
VIBRATIONAL SPECTRA AND THERMODYNAMIC PROPERTIES OF THIAZOLE, 2-AMINOTHIAZOLE, 2-AMINO-[²H]-THIAZOLE AND 2-AMINO-[²H₂]-THIAZOLEJuan F. ARENAS^a, Jesús PEREZ-PEÑA*^b and Melchor GONZALEZ-DAVILA^b^a *Department of Physical Chemistry, University of Málaga, 29071 Málaga, Spain and*^b *Department of Chemistry, Polytechnic University of Canary Islands, Las Palmas, Spain*

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Infrared and Raman spectra of thiazole have been reinvestigated with new assignments of overtone and combination bands being proposed. Infrared spectra in the solid phase and in different solutions for 2-aminothiazole and 2-amino-[²H₂]-thiazole, as well as Raman spectrum of microcrystalline powder for 2-aminothiazole were also studied and a general assignment for all the observed bands have been proposed. The present assignment satisfies the isotopic product rule for i.r. fundamentals. On this basis thermodynamic functions have been computed.

The vibrational spectrum of thiazole has been the subject of several studies dealing with both infrared and Raman spectroscopy¹⁻⁵. However, we decided to carry out a new study of thiazole in order to confirm the existing assignment and to propose new assignments for fundamentals, overtone, combination and difference bands, thus having a complete vibrational analysis on the different spectra. Moreover, the results obtained have been used as a basis for the establishment of correlations with the corresponding bands in the 2-aminothiazole spectra.

There is virtually no information about the vibrational analysis of the 2-aminothiazole molecule. The only works that can be mentioned are those by Davidovics et al.^{6,7} in which an incomplete assignment in the range 4 000–600 cm⁻¹ for 2-aminothiazole in different solvents is described. So, the aim of the present study was a complete vibrational analysis of the 2-aminothiazole and its corresponding amino-deuterated derivatives (2-amino[²H]-thiazole and 2-amino-[²H₂]-thiazole). The assignments proposed were confirmed by the application of the Teller-Redlich isotopic product rule.

EXPERIMENTAL

The samples used were thiazole with 99% purity from Aldrich and 2-aminothiazole over 98% purity from Merck and were used without further purification. The 2-amino-*d*₂-thiazole was

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prepared by direct exchange of 2-aminothiazole with D_2O . The 2-amino- $[-^2H_2]$ -thiazole after three exchanges contained about 20 per cent of 2-aminothiazole and about 35 per cent of 2-amino- $[-^2H]$ -thiazole. Drying of the samples was done with anhydrous sodium sulfate.

Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer in the 4 000 to 200 cm^{-1} range. Vapour-phase spectra were obtained with a 10 cm path-length cell fitted with CsI or NaCl windows at a pressure in equilibrium with the liquid at room temperature. Results for the solutions in CCl_4 , $HCCl_3$, C_2Cl_4 and CS_2 were obtained with cells of different path lengths fitted with CsI and KBr windows. Standards for wave-number determinations were polystyrene film and indene-camphor-cyclohexanone mixtures as described in ref.⁸. Raman spectra were taken on a Jobin Yvon U-1000 spectrometer using the 5 145 Å exciting line of a Spectra Physics 2020 Ar⁺ laser for the study of liquid thiazole and the 6 471 Å exciting line of a Spectra Physics 2020 Kr⁺ laser for microcrystalline 2-aminothiazole.

RESULTS AND DISCUSSION

The molecular structure of thiazole has been determined by microwave spectroscopy⁹, confirming the generally accepted hypothesis of a planar structure. The equilibrium configuration of the 2-aminothiazole molecule is not accurately known. In this work, a planar structure has been maintained in which the lone-pair electrons of the nitrogen atom participates in the π system of the aromatic ring. Therefore, the molecule is assumed to be planar and the normal modes of vibration can be classified under C_s as the relevant point group.

ASSIGNMENT OF SPECTRA

Thiazole

The thiazole spectrum was recorded in different phases and proposed assignments are shown in Table I. Table II summarizes our assignments together with the proposed ones by Sbrana et al. and Davidovics et al. A good agreement is observed except for the assignment proposed for the fundamentals W_4 and $\gamma_1(CH)$. The fundamental W_4 is assigned to a band at 888.2 cm^{-1} , appearing in the vapour-phase spectrum as a Q -branch, and clearly resolved in the pure liquid spectrum with regard to the nearby W_5 . These features occur in other compounds studied¹⁰, which induce to propose, in agreement with Sbrana et al., the assignment of the fundamental W_4 at 888.2 cm^{-1} , the value which Davidovics establishes for the $\gamma_1(CH)$ vibration. Sbrana tentatively assigned a weak band, not seen by us, in the liquid spectrum at 849 cm^{-1} and resolved in the crystal spectrum at the temperature of liquid nitrogen, to the fundamental $\gamma_1(CH)$; A'' . Taking into account the assignment proposed for similar molecules, like thiophene and isothiazole^{11,12}, we tentatively assigned this fundamental to a band in the shape of a shoulder, measured at 809.4 cm^{-1} .

Finally, based on previous considerations, new assignments were proposed regarding overtone, combination and difference bands, some of which are being

TABLE I
Summary of frequencies and assignments in the infrared and Raman spectra of thiazole

vapour		Infrared				Raman liquid			Assignment
$\tilde{\nu}$	$\Delta\tilde{\nu}_{PR}$	<i>I</i>	$\tilde{\nu}$	<i>I</i>	$\tilde{\nu}$	<i>I</i>	$\tilde{\nu}$	<i>q</i>	
586·5P		w	467·5	vw	465·5	vw	468·4		$\Gamma_2; A''$
605·3Q	30·6	s	607·9	s	604·9				$\Gamma_1; A''$
617·1R						s	611·8	p	$W_7; A'$
703·1P									$\gamma_3(\text{CH}); A''$
722·0Q	28·9	s	726·4	s	725·0				
732·0R									$W_6; A'$
795·4Q		s	761·8	sh	754·3	w	756·2		$2\gamma_2(\text{CH}) - \gamma_2(\text{CH}); A''$
782·9P									
799·4Q	30·5	vs	802·6	vs	796·8				$\gamma_2(\text{CH}); A''$
813·4R									$\gamma_1(\text{CH}); A''$
857·3P		sh	809·4						
867·5Q	18·6	vs	865·5	vs	864·9	s	865·5	p	$W_5; A'$
875·9R									
888·2Q		m	881·2	m	881·0				$W_4; A'$
924·3P									
937·5R	13·2	w	932·7	vw	930·6				$2\Gamma_2; A'$
1 033·8P									

TABLE I
(Continued)

vapour		Infrared				Raman liquid			Assignment	
$\tilde{\nu}$	$\Delta\tilde{\nu}_{PR}$	liquid		solution ^a		<i>I</i>	$\tilde{\nu}$	<i>q</i>		
		<i>I</i>	$\tilde{\nu}$	<i>I</i>	$\tilde{\nu}$					
			vw	1 986.2	vw	1 985.3			$W_5 + \delta_2(\text{CH}); A'$	
			vw	2 083.9	vw	2 078.7			$2\delta_3(\text{CH}); A'$	
			vw	2 105.1	vw	2 101.4			$W_5 + \delta_1(\text{CH}); A'$	
			vw	2 134.7	vw	2 134.7			$\delta_2(\text{CH}) + \delta_3(\text{CH}); A'$	
2 245.5 <i>Q</i>			vw	2 238.7	vw	2 243.7			$2\delta_2(\text{CH}); A'$	
			w	2 277.9					$\delta_1(\text{CH}) + \delta_3(\text{CH}); A'$	
2 341.9 <i>P</i>										
2 359.9 <i>R</i>	18.0		w	2 347.4	vw	2 349.5			$\delta_1(\text{CH}) + \delta_2(\text{CH}); A'$	
			w	2 690.7	w	2 692.6			$W_2 + W_3; A'$	
2 742.7 <i>P</i>										
2 752.8 <i>Q</i>	19.7		w	2 746.2	w	2 745.2			$2W_2; A'$	
2 762.4 <i>R</i>										
2 847.0 <i>Q</i>			w	2 848.7	w	2 840.3			$W_1 + W_2; A'$	
3 092.7 <i>P</i>										
3 107.4 <i>R</i>	14.7		s	3 080.5	s	3 083.1	m	3 084.6	$\nu_2(\text{CH}), \nu_3(\text{CH}); A'$	
3 124.1 <i>P</i>										
3 135.7 <i>Q</i>	21.8		m	3 118.4	m	3 120.9	m	3 117.0	p	$\nu_1(\text{CH}); A'$
3 145.9 <i>R</i>										
3 698.0 <i>P</i>										
3 725.4 <i>R</i>	27.4								$3\delta_1(\text{CH}); A'$	

^a Values for 0.05M-CCl₄ and 0.05M-CS₂ solutions.

proposed for the first time: $2\gamma_2(\text{CH}) - \gamma_2(\text{CH})$; A'' , $2\delta_3(\text{CH})$; A' , $W_5 + \delta_1(\text{CH})$; A' , $2\Gamma_2$; A' (vapour), $W_4 + \gamma_3(\text{CH})$; A'' , $\delta_1(\text{CH}) + \delta_2(\text{CH})$; A' and $W_2 + W_3$; A' and others are assigned based on the observed frequencies for the bands involved: $2W_6$; A' and $2\gamma_1(\text{CH})$; A' . These assignments are included in Table I.

2-Aminothiazole

In accordance with what has been mentioned, the model accepted as a basis for the discussion of the vibrational assignment and for the calculation of the thermodynamic properties was the planar structure model with C_s as relevant point group. The twenty-four normal modes of vibration can be classified as $17A' + 7A''$ both active in the infrared spectra as well as in the Raman one. Molecular vibrations were divided up for the study into three groups: ring vibrations, CH vibrations and vibrations in the $-\text{NH}_2$ group, which must be the ones most affected by isotopic substitution.

TABLE II

Summary of gas phase frequencies (in cm^{-1}) and assignments of thiazole according to different authors

Assignment	Ref. ³	Ref. ⁴	This work
$\nu_1(\text{CH})$	3 140	3 134	3 135.7
$\nu_2(\text{CH})$	3 093	3 083	3 107.4
$\nu_3(\text{CH})$	3 065		
W_1	1 484	1 484	1 484.2
W_2	1 383	1 383	1 382.8
W_3	1 325	1 325	1 325.0
$\delta_1(\text{CH})$	1 239	1 240	1 239.5
$\delta_2(\text{CH})$	1 124	1 124	1 125.2
$\delta_3(\text{CH})$	1 043	1 043	1 042.2
W_4	888	811 ^a	888.2
W_5	867	866	867.5
$\gamma_1(\text{CH})$	849 ^b	888	809.4 ^c
$\gamma_2(\text{CH})$	798	797	799.4
W_6	759 ^a	756	756.2 ^a
$\gamma_3(\text{CH})$	717	716	722.0
W_7	612 ^a	610 ^a	611.8 ^a
Γ_1	603	603	605.3
Γ_2	467 ^a	463 ^a	468.4 ^a

^a Raman, ^b crystal; ^c liquid.

TABLE III
Summary of frequencies (in cm^{-1}) and assignments in the infrared and Raman spectra of 2-aminothiazole

Infrared				Raman solid		Assignment
solid		solution ^a		<i>I</i>	$\tilde{\nu}$	
<i>I</i>	$\tilde{\nu}$	<i>I</i>	$\tilde{\nu}$	<i>I</i>	$\tilde{\nu}$	
				vs	70	
				s	90	
				m	122	
vw	258.9	m	260.3	w	259	$\gamma(\text{CN}); A''$
sh	377.0					$\omega(\text{NH}_2) - \gamma(\text{CN}); A'$
m	398.2	w	399.1	m	397	$r(\text{NH}_2); A''$
		w	469.6			$\Gamma_2; A''$
s	515.7	m	515.5	vw	513	$\delta(\text{CN}); A'$
		m	609.4	w	567	$\Gamma_1; A''$
mb	645.9					$\omega(\text{NH}_2); A''$
				m	677	$W_7; A'$
m	694.6	vs	690.4			$\gamma_3(\text{CH}); A''$
w	709.3					$\nu(\text{CN}) - \Gamma_1; A''$
m	761.9	m	759.6	vs	760	$W_6; A'$
		vw	804.0			$\gamma_2(\text{CH}); A''$
w	864.7	w	863.6	w	863	$W_5; A'$
m	883.9	sh	882.5	m	883	$W_4; A'$
vw	934.8	vw	929.5			$2\Gamma_2; A'$
		sh	1 019.9			$W_6 + \gamma(\text{CN}); A''$
vs	1 033.0	vs	1 036.6	w	1 031	$r(\text{NH}_2); A'$
vw	1 069.6	m	1 073.6	sb	1 073	$\delta_3(\text{CH}); A'$
w	1 140.2	w	1 141.2			$\gamma(\text{CN}) + W_4; A''$
s	1 201.5	vs	1 205.5	m	1 206	$\delta_1(\text{CH}); A'$
m	1 276.1	m	1 272.8	m	1 277	$\nu(\text{CN}); A'$
vw	1 296.7	s	1 297.9			$\Gamma_1 + \gamma_3(\text{CH}); A'$
m	1 326.7	s	1 328.6	vw	1 330	$W_3; A'$
m	1 361.1	mb	1 365.8			$W_2; A'$
w	1 402.1					$W_6 + \omega(\text{NH}_2); A''$
vw	1 445.8					$W_6 + \gamma_3(\text{CH}); A''$
vs	1 498.9	vs	1 498.8	vs	1 498	$W_1; A'$
s	1 525.4	sh	1 525.8			$\gamma(\text{CN}) + \delta(\text{CN}); A''$
						$r(\text{NH}_2) + \delta(\text{CN}); A'$
sh	1 620.8	s	1 603.5			$\delta(\text{NH}_2)_{\text{free}}; A'$
s	1 629.6					$\delta(\text{NH}_2)_{\text{ass}}; A'$
w	1 738.8					$W_5 + W_4; A'$
vw	2 234.3					$W_2 + W_4; A'$
vw	2 308.2					$\nu(\text{CN}) + r(\text{NH}_2); A'$

TABLE III
(Continued)

Infrared				Raman		Assignment
solid		solution		solid		
<i>I</i>	$\tilde{\nu}$	<i>I</i>	$\tilde{\nu}$	<i>I</i>	$\tilde{\nu}$	
vw	2 660.1	vw	2 661.2			$\delta(\text{NH}_2) + r(\text{NH}_2); A'$
w	2 696.5	w	2 697.5			$\delta(\text{NH}_2) + \delta_3(\text{CH}); A'$
w	2 902.9	w	2 902.8			$\delta(\text{NH}_2) + \nu(\text{CN}); A'$
s	3 086.9	s	3 084.6	s	3 086	$\nu_2(\text{CH}); A'$
s	3 120.7	s	3 122.7	s	3 120	$\nu_1(\text{CH}); A'$
m	3 142.7	m	3 161.9			$W_1 + \delta(\text{NH}_2); A'$
m	3 290.6	m	3 280.7			$\nu_s(\text{NH}_2)_{\text{ass.}}; A'$
		s	3 385.9			$\nu_s(\text{NH}_2)_{\text{free}}; A'$
m	3 408.9	w	3 411.2	w	3 404	$\nu_{\text{as}}(\text{NH}_2)_{\text{ass.}}; A'$
		s	3 485.7			$\nu_{\text{as}}(\text{NH}_2)_{\text{free}}; A'$

^a Values given for 0.002M and 0.1M-CCl₄, CS₂ and HCCl₃ solutions and 0.08M-C₂Cl₄ solution of 2-aminothiazole.

Ring vibrations. Vibrations W_1 to W_7 , belonging to species A' and Γ_1 and Γ_2 modes belonging to species A'' correspond to this group, the qualitative form of which are gathered in ref.¹³. Fundamentals W_1 to W_6 were observed in the solid state i.r. spectra as well as in solution and in the Raman, except for W_2 which was not observed in the Raman spectrum. The fundamental W_7 is clearly resolved only in the Raman spectrum, as is Γ_1 , being found at frequencies close to the vibration $\omega(\text{NH}_2)$. Fundamental Γ_2 is recorded at 469.6 cm⁻¹ in solution spectra. In all cases, a strong correlation between the values observed for thiazole and 2-aminothiazole is seen. The isotopic substitution in the amino group does not noticeably alter the frequency at which these fundamentals appear, except for the breathing mode W_5 .

CH vibrations. The substitution of the hydrogen atom in position 2 as regard the thiazole molecule causes only six vibrations to appear, corresponding to the CH bonds in positions 4 and 5 vibrating together, either in phase or not. The two $\nu(\text{CH})$ vibrations were measured in both i.r. and Raman spectra at the same frequencies as for thiazole. Assignment of the vibrations $\delta(\text{CH})$ was carried out by correlation with the spectrum of thiazole and they have been assigned with the same numbers which they were assigned for the thiazole molecule, just as for the $\gamma(\text{CH})$ vibrations

TABLE IV
Summary of frequencies and assignments in the infrared spectra of 2-amino-[²H₂]-thiazole

Solid		Solution ^a		Assignment
<i>I</i>	$\tilde{\nu}$	<i>I</i>	$\tilde{\nu}$	
w	241	w	242	$\gamma(\text{C-ND}_2)$; A''
w	248	w	251	$\gamma(\text{C-NHD})$; A''
		m	260	$\gamma(\text{C-NH}_2)$; A''
w	281.8	w	290.4	$t(\text{ND}_2)$; A''
m	361.7			$t(\text{NHD})$; A''
m	398.4			$t(\text{NH}_2)$; A''
		vw	467.9	Γ_2 ; A''
mb	516.2	mb	511.9	$\delta(\text{C-ND}_2)$; A'
mb	516.2	mb	511.9	$\delta(\text{C-NHD})$; A'
mb	516.2	mb	511.9	$\delta(\text{C-NH}_2)$; A'
sh	534.1			$\omega(\text{ND}_2)$; A''
w	560.5	w	561.6	$\omega(\text{NHD})$; A''
s	623.2	mb	615.4	Γ_1 ; A''
sh	640.8			$\omega(\text{NH}_2)$; A''
s	686.4	s	687.0	$\gamma_3(\text{CH})$; A''
w	708.8			$\nu(\text{CN}) - \Gamma_1$; A''
m	755.8	m	755.8	W_6 ; A'
		vw	803.2	$\gamma_2(\text{CH})$; A''
m	857.3	sh	868.1	W_5 ; A'
s	883.7			W_4 ; A'
		w	784.6	$r(\text{ND}_2)$; A'
		vw	923.9	$r(\text{NHD})$; A'
		vw	980.2	$\delta(\text{CN}) + \Gamma_2$; A''
m	1 032.0	w	1 040.6	$r(\text{NH}_2)$; A'
s	1 059.9	m	1 057.7	$\delta_3(\text{CH})$; A'
vs	1 170.5	m	1 171.6	$\delta(\text{ND}_2)$; A'
m	1 203.4	w	1 203.4	$\delta_1(\text{CH})$; A'
w	1 226.8	w	1 226.2	$\nu(\text{C-ND}_2)$; A'
m	1 260.3	m	1 263.4	$\nu(\text{C-NHD})$; A'
m	1 276.7	m	1 272.9	$\nu(\text{C-NH}_2)$; A'
sb	1 323.8	s	1 322.5	W_3 ; A'
w	1 358.8			W_2 ; A'
w	1 454.4			$\delta(\text{NHD})$; A'
vs	1 494.5			W_1 ; A'
sb	1 521.0			$\nu(\text{CN}) + \gamma(\text{NH}_2)$; A''
				$r(\text{NH}_2) + \delta(\text{CN})$; A'
s	1 629.9			$\delta(\text{NH}_2)$; A'
w	1 726.8			$2W_5$; A'
w	2 333.9			$2\delta(\text{ND}_2)$; A'
sb	2 356.7	m	2 472.2	$\nu_s(\text{ND}_2)$; A'

TABLE IV
(Continued)

Solid		Solution ^a		Assignment
<i>I</i>	$\tilde{\nu}$	<i>I</i>	$\tilde{\nu}$	
w	2 444.1	w	2 445.1	$\nu(\text{CN}) + \delta(\text{ND}_2)$; A'
w	2 514.1	w	2 532.3	$\nu(\text{ND})$; A'
s	2 556.3	m	2 575.4	$\nu_{\text{as}}(\text{ND}_2)$; A'
m	3 087.1	m	3 080.5	$\nu_2(\text{CH})$; A'
m	3 123.3	w	3 120.4	$\nu_1(\text{CH})$; A'
w	3 295.8	w	3 271.9	$\nu_{\text{s}}(\text{NH}_2)_{\text{ass.}}$; A'
		sh	3 380.6	$\nu_{\text{s}}(\text{NH}_2)_{\text{free}}$; A'
m	3 416.4			$\nu_{\text{as}}(\text{NH}_2)_{\text{ass.}}$; A'
		m	3 421.7	$\nu(\text{NH})$; A'
		m	3 457.7	$\nu_{\text{as}}(\text{NH}_2)_{\text{free}}$; A'

^a Values given for 0.05M-CCl₄ and CS₂ solutions.

resolved in the solution spectrum, but not observed in the Raman. All of them, are summarized in Table III.

Vibrations in the —NH₂ group. The amino group can easily undergo associations by hydrogen-bonds. The i.r. study was carried out on different solvents, either inert or proton donors at different concentrations, as well as the solid state spectrum, in order to deduce the type of existing association. From this study, the existence of an intermolecular association by hydrogen bonding between the substituent amino group and the basic thiazolinic nitrogen of another could be concluded¹⁴. In the spectrum in 0.08M-C₂Cl₄ solution, the four bands corresponding to the symmetric and antisymmetric stretching of the corresponding free and associated species are distinguished, bands corresponding only to the associated antisymmetric and symmetric stretching being observed in the solid i.r. spectrum, of which only the last one was visible in the Raman. For these vibrations, a shifting of about 900 cm⁻¹ is produced when proceeding to the deuterated compound, the assignment made being verified with the application of the isotopic product rule. In addition, in the solution spectrum, the fundamentals $\nu(\text{NH})$ and $\nu(\text{ND})$, corresponding to the monodeuterated species, are observed at 3 421.7 cm⁻¹ and 2 523.3 cm⁻¹, respectively.

The NH₂ deformation, or scissoring mode, is measured at 1 620.8 cm⁻¹ in solid spectrum, being at a lower frequency in the diluted solution spectrum, while the corresponding mode of 2-amino-*d*₁-thiazole is assigned at 1 454.4 cm⁻¹. In order to obtain the corresponding value in solution, the isotopic product rule was applied,

being a theoretical value of approximately 1380 cm^{-1} . The $\delta(\text{ND}_2)$ deformation appears at a frequency approximately 500 cm^{-1} lower, in the solid spectrum, at 1170.5 cm^{-1} . The rocking mode, $\nu(\text{NH}_2)$, A'' was assigned at a frequency similar to that of its appearance in the aniline¹⁵, supported by a shifting of about 250 cm^{-1} in the deuterated specie. The two NH_2 modes which remain to be assigned correspond to the wagging mode and the NH_2 torsion mode. The first was assigned to a broad band at 645.8 cm^{-1} in the solid spectrum, and given the frequency at which the fundamentals W_7 and F_1 appear, its intensity is strengthened, appearing broad. In the deuterated species, this band appears at 534 cm^{-1} , with a shifting of

TABLE V

Bond distances and angles for 2-aminothiazole. Corresponding bond angles and distances in the ring are given side by side

Bond	Distance, Å ^a	Bonds	Angle, deg
S(1)—C(2)	1.724	S(1)—C(2)—N(2)	121.3
C(2)—N(3)	1.304	N(2)—C(2)—N(3)	123.6
N(3)—C(4)	1.372	C(2)—N(3)—C(4)	110.1
C(4)—C(5)	1.367	N(3)—C(4)—H(4)	119.4
C(5)—S(1)	1.731	H(4)—C(4)—C(5)	124.8
C(2)—N(2)	1.387	C(4)—C(5)—H(5)	129.0
C(4)—H(4)	1.080	H(5)—C(5)—S(1)	121.4
C(5)—H(5)	1.077	C(5)—S(1)—C(2)	89.3
N(2)—H(6)	0.900	C(2)—N(2)—H(6)	119.0
N(2)—H(7)	0.920	H(6)—N(2)—H(7)	116.0

^a $1\text{ Å} = 10^{-10}\text{ m}$.

TABLE VI

Experimental and theoretical values given by the Teller-Redlich rule

Values	Thiazole-NH ₂ -Thiazole-ND ₂		Thiazole-NH ₂ -Thiazole-NHD		Thiazole-NHD-Thiazole-ND ₂	
	A'	A''	A'	A''	A'	A''
Calculated	0.266	0.534	0.515	0.730	0.516	0.731
Experimental	0.271	0.538	0.523	0.741	—	0.723
% E	1.845	0.743	1.530	1.484	—	1.106

TABLE VII

Thermodynamic functions calculated for thiazole, 2-aminothiazole and 2-amino-[²H₂]-thiazole in the ideal gas state at 101.3 kPa (in J mol⁻¹ · K⁻¹)

T K	Thiazole				2-Aminothiazole				2-Amino-d ₂ -thiazole			
	C_p^0/R	$(H - H_0)/RT$	$-(F - H_0)/RT$	S^0/R	C_p^0/R	$(H - H_0)/R$	$-(F - H_0)/R$	S^0/R	C_p^0/R	$(H - H_0)/RT$	$-(F - H_0)/RT$	S^0/R
200.0	5.62	4.35	26.86	31.21	7.38	4.99	28.06	33.05	7.78	5.20	28.30	33.49
250.0	6.90	4.73	27.87	32.60	9.10	5.64	29.25	34.89	9.55	5.89	29.53	35.42
300.0	8.22	5.20	28.78	33.98	10.76	6.36	30.34	36.69	11.26	6.64	30.67	37.31
350.0	9.49	5.72	29.62	35.34	12.31	7.10	31.37	38.47	12.84	7.42	31.75	39.17
400.0	10.65	6.27	30.42	36.68	13.69	7.84	32.37	40.21	14.25	8.18	32.79	40.98
450.0	11.67	6.81	31.19	38.00	14.92	8.56	33.33	41.89	15.49	8.93	33.80	42.73
500.0	12.57	7.35	31.93	39.28	15.99	9.25	34.27	43.52	16.58	9.64	34.78	44.42
550.0	13.35	7.86	32.66	41.52	16.94	9.91	35.18	45.09	17.54	10.32	35.73	46.04
600.0	14.04	8.34	33.36	42.71	17.77	10.53	36.07	46.60	18.38	10.95	36.65	47.60
650.0	14.65	8.81	34.05	42.86	18.51	11.11	36.94	48.05	19.13	11.55	37.55	49.11
700.0	15.19	9.24	34.72	43.96	19.17	11.67	37.78	49.45	19.80	12.12	38.43	50.55
750.0	15.67	9.65	35.37	45.03	19.76	12.19	38.61	50.79	20.40	12.65	39.28	51.94
800.0	16.11	10.05	36.01	46.05	20.29	12.68	39.40	52.09	20.94	13.15	40.12	53.27
850.0	16.50	10.41	36.63	47.04	20.77	13.14	40.19	53.33	21.43	13.63	40.93	54.56
900.0	16.86	10.76	37.23	47.99	21.22	13.58	40.96	54.53	21.87	14.07	41.72	55.79
950.0	17.18	11.09	37.82	48.91	21.62	13.99	41.70	55.69	22.28	14.49	42.49	56.99
1 000.0	17.48	11.40	38.40	49.80	21.99	14.38	42.43	56.81	22.64	14.89	43.25	58.14
1 050.0	17.76	11.70	38.96	50.66	22.34	14.75	43.14	57.89	22.98	15.27	43.98	59.25
1 100.0	18.01	11.98	39.51	51.49	22.66	15.10	43.83	58.94	23.29	15.63	44.70	60.33
1 200.0	18.45	12.50	41.58	53.08	23.22	15.76	45.18	60.93	23.84	16.29	46.09	62.38
1 400.0	19.16	13.41	42.58	55.98	24.14	16.89	47.69	64.58	24.69	17.43	48.69	66.12

over 100 cm^{-1} . The torsion mode, $\nu(\text{NH}_2)$, A'' was assigned to the band of the solid i.r. spectrum at 398.4 cm^{-1} , and the corresponding $\nu(\text{ND}_2)$ at 281 cm^{-1} .

The last three vibrations involve the C—N bond. These fundamentals will be less sensitive to the isotopic substitution than the others, and they were assigned at 1276.1 cm^{-1} $\nu(\text{CN})$, 515.7 cm^{-1} $\delta(\text{CN})$ and 258.9 cm^{-1} $\gamma(\text{CN})$, values close to those found for aniline.

Tables III and IV summarize the results for the natural and deuterated molecules, respectively.

ISOTOPIC PRODUCT

The Teller–Redlich product rule was applied for the three pairs of compounds, using the structural parameters^{9,16} that are shown in Table V and the atomic masses in ref.¹⁷. The experimental and theoretical values are shown in Table VI. We consider that the agreement between them supports our assignments.

THERMODYNAMIC FUNCTIONS

The thermodynamic functions C_p^0/R , $(H - H_0)/RT$, $-(F - H_0)/RT$ and S^0/R for the different compounds studied were calculated for 21 temperatures in the range 200–1400 K, using the complete set of vibrational frequencies proposed in this work, and by assuming a rigid-rotor, harmonic-oscillator model for the ideal-gas state at a pressure of 101.3 kPa . The rotational constants were computed using the structural parameters mentioned. The symmetric number used was 1. Table VII provides a summary of these thermodynamic functions.

REFERENCES

1. Metzger J. V.: *Thiazole and its Derivatives*. Wiley, London 1979.
2. Chouteau J., Davidovics G., Metzger J., Azzard M., Pointe M.: *Bull. Soc. Chim. Fr.*, 1962, 1794.
3. Sbrana G., Castellucci E., Ginanneschi M.: *Spectrochim. Acta*, A 23, 751 (1967).
4. Davidovics G., Garrigou-Lagrange C., Chouteau J., Metzger J.: *Spectrochim. Acta*, A 23, 1477 (1967).
5. Davidovics G.: *Thesis*. University of Marseille, Marseille 1969.
6. Davidovics G., Chouteau J.: *Spectrochim. Acta*, A 22, 703 (1966).
7. Chouteau J., Davidovics G., Metzger J., Bonzom A.: *Spectrochim. Acta*, A 22, 719 (1966).
8. Cole A. R. H.: *Tables of Wavenumbers for the Calibration of Infrared Spectrometers*. Pergamon Press, New York 1977.
9. Nyggard L., Asmussen E., Hoeg J. H., Maheshwari R. C., Nielsen C. H., Petersen I. B., Rastrup-Andersen J., Soerensen C. O.: *J. Mol. Struct.* 8, 225 (1971).
10. Pérez-Peña J., González-Dávila M., Arenas J. F.: *Applied Spectrosc.*, in press.
11. Rico M., Orza J. M., Morcillo J.: *Spectrochim. Acta*, A 21, 689 (1965).
12. Califano S., Piacenti F., Sbrana G.: *Spectrochim. Acta*, A 20, 339 (1964).

13. Colthup N. B., Daly L. H., Wiberley A. E.: *Introduction to Infrared and Raman Spectroscopy*. Academic Press, New York 1975.
14. González-Dávila M., Pérez-Peña J., Arenas J. F.: *Tetrahedron*, in press.
15. Evans C.: *Spectrochim. Acta*, A 22, 719 (1966).
16. Prusiner P., Sundaralingam M., Ito T., Sakurai T.: *Acta Crystallogr.*, B 32, 853 (1976).
17. Weast R. C.: *Handbook of Chemistry and Physics*. CRC Press, Boca Raton 1984.