

Normal Coordinate Analysis of the Non-Planar Vibrations of 1,3,4-Thiadiazole

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Harmonic potential functions for the out-of-plane vibrations of 1,3,4-thiadiazole have been calculated by using deuterium isotopic frequency data.

Normal coordinates have been calculated for the two possible sets of force constants in each symmetry species.

An attempt has been made to select the set of force constants with physical significance from ^{13}C isotopic frequency data and ^{15}N isotopic frequency data.

The assignments of the fundamental vibration frequencies of 1,3,4-thiadiazole (I), 2D-1,3,4-thiadiazole (II), 2,5D₂-1,3,4-thiadiazole (III), 2- ^{13}C -1,3,4-thiadiazole (IV) and 3- ^{15}N -1,3,4-thiadiazole (V)¹ provide us with sufficient frequency data to calculate the most general quadratic potential function for the out-of-plane vibrations of 1,3,4-thiadiazole.

The normal frequencies of I and III should in principle determine the six symmetry force constants in the harmonic potential function.

To obtain a potential function, which accounts for all the observed normal frequencies, we have used the experimental data in the following way:

1. Root mean square adjustments of the frequencies of I, II, and III to obtain a consistent set of frequencies according to the isotopic rules.
2. Calculation of the force constants by solving the secular equations of I and III.
3. An attempt to select the set with physical significance using the isotopic frequency shifts of IV and V.

CALCULATIONS

We started from the conventional coordinates:²

2 out-of-plane bond bendings γ and γ' and
5 bond torsions $\varrho, \varrho', \delta, \delta'$ and τ

as shown in Fig. 1. Using a set of symmetry coordinates from Table 1 similar to those previously used on thiophene³ we are able to compare the results

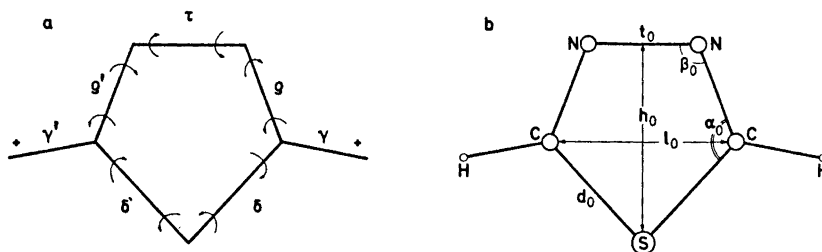


Fig. 1. 1,3,4-Thiadiazole. Non-planar internal coordinates and geometrical parameters.

Table 1. 1,3,4-Thiadiazole. Non-planar redundant and symmetry coordinates.

A_2 species			
Redundant coordinates:			
I	$\tau - \cos \beta_0 (\varrho + \varrho') + \cos (\alpha_0 + \beta_0) (\delta + \delta')$	= 0	
IIa	$t_0 \sin \beta_0 \tau - l_0 \sin \alpha_0 (\delta + \delta')$	= 0	
IIb	$h_0 \tau + d_0 \sin \alpha_0 (\varrho + \varrho')$	= 0	
Symmetry coordinates:			
S	$\gamma - \gamma'$		
T	$-2l_0 d_0 \sin \alpha_0 \tau + h_0 t_0 (\varrho + \varrho') - t_0 d_0 \sin \beta_0 (\delta + \delta')$		
B_2 species			
Redundant coordinate:			
III	$\sin (\alpha_0 + \beta_0) (\delta - \delta') - \sin \beta_0 (\varrho - \varrho')$	= 0	
Symmetry coordinates:			
S	$\gamma + \gamma'$		
T	$\sin \beta_0 (\delta - \delta') + \sin (\alpha_0 + \beta_0) (\varrho - \varrho')$		

h_0 , d_0 , t_0 , l_0 , α_0 , and β_0 are geometrical parameters of the pentagonal ring.

The redundant coordinate II should be a linear combination of IIa and IIb orthogonal to the redundant coordinate I. All coordinates should be normalized.

from this work with the potential function of thiophene. The kinetic energy matrix \mathbf{G} was calculated from the structure, determined in this laboratory.⁴

The experimental frequencies were adjusted in order to fulfill exactly the product rules and the complete isotopic rule between I, II, and III. This adjustment was made in such a way, that the root mean square of the cor-

rections of the square of the frequencies $\sqrt{\frac{1}{n} \sum (\nu_{\text{adj}}^2 - \nu_{\text{obs}}^2)^2}$ was minimized,

Table 2. The secular determinant equation:

$$|GF - \lambda E| = 0$$

was expanded directly, yielding the two relations:

Table 2. 1,3,4-Thiadiazole and its deuterated species. Normal frequencies, observed and adjusted (cm^{-1}).

Frequency	obs.	adj.	Compound		obs.	adj.
			obs.	adj.		
ν_7	796	796.5	635	635.0	626	625.6
ν_8	616	616.2	613	613.1	603	602.4
ν_{14}	820	820.2	809	809.0	650	649.7
ν_{15}	483	483.5	459	458.7	437	436.8

$$\lambda_i + \lambda_j = F_{SS}G_{SS} + 2F_{ST}G_{ST} + F_{TT}G_{TT} \quad (\text{i})$$

$$\lambda_i \lambda_j = (F_{SS}F_{TT} - F_{ST}^2)(G_{SS}G_{TT} - G_{ST}^2) \quad (\text{ii})$$

where i and j refer to the two normal frequencies of the symmetry species, and S and T refer to the two symmetry coordinates of the species; Table 1.

Using frequency data from I and III, we obtained in each symmetry species, A_2 and B_2 , three independent equations for determination of F_{SS} , F_{ST} and F_{TT} . Because of the second order eqn. (ii), we obtained two sets of F_{ST} and F_{TT} in each species. Only the CH-deformation force constant F_{SS}

Table 3. 1,3,4-Thiadiazole. Non-planar symmetry force constants ($\text{mdyn } \text{\AA}/\text{rad}^2$).

	A_2 species		B_2 species	
	set a	set b	set a	set b
F_{SS}	0.3584	0.3584	0.4048	0.4048
F_{ST}	0.1904	0.1695	-0.2264	-0.5086
F_{TT}	0.3309	0.3100	0.4228	0.9353

is uniquely determined; Table 3. It means, that in the non-planar species there are four different potential functions, each accounting for the observed frequencies of I, II, and III. Calculation of the normal coordinates of I, (Fig. 2), shows, at least for the B_2 vibrations, a pronounced difference between the two different sets of F_{ST} and F_{TT} .

CONSIDERATIONS

In Table 4 we compare the observed and the calculated isotopic shifts of IV and V. It is seen, that the observed isotopic shifts of ν_7 , ν_8 , ν_{14} , and ν_{15} of IV are found as 3 cm^{-1} , 2 cm^{-1} , 2 cm^{-1} , and 6 cm^{-1} , respectively. The best agreement with the calculated isotopic shifts are given using the potential function consisting of set b of the A_2 species and set a of the B_2 species. The uncertainties of the observed isotopic shifts are, however, too large to justify an unambiguous selection of a potential function from these experimental

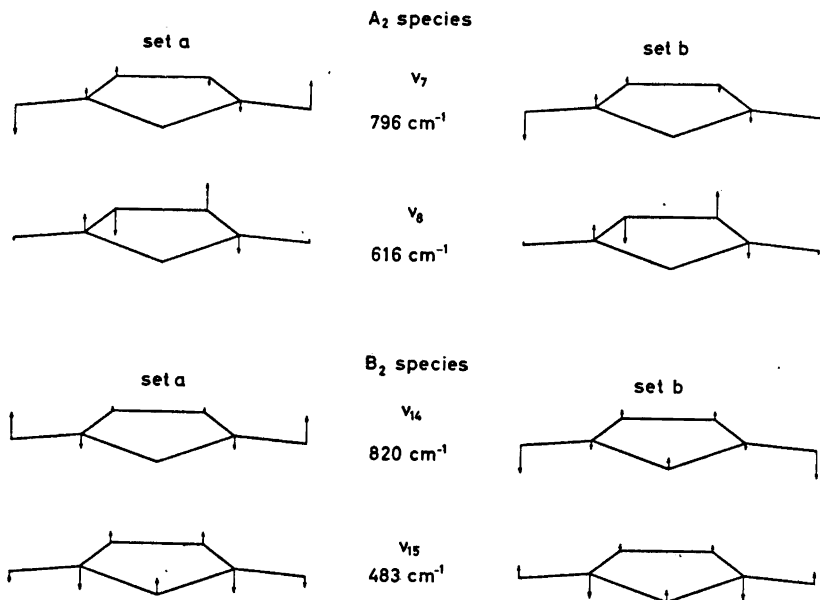


Fig. 2. 1,3,4-Thiadiazole. Normal coordinates. A graphic representation of the normal coordinates in terms of the mass reduced cartesian coordinates calculated on the bases of two different potential functions in each symmetry species.

Table 4. 1,3,4-Thiadiazole. Calculated and observed isotopic frequency shifts (cm^{-1}).

Frequency	calculated				observed
	<i>a a</i>	<i>a b</i>	<i>b a</i>	<i>b b</i>	
2- ¹³ C-1,3,4-Thiadiazole					
ν_7	1.7	1.6	2.6	2.4	3 ± 1
ν_8	3.6	3.6	3.1	3.0	2 ± 1
ν_{14}	2.5	1.0	2.4	1.0	2 ± 0.5
ν_{15}	5.4	6.3	5.4	6.3	6 ± 0.5
3- ¹⁵ N-1,3,4-Thiadiazole					
ν_7	1.0	1.0	0.4	0.4	< 2
ν_8	7.1	7.1	7.6	7.6	—
ν_{14}	0.1	0.7	0.1	0.7	< 0.5
ν_{15}	1.3	1.0	1.3	1.0	—
1- ³⁴ S-1,3,4-Thiadiazole					
ν_7	0	0	0	0	—
ν_8	0	0	0	0	—
ν_{14}	0.1	1.4	0.1	1.4	—
ν_{15}	2.0	1.2	2.0	1.2	—

The calculated frequency shifts are based on four different potential functions, each consisting of one set from A_2 species and one from B_2 species as indicated of the two small letters above the columns. The first refers to A_2 species the other to B_2 species.

data. The observed isotopic shifts of ν_7 , ν_8 , ν_{14} , and ν_{15} of V are found as 1 cm^{-1} , 7 cm^{-1} , 0 cm^{-1} , and 1 cm^{-1} , respectively. Unfortunately, they are all reproduced within the experimental error by the four different potential functions. The calculated isotopic shifts of the B_2 frequencies ν_{14} and ν_{15} of 1- ^{34}S -1,3,4-thiadiazole VI are also given in Table 4. However, the observed splitting of ν_{14} in the vapor spectrum of I observed as 6 cm^{-1} might as well be due to a "hot band". No splitting of ν_{15} is observed in the spectrum of I.

Table 5. 1,3,4-Thiadiazole. Non-planar species. L -matrices ($S=LQ$) for the two sets of force constants in each symmetry species.

		Set a		Set b	
A_2	S	ν_7 0.9829	ν_8 0.5661	ν_7 1.0526	ν_8 0.4226
	T	0.0692	-0.9852	-0.0697	-0.9852
B_2	S	ν_{14} 1.1202	ν_{15} 0.2230	ν_{14} -0.5939	ν_{15} 0.9756
	T	0.2899	0.6601	0.2897	0.6602

Table 5 shows the L -matrix corresponding to the possible F -matrices and Fig. 2 shows the normal coordinates of I represented in terms of the mass reduced cartesian coordinates calculated from the possible F -matrices. It is seen, that set b of A_2 species and set a of B_2 species yields the most characteristic normal modes. That is ν_7 and ν_{14} are mainly CH deformation modes and ν_8 and ν_{15} are mainly ring deformation modes.

Table 6. 1,3,4-Thiadiazole and thiophene.³ Valence force constants (mdyn $\text{\AA}/\text{rad}^2$).

	1,3,4-Thiadiazole	Thiophene
$f_{\nu_{\alpha}\nu_{\alpha}}$	0.382	0.339
$f_{\nu_{\alpha}\nu_{\alpha}'}$	0.023	0.046
$f_{\nu_{\beta}\nu_{\beta}}$	-	0.395
$f_{\nu_{\beta}\nu_{\beta}'}$	-	-0.031
$F_{\Gamma(\text{A}_2)\Gamma(\text{A}_2)}$	0.310	0.440
$F_{\Gamma(\text{B}_2)\Gamma(\text{B}_2)}$	0.423	0.443
$f_{\nu_{\alpha}\Gamma(\text{A}_2)} = -f_{\nu_{\alpha}'\Gamma(\text{A}_2)}$	0.120	0.123
$f_{\nu_{\alpha}\Gamma(\text{B}_2)} = f_{\nu_{\alpha}'\Gamma(\text{B}_2)}$	-0.160	-0.169
$f_{\nu_{\beta}\Gamma(\text{A}_2)} = -f_{\nu_{\beta}'\Gamma(\text{A}_2)}$	-	-0.179
$f_{\nu_{\beta}\Gamma(\text{B}_2)} = f_{\nu_{\beta}'\Gamma(\text{B}_2)}$	-	0.091

In thiophene the same difference between the two sets of force constants was observed.³ Orza, Rico and Biarge selected, somewhat arbitrarily, the set which gave the most characteristic normal coordinates as the more physical reliable. From the same point of view we shall select set *b* of the A_2 species and set *a* of the B_2 species as the potential function with physical significance. These sets, also, best reproduce the observed isotopic splittings of IV. It should, however, be emphasized, that the present experimental data are insufficient to select unambiguously the true potential function of the out-of-plane vibrations of 1,3,4-thiadiazole.

CONCLUSION

In spite of our difficulties in selecting the true potential function, the two symmetry force constants, $F_{SS(A_2)}$ and $F_{SS(B_2)}$ are unambiguously determined. This makes us able to determine the valence force constants $\gamma_{\gamma\gamma}$ and $f_{\gamma\gamma}'$ attached to the CH-out-of-plane movement:

$$f_{\gamma\gamma} = 0.382 \text{ mdyn } \text{\AA}/\text{rad}^2; \quad f_{\gamma\gamma}' = 0.023 \text{ mdyn } \text{\AA}/\text{rad}^2$$

Table 6 compares the selected potential function of 1,3,4-thiadiazole with that of thiophene calculated by Orza, Rico and Biarge.³ It is seen, that $f_{\gamma\gamma}$ for 1,3,4-thiadiazole is considerably greater than the corresponding force constant for the α -H atoms in thiophene. This seems to be in agreement with equivalent calculation for 1,3,4-oxadiazole and 1,2,5-oxadiazole to be published later.⁵

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