at 614 cm^{-1} which had previously been assigned to this mode by Sidman and McClure.¹⁸ In essence the assignment of the 685 cm^{-1} Raman line to the skeletal bending modes results in too many Raman lines in the skeletal bending region to be assigned to the fundamentals of the biacetyl molecule for only the trans form. Also the C-CH₃ symmetrical stretching mode was not assigned by Noack and Jones; yet it should be one of the most intense Raman lines. Sidman and McClure assigned the 1004 cm^{-1} Raman line to the C-CH₃ stretching mode, but Noack and Jones have suggested that this band is the central C-C stretching vibration. Thus, there are still several uncertainties in the vibrational assignment for biacetyl and it was hoped that an investigation of the infrared and Raman spectra of solid biacetyl would clear up these discrepancies. No vibrational studies have previously been reported for the solid.

It was hoped that a vibrational study of the solid would provide the necessary data to determine the symmetry in the solid as well as the crystal site occupied by the molecules. In addition, factor group splitting could be investigated and it was hoped that the frequencies for the methyl torsional modes might be determined. The frequency for the skeletal C-C torsional mode was also of particular interest since it had been previously reported to be at 35 cm^{-1} from a study of the electronic spectrum of the solid²¹ although Fateley et al.²⁰ have reported a frequency of 48 cm^{-1} for this normal mode in the vapor state. Noack and Jones had suggested a trans, C_{2h}, structure for the molecule

in the liquid although they pointed out that such a structure was contrary to the dipole moment reported by Bloom and Sutton²³ for this molecule in both the gas and liquid states. Therefore, a reinvestigation of both the liquid and gas was carried out to obtain data for comparison with the solid phase studies.

The infrared spectra of biacetyl $[\text{CH}_3\text{CO}]_2$ and biacetyl- d_5 $[\text{CD}_3\text{CO}]_2$ were recorded over the range 33 to 400 cm^{-1} for the samples in the gaseous, liquid and polycrystalline states. The Raman spectra of the liquid and polycrystalline solids were also observed, and quantitative depolarization ratios were measured. The vibrational spectra of the crystalline materials were interpreted on the basis of C_{2h} molecular symmetry and the values observed for the fundamentals were compared with those previously reported for the fluid states. A comparison of the infrared and Raman bands in the crystal shows that the mutual exclusion principle was operative. It was concluded from this alternate forbiddance that the molecule has a centrosymmetric structure in the crystal and that each molecule occupies a $C_i(\bar{1})$ site. The factor group of the crystal is believed to be either $C_{2h}(2/m)$ or $C_{2h}(mmm)$ with two or four molecules per primitive unit cell. No evidence could be found for the existence of the cis isomer in the fluid states. Possible reasons for its absence are discussed in detail in the paper which is presented in Appendix I. The infrared active methyl torsion was observed at 217 and 157 cm^{-1} for the "light" and "heavy" molecules in the solid state, respectively, and the barriers to internal rotation were calculated to be 3.1 kcal/mole. Barriers of 2.7 and 2.8 kcal/mole were calculated from rather broad bands in the spectra of gaseous $[\text{CH}_3\text{CO}]_2$ and $[\text{CD}_3\text{CO}]_2$, respectively. The barrier values were compared to those obtained for other acetyl compounds (see Appendix I). Calculation of thermodynamic properties is underway and will be reported in the next progress report.

Crystallographic studies^{24,2} have established the structures of oxamide and dithiooxamide as being trans C_{2h} in space groups of $P\bar{1}$. Oxamide has one molecule per unit cell, whereas the sulfur analog contains two. Infrared and Raman studies have been reported²⁶⁻²⁸ for oxamide as has infrared data for dithiooxamide²⁶, but none of the studies have examined the region below 200 cm^{-1} and most studies extended only to 400 cm^{-1} . This has left six fundamentals unassigned in oxamide, four of which are Raman active and two which are infrared active. The modes remaining to be found in the infrared spectrum are the OCN torsion of a_u symmetry and the OCN rock of b_u symmetry. Raman assignments are lacking for two a_g modes, the OCN bend and rock, and two b_g vibrations, the NH_2 torsion and OCN out-of-plane bend. There is no Raman information available for dithiooxamide at all and the SCN out-of-plane bend (a_u), SCN torsion (a_u), SCN bend (b_u), and SCN rock (b_u) have not been observed in the infrared spectrum. The interesting lattice region has also been neglected. Therefore, work was undertaken to reexamine the spectra of these compounds in an attempt to complete the assignments and provide new information concerning the lattice vibrations of the two molecules.

Re-examination of the infrared and Raman spectra of oxamide led to the assignment of all the fundamental vibrations of this molecule, with the exception of the Raman-active OCN rock. Similarly, the infrared assignments were completed for dithiooxamide, and nine out of twelve fundamentals assigned from the previously unobserved Raman spectrum. The weakness of the Raman lines of dithiooxamide prevented us from observing the 2 N-H stretching modes and the NH_2 scissors because the phototube is less sensitive in the high-frequency range.

The lattice regions of the spectra have been examined and the external modes were observed as predicted from group theoretical considerations. Oxamide exhibits three Raman-active librations, which occur at 106, 134, and

157 cm^{-1} . For dithiooxamide, three infrared-active translations and six Raman librations are expected. The infrared bands were observed at 79, 92, and 99 cm^{-1} . The Raman lines occur as three doublets; three strong lines were seen at 74, 98, and 112 cm^{-1} , and the first two had weaker shoulders on the low-frequency side. The sixth libration was not seen, but is probably contained in the assumed unsplit line at 112 cm^{-1} .

Factor group splitting of the internal fundamentals is a possibility in dithiooxamide, but the only indication of it was seen in the splitting of the SCN out-of-plane bend. The forces in the crystals of oxamide and dithiooxamide appear to be similar, as evidence by the shift of librations from one molecule to the other of approximately 1.4 and the similarity of the calculated force constants.

FUTURE WORK (NGR-41-002-033)

We are continuing our investigation of the vibrational spectra of small molecules which may be possible constituents of the Jovian atmospheres. The data will be used to calculate thermodynamic properties, force constants and other useful molecular properties when possible. At present work is still continuing on methylhydrazine. Also the vibrational study of azomethane is nearing completion. The results of these studies will be in the next progress report. We have also begun an investigation of oxalyl chlorofluoride which is a continuation in our study of molecules containing carbonyls. The results of this work should appear in a future report. We have also initiated studies on dimethyl phosphine which fits the criteria as a possible constituent of the Jovian atmospheres.

We believe we are combining good science with studies that will prove to be very valuable when better infrared data becomes available of the atmospheres of the Jovian planets. We are emphasizing the data on the infrared spectra of the solids and showing how this information can be as definitive in the identification of chemical substances as the frequently used gas phase data.

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Appendix I

VIBRATIONAL SPECTRA AND STRUCTURE OF CIACETYL

Abstract --- The infrared spectra of biacetyl $[\text{CH}_3\text{CO}]_2$ and biacetyl- d_6 $[\text{CD}_3\text{CO}]_2$ have been recorded over the range 33 to 400 cm^{-1} for the samples in the gaseous, liquid and polycrystalline states. The Raman spectra of the liquid and polycrystalline solids have also been observed, and quantitative depolarization ratios have been measured. The vibrational spectra of the crystalline materials have been interpreted on the basis of C_{2h} molecular symmetry and the values observed for the fundamentals are compared with those previously reported for the fluid states. A comparison of the infrared and Raman bands in the crystal shows that the mutual exclusion principle is operative. It is concluded from this alternate forbiddance that the molecule has a centrosymmetric structure in the crystal and that each molecule occupies a $\text{C}_i(\bar{1})$ site. The factor group of the crystal is believed to be either $\text{C}_{2h}(2/m)$ or $\text{C}_{2h}(\text{mmm})$ with two or four molecules per primitive unit cell. No evidence could be found for the existence of the cis isomer in the fluid states. Possible reasons for its absence are discussed. The infrared active methyl torsion was observed at 217 and 157 cm^{-1} for the "light" and "heavy" molecules in the solid state, respectively, and the barriers to internal rotation were calculated to be 3.1 kcal/mole. Barriers of 2.7 and 2.8 kcal/mole were calculated from rather broad bands in the spectra of gaseous $[\text{CH}_3\text{CO}]_2$ and $[\text{CD}_3\text{CO}]_2$, respectively. The barrier values are compared to those obtained for other acetyl compounds.

Introduction

We have recently recorded the vibrational spectra of several molecules of chemical formula, $[\text{COX}]_2$, where $X = \text{F}, \text{Cl}, \text{Br}$ and H and determined their molecular symmetries in the solid and fluid states.¹⁻⁴ For the halogen containing molecules, the spectra for the fluid states showed the presence of two geometric isomers and the data have been shown to be consistent for that expected for the cis and trans isomers. In these studies it has been shown that structural conclusions can only be correctly made if the infrared and Raman spectra are obtained for these compounds in at least two different physical states with one of them being the solid. Closely related to these studies is our investigation of the infrared and Raman spectra of 2,3-butanedione which is commonly called biacetyl.

There have been several previous vibrational studies⁵⁻⁸ of biacetyl with the more recent one by K. Noack and R. N. Jones⁷ being the most complete. However, there are some inconsistencies in the work of Noack and Jones which cannot be readily explained. For example, they have assigned the Raman lines at 240 and 538 cm^{-1} to out-of-plane bending modes of b_g symmetry whereas there should be only one mode of such symmetry unless one gives the methyl torsional mode such a description. However 240 cm^{-1} is too high a frequency for the methyl torsional mode for this type of molecule. Noack and Jones⁷ as well as Harris and Witkowski⁸ have assigned the strong Raman line at 685 cm^{-1} as the skeletal bending mode of a_g symmetry but such an assignment leaves no reasonable explanation for the Raman line at 614 cm^{-1} which had previously been assigned to this mode by Sidman and McClure.⁶ In essence the assignment of the 685 cm^{-1} Raman line to the skeletal bending mode results in too many Raman lines in the skeletal bending region to be assigned to the fundamentals of the biacetyl molecule for only the trans form. Also the $\text{C}-\text{CH}_3$ symmetrical stretching mode was not assigned by Noack and Jones; yet it should be one of the most intense Raman lines, Sidman

and McClure assigned the 1004 cm^{-1} Raman line to the C - CH₃ stretching mode but Noack and Jones have suggested that this band is the central C - C stretching vibration. Thus, there are still several uncertainties in the vibrational assignment for biacetyl and it was hoped that an investigation of the infrared and Raman spectra of solid biacetyl would clear up these discrepancies. No vibrational studies have previously been reported for the solid.

It was hoped that a vibrational study of the solid would provide the necessary data to determine the symmetry in the solid as well as the crystal site occupied by the molecules. In addition, factor group splitting could be investigated and it was hoped that the frequencies for the methyl torsional modes might be determined. The frequency for the skeletal C-C torsional mode was also of particular interest since it had been previously reported to be at 35 cm^{-1} from a study of the electronic spectrum of the solid⁹ although Fateley et al.¹⁰ have reported a frequency of 48 cm^{-1} for this normal mode in the vapor state. Noack and Jones had suggested a trans, C_{2h}, structure for the molecule in the liquid although they pointed out that such a structure was contrary to the dipole moment reported by Bloom and Sutton¹¹ for this molecule in both the gas and liquid states. Therefore, a reinvestigation of both the liquid and gas was carried out to obtain data for comparison with the solid phase studies.

EXPERIMENTAL SECTION

The 2,3-butanedione sample was obtained from the Aldrich Chemical Co. It was degassed and stored over drying agent. The 2,3-butanedione- d_6 sample was made by deuterium exchange. Fifteen ml of the biacetyl was refluxed for 48 hours with 35 ml of D_2O made approximately 0.5N with D_2SO_4 . The biacetyl was distilled out of the solution and dried. After four such exchanges the NMR spectra showed no indication of hydrogen atoms.

Vapor phase and solid phase infrared spectra between 4000 and 200 cm^{-1} were recorded on a Perkin-Elmer Model 621 spectrophotometer and between 500 and 33 cm^{-1} on a Beckman IR-11 spectrophotometer. Both instruments were purged with dry air and calibrated with standard gases.^{12,13} For studies of the vapor phases, 20-cm cells with cesium iodide windows were used in the mid infrared, whereas a Beckman 10-m variable path cell with polyethylene windows was used for recording the far infrared spectra. The spectra of the solids were obtained by condensing the vapor onto a cesium iodide or silicon window cooled with boiling nitrogen. The infrared spectrum of the liquid was obtained as a capillary film between cesium iodide plates. The infrared spectra of biacetyl and biacetyl- d_6 in the solid and gaseous phases are presented in Fig. 1.

The Raman spectra were recorded on a Cary Model 81 spectrophotometer equipped with a Spectra Physics Model 125 helium-neon laser. The instrument was calibrated with emission lines from a neon lamp over the spectral range $0\text{-}4000\text{ cm}^{-1}$. The Raman spectra of the solids were obtained by use of a low temperature cell similar to that described by Carlson.¹⁴ The Raman spectra of the liquids were obtained by means of small samples sealed in glass capillaries. The Raman spectra of biacetyl and biacetyl- d_6 in the solid and liquid phases are presented in Fig. 2. The frequencies for the bands observed in the infrared and Raman spectra of biacetyl are listed in Table I and those of biacetyl- d_6 in Table II. The observed frequencies are believed to be accurate to $\pm 1\text{ cm}^{-1}$ for all sharp bands.

Results and Discussion

No X-ray data are available for solid biacetyl. However, it is expected that the molecule will have the trans configuration in the solid. Studies of similar molecules¹⁻⁴ have shown that a center of symmetry is maintained at the site in the unit cell; thus, the rule of mutual exclusion is expected to hold in the solid and one should be able to easily determine the configuration from the spectral data. Several of the infrared bands appear to be split by either the static or the correlation field. However; the magnitude of this splitting is in general small compared to the separation of the fundamental vibrations so there is little difficulty in determining the frequency limits of each band. The bands in the solid phase are quite sharp and it is possible to separate fundamentals that are badly overlapped in the gas and liquid phases. Thus, it is possible to make assignments for most of the fundamental vibrations of biacetyl and biacetyl-d₆ in the solid phase.

The results of the studies of the solid state spectra coupled with improved data for the other phases make a more detailed analysis possible and require the reassignment of some of the bands. Since some of the bands are better delineated in the solid only the solid state spectra will be discussed in detail with references to the spectra of the other phases being made only as they relate to the assignment of the normal modes.

The highest frequency vibrations of biacetyl arise from the C-H stretching motions of the two methyl groups. The two symmetric and four antisymmetric C-H stretching modes are divided among the symmetry species of the C_{2h} point group with the two symmetric stretching motions being of a_g and b_u symmetry and the antisymmetric stretching modes having a_g, b_g, a_u and b_u symmetry. The Raman active C-H stretching modes are found at 3018, 2983 and 2922 cm⁻¹ in solid

biacetyl. In the liquid the band corresponding to the 2922 cm^{-1} band is strongly polarized whereas the bands corresponding to the 2983 and 3018 cm^{-1} bands appear depolarized and polarized respectively. The 2922 cm^{-1} band is assigned to the symmetric stretching motion whereas the 2983 and 3018 cm^{-1} bands are assigned to the antisymmetric stretching motions of b_g and a_g symmetry, respectively. In the spectra of biacetyl- d_6 these bands are shifted to 2142 , 2228 and 2267 cm^{-1} , respectively. The infrared active modes occur at 3012 , 2975 and 2925 cm^{-1} in solid biacetyl and are assigned to the antisymmetric C-H stretching motions of b_u and a_u symmetry and to the symmetric stretching motion of b_u symmetry, respectively. In the spectrum of biacetyl- d_6 these modes are shifted, respectively, to 2267 , 2216 and 2120 cm^{-1} .

It is difficult to give realistic descriptions to the motions causing the bands in the 1500 to 650 cm^{-1} region where the bands arising from the motions of the methyl group and those arising from the high frequency skeletal motions are expected to occur. Miyazawa¹⁵ has suggested that the C-CH₃ stretching modes of biacetyl might be expected to mix with the appropriate CH₃ rocking modes. As will be shown later these bands all shift upon deuteration in such a manner that it is not possible to consider them as isolated normal modes of the methyl group or the heavy skeleton; thus the descriptions given for these modes can only be considered as very poor approximations of the true normal modes.

Eight bands appear in the Raman spectra of solid biacetyl in the region 1500 to 650 cm^{-1} . The pair of bands at 1435 and 1421 cm^{-1} is assigned to the antisymmetric methyl deformations. These bands appear as one broad band in the liquid so it was not possible to obtain depolarization data for them. However, in the solid the 1421 cm^{-1} band is a medium sharp band whereas the 1435 cm^{-1} band appears as a weak broad band. Since modes of a_g symmetry are generally sharp

the 1421 cm^{-1} band is assigned to the antisymmetric deformation of species a_g and the 1435 cm^{-1} line is taken to be the b_g deformation.

The symmetric methyl deformation is assigned to the band at 1367 cm^{-1} which is polarized in the liquid. The Raman active methyl rocking modes are assigned to the bands at 1288 and 1280 cm^{-1} . There is no indication in the solid or liquid as to the symmetry of these bands. The central carbon-carbon stretching mode occurs at 1001 cm^{-1} . This mode occurs at 1078 cm^{-1} in glyoxal⁴, 1093 cm^{-1} in oxalyl chloride¹ and 1052 cm^{-1} in oxalyl bromide.²

The symmetric C-CH₃ stretching mode is expected to give rise to an intense band at a somewhat lower frequency than the central C-C stretching mode. This mode corresponds to the C-X stretch of the oxalyl halides which occurs at 620 cm^{-1} in oxalyl chloride¹ and 582 cm^{-1} in oxalyl bromide.² This mode is assigned to the intense, highly polarized band at 693 cm^{-1} . As stated earlier, the assignment of this band to a bending mode would place too many bands in the bending region of the Raman spectrum. None of these bands disappeared with solidification so they cannot be attributed to another isomer. Also the intensity of the 693 cm^{-1} band suggests that it should be assigned to the carbon-carbon stretching motion rather than to a skeletal bending mode.

The Raman spectrum of solid biacetyl-d₆ has the corresponding bands at 1301 , 1062 , 1035 , 1018 , 1009 , 847 and 619 cm^{-1} with the 1301 , 1062 , 847 and 619 cm^{-1} lines being polarized in the liquid. The 847 and 619 cm^{-1} bands are readily assigned to the central C-C and C-CD₃ stretching motions. This yields shift factors ν_H/ν_D of 1.18 and 1.12 , which should be compared with the expected values of 1.05 and 1.10 for the C-C and C-CH₃ stretching modes, respectively. These larger shifts are due to the coupling of these motions with some of the methyl motions of a_g symmetry giving them shift factors greater than expected. Since the 1301 and 1062 cm^{-1} bands are polarized they must arise from motions of a_g

symmetry and are thus assigned to the two highest frequency bending modes, the antisymmetric and symmetric methyl deformations of symmetry a_g . The antisymmetric deformation of b_g symmetry is assigned to the 1035 cm^{-1} band. The rocking motions for the " d_6 " compound are assigned to the bands at 1018 and 1009 cm^{-1} .

The infrared active modes occurring in the $1500\text{-}650\text{ cm}^{-1}$ region are also badly mixed. The bands at 1418 and 1400 cm^{-1} in biacetyl are assigned to the antisymmetric deformations and the 1350 cm^{-1} band is assigned to the symmetric deformation. In the infrared spectrum of solid biacetyl- d_6 these bands appear at 1143 cm^{-1} and as doublets at 1041 , 1034 cm^{-1} and 1026 , 1021 cm^{-1} . A comparison of the intensities of the bands in the spectra of solid biacetyl with those of solid biacetyl- d_6 suggests that 1143 cm^{-1} band should be assigned to the symmetric deformation and the 1041 , 1034 cm^{-1} and 1026 , 1021 cm^{-1} bands to the antisymmetric deformations split by crystal field effects. The spectra of the samples in the gaseous state give even stronger evidence for this assignment. The corresponding gas phase bands of both the 1350 cm^{-1} (Fig. Ia) and the 1143 cm^{-1} (Fig. Ib) bands have A type contours whereas the gas phase bands corresponding to the antisymmetric deformations in each case have no definite contours.

Some previous investigators have assigned the infrared bands at 953 and 912 cm^{-1} in biacetyl as a Fermi resonance doublet. The 953 cm^{-1} band is split in the crystal and appears as a doublet at 956 and 950 cm^{-1} . However, the spectrum of the gas phase shows that these two bands have different band contours, an indication that they arise from motions of different symmetry. The infrared spectrum of solid biacetyl- d_6 reveals bands at 790 and 769 cm^{-1} indicating that both the 953 cm^{-1} and the 912 cm^{-1} bands shift upon deuteration. Thus, both bands must be due to fundamental vibrations. Since only the rocking modes and the antisymmetric C-CH₃ stretching modes are expected in this frequency region these two bands are assigned to the rocking modes. The 953 cm^{-1} (790 cm^{-1} for " d_6 ") band is assigned to the b_u rocking

mode whereas the 912 cm^{-1} (769 cm^{-1} for " d_6 ") band is assigned to the a_u rocking mode. The band contours of the 953 and 790 cm^{-1} bands are the same as those for other bands assigned to modes of b_u symmetry. The C-CH₃ antisymmetric stretching mode is then assigned to the 1131 cm^{-1} band, with the corresponding vibration in the d_6 compound occurring at 969 cm^{-1} . The extremely large shift of this band with deuteration clearly shows that this mode as involves considerable methyl rocking motion and the description of this mode as a C-CH₃ antisymmetric stretching mode is a very poor approximation of the actual normal mode.

The skeletal bending and rocking motions lie below 650 cm^{-1} and in the Raman spectrum of solid biacetyl there are three bands

found at 614 , 526 and 380 cm^{-1} . The band in the liquid corresponding to the 614 cm^{-1} band is depolarized and is assigned to the COCH₃ antisymmetric out-of-plane bending mode. The 526 cm^{-1} band is assigned to the COCH₃ symmetric bending motion and the 380 cm^{-1} band to the COCH₃ symmetric rocking mode. These bands are shifted upon deuteration to 515 , 500 and 340 cm^{-1} , respectively. The infrared active bands occur at 544 , 360 and 261 cm^{-1} . The gas phase bands corresponding to the 544 and 261 cm^{-1} bands have A-type band contours and are thus due to modes of b_u symmetry. They are assigned to the COCH₃ antisymmetric bending and rocking modes, respectively. The 360 cm^{-1} band is assigned to the COCH₃ symmetric out-of-plane bend of a_u symmetry. The corresponding bands in biacetyl- d_6 occur at 488 , 237 and 324 cm^{-1} , respectively.

There are three torsional modes to be assigned: an infrared active methyl torsion, a Raman active methyl torsion and an infrared active acetyl torsion. The infrared active methyl torsion is assigned to a weak band at 217 cm^{-1} which is shifted to 158 cm^{-1} in the spectrum of biacetyl- d_6 (see Figures 3 and 4). This yields a shift factor of 1.37. Although this is less than the theoretical 1.41, it is as close as could be expected. The Raman active methyl torsion

was not observed. Although a very weak broad band was observed in the Raman spectrum of liquid biacetyl at approximately 246 cm^{-1} , such a frequency seems too high for this normal mode. Also it was not possible to locate any band with a proper shift factor for a torsional motion in the Raman spectrum of biacetyl- d_6 . The acetyl torsion has been reported¹⁰ to have a frequency of 48 cm^{-1} in the gas phase. We observed this mode as a band centered at 52 cm^{-1} , which is shifted to a slightly higher frequency in the solid and occurs at 66 cm^{-1} . In the infrared spectrum of solid biacetyl- d_6 this mode occurs at 61 cm^{-1} . The shift factor corresponds very closely to the theoretical value and removes any doubt of the assignment. The previous assignment⁹ of 35 cm^{-1} for the torsional frequency in the solid from a study of the electronic spectrum is apparently in error.

The infrared active methyl torsions have been observed in the vapor phase samples of biacetyl and biacetyl- d_6 at $\sim 200\text{ cm}^{-1}$ and 150 cm^{-1} , respectively. The threefold barrier to rotation has been calculated for each case, using the method based on the Mathieu equation as illustrated by Fateley and Miller¹⁶ with eigenvalues from Herschbach's¹⁷ tables. Reduced moment of inertia constants of 5.426 and 2.785 cm^{-1} yield barriers of 2.65 and 2.79 kcal/mole for CH_3 and CD_3 , respectively. These are higher than barriers found for other acetyl compounds in the vapor phase: acetaldehyde,¹⁸ 1.16 kcal/mole ; acetyl bromide,¹⁹ 1.30 kcal/mole ; and acetyl chloride,²⁰ 1.30 kcal/mole . The breadth and weakness of the torsional band in gaseous biacetyl casts some doubt on its exact position. However, for both solids the methyl torsion is sharp and well defined. Barriers calculated from the solid frequencies are 3.07 and 3.05 kcal/mole for biacetyl and biacetyl- d_6 , again using the simple cosine function and neglecting intermolecular forces. The small shift in the torsion seems to justify this treatment. The barriers for solid acetyl bromide²¹ and chloride²¹ are 1.97 and 1.81 kcal/mole . Therefore, there

is clear evidence that the barrier to methyl rotation in biacetyl is considerably higher than the barriers found for other acetyl compounds studied to date. It is not at all clear why the barrier values should differ by so much but the relatively short distance between the hydrogen and the "other" carbonyl may explain part of the effect.

Although assignment of the fundamental vibrations has been made using frequencies for the solid phase, there is no significant difference between the spectra of the three phases. Comparison of curves A and C (for gaseous and solid biacetyl, respectively) in Fig. 1 demonstrates a one-to-one correspondence of bands for the two phases. Only a sharpening of lines and splitting due to crystal field effects can be seen for the solid. A similar correspondence is seen in the Raman spectra. The fact that no band present in the gas or liquid phase disappears or shifts significantly points to the presence of only one isomeric form in all phases, the trans form. This is in contrast to our findings for $(\text{COCl})_2$ ¹, $(\text{COBr})_2$ ², and $(\text{COF})_2$ ³, all of which exhibit two isomeric forms in the fluid states and one in the solid. Glyoxal⁴, $(\text{COH})_2$, on the other hand, is similar to biacetyl. It thus appears that the halogens provide some stabilizing influence for the cis isomer that cannot be realized when they are replaced by hydrogen atoms or methyl groups. A non-bonded interaction probably exists between the halogens on adjacent carbons that becomes insignificant or does not exist for the H and CH_3 cases.

A consideration of the infrared and Raman spectra of solid biacetyl reveals that none of the Raman frequencies appear in the infrared spectrum and none of the infrared frequencies appear in the Raman spectrum. Also, all of the combination bands observed in the infrared spectrum could be assigned as arising from the combination of one ungerade and one gerade fundamental. In the Raman spectrum the few bands not assigned to fundamental modes could be readily assigned to overtones or combinations of Raman fundamentals. On this basis the biacetyl molecule must be in the trans form and occupying sites of at least C_i symmetry in the crystal. With C_i sites, packing considerations imply that the most probable space group would be one of the C_{2h} or D_{2h} space groups.

A consideration of the factor group splitting provides a basis for the differentiation between the C_{2h} and D_{2h} space groups. The C_i - C_{2h} site-factor group combination predicts a splitting of each infrared and each Raman vibration into two components. However, the C_i - D_{2h} combination predicts the splitting of each infrared vibration into three components and each Raman vibration into four components. In the infrared spectrum of solid biacetyl- d_6 (see Fig. Id) several of the bands showed pronounced splitting. In each case the bands are split into two components which would imply a C_{2h} space group.

Two lattice vibrations appear in the infrared spectrum of biacetyl at 136 and 104 cm^{-1} and at 115 and 93 cm^{-1} in the spectrum of biacetyl- d_6 . These bands must be due to optic translational modes since these modes are active only in the infrared for molecules on C_i sites. Five Raman active librational modes appear in the Raman spectrum of biacetyl. These bands occur as two pairs at $74, 67\text{ cm}^{-1}$, at $87, 85\text{ cm}^{-1}$ and a weak band at 97 cm^{-1} . The appearance of the optical translational modes in the infrared and the doubling of the optical librational modes in the Raman implies that there are at least two molecules per unit cell. The splitting of the lattice modes is not expected to be large so

the observed bands may be the result of more components than were actually resolved. Thus the crystal structure is most likely C_{2h} with two or possibly four molecules per unit cell; however, D_{2h} can not conclusively be ruled out as the space group.

Bloom and Sutton¹¹ have reported that biacetyl vapor has a dipole moment of approximately one debye at room temperature, which increases with increasing temperature. They proposed two possible explanations; one was that there were cis and trans isomers and the observed dipole moment arose from the cis isomer. The other suggestion was that the dipole moment was the result of bond moments of the trans form not canceling during the vibration from the non-polar equilibrium position. They decided that it was not possible to differentiate between these two explanations by means of dipole measurements. However, it seems unlikely that such a large dipole moment could arise as the result of the sum of small instantaneous dipoles.

The present investigation has eliminated the possibility of the presence of a cis isomer in the solid phase, and there is no indication of a second isomer in the liquid or vapor phases. Bloom and Sutton encountered some difficulty in purification of their sample and at least two of their runs produced erratic results. They suggested that the work should be rechecked using a sample purified by a different technique but were not able to continue the project because of the war. In light of the spectroscopic evidence and the element of doubt in the dipole moment measurements, the conclusion that biacetyl exists in only the trans configuration in all phases seems justified.

Conclusions

Vibrational assignments have satisfactorily been made for solid biacetyl according to C_{2h} symmetry. Spectra of the liquid and vapor phases show no indication of a second isomeric form, and it is concluded that the non-bonded forces between halogens which stabilize the cis isomer of the oxalyl halides are not present between the methyls of biacetyl. The mutual exclusion between infrared and Raman spectra of crystalline biacetyl necessitates a centrosymmetric structure and the space group is probably C_{2h} or D_{2h} . The splitting of the Raman-active librational modes and the appearance of translational bands in the far infrared spectrum indicate that there are at least two and possibly four molecules per unit cell. The barrier to methyl rotation has been calculated to be 2.65 kcal/mole, considerably higher than those found for other acetyl compounds.

Acknowledgment

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Table I. Vibrational Data on Biacetyl.

Gas	Infrared(cm^{-1})		Raman(cm^{-1})		Assignment
	Liquid	Solid	Liquid	Solid	
3437 w	3417 m	3415 m			1706 + 1719 = 3425
3021 w	3010 w	3012 w			antisymmetric C-H stretch (b_u)
2978 w	2999 w	2975 w	3016 vw	3018 w	antisymmetric C-H stretch (a_g)
2944 w	2935 w	2925 w	2978 vw	2983 w	antisymmetric C-H stretch (a_u)
					antisymmetric C-H stretch (b_g)
					symmetric C-H stretch (b_u).
			2928 s	2922 m	symmetric C-H stretch (a_g)
1775 w(sh)	1807 w(sh)	1819 w			1131 + 693 = 1824
1734 R s	1770 w(sh)	1751 w			
1719 P s	1715 vs	1706 vs			antisymmetric C=O stretch (b_u)
			1720 vs	1719 vs	symmetric C=O stretch (a_g)
		1683 vw			261 + 1421 = 1682
			1680 vw		693 + 1001 = 1694
1680 w(sh)	1678 w(sh)	1676 w			
		1645 w			360 + 1288 = 1648
		1604 vw			912 + 693 = 1605
			1431 w(sh)	1435 w	antisymmetric CH_3 deformation (b_g)
			1424 m	1421 m	antisymmetric CH_3 deformation (a_g)
		1432 w(sh)			
		1428 w(sh)			912 + 526 = 1438; 1367 + 66 = 1433

Table I (continued)

Gas	Infrared (cm^{-1})		Raman (cm^{-1})		Assignment
	Liquid	Solid	Liquid	Solid	
1424 m	1419 s	1418 s 1400 m	1364 w	1367 w	antisymmetric CH_3 deformation (a_u or b_u) antisymmetric CH_3 deformation (a_u or b_u)
1365 R	1381 w(sh)				symmetric CH_3 deformation (a_g)
1358 Q s	1352 s	1350 s			symmetric CH_3 deformation (b_u)
1352 P	1315 w(sh)				
			1275 w	1288 w(sh) 1280 w	symmetric CH_3 rock (a_g or b_g) symmetric CH_3 rock (a_g or b_g) $261 + 1001 = 1262$
	1260 vw	1256 vw			
		1238 vw			
	1200 vw(sh)	1226 vw			$544 + 693 = 1237$
	1171 vw(sh)	1167 vw			$544 + 614 = 1158$
1122 R					
1114 Q s	1114 s	1131 s			antisymmetric C- CH_3 stretch (b_u)
1107 P		1119 sh			
	1082 vw(sh)				
	1063 vw(sh)	1045 vw			$360 + 693 = 1053$
			1050 vw	1052 vw	$2 \times 526 = 1052$
			1005 m	1001 m	C-C stretch (a_g)
955 R		956 m			
949 Q w	946 m	950 m			antisymmetric CH_3 rock (b_u)
945 P					

Table I (continued)

Gas	Infrared(cm^{-1})		Raman(cm^{-1})		Assignment
	Liquid	Solid	Liquid	Solid	
910 m	913 m	912 m			antisymmetric CH_3 rock (a_u)
543 R			685 vs	693 vs	symmetric C- CH_3 stretch (a_g)
538 Q s			608 w	614 vw	antisymmetric COCH_3 out-of-plane bend (b_g)
531 P	537 s	544 s			antisymmetric COCH_3 bend (b_u)
348 R			537 m	526 m	symmetric COCH_3 bend (a_g)
327 P	345 w	360 m			symmetric COCH_3 out-of-plane bend (a_u)
262 R			369 s	380 m	symmetric COCH_3 rock (a_g)
252 Q w	264 w	261 m			antisymmetric COCH_3 rock (b_u)
246 P			246 vw(br)		
~ 200 vw		217 vw			CH_3 torsion (a_u)
		136 w			translational mode
		104 w			translational mode
				97 w	librational mode
				87 m	librational mode
				85 sh	librational mode
				74 s	librational mode
				67 sh	librational mode
				66 vw	acetyl torsion (a_u)

Table II. Vibrational Data on Biacetyl-d₆.

Infrared(cm^{-1})		Raman(cm^{-1})		Assignment
Gas	Solid	Liquid	Solid	
3427 w	3407 m			1706 + 1716 = 3422
3006 w	3011 w			790 + 2228 = 3018
	3005 w			1301 + 1706 = 3007
	2557 vw			1706 + 847 = 2553; 2216 + 340 = 2556
	2443 w			2120 + 340 = 2460; 324 + 2142 = 2466 237 + 2228 = 2465
	2329 vw			1716 + 619 = 2335
		2263 w	2267 s	antisymmetric C-D stretch (a_g)
2272 w	2267 w			antisymmetric C-D stretch (b_u)
		2229 w	2228 w	antisymmetric C-D stretch (b_g)
2235 w	2216 w			antisymmetric C-D stretch (a_u)
	2166 vw			1143 + 1018 = 2161; 1143 + 1035 = 2178
		2135 s	2142 s	symmetric C-D stretch (a_g)
	2120 m			symmetric C-D stretch (b_u)
	2085 vw			1024 + 1062 = 2086
	2080 vw			1038 + 1035 = 2073
		2042 vw	2065 vw	2 x 1035 = 2070
	2024 vw			969 + 1062 = 2031
	1991 vw			969 + 1035 = 2005
	1780 m			1301 + 488 = 1789
1766 sh	1761 m			1143 + 619 = 1762
		1716 vs	1716 vs	symmetric C=O stretch (a_g)
1729 R 1718 P vs	1706 vs			antisymmetric C=O stretch (b_u)
1679 sh	1680 m 1679 m 1669 m			
	1643 w			1143 + 500 = 1643
	1583 vw			969 + 619 = 1588
	1547 w			488 + 1062 = 1550

Table II (continued)

Infrared(cm^{-1})		Raman		Assignment
Gas	Solid	Liquid	Solid	
1334 w	1400 w			790 + 619 = 1409
	1322 vw			324 + 1009 = 1333
		1282 w	1301 w	antisymmetric CD_3 deformation (a_g)
	1276 w			237 + 1038 = 1275
	1264 w			237 + 1030 = 1267
	1252 m			237 + 1018 = 1255
1241 w				
	1231 w			
	1223 m			158 + 1062 = 1220
1145 R				
1139 Q s	1143 vs			symmetric CD_3 deformation (b_u)
1132 R				
	1118 m			340 + 790 = 1130
	1110 m			488 + 619 = 1107; 340 + 769 = 1109
		1053 w	1062 w	symmetric CD_3 deformation (a_g)
1038	1041 m			antisymmetric CD_3 deformation
	1034 m			(a_u or b_u)
		1028 w	1038 w	antisymmetric CD_3 deformation (b_g)
			1030 w	
1028 m	1026 s			antisymmetric CD_3 deformation
	1021 s			(a_u or b_u)
		1018 w	1018 w	symmetric CD_3 rock (a_g or b_g)
			1009 w	symmetric CD_3 rock (a_g or b_g)
	1000 w			488 + 515 = 1003
	992 w			488 + 500 = 988
967 R				
960 Q s	969 s			antisymmetric C- CD_3 stretch (b_u)
953 P				
	952 sh			
		935 wv	944 wv	340 + 619 = 959
		845 m	847 m	C-C stretch (a_g)

Table II (continued)

Infrared(cm^{-1})		Raman(cm^{-1})		Assignment
Gas	Solid	Liquid	Solid	
782 sh	790			antisymmetric CD_3 rock (b_u)
772 m	770 768			antisymmetric CD_3 rock (a_u)
		607 vs	619 vs	symmetric C- CD_3 stretch (a_g)
		517 s	515 m	antisymmetric COCD_3 out-of-plane bend (b_g)
			500 m	symmetric COCD_3 bend (a_g)
	506 w			
489				
483 s	488 s			antisymmetric COCD_3 bend (b_u)
476				
		335 s	340 s	symmetric COCD_3 rock (a_g)
314 s	324 s			symmetric COCD_3 out-of-plane bend (a_u)
225 m	237 m			antisymmetric COCD_3 rock (b_u)
150 vw	158 vw			CD_3 torsion (a_u)
	115 w			translational mode
			94 w	librational mode
	93 m			translational mode
			80 sh	librational mode
			72 s	librational mode
			60 sh	librational mode
56				
47	61 vw			acetyl torsion (a_u)

Table III. Fundamental Frequencies of Solid biacetyl and biacetyl-d₆

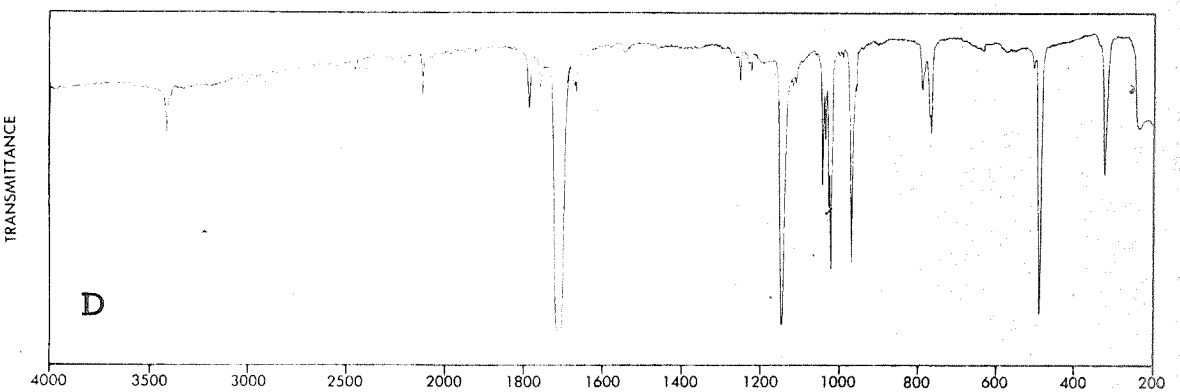
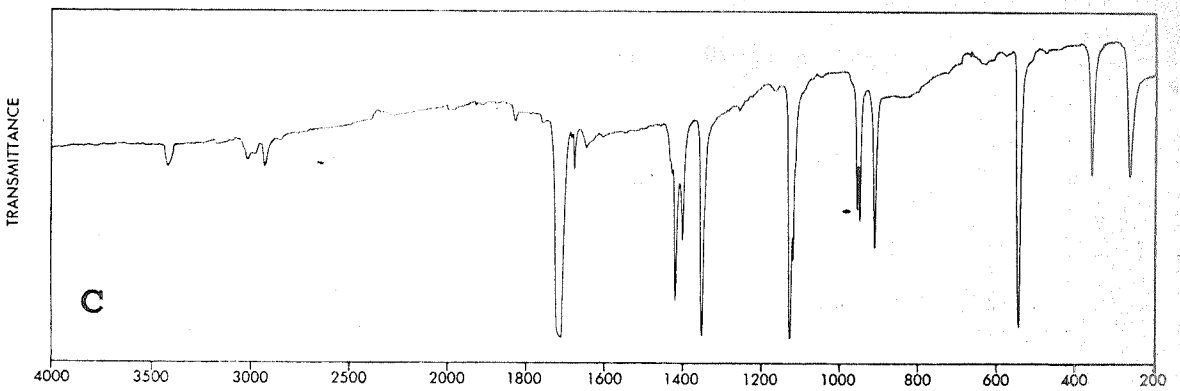
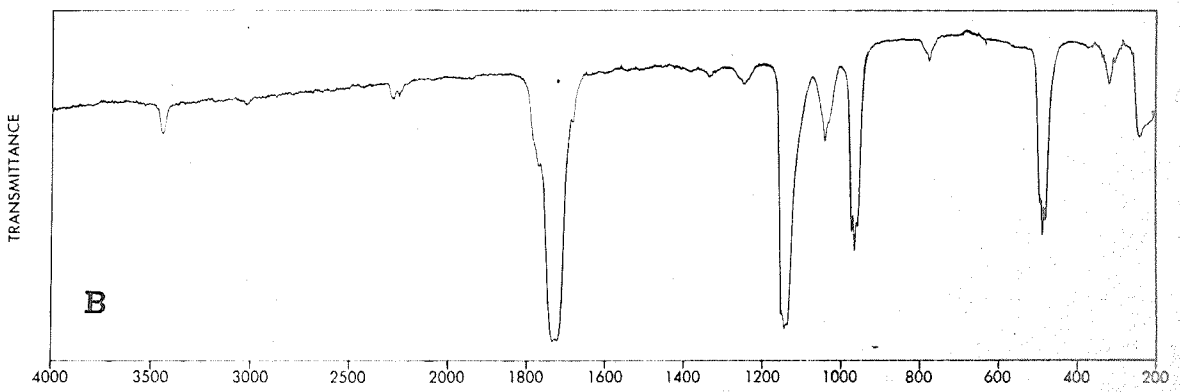
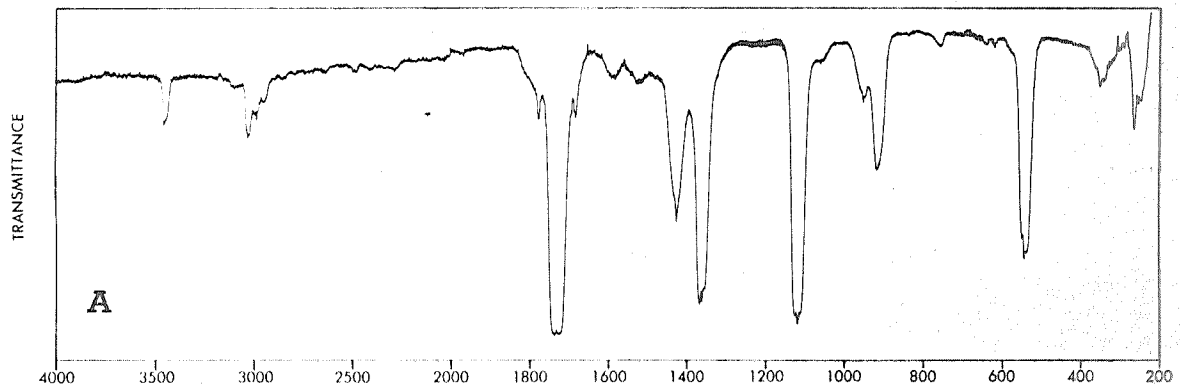
Vibration	Symmetry species and approximate description of the normal modes	Raman ($\Delta \text{ cm}^{-1}$)	biacetyl Infrared (cm^{-1})	Raman ($\Delta \text{ cm}^{-1}$)	biacetyl-d ₆ Infrared (cm^{-1})
a_g					
1	C-H antisymmetric stretch	3018		2267	
2	C-H symmetric stretch	2922		2142	
3	C=O symmetric stretch	1719		1716	
4	CH ₃ antisymmetric deformation	1421		1301	
5	CH ₃ symmetric deformation	1367		1062	
6	CH ₃ symmetric rock	1288 or 1280		1018 or 1009	
7	C-C stretch	1001		847	
8	C-CH ₃ symmetric stretch	693		619	
9	COCH ₃ symmetric bend	526		500	
10	COCH ₃ symmetric rock	380		340	
a_u					
11	C-H antisymmetric stretch		2975		2216
12	CH ₃ antisymmetric deformation		1418 or 1400		1038 or 1024
13	CH ₃ antisymmetric rock		912		769
14	COCH ₃ symmetric out-of-plane bend		360		324
15	CH ₃ torsion		217		158
16	acetyl torsion		66		61
b_g					
17	C-H antisymmetric stretch	2983		2228	
18	CH ₃ antisymmetric deformation	1435		1035	

Table III (Continued)

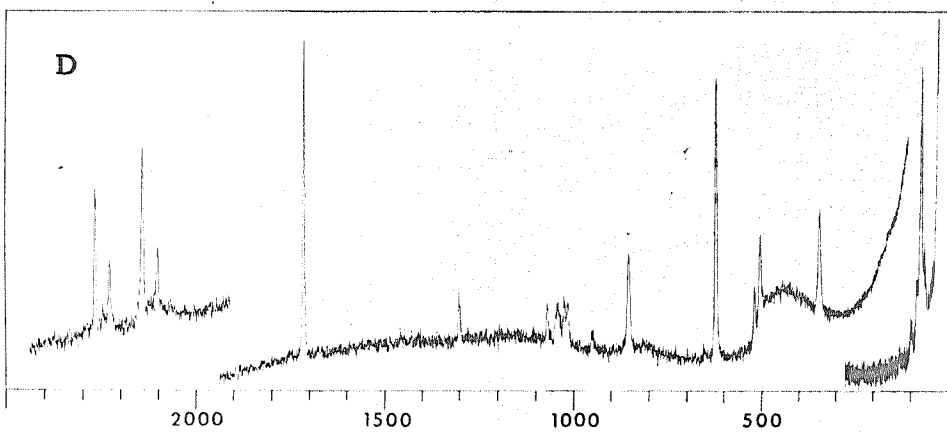
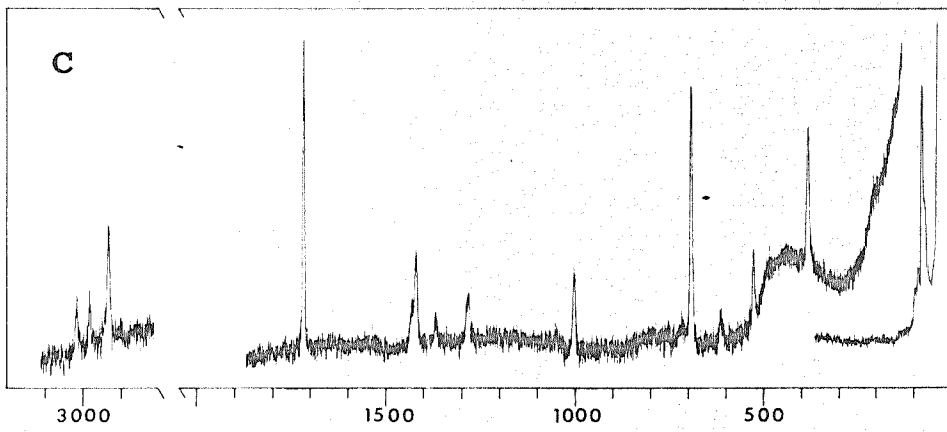
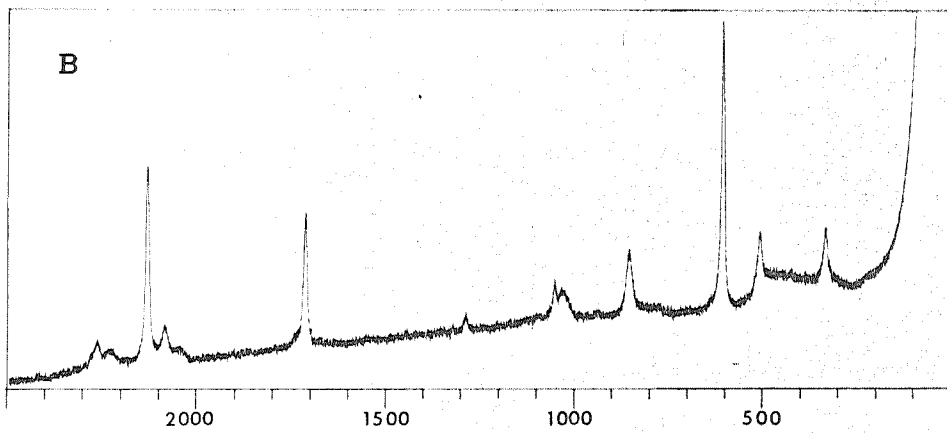
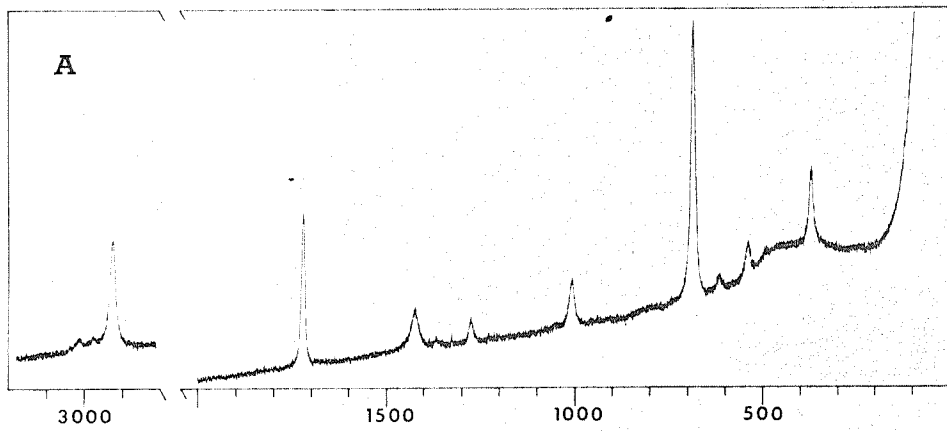
Vibrations	Symmetry species and approximate description of the normal modes	biacetyl		biacetyl-d ₆	
		Raman (Δ cm ⁻¹)	Infrared (cm ⁻¹)	Raman (Δ cm ⁻¹)	Infrared (cm ⁻¹)
19	CH ₃ symmetric rock	1288 or 1280		1018 or 1009	
20	COCH ₃ antisymmetric out-of-plane bend	614		515	
21	CH ₃ torsion	----		----	
	b _u				
22	C-H antisymmetric stretch		3012		2267
23	C-H symmetric stretch		2925		2120
24	C=O antisymmetric stretch		1706		1706
25	CH ₃ antisymmetric deformation		1418 or 1400		1038 or 1024
26	CH ₃ symmetric deformation		1350		1143
27	C-CH ₃ antisymmetric stretch		1131		969
28	CH ₃ antisymmetric rock		953		790
29	COCH ₃ antisymmetric bend		544		488
30	COCH ₃ antisymmetric rock		261		237

Figure Captions

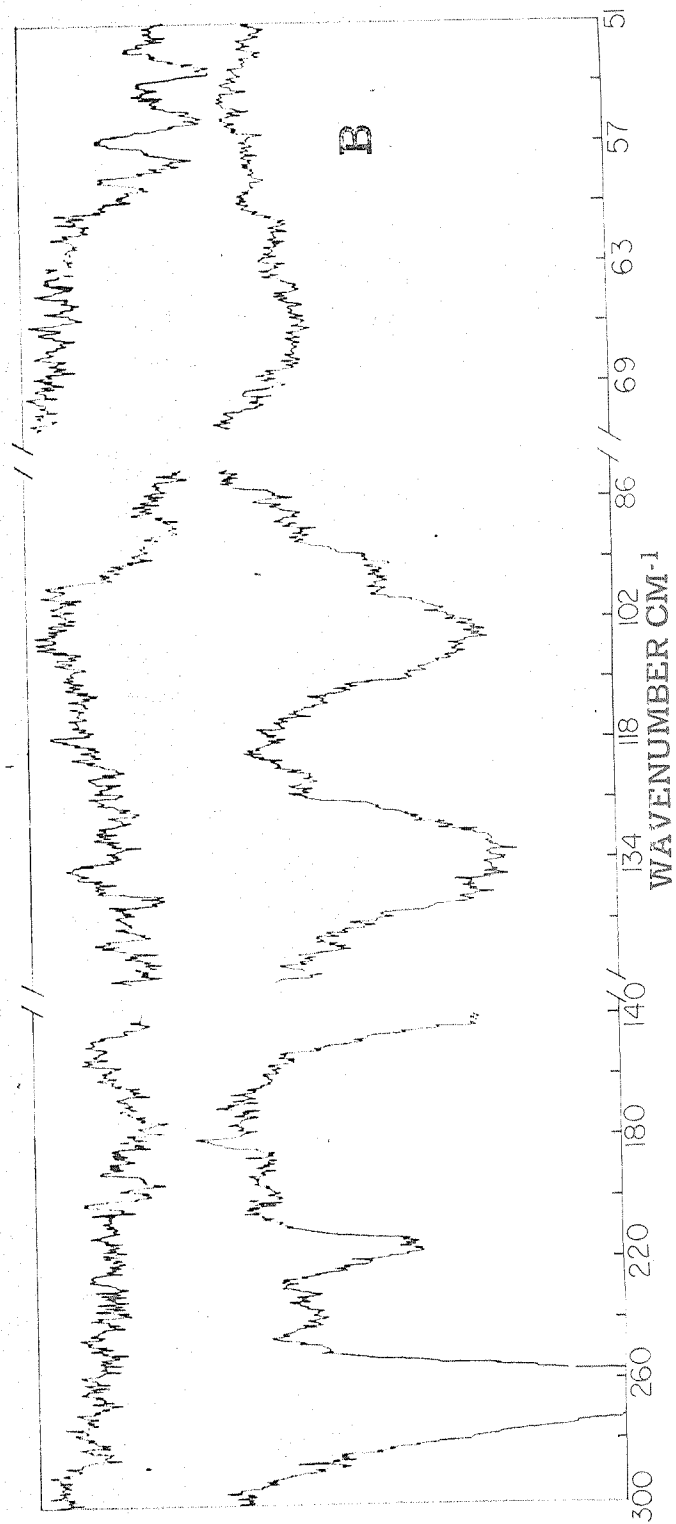
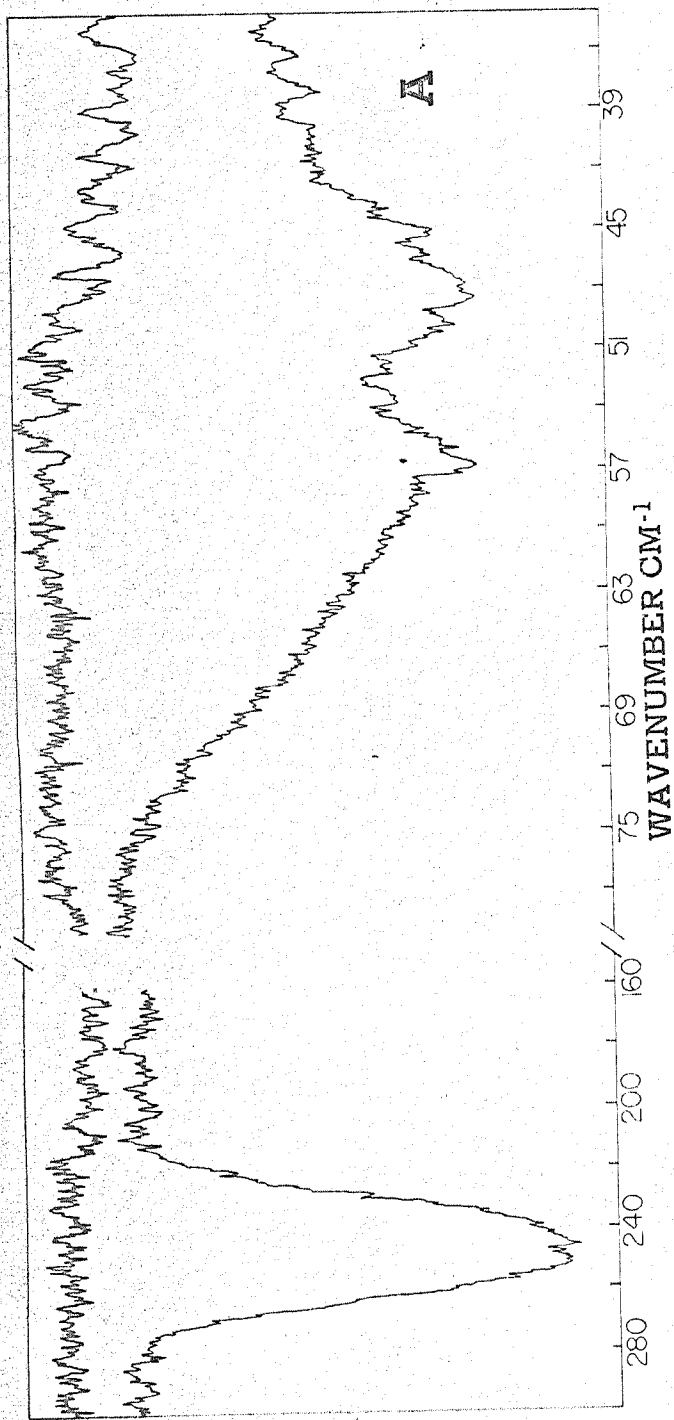
- Fig. 1 - Infrared spectra of biacetyl: A, gaseous biacetyl; B, gaseous biacetyl-d₆; C, solid biacetyl; D, solid biacetyl-d₆.
- Fig. 2 - Raman spectra of biacetyl: A, liquid biacetyl; B, liquid biacetyl-d₆; C, solid biacetyl; D, solid biacetyl-d₆.
- Fig. 3 - Far infrared spectra of biacetyl: A, vapor phase; B, solid phase.
- Fig. 4 - Far infrared spectra of biacetyl-d₆: A, vapor phase; B, solid phase.

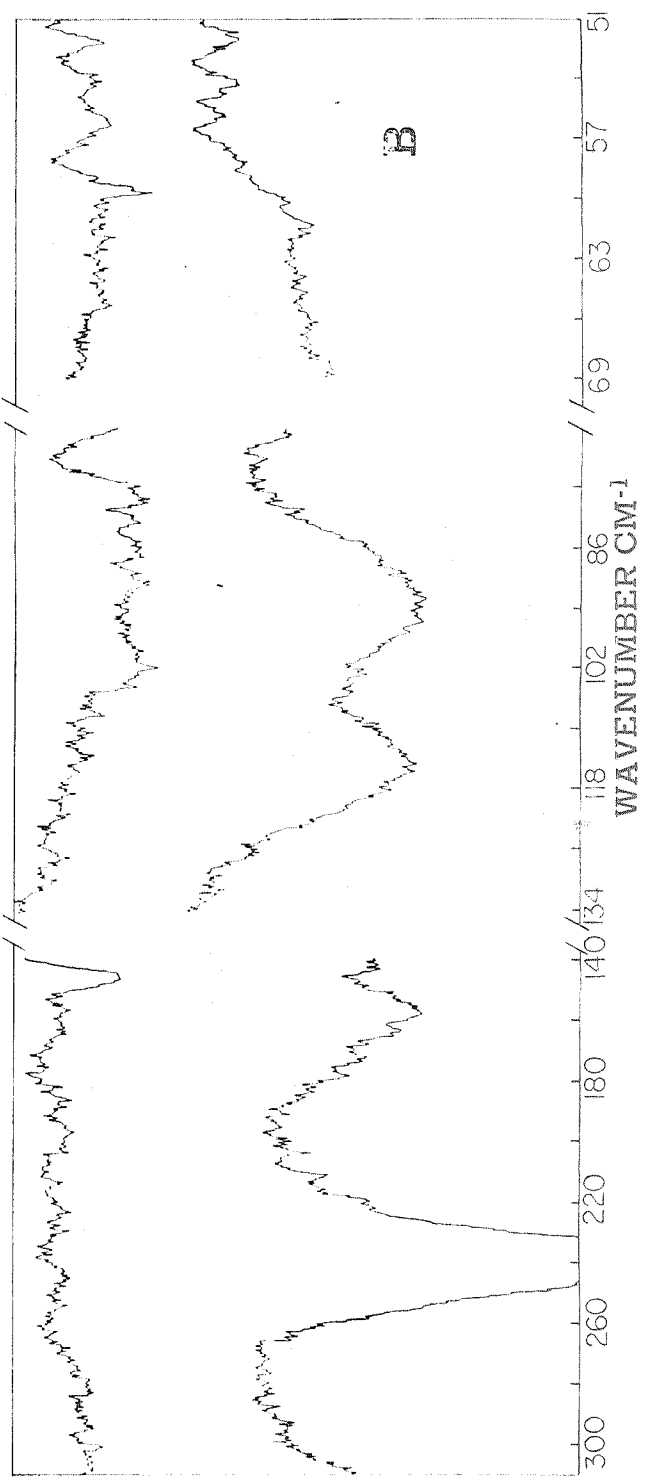
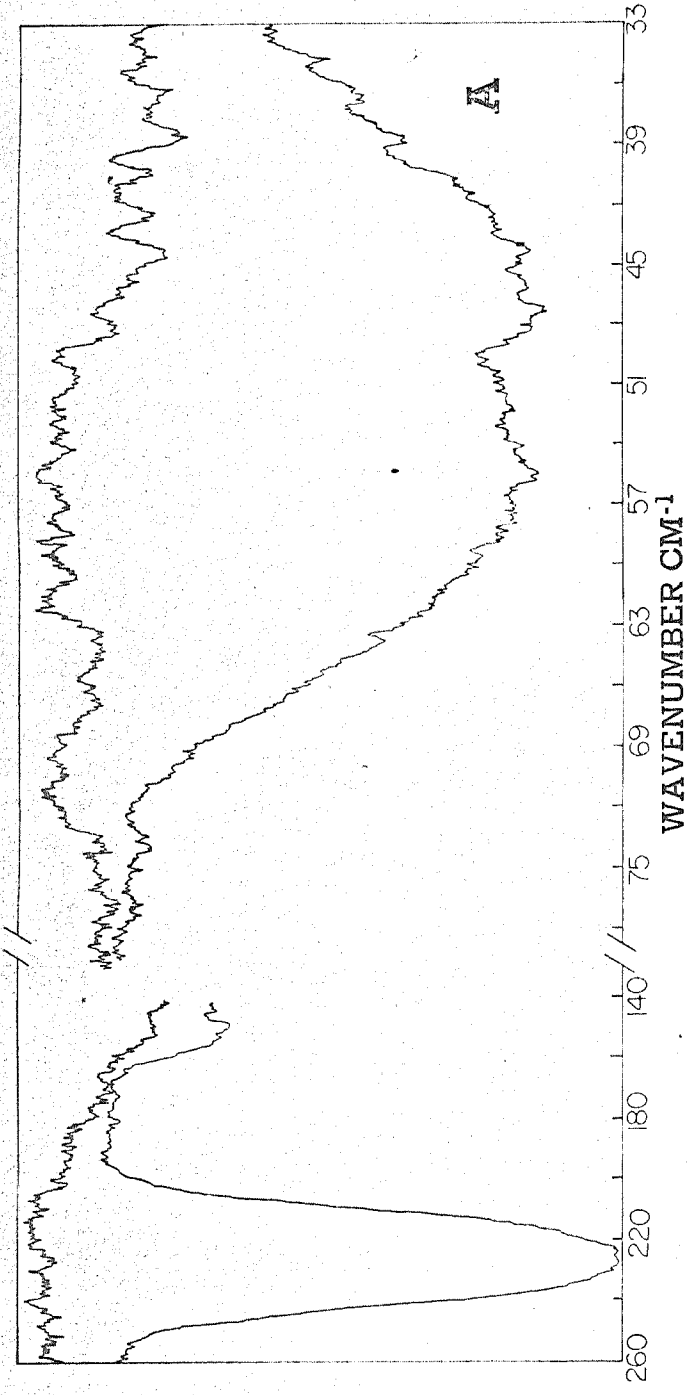


WAVENUMBER CM^{-1}



WAVENUMBER CM^{-1}





Appendix II

LOW-FREQUENCY MODES OF MOLECULAR CRYSTALS. OXAMIDE AND DITHIOOXAMIDE.

Abstract --- The infrared spectra of oxamide and dithiooxamide have been reexamined and the low frequency limit extended to 33 cm^{-1} . The Raman spectrum of oxamide has likewise been studied in the low-frequency range. Assignments have been made for two infrared bands and three of the four Raman bands previously unobserved. The Raman spectrum of dithiooxamide, a red solid, has been reported for the first time, and assignments have been made for the fundamental vibrations of this molecule. In addition, the external modes of both molecules have been studied. The three predicted intermolecular fundamentals were observed in the Raman spectrum of oxamide. The three translational and five of the six librational modes were observed in the far infrared and Raman spectra, respectively, of dithiooxamide. Ranges for the intermolecular force constants have been calculated.

INTRODUCTION

Crystallographic studies^{1,2} have established the structures of oxamide and dithiooxamide as being trans C_{2h} in space groups of $P\bar{1}$. Oxamide has one molecule per unit cell, whereas the sulfur analog contains two. Infrared and Raman studies have been reported³⁻⁵ for oxamide as has infrared data for dithiooxamide³, but none of the studies have examined the region below 200 cm^{-1} and most studies extended only to 400 cm^{-1} . This has left six fundamentals unassigned in oxamide, four of which are Raman active and two which are infrared active. The modes remaining to be found in the infrared spectrum are the OCN torsion of a_u symmetry and the OCN rock of b_u symmetry. Raman assignments are lacking for two a_g modes, the OCN bend and rock, and two b_g vibrations, the NH_2 torsion and OCN out-of-plane bend. There is no Raman information available for dithiooxamide at all and the SCN out-of-plane bend (a_u), SCN torsion (a_u), SCN bend (b_u), and SCN rock (b_u) have not been observed in the infrared spectrum. The interesting lattice region has also been neglected. Therefore, work has been undertaken to reexamine the spectra of these compounds in an attempt to complete the assignments and provide new information concerning the lattice vibrations of the two molecules.

EXPERIMENTAL TECHNIQUES

The samples of oxamide and dithiooxamide were obtained from Aldrich Chemical Company and were used without further purification. Deuterium compounds were prepared by exchange with hot D_2O .

Infrared spectra were recorded on a Perkin Elmer Model 621 spectrophotometer between 4000 and 200 cm^{-1} and on a Beckman IR-11 between 500 and 33 cm^{-1} . Both instruments were purged with dry air and calibrated with standard gases.⁶

Samples were examined in the mid-infrared region as CsI pellets and as thin films sublimed onto a silicon plate. The far-infrared sample of dithiooxamide was obtained by repeated sublimation onto a thin sheet of polyethylene, while oxamide was examined as a mineral oil mull.

Raman spectra were recorded with a Cary 81 spectrophotometer equipped with a helium-neon laser for excitation. The instrument was calibrated with emission lines from a neon lamp over the spectral range 0-4000 cm^{-1} . Samples were examined as powders and as a thick paste made by mulling the powder with mineral oil. Some samples were also cooled in a variable-temperature cell which has been described previously.⁷

RESULTS

Comparison of results of this study with those of previous workers is given in Table 1. Our infrared data is essentially in agreement with that of Scott and Wagner³, with the addition of low-frequency data. The Raman spectra of oxamide and dithiooxamide are presented in Figures 1 and 2, and the far-infrared spectra of the compounds are given in Figures 3 and 4. The Raman spectrum of dithiooxamide has not been previously published, and the bands observed are tabulated in Table 2. Its orange color prevented observation of the spectrum by Hg arc excitation, but the versatile lasers now provide a suitable source. The intensity of the spectrum is still somewhat of a problem, with the one strong band at 932 cm^{-1} dominating the spectrum of weak bands, even at high sensitivity. This is so much the case that the weak N-H stretching vibrations were not even observed. The spectrum was not improved by cooling the sample in a variable-temperature cell. The totally deuterated analogs were prepared to aid in assignment of the Raman bands. Tables 2 and 3 summarize the available infrared and Raman data for the two isotopic molecules of oxamide

and dithiooxamide, respectively. The lattice bands are prominent in the Raman spectra of both compounds, even at room temperature.

The one area of disagreement between our work and that of Kahovec and Wagner⁴ is in the Raman spectrum of oxamide. They report a weak band at 809 cm^{-1} whereas in the same region, we find two bands, 806 cm^{-1} having medium intensity and 831 cm^{-1} , weak. Possibly, this splitting is beyond the limit of the resolution of their instrument.

DISCUSSION

The established molecular symmetry of oxamide and dithiooxamide is C_{2h} . The molecules have centers of symmetry, which leads to mutual exclusion between the infrared and Raman spectra. Thus, there are 24 fundamental vibrations, 12 of which are infrared active and 12 of which are Raman active. Table 4 gives the group theory for molecules having these point, site, and factor group symmetries.

Assignment of Oxamide Fundamentals

Partial assignments were made for the fundamental vibrations of oxamide by Scott and Wagner³, but the low-frequency limitation of their instrumentation left two infrared fundamentals unassigned along with four Raman-active modes not assigned by earlier workers. We have added these to the previous assignments to complete the information (see Table 5). The vibrational analysis of oxamide, although complicated by mixing of modes, is rather straightforward based on comparison with other amides. We are in agreement with the infrared assignments of Scott and Wagner. The two unassigned fundamentals were found as a strong band at 337 cm^{-1} and a weak band at 165 cm^{-1} , the only line seen in the far-infrared spectrum. The 337 cm^{-1} band is assigned as the OCN rock and the 165 cm^{-1} band as the OCN torsion.

Minor changes and additions have been made in the assignment of the Raman spectrum of oxamide. Two bands were observed in oxamide between 800 and 850 cm^{-1} (831 w, 806 m) where Kahovec and Wagner⁴ had seen only one weak peak (809 w). We have assigned the band having medium intensity, 806 cm^{-1} , to ν_{14} , the NH_2 wag and the weak 831 cm^{-1} band to ν_7 , the C-C stretching vibration. We are in agreement with the other assignments given by Scott and Wagner based on the spectra of Kahovec and Wagner; isotopic shift factors lend support to these assignments. They made no assignments below 800 cm^{-1} , and we have added this information. Bands were observed at 627 (w, br), 536 (m), and 454 (s). There should be one more fundamental, but it was not observed. The assignment of these bands is as follows: 627 to ν_{15} , the NH_2 torsion; 536 to ν_8 , the OCN bend; and 454 to ν_{16} , the OCN out-of-plane bend; the OCN rock was not observed. A band was seen in the deuterated compound at 275 cm^{-1} , which is tentatively assigned as the OCN rock of the heavy compound.

Assignment of Dithiooxamide Fundamentals

The assignments for the Raman spectrum of dithiooxamide are more difficult to make. Although the red He-Ne laser line does permit observation of the spectrum, the compound evidently absorbs some of the red light, making the spectrum generally weak. The color of the deuterated compound changes slightly toward brown, and no spectrum of this compound could be obtained.

Our assignments agree with those made by Scott and Wagner for the infrared bands, but there seems to be some disagreement in the literature concerning the assignment of C=S and C-N stretching modes. Bellamy⁸ gives the range 1050-1200 cm^{-1} for the C=S stretch in the infrared, and extending up to 1400 cm^{-1} in thioureas. Assignments for this vibration in the infrared spectra of several compounds have varied from 843 cm^{-1} in thioformamide⁹ to ~1000 cm^{-1} in a series of secondary thioamides¹⁰ to 1413 cm^{-1} in thiourea.¹¹ Jones *et al.*¹² concluded from studying infrared spectra of analogous oxygen and sulfur-containing

compounds that the C=S stretch occurs at 1408 cm^{-1} in thiourea, 1344 cm^{-1} in thiocarbonilide, and 1425 cm^{-1} in thiooxamide, although the spectra are not presented and no mention was made of other bands. In the cases where the C=S stretch has been assigned around 1400 cm^{-1} , a strong band near 730 cm^{-1} has been assigned as a C-N stretching mode. This represents a shift of 700 cm^{-1} from the other C-N stretching vibration, a rather large difference between the antisymmetric and symmetric counterparts. When this is compared with Raman data on thioamides, a strong case is made for assigning the C=S stretch to a band near 800 cm^{-1} with the weaker band around 1400 cm^{-1} being associated with the second C-N stretch. The size of the sulfur atom should lead to strong Raman bands involving motions in which it participates. Indeed, the strongest band in the Raman spectra of thiourea,¹³ thioacetamide,¹⁴ and dithiooxamide occurs at 735 , 722 , and 931 cm^{-1} , respectively. It seems unlikely that a band of this intensity and position should be assigned to a C-N stretching mode. We feel that a reasonable range for the C=S stretch of thioamides is $700\text{-}900\text{ cm}^{-1}$. This is only slightly higher than the range Bellamy⁸ cites for single bonded C-S stretching ($600\text{-}700\text{ cm}^{-1}$), suggesting that the C=S bond of thioamides possesses considerable single bond character. This corresponds to a similar lowering in frequency which occurs for the C=O stretch in amides as compared with that of acids and ketones. The C-N stretching vibration occurs at a higher frequency in amides ($\sim 1400\text{ cm}^{-1}$) than in amines ($1020\text{-}1250\text{ cm}^{-1}$), due to increased double bond character. Thioamides appear to be essentially analogous to amides.

The assignments for the fundamental vibrations of dithiooxamide are summarized in Table 6. Infrared bands assignments are in complete agreement with those of Scott and Wagner³ (the C=S stretching fundamental is observed at 832 cm^{-1} and the 1428 cm^{-1} band assigned by Jones et al.¹² to this vibration is taken to be the C-N stretching mode). In addition, the low-lying skeletal modes are assigned

as follows: $392-405\text{ cm}^{-1}$ doublet to ν_{12} , the SCN out-of-plane bend; 112 cm^{-1} to ν_{13} , the SCN torsion; 470 cm^{-1} to ν_{23} , the SCN bend; and 301 cm^{-1} to ν_{24} , the SCN rock. The assignment of the Raman-active fundamentals is rather analogous, complicated by the non-observance of several lines. This is believed to be caused by the weakness of the spectrum. The two N-H stretching modes were not found in the expected region, as well as the NH_2 scissors. The highest frequency line occurs at 1439 cm^{-1} . This is considered to be too low to be the NH_2 scissors, by comparison with similar compounds^{13,15,16} and the position of infrared-active NH_2 scissors of the same compound. The NH_2 scissors, thus, should occur near $1570-1600\text{ cm}^{-1}$, but was not observed; the band at 1439 cm^{-1} has been assigned to ν_4 , the C-N stretching vibration. The Raman assignments are completed as follows: 1291 cm^{-1} to ν_5 , NH_2 rock; 931 cm^{-1} to ν_6 , C=S stretch; 435 cm^{-1} to ν_8 , SCN bend; 177 cm^{-1} to ν_9 , SCN rock; 665 cm^{-1} to ν_{14} , NH_2 wag; 492 cm^{-1} to ν_{15} , NH_2 torsion; and 339 cm^{-1} to ν_{16} , SCN out-of-plane bend. The C-C stretch, ν_7 , has tentatively been assigned to the 670 cm^{-1} shoulder on the NH_2 wag. This is rather lower than the expected range for this vibration, and it is possible that it occurs at a higher frequency but was not observed, since it was not particularly strong in oxamide.

Lattice Vibrations

In addition to the fundamental vibrations, there are external modes to be considered, 6 for oxamide and 12 for dithiooxamide. From a consideration of Table 4, it can be shown that the optical librations (OL), acoustical translations (AT), and optical translations (OT) are distributed in the following manner among the vibrational species:

Oxamide (1 molecule per unit cell)

Γ (OL) = $3a_g$	Raman
Γ (AT) = $3a_u$	Inactive
Γ (OT) = 0	

Dithiooxamide (2 molecules per unit cell)

Γ (OL) = $6a_g$	Raman
Γ (AT) = $3a_u$	Inactive
Γ (OT) = $3a_u$	Infrared

Oxamide, thus, should exhibit three Raman active librations whereas six Raman librations and three infrared translations are predicted for dithiooxamide. The three lattice bands are very prominent features of the Raman spectrum of oxamide, occurring at 106, 134, and 157 cm^{-1} , with corresponding bands at 100, 137, and 156 cm^{-1} in the d_4 compound. In agreement with the group theory no lattice bands were observed in the far-infrared spectrum. It was not possible to associate the librations with a particular librational axis because the predicted shift factors for all three moments were very small and nearly the same (1.0452, 1.0548, and 1.0510 for I_A , I_B , and I_C , respectively). It seems possible that the 106 cm^{-1} band should be associated with motion around the B axis, however, because of its somewhat larger shift factor. An estimated range for the force constant of the librations was calculated using an equation of the form $k = \frac{\lambda I}{4r^2}$, where an arbitrary r of 1A is used to keep the units consistent. By associating the highest librational frequency with the largest moment of inertia and the lowest frequency with the smallest moment, the widest possible range for k is found to be 0.14-0.79 mdyne/A. This is considerably larger than several other reported librational force constants¹⁷ and probably reflects the high degree of hydrogen bonding in this compound.

The three infrared translations of dithiooxamide were observed at 79, 92, and 99 cm^{-1} , along with a combination band at 211 cm^{-1} , taken to be the combination of the 112 cm^{-1} torsion and a Raman-active lattice mode at 98 cm^{-1} . The six Raman-active librations apparently occur as three doublets; five bands have been observed, with three being strong bands and two of these having

less pronounced shoulders. Presumably the remaining mode is contained in the unsplit band of highest frequency. The observed bands are 67, 74, 93, 98 and 112 cm^{-1} at room temperature. These were found to shift to 72, 77, 100, 106 and 116 cm^{-1} when the sample was cooled with liquid nitrogen. The weak band seen in the spectrum at 57 cm^{-1} arises from an instrumental "ghost"; it did not change position with temperature.

Librational force constants calculated for this molecule fall in the range 0.089-0.75 mdyne/A. These values were calculated by using the moments of inertia of the molecule, rather than of the unit cell. The fact that the observed frequencies for dithiooxamide are shifted from those of oxamide by about 1.4 suggests that the forces are about the same in the two crystals and the difference in the number of molecules per unit cell has little effect.

Factor group splitting is possible in dithiooxamide, since there are two molecules per unit cell. The only indication of such splitting was seen in ν_{12} , the SCN out-of-plane bend, which exhibited a splitting of 13 cm^{-1} in $(\text{CSNH}_2)_2$ and 17 cm^{-1} in $(\text{CSND}_2)_2$. Wheatley² reported a significant difference between the C-S and C-N bond lengths of the two molecules in the unit cell of dithiooxamide, the C-S bond being 0.032 Å and the C-N 0.025 Å shorter in molecule 2 than in molecule 1. Such a difference, if real, should enhance factor group splitting. Since such is not the case, it appears that there is no real difference in bond lengths between the two molecules.

CONCLUSIONS

Re-examination of the infrared and Raman spectra of oxamide has led to the assignment of all the fundamental vibrations of this molecule, with the exception of the Raman-active OCN rock. Similarly, the infrared assignments have been completed for dithiooxamide, and nine out of twelve fundamentals assigned from the previously unobserved Raman spectrum. The weakness of the Raman lines of dithiooxamide has prevented us from observing the 2 N-H stretching modes and the NH_2 scissors because the phototube is less sensitive in the high-frequency range.

The lattice regions of the spectra have been examined and the external modes were observed as predicted from group theoretical considerations. Oxamide exhibits three Raman-active librations, which occur at 106, 134, and 157 cm^{-1} . For dithiooxamide, three infrared-active translations and six Raman librations are expected. The infrared bands were observed at 79, 92, and 99 cm^{-1} . The Raman lines occur as three doublets; three strong lines were seen at 74, 98, and 112 cm^{-1} , and the first two had weaker shoulders on the low-frequency side. The sixth libration was not seen, but is probably contained in the assumed unsplit line at 112 cm^{-1} .

Factor group splitting of the internal fundamentals is a possibility in dithiooxamide, but the only indication of it was seen in the splitting of the SCN out-of-plane bend. The forces in the crystals of oxamide and dithiooxamide appear to be similar, as evidenced by the shift of librations from one molecule to the other of approximately 1.4 and the similarity of the calculated force constants.

ACKNOWLEDGMENT

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Table I

Reported Spectra of Oxamide

<u>This Work</u>	<u>Raman</u>		<u>This Work</u>	<u>Infrared</u>	
	<u>Kahovec and Wagner*</u>	<u>Miyazawa[†]</u>		<u>Scott and Wagner[‡]</u>	<u>Miyazawa[†]</u>
3385 w	3384 m		3363 (92)	3370 vs	
			3250 (4)		
			3185 (100)	3160 vs	
3153 w, br	3141 m		2818 (4)		
			1878 (2)		
1700 m	1699 w	1692 (2)	1656 (76)	1661 vs	
			1608 (15)	1608 s	
1596 w	1593 w				
1491 s	1490 s	1493 (3)	1440 (5)		
			1348 (25)	1350 s	
			1300 (4)	1292 vw	
				1250 vw	
1105 s	1106 s	1100 (3)			
			1103 (14)	1105 m	

Table I (continued)

Raman		Reported Spectra of Oxamide		
<u>This Work</u>	<u>Kahovec and Wagner*</u>	<u>Miyazawa⁺</u>	<u>This Work</u>	<u>Infrared</u>
831 w				<u>Scott and Wagner^δ</u>
806 m	809 w	800 (1)		<u>Miyazawa⁺</u>
				792 (10)
				678 (31)
627 w, br	624 vw		471 m	629 (7)
536 m				
		448 (0)		
		357 (0)		
		240 (0)	337 s	
			165 w	
157 s				
134 s				
106 vs				

* Ref. 4

+ Ref. 5

δ Ref. 3

Abbreviations: s, strong; m, medium; w, weak; v, very; br, broad

Table III

Spectra of Oxamide and Oxamide-d₄

<u>Raman</u> [*]		<u>Infrared</u> ⁺	
<u>Light</u>	<u>Heavy</u>	<u>Light</u>	<u>Heavy</u>
106 vs	100 vs		
134 s	137 s		
157 s	156 m		
	275 vw	165	
454 s	412 m	337 s	312
	455 (residual)	471 w	489
536 m	521 m	629 w	569 w
627 w, br	480 w, br	678 m	495 w
806 m	824 m		
831 w	721 m	792 w	622 w
1105 s	939 s	1103 w	927 m
	1105 w (residual)	1300 w	1030 w
1491 s	1491 s	1348 m	1374 m
		1440 w	1426 w
1596 w	1206 w	1608 w	1121 w
1700 m	1657 m	1656 s	1647 s
		1878 w	1770 w
		2818 w	2861 w
3153 w, br	2339 w, br	3185 s	2384 s
		3250 w	2326 w
3385 w	2540 w	3363 s	2564 s

* This work

⁺ Infrared frequencies above 500 cm⁻¹ are taken from ref. 3.
All others are from this work.

Abbreviations: s, strong; m, medium; w, weak; v, very; br, broad

Table IV

<u>Molecule</u>	<u>Site</u>	<u>Factor</u>
C_{2h}	C_i	C_i'
R_z a_g } z a_u }	a_g	a_g R_x, R_y, R_z
R_x, R_y b_g } x, y b_u }	a_u	a_u x, y, z

Table V

Vibrational Assignments of Oxamide and Oxamide-d₄

Vibration No.	Approximate Description	Oxamide		Oxamide-d ₄	
		Raman	Infrared	Raman	Infrared
a_g					
ν_1	N-H stretch	3385		2540	
ν_2	N-H stretch	3153		2239	
ν_3	C=O stretch	1700		1657	
ν_4	NH ₂ scissors	1596		1206	
ν_5	C-N stretch	1491		1491	
ν_6	NH ₂ rock	1105		939	
ν_7	C-C stretch	831		721	
ν_8	OCN bend	536		521	
ν_9	OCN rock	-		275	
a_u					
ν_{10}	NH ₂ wag		792		622
ν_{11}	NH ₂ torsion		678		495
ν_{12}	OCN out-of-plane bend		471		489
ν_{13}	OCN torsion		165		-
b_g					
ν_{14}	NH ₂ wag	806		824	
ν_{15}	NH ₂ torsion	627		480	
ν_{16}	OCN out-of-plane bend	454		412	
b_u					
ν_{17}	N-H stretch		3363		2564
ν_{18}	N-H stretch		3185		2384
ν_{19}	C=O stretch		1656		1647
ν_{20}	NH ₂ scissors		1608		1121
ν_{21}	C-N stretch		1348		1374
ν_{22}	NH ₂ stretch		1103		927
ν_{23}	OCN bend		629		569
ν_{24}	OCN rock		337		312

Table VI

Vibrational Assignments of Dithiooxamide and Dithiooxamide-d₄

Vibration No.	Approximate Description	Dithiooxamide		Dithiooxamide-d ₄	
		Raman	Infrared	Raman	Infrared
a_g					
v ₁	N-H stretch	-			
v ₂	N-H stretch	-			
v ₃	NH ₂ scissors	-			
v ₄	C-N stretch	1439			
v ₅	NH ₂ rock	1291			
v ₆	C=S stretch	931			
v ₇	C-C stretch	670			
v ₈	SCN bend	435			
v ₉	SCN rock	177			
a_u					
v ₁₀	NH ₂ wag		695		523
v ₁₁	NH ₂ torsion		623		460
v ₁₂	SCN out-of-plane bend		405-392		380-363
v ₁₃	SCN torsion		112		
b_g					
v ₁₄	NH ₂ wag	665			
v ₁₅	NH ₂ torsion	492			
v ₁₆	SCN out-of-plane bend	339			
b_u					
v ₁₇	N-H stretch		3275		2500
v ₁₈	N-H stretch		3144		2342
v ₁₉	NH ₂ scissors		1582		1145-1124
v ₂₀	C-N stretch		1428		1465
v ₂₁	NH ₂ rock		1201		1048
v ₂₂	C=S stretch		832		746
v ₂₃	SCN bend		470		423
v ₂₄	SCN rock		301		289

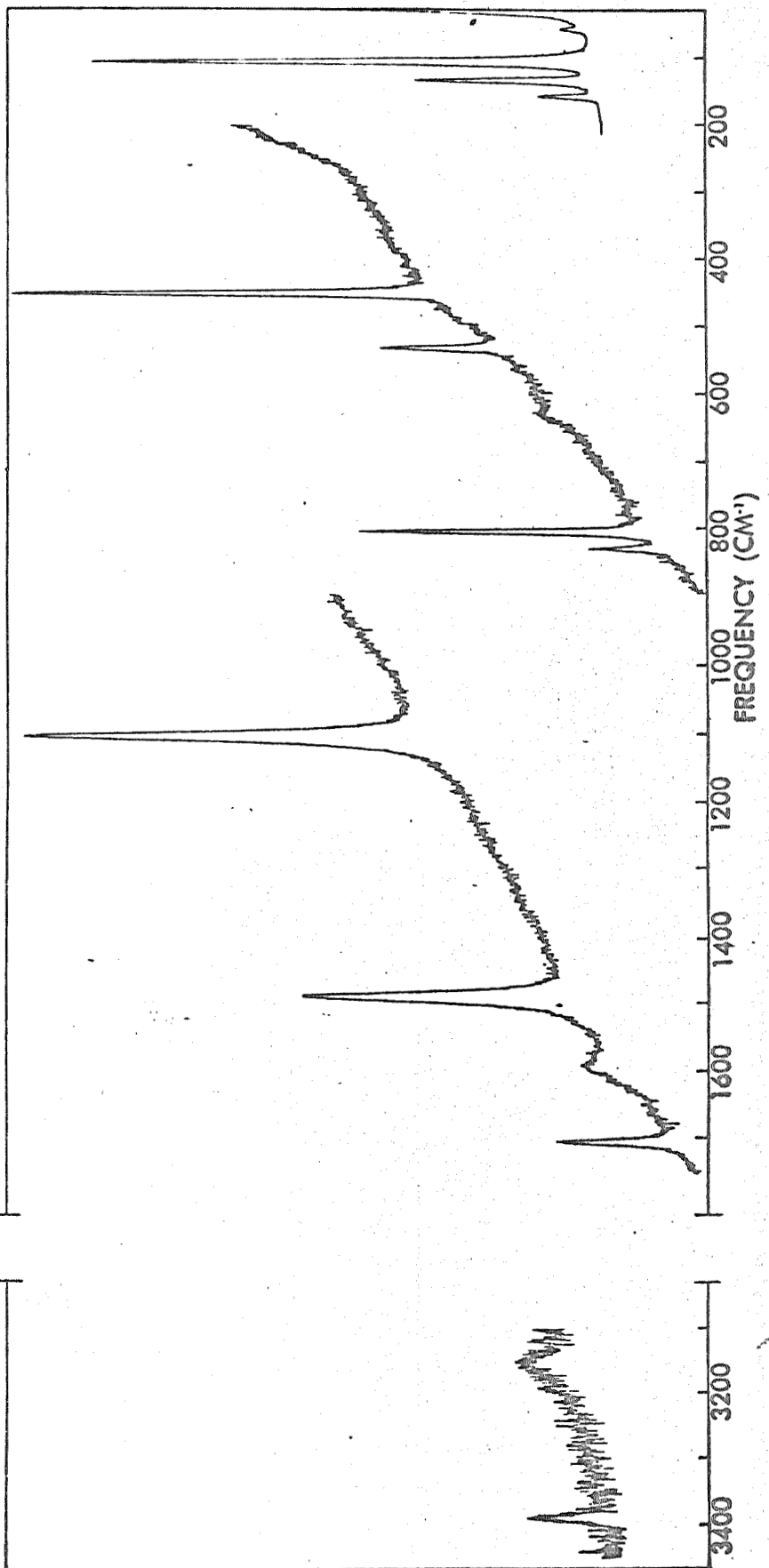
Figure Captions

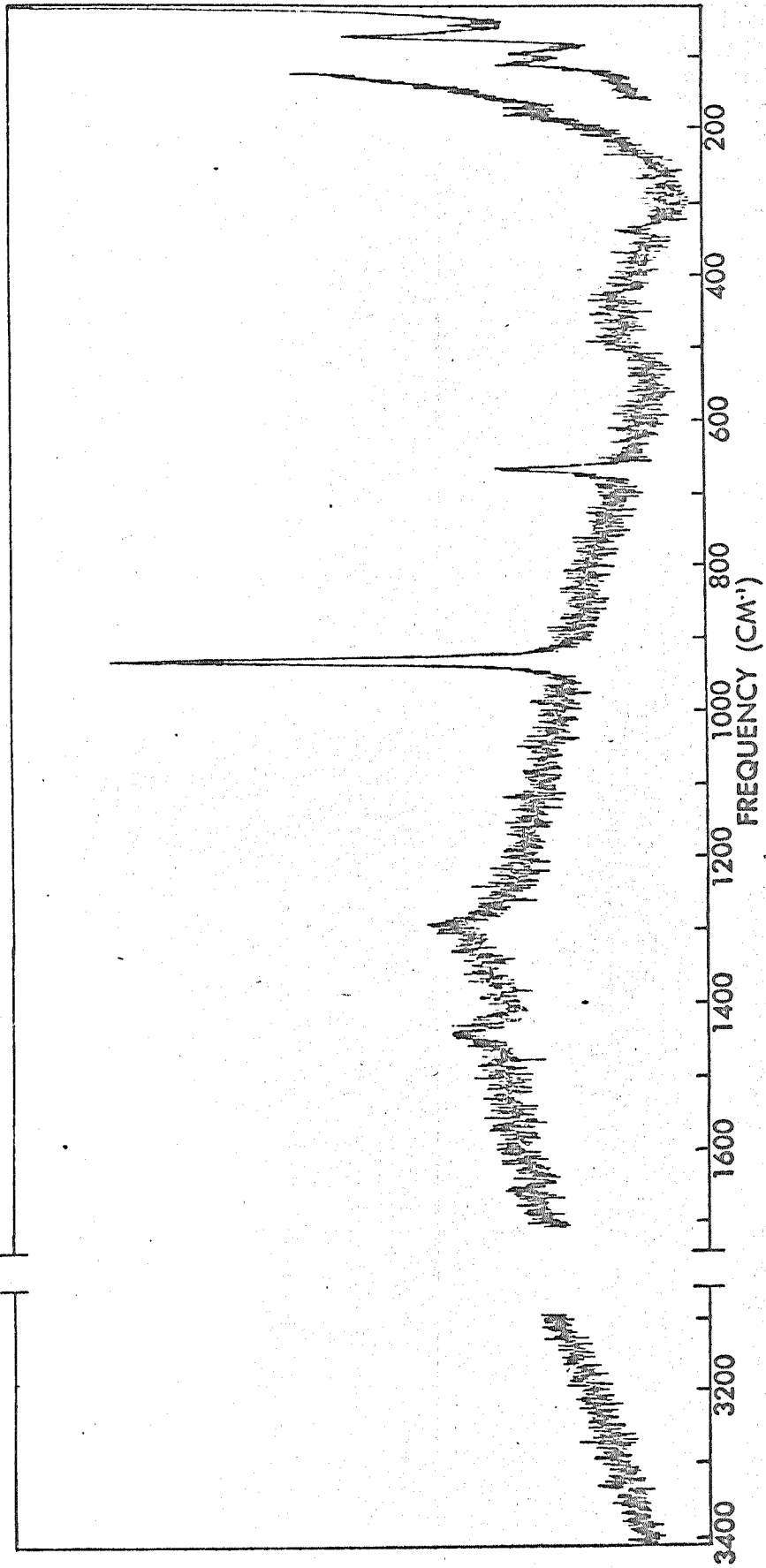
Fig. 1 - Raman spectrum of oxamide powder

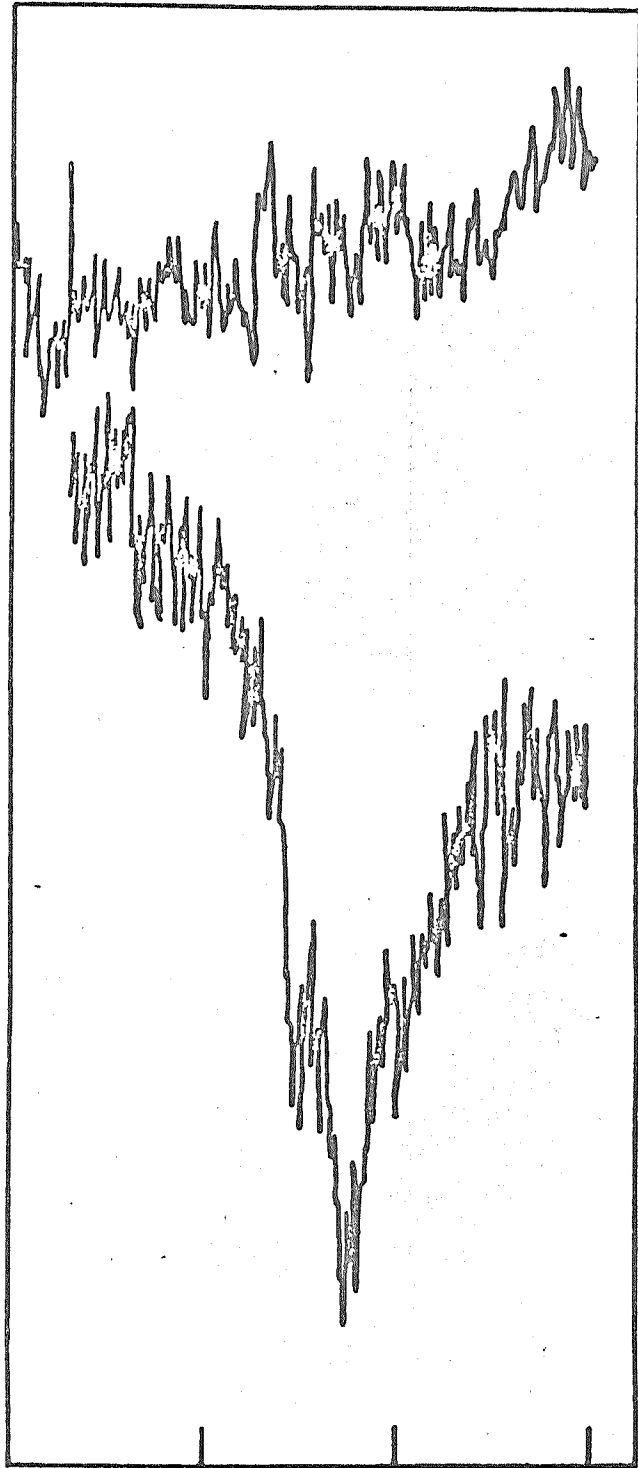
Fig. 2 - Raman spectrum of dithiooxamide powder

Fig. 3 - Far-infrared spectrum of oxamide in Nujol mull

Fig. 4 - Far-infrared spectrum of sublimed film of dithiooxamide







180
FREQUENCY (CM^{-1})
140

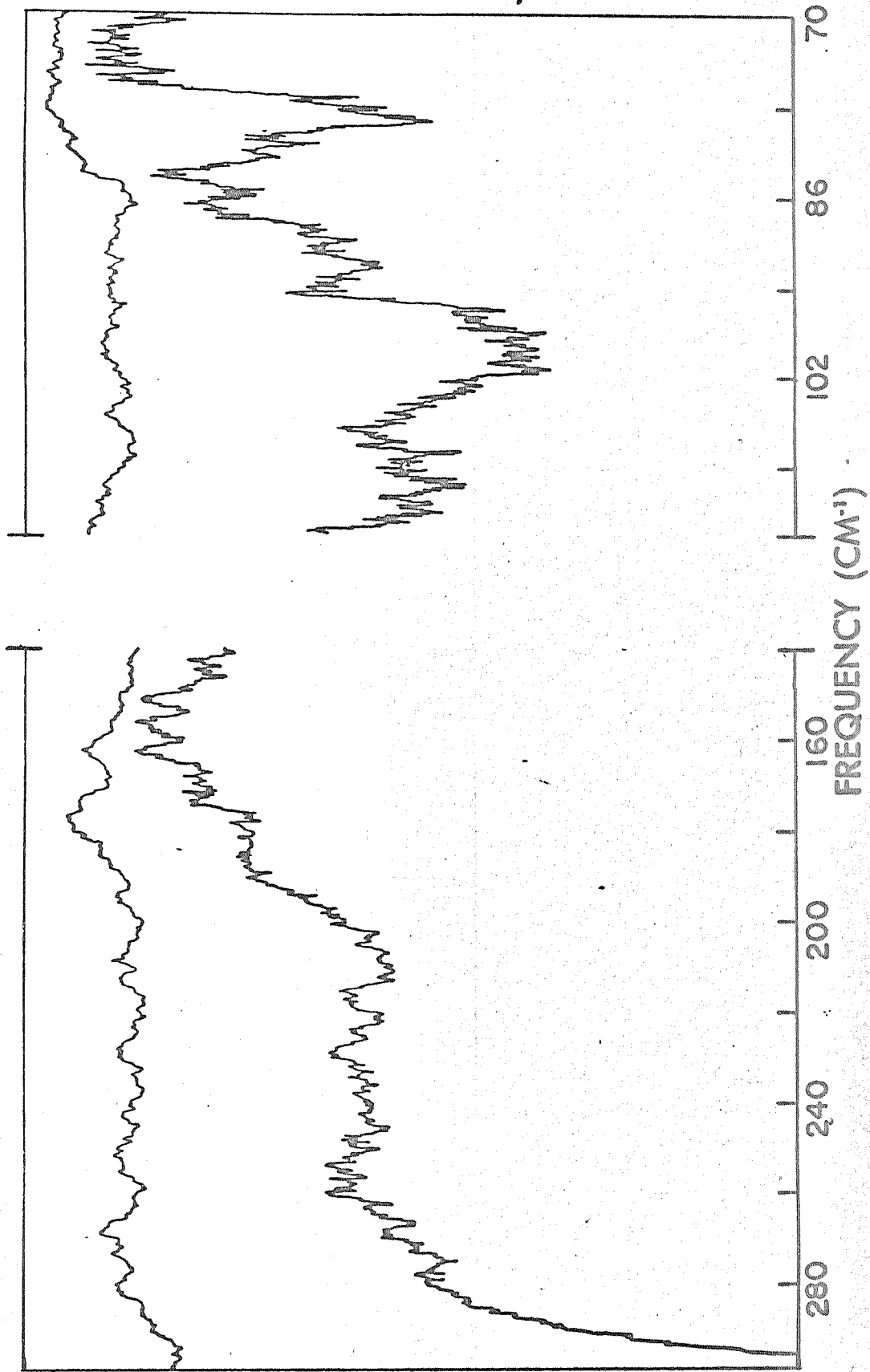


Fig. 4

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