Molecular Crystals and Liquid Crystals

Low-Frequency Modes of Molecular Crystals: XVI. Oxamide and Dithiooxamide

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Low-Frequency Modes of Molecular Crystals
XVI.† Oxamide and Dithiooxamide

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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 reported[3-5] for oxamide as has infrared data for dithiooxamide,[3] 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

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are the OCN torsion of a_u symmetry and the OCN rock of b_u symmetry. Raman assigments 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 Wagner,[3] with the addition of low-frequency data.

TABLE 1 Reported Spectra of Oxamide

This Work	Raman Kahovec and Wagner†	Miyazawa‡	This Work	Infrared Scott and Wagner§	Miyazawa‡
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
		1205 (0)?			
					1250 vw
1105 s	1106 s	1100 (3)			
				1103 (14)	1105 m
831 w					
806 m	809 w	800 (1)			
				792 (10)	788 w
				678 (31)	
					640 m
				629 (7)	
627 w, br	624 vw				
536 m					
			471 m	464 (2)	
454 s		448 (0)			
		357 (0)			
			337 s		
		240 (0)			
157 s			165 w		
134 s					
106 vs					

† Ref. 4.
‡ Ref. 5.
§ Ref. 3.
　　Abbreviations: s, strong; m, medium; w, weak; v, very; br. broad.

The Raman spectra of oxamide and dithiooxamide are presented in Figs. 1 and 2, and the far-infrared spectra of the compounds are given in Figs. 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

TABLE 2   Spectra of Dithiooxamide and Dithiooxamide-d_4

Raman†		Infrared‡	
Light	Heavy	Light	Heavy
67			
74		79	
93		92	
98		99	
112			
		112	
177 w			
		211	
		301 s	289
339 w			
		405, 392 m	380, 363
435 vw, br		470 w	423
492 vw, br			
		623 s	460 w
665 m			
670 sh			
		695 m	532 w
		832 s	746 m
931 vs			
		1201 m	1048 m
1291 m			
		1327 w	
1325 w			
		1396 w	
		1428 m	1465 s
1439 m			
		1582 s	1145, 1124 w
		1756 w	
		2503 vw	
		2799 vw	
		3144 vs	2342 s
		3211 s	
		3275 vs	2500 s

† This work.

‡ Infrared frequencies above 500 cm⁻¹ for $(CSNH_2)_2$ and above 450 cm⁻¹ for $(CSND_2)_2$ are taken from ref. 3. All others are from this work.

Abbreviations: s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder.
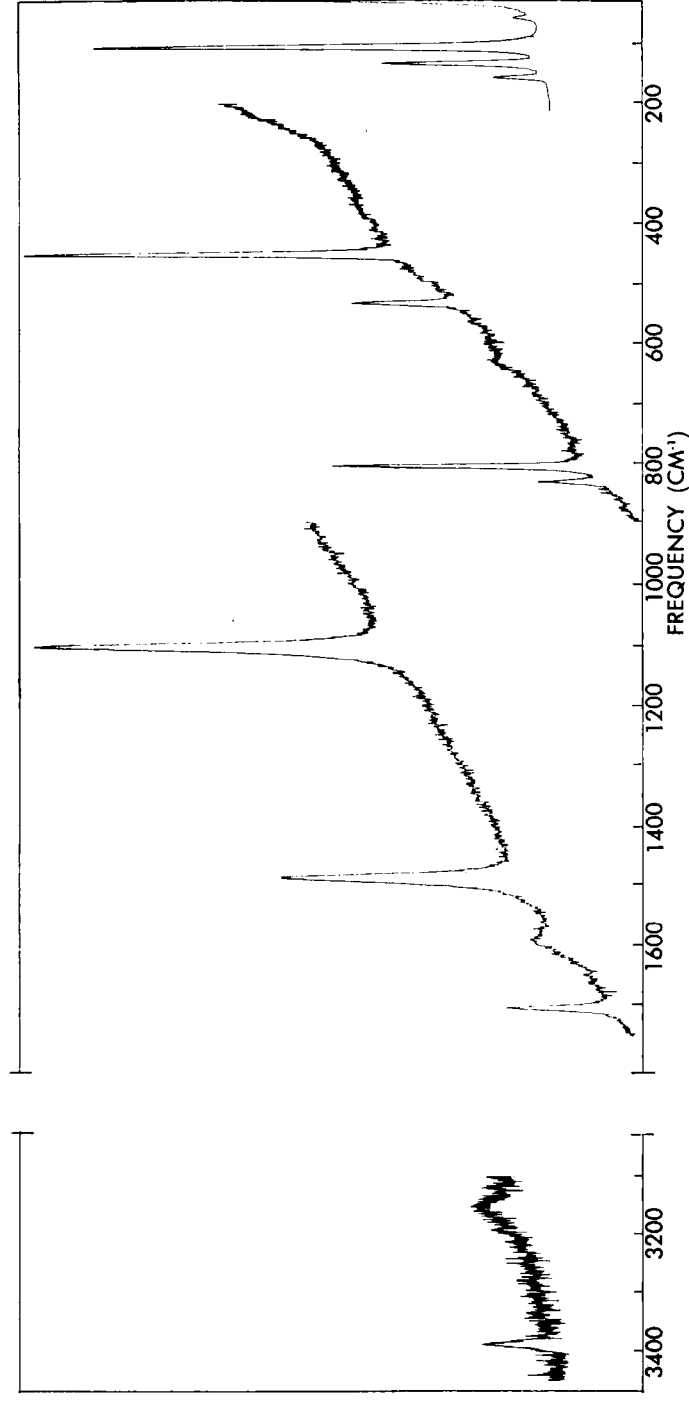
Figure 1. Raman spectrum of oxamide powder.
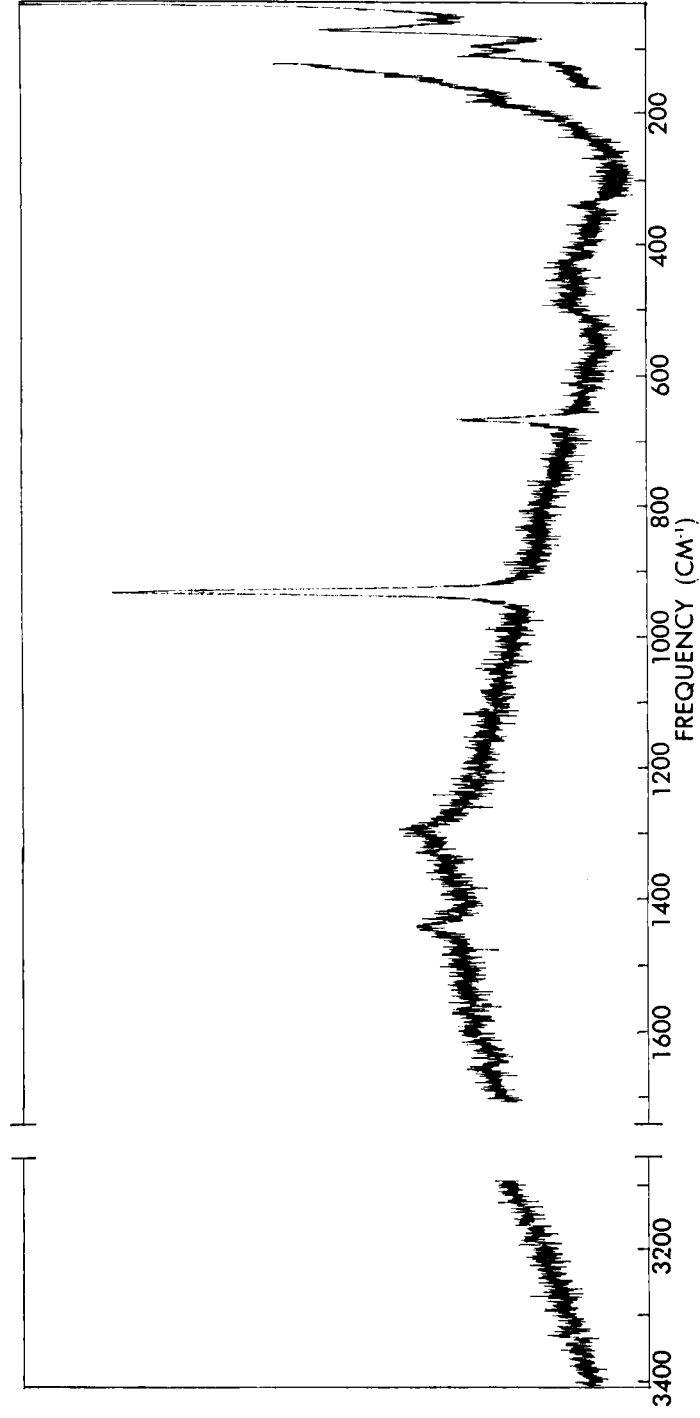
Figure 2. Raman spectrum of dithiooxamide powder.

180   140
FREQUENCY (CM⁻¹)
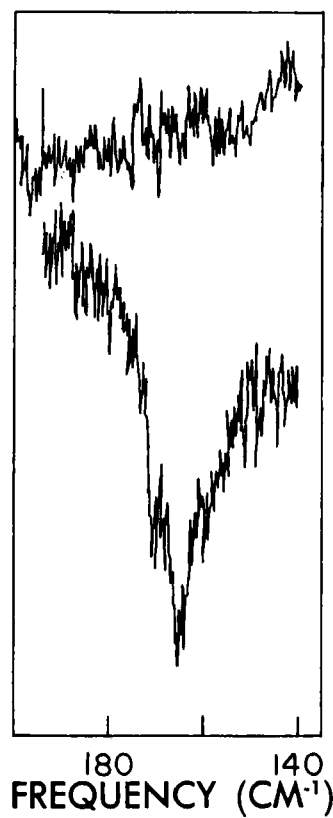
Figure 3.   Far-infrared spectrum of oxamide in Nujol mull.

280   240   200   160   102   86   70
FREQUENCY (CM⁻¹)
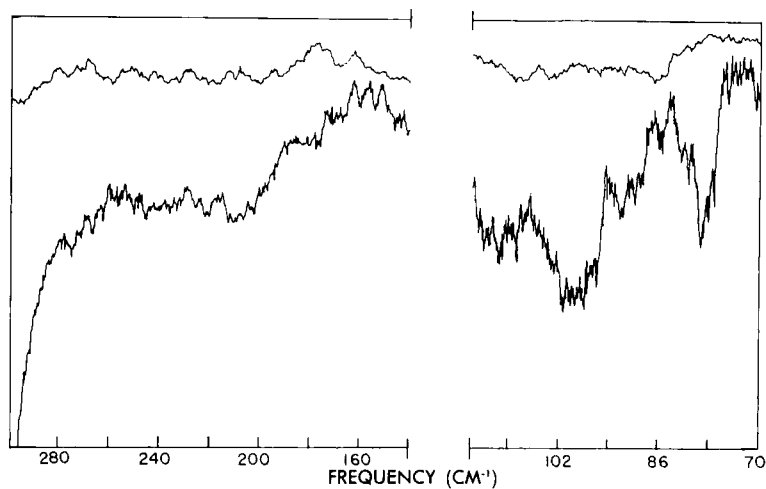
Figure 4.   Far-infrared spectrum of sublimed film of dithiooxamide.

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

TABLE 3   Spectra of Oxamide and Oxamide-d$_4$

| Raman† | | Infrared‡ | |
Light	Heavy	Light	Heavy
106 vs	100 vs		
134 s	137 s		
157 s	156 m		
		165	
	275 vw	337 s	312
454 s	412 m	471 w	489
	455 (residual)		
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.

The one area of disagreement between our work and that of Kahovec and Wagner[4] 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.

TABLE 4

Molecule		Site	Factor	
C_{2h}		C_i	C_i^1	
R_z	a_g	a_g	a_g	$R_x,\ R_y,\ R_z$
z	a_u			
$R_x,\ R_y$	b_g	a_u	a_u	$x,\ y,\ z$
$x,\ y$	b_u			

ASSIGNMENT OF OXAMIDE FUNDAMENTALS

Partial assignments were made for the fundamental vibrations of oxamide by Scott and Wagner,[3] 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.

Table 5   Vibrational Assignments of Oxamide and Oxamide-d_4

Vibration No.	Approximate Description	Oxamide		Oxamide-d_4	
		Raman	Infrared	Raman	Infrared
	a_g				
v_1	N-H stretch	3385		2540	
v_2	N-H stretch	3153		2239	
v_3	C = O stretch	1700		1657	
v_4	NH_2 scissors	1596		1206	
v_5	C-N stretch	1491		1491	
v_6	NH_2 rock	1105		939	
v_7	C-C stretch	831		721	
v_8	OCN bend	536		521	
v_9	OCN rock	—		275	
	a_u				
v_{10}	NH_2 wag		792		622
v_{11}	NH_2 torsion		678		495
v_{12}	OCN out-of-plane bend		471		489
v_{13}	OCN torsion		165		—
	b_g				
v_{14}	NH_2 wag	806		824	
v_{15}	NH_2 torsion	627		480	
v_{16}	OCN out-of-plane bend	454		412	
	b_u				
v_{17}	N-H stretch		3363		2564
v_{18}	N-H stretch		3185		2384
v_{19}	C = O stretch		1656		1647
v_{20}	NH_2 scissors		1608		1121
v_{21}	C-N stretch		1348		1374
v_{22}	NH_2 stretch		1103		927
v_{23}	OCN bend		629		569
v_{24}	OCN rock		337		312

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 Wagner[4] had seen only one weak peak (809 w). We have assigned the band having medium intensity, 806 cm^{-1}, to v_{14}, the NH_2 wag and the weak 831 cm^{-1} band to v_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. Bellamy[8] 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 thioformamide[9] to $\sim$1000 cm^{-1} in a series of secondary thioamides[10] 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 anti-symmetric 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^{-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 700–900 cm^{-1}. This is only slightly higher than the range Bellamy[8] cites for single bonded C—S stretching (600–700 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 (~ 1400 cm^{-1}) than in amines (1020–1250 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 band assignments are in complete agreement with those of Scott and Wagner[3] (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 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 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;

TABLE 6 Vibrational Assignments of Dithiooxamide and Dithiooxamide-d_4

Vibration No.	Approximate Description	Dithiooxamide Raman	Dithiooxamide Infrared	Dithiooxamide-d_4 Raman	Dithiooxamide-d_4 Infrared
	a_g				
ν_1	N-H stretch	—			
ν_2	N-H stretch	—			
ν_3	NH_2 scissors	—			
ν_4	C-N stretch	1439			
ν_5	NH_2 rock	1291			
ν_6	C = S stretch	931			
ν_7	C-C stretch	670			
ν_8	SCN bend	435			
ν_9	SCN rock	177			
	a_u				
ν_{10}	NH_2 wag		695		523
ν_{11}	NH_2 torsion		623		460
ν_{12}	SCN out-of-plane bend		405–392		380–363
ν_{13}	SCN torsion		112		
	b_g				
ν_{14}	NH_2 wag	665			
ν_{15}	NH_2 torsion	492			
ν_{16}	SCN out-of-plane bend	339			
	b_u				
ν_{17}	N-H stretch		3275		2500
ν_{18}	N-H stretch		3144		2342
ν_{19}	NH_2 scissors		1582		1145–1124
ν_{20}	C-N stretch		1428		1465
ν_{21}	NH_2 rock		1201		1048
ν_{22}	C = S stretch		832		746
ν_{23}	SCN bend		470		423
ν_{24}	SCN rock		301		289

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:

<div align="center">

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

</div>

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 $k = \lambda I/4r^2$, 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 constants[17] 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 (CSNH$_2$)$_2$ and 17 cm^{-1} in (CSND$_2$)$_2$. Wheatley[2] 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 A and the C—N 0.025 A 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.

Acknowledgement

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