Infrared and Raman spectra of 1,2,5-thiadiazole

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Abstract—The infrared spectra of 1,2,5-thiadiazole and 1,2,5-thiadiazole-d_2 in the gaseous and liquid states, have been measured between 4000 and 400 cm^{-1}. The Raman spectrum of liquid 1,2,5-thiadiazole has also been obtained. An assignment of all the infrared active modes was based on the rotational envelope contours of the gas phase spectra, the isotope shift and the polarization measurements of the Raman spectrum. The two infrared inactive but Raman active A_2 modes were not detected.

1. Introduction

THE COMPLETE vibrational assignment of five-membered heterocyclic molecules is an interesting and far from exhausted field, although considerable work has been done since the appearance of the paper by LORD and MILLER on pyrrole [1]. The objective of the present work was, therefore, to make a contribution to the research going on in this field by completely analysing the infrared and Raman spectra of 1,2,5-thiadiazole first synthesized by Prof. MARVIN CARMACK and his research group at Indiana University [2–6].

Attempts to analyse its spectrum were made from the very earliest stages of the study of 1,2,5-thiadiazole. From comparison of the parent compound and its various substitution derivatives, WEINSTOCK [2] and SHEW [3] identified the C—H stretching mode and several ring vibrations. Much more complete, although still purely empirical, was the analysis done by MARQUARDT [4] who made use of the liquid-phase spectra of 1,2,5-thiadiazole and 1,2,5-thiadiazole-d_2 and of the gas-phase spectra of these two and of 1,2,5-thiadiazole-d. MARQUARDT, however, did not examine the region beyond 15 μ and did not have Raman data so was unable to make a complete vibrational assignment.

2. Experimental

The sample of 1,2,5-thiadiazole (b.p. 94·2°C) was kindly furnished by. Prof. Carmack's group. The sample was, evidently, of very good purity and no bands that could be attributed to impurities were observed in its gas chromatogram. 1,2,5-thiadiazole-d_2 was prepared following, in essence, the procedure described by MARQUARDT [4]. The starting material, 1,2,5-thiadiazole-3,4-dicarboxylic acid,

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[1] R. C. LORD, JR, and F. A. MILLER, *J. Chem. Phys.* **10**, 328 (1942).
[2] L. M. WEINSTOCK, Ph.D. Dissertation, Indiana University (1958).
[3] D. SHEW, Ph.D. Dissertation, Indiana University (1959).
[4] F. H. MARQUARDT, Ph.D. Dissertation, Indiana University (1960)
[5] R. G. COLLINS, Ph.D. Dissertation, Indiana University (1965).
[6] M. CARMACK, L. M. WEINSTOCK and D. SHEW, *Abstracts*, 136th *National Meeting of the American Chemical Society*, p. 37-P. Altantic City, New Jersey, September (1959).

however, was obtained using a method given by COLLINS [5]. The carboxylic groups of the acid were then deuterated by treating three 3 g samples of it with several portions of deuterium oxide (totaling 17 ml) and evaporation, on a vacuum line, of each portion, after the equilibrium was established, by short heating to boiling. The whole procedure was carried out in Carius tubes which were then sealed and the deuterated acid was decarboxylated by pyrolysis for 16 hr at 200°C. The product after pyrolysis was purified as recommended by Marquardt. The gas chromatogram showed purity of about 99 percent.

The infrared spectra were taken using, for the most part, a double-beam Perkin–Elmer Model 21 spectrophotometer equipped with LiF, NaCl or KBr prisms. In clarifying some complex rotational envelopes and using long path length cells for the gas-phase a single-beam grating instrument, the Perkin–Elmer Model 210 was used. A Cary Model 81 was used to record the Raman spectrum.

The gas-phase i.r. spectra were measured using 10 cm gas-cells with NaCl or KBr windows. A 150 cm cell was also used in two cases. The cells were evacuated on a vacuum line and then filled with vapor to a pressure of about 50 mm Hg at room temperature. The liquid-phase i.r. spectra were taken using a 0·025 mm micro-cell with NaCl windows, except in the KBr region where a capillary film between two KBr plates was used. Raman spectra of the liquid-phase were taken using 7 ml samples.

3. RESULTS AND DISCUSSION

The infrared spectra of gaseous and liquid 1,2,5-thiadiazole and 1,2,5-thiadiazole-d_2 are shown in Figs. 1 and 2. The wavelengths (in microns) and the frequencies (in cm^{-1}) of the i.r. bands together with an estimation of their intensity are listed in Tables 1 and 2. The spectrometer was calibrated with spectra of water vapor, CO_2 and NH_3 and the frequencies are believed to be accurate to ± 5 cm^{-1}. The Raman frequencies believed to be accurate to ± 10 cm^{-1} and qualitative estimation of depolarization ratios and intensities for liquid 1,2,5-thiadiazole are listed in Table 3.

Both electron diffraction work by BONHAM and MOMANY [7] and the microwave study by DOBYNS and PIERCE [8] showed that 1,2,5-thiadiazole is planar with C_{2v} symmetry. The moments of inertia (in amu-Å^2) of the molecule are $I_A = 59 \cdot 2057$, $I_B = 79 \cdot 8245$, and $I_C = 139 \cdot 1126$. The A inertial axis coincides with the two-fold symmetry axis. Perpendicular to the A-axis is the B inertial axis which is also located in the plane of the molecule and lies very close to the nitrogen atoms. The C-axis is perpendicular to the plane of the molecule.

The fifteen normal modes of vibration may be classified into four symmetry species [9]. Six vibrations are the totally symmetric A_1 species and are infrared and Raman (polarized) active. Five modes of B_1 symmetry and two of B_2 symmetry are infrared and Raman (depolarized) active. The remaining two vibrations, A_2, are infrared inactive but have allowed depolarized Raman scattering.

[7] (a) R. A. BONHAM and F. A. MOMANY, J. Am. Chem. Soc. **83**, 4475 (1961); (b) F. A. MOMANY and R. A. BONHAM, J. Am. Chem. Soc. **86**, 162 (1964).

[8] Sr. V. DOBYNS and L. PIERCE, J. Am. Chem. Soc. **85**, 3553 (1962).

[9] G. HERZBERG, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand, N.Y. (1964).
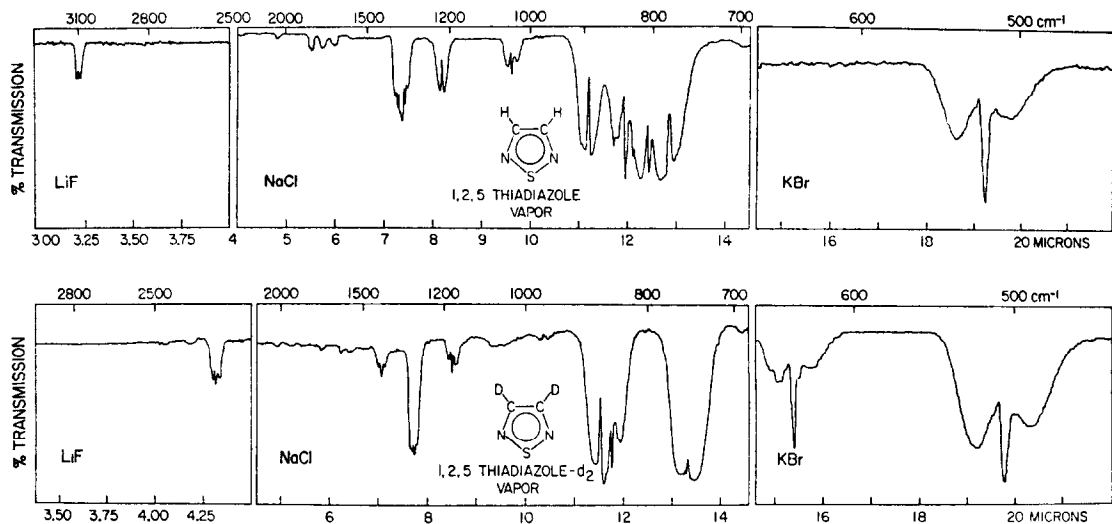
Fig. 1. The gas-phase infrared spectra of 1,2,5-thiadiazole and 1,2,5-thiadiazole-d_2 in the LiF, NaCl and KBr prism regions. The pathlength was 10 cm and the gas pressure was 50 mm Hg.
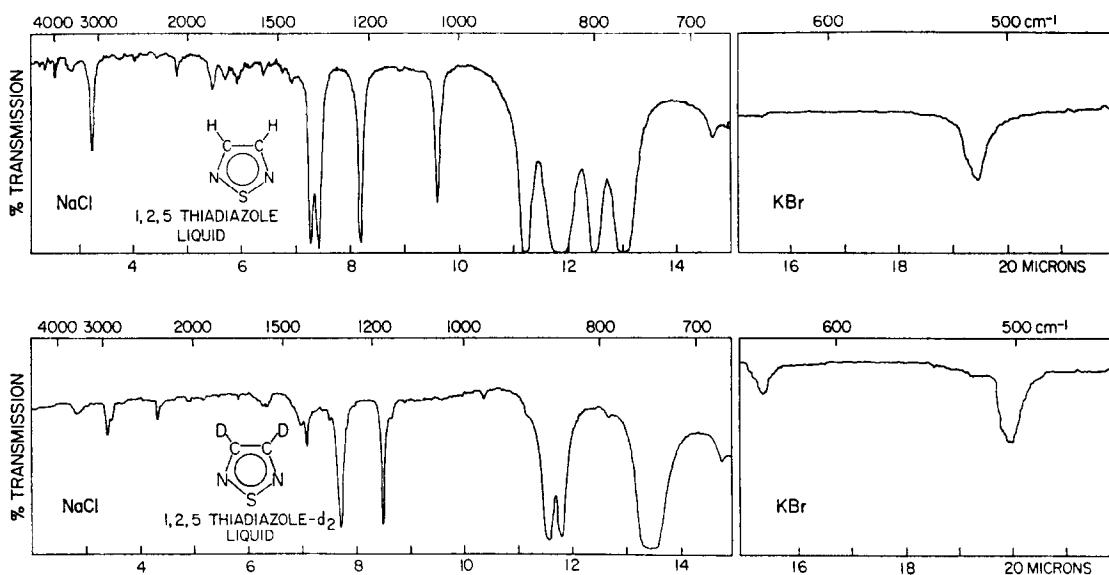

Fig. 2. The liquid-phase infrared spectra of 1,2,5-thiadiazole and 1,2,5-thiadiazole-d_2. The path length in the NaCl region was 0·025 mm and a capillary film was used in the KBr region.

Table 1. Infrared spectrum of $C_2H_2N_2S$*

Liquid phase			Vapor				Assignment
λ	ν	I	λ	ν	Rot. str.	I	
2·315	4320	vw					$3106 + 1227 = 4333$
2·425	4124	vw					$3106 + 1041 = 4147$
2·510	3984	w	2·500	4000	Q	vw	$3108 + 895 = 4003$
2·798	3575	w					$3108 + 500\dagger = 3608$
			3·205	3120	R		
			3·212	3113	R	w	B_1 fundamental
3·235	3091	m	3·220	3106	Q	w	A_1 fundamental
			3·224	3102	P		
			3·228	3098	P		
3·735	2677	vw					$1461 + 1227 = 2688$
4·005	2497	vw					$1461 + 1041 = 2502$
4·420	2262	vw					$1227 + 1041 = 2268$
			4·779	2092	R		
4·801	2083	w	4·803	2082	Q	w	$2 \times 1041 = 2082$
			4·828	2071	P		
			5·472	1827	R		
5·450	1834	w	5·501	1818	Q	w	$2 \times 908\dagger = 1816$
			5·530	1808	P		
			5·717	1749	R		
5·695	1756	w	5·746	1740	P	w	$838 + 908\dagger = 1746$
			5·884	1700	R		
5·910	1692	w	5·912	1691	P	w	$895 + 806 = 1701$
6·400	1562	w					$802 + 769 = 1571$
			6·821	1466	R		
6·890	1451	w	6·863	1457	P	vw	B_1 fundamental
			7·215	1386	R		
7·263	1377	vs	7·262	1377	Q	s	$2 \times 688 = 1376$
			7·294	1371	Q		?
			7·321	1366	R		
7·410	1349	vs	7·407	1350	Q	s	A_1 fundamental
			7·463	1340	P		
			7·930	1261	R		
8·030	1245	sh	7·992	1251	Q	sh	A_1 fundamental
			8·117	1232	R		
8·170	1224	s	8·183	1222	P		B_1 fundamental
			9·497	1053	R		
9·588	1043	s	9·606	1041	Q	m	A_1 fundamental
			9·690	1032	P		
11·210	892	vs	11·123	899	R		
			11·249	889	P	s	B_1 fundamental
			11·696	855	R		
11·930	838	vs	11·933	838	Q	vs	B_2 fundamental
			12·077	828			
			12·240	817	P,R		
12·475	802	vs	12·407	806	Q	vs	A_1 fundamental
			12·560	796	P		
12·999	769	vs	12·739	785	R	vs	B_1 fundamental
			12·920	774	P		
			14·314	698	R		
14·665	682	w	14·535	688	Q	vw	A_1 fundamental
			14·727	679	P		
			18·622	537	R		
19·420	515	vs	19·231	520	Q	vs	B_2 fundamental
			19·802	505	P		

* λ: wavelength in microns; ν: frequency in cm^{-1}; I: intensity; vw: very weak; w: weak; m: medium; s: strong; vs: very strong; sh: shoulder; Rot. str.: rotational structure.
    † 908 and 500 cm^{-1} are non-observed frequencies, supposed to belong to the A_2 class.

Table 2. Infrared spectrum of $C_2D_2N_2S$*

Liquid phase			Vapor				Assignment
λ	ν	I	λ	ν	Rot. str.	I	
3·143	3500	vw					$2320 + 681 + 506 = 3507$
3·380	2958	vw	3·370	2967	Q	vw	$2318 + 650 = 2968$
3·407	2935	w					Impurity?
3·491	2864	w					Impurity?
4·054	2467	w	4·050	2467	R	vw	$968 + 2 \times 753 = 2474$
			4·070	2457	P		
			4·297	2327	R		
			4·299	2326	R	w	B_1 fundamental
4·346	2301	m	4·314	2318	Q	w	A_1 fundamental
			4·321	2314	P		
			4·332	2308	P		
4·415	2265	vw					$1417 + 849 = 2266$
4·885	2047	vw					$1183 + 869 = 2052$
4·926	2030	vw					$1183 + 849 = 2032$
5·770	1733	vw					$2 \times 869 = 1738$
5·831	1715	vw					$869 + 849 = 1718$
6·289	1590	w					Impurity?
6·373	1569	w					Impurity?
6·973	1434	w	6·969	1435	R	m	$751 + 681 = 1432$
7·102	1408	m	7·027	1423	P, R	m	B_1 fundamental
			7·087	1411	P		
7·380	1355	vw					$849 + 506 = 1355$
7·508	1332	vw					$681 + 650 = 1331$
			7·634	1310	R		
			7·686	1301	Q	s	$2 \times 650 = 1300$
			7·710	1297	Q		?
7·722	1295	vs	7·728	1294	Q	s	A_1 fundamental
			7·782	1285	P		
			8·382	1193	R		
8·470	1181	vs	8·452	1183	Q	m	A_1 fundamental
			8·532	1172	P		
8·640	1157	w					$650 + 506 = 1156$
10·352	966	w	10·277	973	R	vw	B_1 fundamental
			10·395	962	P		
11·130	898	w					$2 \times 450\dagger = 900$
11·547	866	vs	11·416	876	R	vs	B_1 fundamental
			11·561	865	P		
11·848	844	vs	11·778	849	Q	vs	A_1 fundamental
			11·919	839	P		
			13·123	762	R		
			13·228	756	R		
13·316	751	vs	13·280	753	Q	vs	A_1 fundamental
			13·405	746	P	vs	B_1 fundamental
			14·450	692	R		
14·749	678	w	14·680	681	Q	vw	A_1 fundamental
			15·038	665	R		
15·300	654	s	15·385	650	Q	s	B_2 fundamental
			15·798	633	P		
			19·157	522	R		
19·920	502	s	19·763	506	Q	s	B_2 fundamental
			20·325	492	P		

* λ: wavelength in microns; ν: frequency in cm^{-1}; I: intensity; vw: very weak; w: weak; m: medium; s: strong; vs: very strong; sh: shoulder; Rot. Str.: rotational structure.

† 450 cm^{-1} is a non-observed frequency assumed to belong to the A_2 class.

Table 3. Raman spectrum of $C_2H_2N_2S$

Frequency (cm^{-1})	Intensity[a]	Polarization Ratio[b]
3095	vs	p
3085	s	dp
1455	vw	dp
1375	m	dp
1350	m	dp
1250	m	p
1215	w	dp
1045	m	dp
890	vw	dp
805	s	p
770	w	dp
685	m	p
520	vw	?

[a] vw: very weak; w: weak; m: medium; s: strong; vs: very strong.
[b] p: polarized; dp: depolarized.

Assignment of the gas-phase spectra is made easier by examination of the contour of the vibration-rotation envelope. Using the moments of inertia of 1,2,5-thiadiazole and the figures of BADGER and ZUMWALT [10], the vibrational bands of A_1 symmetry are predicted to have a rather sharp Q branch comparable in intensity to the R and P branches which will be separated by about 19 cm^{-1}. Since these bands correspond to dipole moment oscillations along the A inertial axis they are referred to as A-type bands. Vibrations of B_1 symmetry have dipole moment oscillations along the B-axis and are responsible for B-type band contours with unresolved Q and P and Q and R branches, exhibiting two maxima separated by 10 cm^{-1}. An intense Q branch should be characteristic for the C-type bands, with the P and R branches of much lesser intensity separated by 32 cm^{-1}. Dipole moment oscillations along the C-axis are produced by vibrations of the B_2 symmetry species.

As a final check on the consistency of the vibrational assignment the Redlich-Teller product rule is used [9]. The calculated ratio of the product of frequencies of the deuterated and protonated molecule for each symmetry species is denoted τ_{calc} and is listed in Table 4.

3.1 *Vibrations of* A_1 *class*

Five of the A_1 vibrations are immediately identified by their strongly polarized Raman bands (3095, 1250, 1045, 805, 685 cm^{-1}). The symmetric C—H stretching mode can be associated with the highest Raman frequency. In the infrared absorption of gas-phase $C_2H_2N_2S$ a sharp peak at 3106 cm^{-1} with a P and an R branch separated by about 22 cm^{-1} is readily recognizable as an A-type band. Isotopic substitution shifts this mode to 2318 cm^{-1}. In the gas-phase infrared spectrum of $C_2H_2N_2S$ A-type bands are also found at 1041 and 806 cm^{-1} with corresponding bands at 849 and 753 cm^{-1} in the spectrum of $C_2D_2N_2S$. The big shift upon isotopic substitution

[10] R. M. BADGER and L. R. ZUMWALT, *J. Chem. Phys.* **6,** 711 (1938).

Table 4. Fundamental frequencies of $C_2H_2N_2S$ and $C_2D_2N_2S$

Species	No.	$C_2H_2N_2S$	$C_2D_2N_2S$	R†	Approximate description
A_1	1	3106	2318	1·340	C—H stretching
	2	1350	1294	1·043	Ring stretching
	3	1251	1183	1·057	Ring stretching
	4	1041	849	1·226	C—H in-plane bending
	5	806	753	1·070	Ring in-plane bending
	6	688	681	1·010	Ring in-plane bending
		Product rule: $\tau_{obs} = 0·510$		$\tau_{calc} = 0·506$	
A_2	7	(908)*	(735)*		C—H out-of-plane bending
	8	(500)*	(450)*		Ring out-of-plane bending
		Product rule:		$\tau_{calc} = 0·729$	
B_1	9	3108	2320	1·339	C—H stretching
	10	1461	1417	1·031	Ring stretching
	11	1227	968	1·267	C—H in-plane bending
	12	895	869	1·029	Ring in-plane bending
	13	780	751	1·039	Ring in-plane bending
		Product rule: $\tau_{obs} = 0·535$		$\tau_{calc} = 0·528$	
B_2	14	838	650	1·289	C—H out-of-plane bending
	15	520	506	1·028	Ring out-of-plane bending
		Product rule: $\tau_{obs} = 0·753$		$\tau_{calc} = 0·755$	

( )* Non-observed frequencies   R† Ratio of protonated to deuterated frequency

of the 1041 cm^{-1} band characterizes it as a C—H vibration and its position as a bending mode. The isotopic shift of the 806 cm^{-1} band is considerably less—an indication of a ring vibrational mode. An A-type band at 688 cm^{-1} in the infrared spectrum of 1,2,5-thiadiazole is extremely weak but was observed using a 150 cm cell. In the gas-phase spectrum of $C_2D_2N_2S$ only the R branch of the corresponding band is clearly visible, with a maximum at 692 cm^{-1}, whereas the Q branch appears only as a shoulder and the P branch is completely hidden under the very intense absorption of a B_2 band. Another band of A_1 symmetry in the infrared spectrum of $C_2D_2N_2S$ is of medium intensity and is centered at 1183 cm^{-1}. The corresponding band in the spectrum of $C_2H_2N_2S$, apparently much weaker, is hidden by the absorption of a B_1 band at 1227 cm^{-1}, but undoubtedly corresponds to the intense and polarized 1250 cm^{-1} Raman feature.

The last of the A_1 fundamentals (ν_2) is found in the complex infrared feature centered around 1365 cm^{-1} in which two sharp and strong and one sharp but weaker peaks are easily seen (1377, 1371 and 1350 cm^{-1}). In the liquid-phase i.r. spectrum there are two equally intense peaks at 1377 and 1349 cm^{-1} which match closely two Raman bands of medium intensity at 1375 and 1350 cm^{-1} which apparently are very weakly polarized. The corresponding complex band in the spectrum of $C_2D_2N_2S$ also has three sharp peaks, apparently Q branches, at 1301, 1297 and 1294 cm^{-1} of which the central is the weakest. In the liquid spectrum of the deuterated species there is a single, somewhat broad band with center at 1295 cm^{-1}. In both the spectra of the protonated and deuterated species we assigned the lowest Q branch as center of the A_1 fundamental in order to best satisfy the product rule.

With the presented assignment which is summarized in Table 4 the product rule is satisfied to about 0·8 percent.

3.2 *Vibrations of* A_2 *class*

The Raman data, unfortunately, give no indication of the location of the two frequencies of this class: a C—H out-of-plane bending mode and a ring out-of-plane deformation mode. By comparison with the spectra of isothiazole [11] and thiophene [12] which are isoelectronic with 1,2,5-thiadiazole one would expect to find the C—H bending mode around 800–900 cm^{-1} and the ring deformation mode around 400–500 cm^{-1}. In the assignment of some overtones and combination bands we used 908 and 500 cm^{-1} as values for these two frequencies. The corresponding bands in the spectrum $C_2D_2N_2S$ are then expected around 735 and 450 cm^{-1}.

3.3 *Vibrations of* B_1 *class*

Three of the five B_1 frequencies are very easy to locate due to their characteristic profile and intensity in the gas-phase infrared spectrum of $C_2H_2N_2S$. These three frequencies, 1227, 895 and 780 cm^{-1} correspond to the 1215, 890 and 770 cm^{-1} bands in the liquid-phase Raman spectrum. From their isotopic shifts the high frequency band and two low frequency bands can be attributed to the C—H in-plane bending, and ring vibrational modes respectively. It is interesting to note that to the rather intense 1227 cm^{-1} band in the spectrum of $C_2H_2N_2S$ corresponds a weak band at 968 cm^{-1} in the spectrum of $C_2D_2N_2S$, although such dramatic intensity changes upon deuteration do not seem to be very unusual.

One remaining ring vibration needs to be identified. In the spectrum of $C_2D_2N_2S$ there is a rather intense feature which can be interpreted as two bands of B_1 symmetry—one centered at about 1429 cm^{-1} and the other at 1417 cm^{-1}. The higher frequency is much weaker in the liquid-phase spectrum and is, therefore, hardly the fundamental one is looking for. If one chooses the 1417 cm^{-1} band as a fundamental, the expected position of the corresponding band in the spectrum of $C_2H_2N_2S$ is about 1460–1470 cm^{-1}. An extremely weak band was indeed observed in that region using a gas-cell 10 cm long. With a gas-cell 150 cm long a band of clearly B-type was observed with maxima at 1466 and 1457 cm^{-1}. A weak band at 1451 cm^{-1} in the liquid i.r. spectrum and a very weak feature at 1455 cm^{-1} in the Raman spectrum also supports the assignment of this band as a B_1 fundamental.

The remaining frequency of this class is a C—H stretching mode and it is expected around 3000 cm^{-1}. In the complex structure of the gas phase infrared band around 3100 cm^{-1} the two shoulders separated by about 11 cm^{-1} (3113 and 3102 cm^{-1}) are easy to attribute to a B-type band with center at 3108 cm^{-1}. This value was accepted for the ν_9 mode.

With this assignment of the B_1 fundamental vibrational modes, the product rule is satisfied to about 1·3 percent.

3.4 *Vibrations of* B_2 *class*

Due to their limited number and distinct appearance (a strong Q branch flanked with P and R branches about 32 cm^{-1} apart) the frequencies of this class are the easiest to locate.

[11] S. Califano, F. Piacenti and G. Sbrana, *Spectrochim. Acta* **20**, 339 (1964).
[12] M. Rico, J. M. Orza and J. Morcillo, *Spectrochim. Acta* **21**, 689 (1965).

The intense sharp peak at 838 cm^{-1} in the infrared spectrum of gaseous $C_2H_2N_2S$ immediately suggests location of one of the two frequencies of this class. Its shift, upon deuteration, to 650 cm^{-1} characterizes it as a C—H bending mode. The ring out-of-plane mode gives rise to a band whose Q branch lies at 520 cm^{-1} and is shifted to 506 cm^{-1} in the spectrum of $C_2D_2N_2S$. Due to their isolated position these two bands, as well as the 650 cm^{-1} band of the deuterated species clearly exhibit the contour of a C-type band.

The product rule is satisfied to about 0·3 percent, but the calculated value is higher than that observed. This deviation from the usual rule (that the observed value for τ is higher than the calculated) is small and not necessarily significant since it can be explained by small inaccuracies in the determination of the values of the frequencies.

3.5 Overtone and combination bands

Table 1 and Table 2 list a number of bands for both $C_2H_2N_2S$ and $C_2D_2N_2S$ which are interpreted as overtones or combination bands. Whereas the assignment of many of them seems clear cut, several instances exist where the situation is a little bit more complicated and requires some explanation.

The use of estimated A_2 frequencies is needed to explain some of the weak bands in the infrared spectra of both 1,2,5-thiadiazole and 1,2,5-thiadiazole-d_2. In the spectrum of $C_2H_2N_2S$ such frequencies are 3575 cm^{-1} (liquid) interpreted as $3108 + 500 = 3608$ cm^{-1}, 1818 cm^{-1} (vapor) interpreted as an overtone of the ν_7 mode assumed to lie around 908 cm^{-1} and the gas-phase band at 1745 cm^{-1} interpreted as $838 + 908 = 1746$ cm^{-1}. Whereas the band at 1818 cm^{-1} could be interpreted without using A_2 frequencies, although much less satisfactorily ($1041 + 806 = 1847$), there is no reasonable interpretation for the bands at 3575 and 1745 cm^{-1}. The symmetry of the combination bands interpreted as involving A_2 frequencies corresponds to the observed rotational envelopes of the 1818 and 1745 cm^{-1} bands. The band at 3575 cm^{-1} was not detected in the gas-phase spectrum. Similarly, the weak band at 898 cm^{-1} in the liquid-phase spectrum of 1,2,5-thiadiazole-d_2 can be interpreted as an overtone of a low lying fundamental. The only low enough fundamental is possibly the A_2 ring bending mode and, if the 898 cm^{-1} is to be interpreted as its overtone, the frequency of the fundamental should be around 450 cm^{-1}. The product rule would then place the other A_2 band in the spectrum of the deuterated species around 735 cm^{-1}.

A further word should be said about the assignment of the 1377 and 1371 cm^{-1} peaks in the infrared spectrum of $C_2H_2N_2S$ and those at 1301 and 1297 cm^{-1} in the spectrum of $C_2D_2N_2S$. The former peak in each pair is stronger and almost equally strong as the peaks attributed to A_1 fundamentals (1350 and 1294 cm^{-1} respectively). With the data in hand we are able to assign only one peak in each pair as overtones: the 1377 cm^{-1} band as an overtone of ν_6 ($2 \times 688 = 1376$) and that at 1301 cm^{-1} (the deuterated species) as an overtone of ν_{14} ($2 \times 650 = 1300$). The intensity of these two bands, rather unusual for overtone frequencies, can be explained as a result of almost complete Fermi resonance with the neighboring A_1 fundamentals with which they share the same symmetry. This would also explain the slight upwards shift from the predicted value of the frequency. The peaks at 1371 and 1297 cm^{-1} could not be

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interpreted as binary combinations of the fundamental frequencies we know. Another case where Fermi resonance is apparently present and acts to enhance the intensity of a combination band is found with the B_1 bands at 1429 cm^{-1} (interpreted as $\nu_4 + \nu_{15}$) and 1417 cm^{-1} (interpreted as a B_1 fundamental) in the spectrum of $C_2D_2N_2S$.

4. Conclusions

The presented assignment of the fundamental modes of 1,2,5-thiadiazole is summarized in Table 4. The parallel analysis of the spectra of the protonated and deuterated species enables easy classification of the modes into those which are mainly oscillations of the ring and those which are best described as C—H vibrations. Further approximate classification follows the suggestions of Rico [12] for vibrations of thiophene which should be qualitatively similar to those of 1,2,5-thiadiazole.