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VIBRATIONAL SPECTRUM AND THERMODYNAMIC PROPERTIES OF PYRIDAZINE

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Abstract

Vibrational spectrum of pyridazine was recorded. Assignment of frequencies to normal vibrations was made. Tellr-Redlich product rule was applied for symmetry species A_1, A_2, B_1 and B_2. Thermodynamic functions were calculated from spectroscopic data.

Introduction

Spectroscopic data of diazines was reported few decades ago[1]. Schneider[2] has measured the dipole moments of pyridazine while Huckel and Johnentz[3] have determined a number of physical properties of pyridazine and measured its association. The vibrational spectra of diazines[4,5] were investigated and vibrational assignment was suggested based on analogy with benzene and pyridine spectra. Spectroscopic and electrochemical studies[6] on chloropyridazine derivatives were investigated. The results indicate an intramolecular charge transfer band in the UV region which depend substantially on the nature of both donor and acceptor moieties. Pyridazine derivatives were found to have antibacterial analgesic[7,8], anti-inflammatory[9], anticonvulsant[10] and antioxidant[11] properties

Thermodynamic properties are difficult to measure directly because of experimental difficulties. However these properties may be calculated from spectroscopic data. In the present communication, the infrared spectrum of pyridazine was studied to calculate thermodynamic properties from spectroscopic data.

Experimental:

Pure sample of pyridazine was obtained and the infrared spectrum was recorded in the liquid phase using Shimadzu IR – 440 spectrometer over the vibrational range 300-4000 cm^{-1}.

Results and Discussion

Pyridazine is particularly interesting molecule because it has two sets of equivalent hydrogen nuclei. The molecule is planar and belongs to the point group C_{2v}. The structure of the vibrational representation is grouped into four symmetry species and given by the following equation:

$$\Gamma_{vib} = 9A_1 + 4A_2 + 8B_1 + 3B_2$$

Under the selection rule of C_{2v} point group, A_1, B_1 and B_2 are infrared and raman active while A_2 is raman active only. The numbering of the vibrational degrees of freedom is in accordance with deutrated benzene notation proposed by Wilson[12].

The infra-red spectrum of pyridazine is shown in figure (1) and absorotion peaks are listed in table (1) with assignment. Vibrations of A_1 species are totally symmetric modes. CH stretching vibration v_2 and v_{20b} are expected to be observed in the high frequency region at 3050 and 3066 cm^{-1} respectively. Ring vibrations v_1, v_{6a}, v_{8a} and v_{19b} are observed as strong-medium absorptions at 965, 625, 1570 and 1416 cm^{-1} respectively. While ring vibration v_{14} is expected[4] to appear in the region 1300-1350 cm^{-1}, it is observed as weak absorption at 1340 cm^{-1}. On the basis of frequency shift expected on deuteration, vibration v_{9a} essentially a CH bending motion of the fourth and fifth protons while vibration v_{15} may be involving the third and sixth protons. v_{9a} and v_{15} are observed at 1158 and 1062 cm^{-1} respectively. A_2 vibrations are raman active only and can be located by their infra-red inactivity. v_5 and v_{17a} are resolved as very weak peaks at 938 and 861 cm^{-1} respectively. v_4 and v_{16a} were observed[5] in the Raman spectrum at 753 and 410 cm^{-1} respectively. B_1 vibrations v_{12} and v_{13} are observed as weak absorption features at 1010 and 3080 cm^{-1} respectively. The remaining B_1 vibrations are observed as strong-medium absorption features in the infra-red spectrum and assignment is listed in Table (1). B_2 vibrations v_{10a} and v_{11} are attributed to CH bending modes and resolved at 870 and 760 cm^{-1} respectively. Ring vibration v_{16b} was previously[5] observed at 370 cm^{-1}.

Molecular geometry of pyridazine has been obtained from microwave spectroscopy[13] and the Cartesian coordinates for each atom were calculated. The principal moments of inertia I_x, I_y and I_z were estimated using the equation[14]:

$$I = \sum m_i p_i^2$$

Where p_i is the perpendicular distance of the mass element mi from the axis.

The values of moments of inertia for pyridazine and pyridazine-d_4 are listed in Table (2) and used in product rule calculations. The reported normal vibrations of pyridazine-d_4 were employed to apply Teller-Redlich product rule[14]. Since the product of v_i/v values of all vibrations of a given symmetry type is independent of the potential constants and depends only on the atomic masses and the molecular structure. For A_1 symmetry species, no rotation is involved while transition moment is parallel to the z-axis and the contributions of carbon, hydrogen and nitrogen atoms to A_1 vibrations are four, four and two respectively. For A_2 symmetry species, rotation is involved around the z-axis while no translation is involved. The contributions of carbon, hydrogen and nitrogen atoms to A_2 vibrations are two, two and one respectively. For B_1 symmetry species, rotation is involved around the y-axis and transition moment is parallel to the x-axis. The contributions of carbon, hydrogen and nitrogen atoms to B_1 vibrations are four, four and two respectively. For B_2 symmetry species, rotation is involved around the x-axis while transition moment is paralled to the y-axis. The contributions of carbon, hydrogen and nitrogen atoms to B_2 vibrations are two, two and one respectively.

The results of product rule calculations are listed in Table (3). The agreement between observed and calculated values is sufficient to insure that the correct assignment of vibrational frequencies are made.

One the basis of vibration frequencies obtained from the IR spectrum. It is possible to predict with great precision thermodynamic quantities. The values calculated from vibrational data are more accurate than those determined by direct experimental methods. Using harmonic oscillator approximation, the vibrational partition function, Q_v, for diatomic molecule[15] is given by the following equation:

$$Q_v = [\ 1\text{-}e^{-\,hc\nu/KT}\ ]^{-1}$$

Where: h planh's constant, c velocity of light, ν vibrational frequency However for polyatomic molecule[16,17], Q_v is evaluated for each vibrational degree of freedom. The overall vibrational partition function is the product of the individual partition functions according to the equation :

$$Q_v = [\ 1\text{-}e^{-\,hcv_1/KT}\ ]^{-d_1} \cdot [\ 1\text{-}e^{-\,hcv_2/KT}\ ]^{-d_2} \ldots\ldots\ldots\ldots\ldots\ldots$$

Where d_1, d_2, ………… are the degrees of degeneracy of the vibrations v_1, v_2, …………. respectively. K is Boltzmann's constant, T is the absolute temperature, h is plank's constant and c is the velocity of light. Thus its possible to predict the value of the partition function, Q_v, if the frequencies of the fundamental vibrations and their degrees of degeneracy are known, the internal partition function, Q_{int}, is evaluated[17] from knowing the values of moments of inertia and the value of symmetry number, σ. The rotational contribution to partition function, Q_r, is evaluated[15,17] using the values of calculated moments of inertia. The vibrational contribution to the heat content, H^0_v, and heat capacity, C^0_p, can be evaluated using Einstein functions[16,17]. The translational contribution to entropy, S^0_{tr}, is computed using Sackur-Tetrode equation[17,18]. The vibrational contribution to entropy, $S^0_{vib,}$ the rotational contribution to entropy, S^0_{rot}, and the free energy functions are computed as reported in our work[17]. Thermodynamic properties were computed over the temperature range 100-400 K°. The values of thermodynamic functions for pyridazine and pyridazin-d_4 are listed in Tables (4) and (5) respectively.

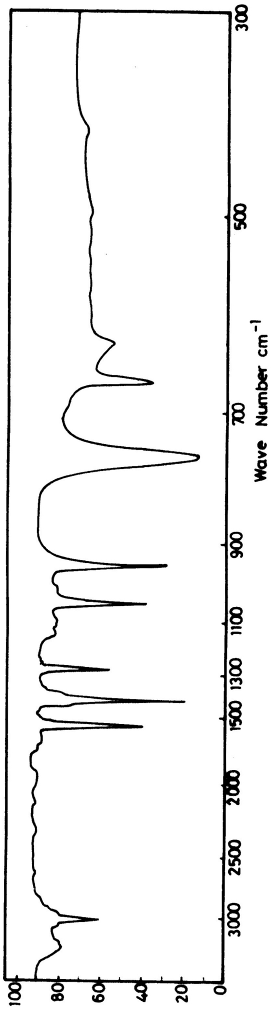
100
80
60
40
20
0
3000
2500
2000
1500
1300
1100
900
700
500
300
Wave Number cm^{-1}

Fig. 1

Table (1): Fundamental vibrations of pyridazine and pyridazine-d_4 (cm^{-1}).

pyridazine				pyridazine-d_4[5]			
Symmetry Species		Assignment	Frequency	Symmetry Species		Assignment	Frequency
A_1	ν_1	Ring	965	A_1	ν_1	Ring	950
	ν_2	CH stretch	3050		ν_2	CD stretch	2272
	ν_{6a}	Ring	625		ν_{6a}	Ring	608
	ν_{8a}	Ring	1570		ν_{8a}	Ring	1545
	ν_{9a}	CH bend	1158		ν_{9a}	CD bend	894
	ν_{14}	Ring	1340		ν_{14}	Ring	1203
	ν_{15}	CH bend	1062		ν_{15}	CD bend	835
	ν_{19b}	Ring	1416		ν_{19b}	Ring	1270
	ν_{20b}	CH stretch	3066		ν_{20b}	CD stretch	2303
A_2	ν_4	Ring	753	A_2	ν_4	Ring	686
	ν_5	CH bend	938		ν_5	CD bend	766
	ν_{16a}	Ring	410		ν_{16a}	Ring	351
	ν_{17a}	CH bend	861		ν_{17a}	CD bend	727
B_1	ν_3	CH bend	1288	B_1	ν_3	CD bend	1038
	ν_{6b}	Ring	670		ν_{6b}	Ring	642
	ν_{7b}	CH stretch	3085		ν_{7b}	CD stretch	2259
	ν_{8b}	Ring	1570		ν_{8b}	Ring	1528
	ν_{12}	Ring	1010		ν_{12}	Ring	973
	ν_{13}	CH stretch	3080		ν_{13}	CD stretch	2303
	ν_{18a}	CH bend	1145		ν_{18a}	CD bend	853
	ν_{19a}	Ring	1450		ν_{19a}	Ring	1318
B_2	ν_{10a}	CH bend	870	B_2	ν_{10a}	CD bend	710
	ν_{11}	CH bend	700		ν_{11}	CD bend	563
	ν_{16b}	Ring	370		ν_{16b}	Ring	327

Table (2) Calculated moments of inertia in a. m. u. A^{o2}.

Molecule	I_x	I_y	I_z
pyridazine	68.6001	82.4640	160.9995
Pyridazine-d_4	81.6307	92.8500	184.2662

Table (3) Values calculated using Teller-Redlich product rule.

Symmetry	Value Observed	Value Calculated
A_1	0.2583	0.2564
A_2	0.5378	0.5351
B_1	0.2708	0.2564
B_2	0.5801	0.5592

Table (4) Values of thermodynamic functions for pyridazine-d_4 in Cal./deg. mole.

T(K°)	Q_v	Q_r	Q_{int}	H^o_v	C^o_p	S^o_{tr}	$-\frac{F^o-E^o}{T}$	S^o_{rot}	S^o_{vib}
100	1.0079	14134.3987	7125.2856	8.8863	0.5159	33.6138	46.2692	20.5772	0.1045
200	1.1787	39978.1167	23567.9878	224.1561	4.3202	37.0558	52.0872	22.6501	1.4475
273.1	1.5515	63791.0702	49501.9189	693.2799	8.5640	38.6027	55.1082	23.5783	3.4115
298.1	1.7562	72747.8734	63899.2252	924.7408	10.1080	39.0376	56.0502	23.8393	4.2203
300	1.7767	73444.4901	65262.4105	946.8979	10.2258	39.0692	56.1237	23.8582	4.2953
400	3.3200	113075.1898	187761.7050	2272.5220	16.1561	40.4977	59.6513	24.7153	8.0661

Table (5) Values of thermodynamic functions for pyridazine in Cal./deg. mole.

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طـيف الاهــتزاز للبيريدازيـن والخواص الثيرموديناميكية

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تم قياس طيف الاهتزاز للبيريدازين وتم تفسير الاهتزازات الأساسية من الترددات الناتجة وتم التأكد من هذا التفسير بتطبيق قاعدة الضرب لتبلر- ريدلبش. تم حساب دوال ثيرموديناميكية مستخدماً النتائج الطيفية.