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A Reinvestigation of the Normal Vibrations of Thioacetamide

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The normal coordinate treatments of thioacetamide and its seven isotopic molecules have been carried out using Urey-Bradley force constants refined by a least-squares procedure. The laser Raman spectrum of thioacetamide has also been recorded.

A satisfactory assignment of the infrared frequencies of thioacetamide (TAM) and its *N*-deuterated molecule was made by Suzuki[1] with the aid of a normal coordinate analysis using Urey-Bradley force field. Walter and Kubersky[2] reinvestigated the infrared spectra of TAM and its several isotopic molecules. They appear to doubt the applicability of the results of the normal coordinate treatment (of Suzuki) to the isotopic molecules of TAM and have proposed considerable revision of the assignments of the infrared spectrum of TAM. It is of particular interest that the C=S stretching frequency was assigned around 975 cm^{-1}, as was done by some earlier workers[3,4] instead of a band near 720 cm^{-1} as favoured by the normal coordinate treatment.[1] It was therefore considered worthwhile to reinvestigate the infrared spectral assignments of this simplest thioamide, the results of which could be of considerable interest for other molecules. We report here the results of the normal coordinate treatments of TAM and its seven isotopic molecules—CH_3CSND_2, CD_3CSNH_2, CD_3CSND_2, $CH_3CS^{15}NH_2$, $^{13}CH_3CSNH_2$, $^{13}CH_3CSND_2$, and $CH_3{}^{13}CSNH_2$. The laser Raman spectrum of TAM has also been recorded.

Experimental

Infrared Spectra: We recorded the infrared spectra of thioacetamide (E. Merck) and its *N*-deuterated molecule in the range 4000—250 cm^{-1}. The frequency data agree with those of Walter and Kubersky[2] within 2—3 cm^{-1}. In order to utilize the infrared data of other isotopes and for uniformity, the data from the latter were only employed in the calculations.

Raman Spectrum: The Raman spectrum of powdered TAM sealed in a capillary tube was taken on a Cary 81 Raman spectrophotometer using argon laser. The spectrum was kindly recorded for us by Dr. J. R. Scherer of the U. S. Department of Agriculture, Albany, California, to whom we are grateful for this help. The Raman bands are included in Table 2.

Normal Coordinate Treatment

The structural parameters and the internal symmetry coordinates were the same as those employed by Suzuki.[1] The NH and CH stretching modes, however, were retained in the calculations. The initial force constants were taken from Suzuki. Twelve of these force constants were refined by a least-squares technique[5] from 14 frequencies by keeping all stretching constants and three bending constants around the thioamide carbon fixed. The final force constants are given in Table 1. They are comparable to the initial set except for $F_{HNH}(=-0.33\ \text{mdyn/Å})$. We have preferred keeping the force constants within the framework of Urey-Bradley field to the alternate method of keeping F_{HNH} as zero, and introducing a non Urey-Bradley term between two NH bonds, as was done in the case of acetamide and other molecules.[6—8] If the force constant F_{HNH} is kept zero, the NH_2 stretching frequencies deviate largely and the force filed does not converge satisfactorily. The frequencies of the isotopic molecules were calculated employing the refined force constants. All the numerical calculations were made on an IBM 360/44 computer.

Table 1. Force constants (mdyn/Å) for thioacetamide

Stretching		Bending		Repulsion	
K_{CH}	4.50	H_{SCN}	0.240	F_{NCS}	0.991
K_{NH}	5.52	H_{NCC}	0.270	F_{NCC}	0.894
K_{CN}	5.70	H_{CCS}	0.270	F_{CCS}	0.286
K_{CS}	3.40	H_{CNH}	0.308	F_{CCH}	0.479
K_{CC}	2.70	H_{HNH}	0.567	F_{CNH}	0.481
		H_{CCH}	0.279	F_{HCH}	0.122
$k^{a)}{}_{CH_3}$	−0.071	H_{HCH}	0.391	F_{HNH}	−0.332
				F'	$-0.1F$

a) Intramolecular tension in mdyn·Å

Results and Discussion

The observed and calculated frequencies for TAM are given in Table 2, and for *N*- and *C*-deuterated TAM in Table 3, where the assignments obtained from the potential energy distribution (PED) are also shown. The agreement between the observed and calculated frequencies for TAM is excellent and that for isotopes of TAM listed in Tables 3 and 4 is fairly good. The calculated ND stretching frequencies deviate somewhat in the deuterated molecules. This may be attributed to the effects of hydrogen bonding.

The assignments given in Table 2 are practically the same as Suzuki's, and will therefore not be discussed. The satisfactory reproduction of the frequency shifts for several isotopic molecules of TAM (Tables 3 and 4) reflects the validity of the Urey-Bradley force constants and also the assignmtens derived therefrom. The revision of Suzuki's infrared assignments for TAM by Walter and Kubersky[2] therefore finds no support from isotopic molecules. When extensive coupling of the vibrations are involved, correlation by inspection of the frequency variations in the isotopic molecules with the assignments may be difficult as in the case of *N,N*-dimethylformamide.[9]

The C=S stretching mode has been attributed by Suzuki to a band at 720 cm^{-1} which has a mjaor contribution (approx. 60%) from the mode. This

Table 2. Vibrational frequencies (cm^{-1}) and assignments for thioacetamide

Raman	Infrared[a)]	Calcd	Assignments (PED, %)
	3295	3295	ν_aNH(100)
	3080	3080	ν_sNH(98)
	2977	2978	ν_aCH(100); νCH(A″)
	2945	2945	ν_sCH(100)
1650 vw	1650 1648	1650	δNH$_2$(84)+νCN(10)
1474 mb	1479	1479	δ_aCH$_3$(55)+rCH$_3$(21) +νCN(15)
1432 vw	—	—	δCH$_3$(A″)
1406 wb	1390	1390	νCN(54)+δ_aCH$_3$(23)
1370 m	1362	1361	δ_sCH$_3$(88)
1312 wsh 1297 mw	1303	1303	rNH$_2$(42)+νCC(24) +νCS(13)+δNCS(12)
—	1130w[b)]	—	rCH$_3$(A″)
1038 s	1025	1025	rCH$_3$(46)+rNH$_2$(24) +δ_aCH$_3$(11)
975 vw	972	973	νCC(37)+rCH$_3$(21) +rNH$_2$(17)+νCS(11)
—	760wsh[b)]	—	τNH$_2$(A″)
720 vs	719	717	νCS(60)+νCC(16)
712 s	709	—	wNH$_2$(A″)
515 mw	512	—	πCC(A″)
471 s 463	471 460	465	δNCS(74)+νCS(14)
379 w 372 vw	377w[b)]	377	δCS(63)+δNCS(21)
220 w	n.i.	—	—
162 ms	n.i.	—	τCH$_3$(A″)
120 s 101 m 80 s	n.i.		Lattice modes

A″ vibrations are tentatively assigned (*cf.* Table 3) a) From Ref. 2. b) From present investigation. n.i. denotes not investigated.

assignment is supported by the large red shift of the band, by 30—60 cm^{-1}, in metal complexes, where the thiocarbonyl sulfur is the donor[10,11] and the shift of the band to 675 cm^{-1} on *S*-methylation.[12] A comparison of the infrared spectrum of TAM with that of selenoacetamide ("Selenation") has also confirmed this assignment.[12] Thus the attribution of C=S stretching vibration to $\sim$975 cm^{-1} frequency by Walter and Kubersky and others is not supported.[2–4,13] This band has, however, about $\sim$10% C=S stretching mode and shows minor changes on complex formation, *S*-methylation and selenation.[10–12]

The C=S stretching vibration generally occurs as a split band in isotopic molecules. It appears at considerably lower wave numbers in deuterated molecules (Tables 3 and 4) depending on the nature of vibrational coupling.

Out-of-plane Vibrations. A tentative assignment for the seven A″ vibrations of TAM is given in Table 2. The CH$_3$ out-of-plane rocking mode generally occurs at a higher frequency than CH$_3$ in-plane rocking and is of weaker intensity in amides. Accordingly, a weak broad band near 1130 cm^{-1} is attributed to CH$_3$ out-of-plane rocking in TAM, the band being slightly intensified in metal complexes.[10,11] Identification of CH$_3$ torsional mode is difficult since lattice modes

Table 3. Infrared frequencies and their assignments for *N*- and *C*- deuterated thioacetamide

Frequencies, cm^{-1}		CH_3CSND_2
Obsd[a)]	Calcd	Assignments (PED, %)
2981	2978	ν_aCH(100); νCH(A″)
2924	2945	ν_sCH(100)
2485	2443	ν_aND(99)
2285	2238	ν_sND(95)
1506 1486	1487	νCN(30)+δ_aCH$_3$(40) +rCH$_3$(18)
1424	1416	νCN(44)+δ_aCH$_3$(34); δCH(A″)
1360	1361	δ_sCH$_3$(91)
1240	1231	νCC(35)+νCS(21) +rND$_2$(16)+NCS(14)
1164	1179	δND$_2$(73)
979	983	rCH$_3$(62)+δ_aCH$_3$(12) +νCN(11)
836	838	rND$_2$(60)+νCC(33)
700 694	691	νCS(64)+νCC(10)
580 556	—	τND$_2$(A″)
523	—	πCC(A″)
480	—	wND$_2$(A″)
428	420	δNCS(64)+δCS(17) +rND$_2$(13)
—	374	δCS(61)+δNCS(24)

Frequencies, cm^{-1}		CD_3CSNH_2
Obsd[a)]	Calcd	Assignments (PED, %)
3296	3295	ν_aNH(100)
3077	3080	ν_sNH(98)
—	2211	ν_aCD(98); νCD(A″)
—	2112	ν_sCD(99)
1653 1648	1650	δNH$_2$(84)+νCN(10)
1438	—	
1393	1403	νCN(69)
1303	1301	rNH$_2$(43)+νCC(25) +νCS(14)
1234	—	
1094	1086	δ_sCD$_3$(61)+νCC(26) +rNH$_2$(11)
1034	1038	δ_aCD$_3$(87); δCD$_3$(A″)
975	—	rCD$_3$(A″)
957	954	rNH$_2$(31)+νCS(22) +δ_sCD$_3$(17)+νCC(15)
812	817	rCD$_3$(58)+νCN(11); τNH$_2$(A″)
709	—	wNH$_2$(A″)
670 664	663	νCS(55)+rCD$_3$(22) +νCC(13)
461 448	453	δNCS(78)
—	343	δCS(65)+δNCS(15)

a) From Ref. 2.

TABLE 4. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR SOME ISOTOPIC MOLECULES OF THIOACETAMIDE

CD_3CSND_2		$CH_3CS^{15}NH_2$		$^{13}CH_3CSNH_2$		$^{13}CH_3CSND_2$		$CH_3{}^{13}CSNH_2$	
Obsd[a)]	Calcd	Obsd[a)]	Calcd	Obsd[a)]	Calcd	Obsd[a)]	Calcd	Obsd[a)]	Calcd
2477	2443	3288	3285	3292	3295		2967	3297	3295
2285	2238	3081	3075	3082	3080		2942	3082	3080
—	2210	2980	2978	2978 2967	2967		2443	2979	2978
—	2112	2934	2945	2942	2941		2238	2944	2945
1488	—	1654 1640	1642	1652 1648	1650	1506 1502	—	1653 1647	1649
1462	1439	1475	1477	1478	1478	1485	1487	1475	1471
1236	1229	1387 1382	1383	1389	1389	1421	1415	1464	—
1197	—	1361	1361	1364	—	1367	—	1370	1367
1172	1174	1300	1298	1351	1352	1351	1352	1360	1355
—	1056	1024	1022	1303	1299	1236	1225	1304	—
1028	1036	970	969	1022	1018	—	1177	1286	1280
814	809	714	712	973	—	973	976	1026	1022
—	802	704	—	965	964	831	831	963	966
694	—	512	—	718 710	712	700	—	714	713
663									
658	652	466 453	460	703	—	693 689	687	705	—
573	—	—	376	512	—	580	—	512 501	—
546	—	—		470 459	463	— 557	—	471 460	468
523	—	—	—	—	372	523	—	—	379
438	—	—	—	—	—	478	—	—	—
416	410	—	—	—	—	426	418	—	—
—	341	—	—	—	—	—	369	—	—

a) From Ref. 2.

interfere in this region. A band at 162 cm^{-1} in Raman may be favoured to methyl torsion in comparison with that at 155 cm^{-1} in acetamide.[14)]

Both the wagging and torsional vibrations of the NH_2 group in TAM were assigned[1)] earlier to a fairly sharp band at 709 cm^{-1}. In the Raman spectrum also the corresponding band is sharp. Careful observation of the infrared spectrum of TAM shows a weak shoulder at 760 cm^{-1} to the main absorption at 720 cm^{-1}. In metal complexes of TAM, the 760 cm^{-1} band acquires intensity and is sometimes observed as a farily strong band as in the case of copper(I) and palladium(II) chloride complexes.[10,11)] We favour therefore the weak band at 760 cm^{-1} in TAM to NH_2 torsion in comparison with that at 810 cm^{-1} (weak) in acetamide.[14)] The intense band at 709 cm^{-1} is attributed to NH_2 wagging mode in agreement with the earlier assignment.[1)] This is compatible with the NH_2 wagging in acetamide assigned[14)] to a strong band at 700 cm^{-1}.

The remaining three A'' vibrations of TAM are easily assigned as indicated in Table 2. In the deuterated molecules CD_3 out-of-plane rocking is expected near *ca.* 1000 cm^{-1}, and the torsional and wagging modes of ND_2, respectively, around δ 550 and 500 cm^{-1}. It is satisfying to note that bands are observed in this region in deuterated molecules (Tables 3 and 4). For a more definite assignment of the A'' vibrations, a normal coordinate analysis would be helpful.

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