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Vibrational Spectrum of 2-Aminopyrazine

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Infrared and polarized laser Raman spectra in the solid phase and in the solution phase in different solvents have been obtained within the spectral region between 4000 and 200 cm^{-1} and analyzed for the purpose of vibrational assignments. The impact of intermolecular hydrogen bonding on amino group frequencies has been discussed in length. The fundamentals arising out of aromatic nucleus in particular various assignments are consistent with predicted spectral changes due to the presence of strong electron-activating amino group resulting in considerable perturbation of the vibrational levels of "parent" molecule pyrazine.

Out of three diazabenzenes the optical spectroscopy of pyrazine has received considerable attention over the years. The pioneering work on vapor-phase ultraviolet spectrum by Innes et al.[1] is now well-known for the assignments of different transitions in n-π^* electronic transition. Nearly an ambiguous vibrational analysis of pyrazine has been also proposed by Innes et al.[2] and others.[3–13] Normal coordinate analysis of pyrazine has been carried out by many authors.[6,14,15] A complete and coherent vibrational spectral studies has been reported by Zarembowitch et al.[16] for pyrazine which supercedes all the previous reported work. By contrast, the spectroscopic studies of substituted pyrazines have received much less attention except the work on chloro-[17,18] and methylpyrazines.[18]

The present investigation is a part of the extensive program of work being undertaken on spectroscopic studies of various mono- and di-substituted pyrazines. Here the basic purpose of such studies is to study the effects of various electronic resonance interactions induced by different electron-activating and -deactivating substituent groups on electronic and vibrational transitions in pyrazine.

This paper is an endeavor to make precise assignments of the fundamental vibrational modes of 2-aminopyrazine, first time, based on our observations of the infrared and polarized Raman spectra of the solid and solution phases.

An introduction of an electron-activating group NH_2, at ortho position in pyrazine is expected to enhance the various electronic resonances by delocalizing and to some extent by relocalizing the (σ, π, n) electrons between parent molecule and substituent, resulting in the energy redistribution in various vibrational transitions. In the light of these electronic resonance interactions the assignments of different fundamentals have been made. Along with the infrared study of its isotopic modification containing ND_2 group, spectra with state of depolarization of Raman lines have been used in support of the assignments. In addition to these, the data from various papers and in particular by Innes et al.[2] and Zarembowitch et al.[16] on pyrazine,[4,8,11] and by Evans[19] and Tsuboi[20] on aniline have been extensively used.

Experimental

Chemically pure sample of 2-aminopyrazine obtained from M/s. Fluka AG was used without further purification. The solvents CCl_4, CS_2, and $CHCl_3$ used in recording infrared spectra, were of spectroscopic grade.

The infrared spectra of the sample in the solid state using KBr matrix and nujol mull were recorded. Various spectra were recorded carefully by changing the sample, and KBr powder mixture ratio and pressure used to prepare the KBr disc. The average peak values of different scan are used which were definitely differing by 2 to 3 cm^{-1}. Spectra were also recorded of polycrystalline form, formed on sodium chloride disc by using solvent evaporation method. The solution spectra in CCl_4, CS_2, and $CHCl_3$ were recorded at various concentrations using 0.1 mm path length solvent compensated liquid cells.

The isotopic exchange at amino group was obtained by various repeated exchange drying cycles, in a moisture-free nitrogen atmosphere by using 99.4% deuterated water (supplied by Bhabha Atomic Research Centre, Bombay), to obtain for the more complete deuteration. Absolute care was taken during deuterated sample mull preparation and spectra scan to avoid the rehydrogenation.

The maximum isotopic conversion, about 80%, was obtained by monitoring the relative intensity ratio of ND_2 bending mode to NH_2 bending mode.

All infrared measurements were carried out on a polystyrene film run calibrated Perkin-Elmer 397 spectrophotometer in the region 4000—400 cm^{-1}. A nicolet NIC-170SX (Model NIC-170SX) Fourier Transform interferometer was employed to scan the far infrared spectra in the region 400—200 cm^{-1}.

The Raman spectra were recorded on a Jobin Yvon Raman spectrophotometer equipped with double monochromator system consisting of concave halographic gratings with 2000 grooves per mm and one meter focal length. Spectra Physics Model 164 Ar^+ laser excitation at 488.0 nm was used as a excitation source. Calibration was done with the plasma lines from the laser.[21] Spectral widths of 3—5 cm^{-1} were used in recording the Raman spectra. The uncertainty of determination of wavenumber of around ±3 cm^{-1} in, infrared as well as in Raman spectra.

The samples were in the form of solid, sealed in glass capillaries. Polarization measurements were made by rotating the half-wave plate in two different, mutually perpendicular orientation.

Relatively low solubility, less than 25%, of 2-aminopyrazine in usual Raman solvents posed a major problem

Table 1. Correlation Diagram

Modes	Pyrazine D_{2h}	C_{2v}	2-Aminopyrazine C_s
1, 2, 6a, 8a, 9a	A_g (Raman)	A_1[IR, Raman (P)]	A'[IR, Raman(P)]
12, 13, 18a, 19a	B_{1u} (IR)		
3, 6b, 7b, 8b	B_{2g} (Raman)	B_1[IR, Raman(dp)]	
14, 15, 19b, 20b	B_{3u}(IR)		
10a	B_{1g} (Raman)	A_2[Raman (dp)]	A"[IR, Raman(dp)]
16a, 17a	A_u(Inactive)		
4, 5	B_{3g} (Raman)	B_2[IR, Raman(dp)]	
11, 16b	B_{2u} (IR)		

The authors assign the modes, 3, 10a, 13 to (C-X) vibrations in 2-aminopyrazine.

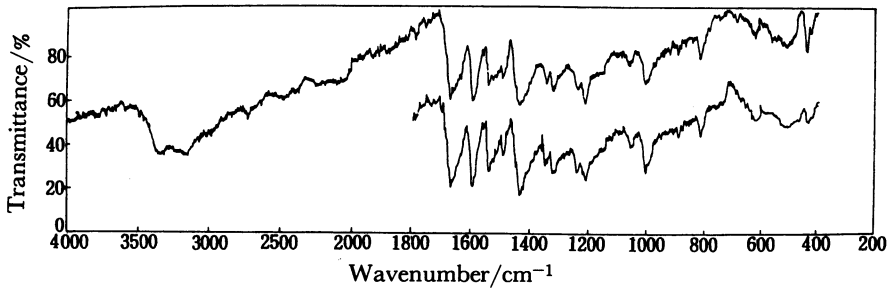

Fig. 1. Infrared spectrum of 2-aminopyrazine in KBr matrix.

to record solution phase Raman spectra. Finally, water was found to be the best Raman solvent in present case. Thus, essentially to ascertain the polarization character of fundamental vibrations obtained in solid phase, the solution phase polarized Raman spectra were recorded in aqueous solution.† Although the degree of polarization is high in aqueous phase rather than the solid phase, the polarizability confirmation in aqueous solution is the same as in the solid state. The uncertainty of measurement in depolarization ratio is of the order of ±0.02 in both the cases.

Results and Discussion

Molecular point group of 2-aminopyrazine has been reduced to C_s, due to inclusion of the nonplanar amino group, from its parent molecule which has D_{2h} point group and the vibrational fundamental modes become active as shown by diagram of correlation of point groups D_{2h}, C_{2v}, and C_s (Table 1).

The total thirty normal vibrations which are active both in the infrared and Raman spectra are divided into two categories:

i. 6 Vibrations of the NH_2 group

ii. 24 Vibrations of the aromatic nucleus

which reduces to 3a'+3a" and 17a'+7a" respectively. The Wilson[22] notation is used to label the various

†Few solution phase Raman spectra scans, were obtained on Spex Ramalog 1401 spectrometer from Spectroscopic Division, BARC, Bombay.

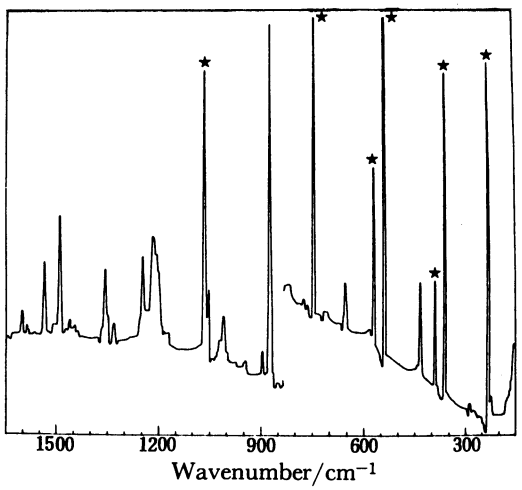

Fig. 2(a): Raman Spectrum of 2-aminopyrazine. Powder in capillary tube. Argon ion 480 nm excitation at 50 mW. Spectral slit width 5 cm^{-1}. ★ Plasma lines. (b): Raman spectrum of 2-aminopyrazine. Recorded on similar conditions as in Fig. 2a.

modes. As per symmetry selection rules, while the species a′ should give rise to polarized Raman lines, the species a″ will have depolarized Raman lines. However, exclusively on the basis of our depolarization measurement, it is interesting to note that some modes obey C_{2v} symmetry selection rules.

To facilitate the proper comparison in this paper, we follow the same set of molecular axis used by Innes et al.[2] for pyrazine, i.e. *Y* axis is taken perpendicular to the molecular plane and the *Z* axis through the two isoelectronic nitrogen atoms.

The infrared spectra recorded in KBr matrix and Raman spectra are reproduced in Figs. 1, 2(a), 2(b), and 3. The experimental observations and assignments are listed in Tables 2 and 3. Predominantly, the various band shapes have been used to relate the corresponding bands recorded in different phases to each other and listed in Table.[††] In following details, the different band values are from spectra recorded in KBr matrix.

Vibrations of the Amino Group: The spectra recorded at different concentrations clearly show that 2-aminopyrazine exhibits the dimer formation (Fig. 4) owing to intermolecular hydrogen bonding similar to 2-aminopyridine.

In general, it has been well established that vibrational spectra are significantly influenced by hydrogen-bond formation. This is particularly noticeable for stretching modes which are displaced to lower frequency upon association. This lowering of frequencies may be attributed to a decrease in force constant arising out of expected increased bond lengths upon association.[24]

All of the six normal fundamental vibrational modes arising out of the $-NH_2$ group and its isotopic modification containing the $-ND_2$ group motions have been assigned and listed in Table 2 along with aniline and 2-aminopyridine for comparison.

The 3500—3400 and 3250—3150 cm^{-1} regions shown two discrete sets of broad band profiles. Clearly, the bands at 3410 and 3510 cm^{-1} are due to symmetric (ν_s) and antisymmetric (ν_{as}), N-H stretches. It is reasonable to assume that the other two bands at 3165 and 3340 cm^{-1} are principally due to similar modes of

††Detail table is available on request.

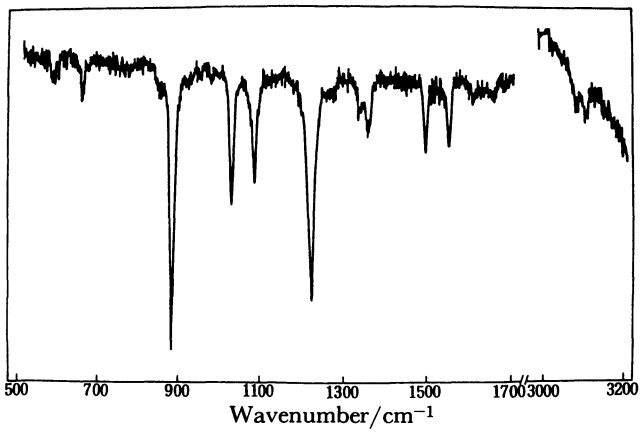

Fig. 3. Solution phase (in H_2O) Raman spectrum of 2-aminopyrazine.

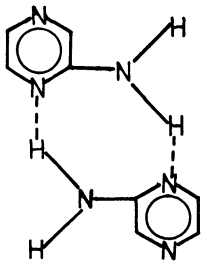

Fig. 4. 2-Aminopyrazine dimer.

Table 2. Internal Vibrational Frequencies (cm^{-1}) of NH_2 Group in 2-Aminopyrazine

Mode	Aniline Ref. 19	Aniline Ref. 20	2-Amino-pyridine Ref. 25, 26	2-Aminopyrazine CS_2	CCl_4	$CHCl_3$	Nujol	KBr	Raman	ND_2AP in nujol
NH_2-Asymm.	3485	3481	3510(M)	3516	3516	3510	—	3510(M)	—	2520(M)
stretch	3440(NHD)	—	3335(D)	—	3347	3342	3330	3340(D)	3327(D)	2438(D)
	2592(ND_2)	—								
NH_2-Symm.	3401	3395	3420(M)	3415	3410	3402	—	3410(M)	—	2485(M)
stretch	2535(NHD)	—	3180(D)	—	3150	3165	3147	3165(D)	3165(D)	2400(D)
	2485(ND_2)	—								
NH_2 scissoring	1618	1619	1634(D)	—	—	1662(D)	—	1662(D)	—	1168(ND_2)
	1441(NHD)	—	1621(M)	—	—	1652(Sh)	—	1652(M)	1650R(L)	1335(NHD)
	1152(ND_2)	1150(ND_2)	—			(M)				
NH_2 twisting	1054	1115	1118	—	—	1200	—	1210	1213	1070(ND_2)
	—	797(ND_2)							1200(Sh)	
									1215R(L)	
NH_2 wagging	670	700	667	—	—	696	—	685	—	482(ND_2)
	420(ND_2)	600(ND_2)								
NH_2 torsion	440/2	—	435/2	—	—	430/2	224	218	218	—
	216.5†								212R(L)	

M=Monomer; D=Dimer; Sh=Shoulder; R(L)=Raman liquid phase in H_2O.
†Ref. 32.

vibration in associated molecules. The corresponding bands in $-ND_2$ species are at 2485 and 2520 cm^{-1}, and 2400 and 2438 cm^{-1} for monomer and dimer respectively. In comparison to 2-aminopyridine[25,26] the large shift in bonded symmetric stretching frequency in present case may be due to the increased $=NH_2^+$ electronic nature[27] of the molecule resulting in increased strength of hydrogen bonding.[24] An advanced anharmonicity of 103 cm^{-1} is observed and calculated[28] bonded symmetric stretching viration resulting in extensive $\angle$HNH angle (143°)[29] opening very well reflects the stronger intermolecular hydrogen bond in present case.

Obviously, the effects of this strong intermolecular bond formation will be most pronounced on the various valence angle deformation modes rather than the resulting electronic activity out of animo group. Although, the enhanced electron attracting character of aromatic nucleus also contributes in raising the frequency and intensity markedly. The established range for NH (δ) scissoring mode is 1650—1590 cm^{-1} and in aniline[19,20] and 2-aminopyridine[25,26] this mode has been assigned to a band at 1620 cm^{-1}. One of the strongest band in present spectrum at 1662 cm^{-1}, with a shoulder at 1650 cm^{-1} has been assigned to this mode. The corresponding ND_2 species mode is found at 1168 cm^{-1}.

Under the same considerations, given for the scissoring mode, the other low frequency modes of the amino group, NH_2 twisting and wagging modes are assigned to the bands at 1210 and 685 cm^{-1} which shift to 1070 and 480 cm^{-1} respectively in the deuterated analog. The corresponding Raman band for twisting mode is at 1213 cm^{-1} and is polarized and weak in intensity.

The band at 218 cm^{-1} with a corresponding weak depolarized Raman band at 218 cm^{-1} is assigned to the low energy torsional motion around the C–N bond with its first overtone located at 431 cm^{-1}. The present torsional frequency agreement, with the value for 2-aminopyridine,[26,30] aniline,[31,32] and *m*-halo-substituted anilines[33] is excellent, and virtually localize the vibrational mode around 200—220 cm^{-1} in these molecules.

A particular aspect concerning the effect of the general anharmonicity induced by torsional motion of the amino group in present case has been visualized in enhanced intensity of combination bands with different amino internal deformation modes which even may contribute to frequency shifts to these characteristic group fundamentals.

Aromatic Nucleus Vibrations: Taking into account the effect of amino group substitution in present case, the phenyl nucleus vibrations are well identified and assigned by reference to instructive comprehensive analysis of the corresponding spectra of pyrazine[2,16] and the present work on 2-amino-d_2-pyrazine. The details are listed in Table 3 which is self explanatory. Only following few comments on spectral characteristic observations specially regarding

Table 3. Fundamental Vibrational Frequencies (in cm^{-1}) of 2-Aminopyrazine (Aromatic Nucleus Part)

Symmetry			Mode No. (22)	Assignment	Pyrazine										2-Aminopyrazine			
					L.M.M. (4)		C.A.S. (8)		S.I.B. (2)		S.S.R. (11)		Z.B.S (16)					
D_{2h}	C_{2v}	C_s			IR	R	IR	R	IR	R	IR	R	IR	R	IR	R(S)	R(L)	(σ_L)
Ag	A_1	A′	6a	βC-C	—	609	609	—	596.1	598	602	600	600	602P	590	582P	585P	0.59
			1	νC-C	—	1015P	1015	—	1015	1016	1016	1011	1016	1016P	862	870P	867P	0.62
			9a	βC-H	—	1232	1232	—	1230	1234	1246	1231	1233	1233P	1240	1245P	—	0.52
			8a	νC-C	—	1584P	1584	—	1578	1578	1581	1574	1580	1580P	1595	1600P	1595P	0.55
			2	νC-H	—	3051P	3060	—	3054	3054	3054	3052	3054	3054	3055	3055P		
A	A_2	A″	16a	γC-C	340	—	400	—	340 (estd)	—	423	—	350	—	355	—	—	
			17a	γC-H	950	—	950	—	950 (estd)	958	997	—	960	—	955	—	—	
B_{1u}	A_1	A′	13	$\nu C\text{-}NH_2$	3065	3069	3090	—	3066	—	3082	—	3012	—	1325	1325P	1320P	—
			19a	νC-C	1490	—	1490	—	1484	—	1491	—	1483	—	1490	1490P	1490P	0.63
			18a	βC-H	1067	—	1135	—	1144	—	1126	—	1130	—	1150	1175P	—	0.43
			12	βC-C	1022	—	1021	—	1110	—	1022	—	1018	—	1009	1009P	1012P	0.58
B_{3u}	B_1	A′	20b	νC-H	3066	—	3070	—	3066	—	3011	—	3063	—	3065	3074	3070P	—
			19b	νC-C	1418	—	1413	—	1418	—	1414	—	1411	—	1438	1445P	1447P	0
			14	νC-C	1342	—	1346	—	1067	—	1149	—	1149	—	1350	1355dp	1360dp	0.85
			15	βC-H	1148	—	1063	—	1022	—	1068	—	1063	—	1060	1050dp	1070dp	0.86
B_{2u}	B_2	A″	16b	γC-C	417	—	417	—	416	—	412	—	418	—	421	433	—	0.54
			11	γC-H	804	—	786	—	804	—	796	—	785	—	818	819dp	—	0.78
B_{1g}	A_2	A″	10a	$\gamma C\text{-}NH_2$	752	753	925	—	757	757	930	919	927	927dp	201	—	—	—
B_{3g}	B_2	A″	4	γC-C	—	641	703	—	703	703	765	—	756	756	745	755p	—	—
			5	γC-H	700	703dp	753	—	981.6	922dp	974	—	983	983	895	895p	—	0.63
B_{2g}	B_1	A′	6b	βC-C	—	516	641	—	516	—	699	701	704	704dp	630	651p	654p	0.30
			3	$\beta C\text{-}NH_2$	—	1118	1350	—	1118	—	1353	1343	1346	1345dp	408	—	—	—
			8b	νC-C	—	1523	1523	—	1524	1524	1522	1524	1525	1525dp	1540	1535dp	1535dp	0.76
			7b	νC-H	—	3038	—	—	3041	3041	3034	3040	3040	3040	3040	3045dp	3048dp	0.77

R(S)-Raman solid phase; R(L)-Raman liquid phase in H_2O; P-Polarized; dp-depolarized; ν-Stretching; β-in-plane deformation; γ-out-of-plane deformation; σ_L-Depolarization ratio liquid phase.

the various corresponding infrared inactive vibrations belonging to Au, B_{2g}, and B_{3g} symmetry species in pyrazine are worth mentioning.

The two infrared inactive Au species fundamentals are little effected in intensity gain due to reduction in symmetry in present case and are identified with weak bands at 355 cm^{-1} (ν_{16a}) and 955 (ν_{17a}) without corresponding Raman lines. Regarding the assignments of the B_{2g} species, planar Raman active fundamentals, our observation of the polarized 651 cm^{-1} Raman line strongly supports the 630 cm^{-1} weak band in infrared for ν_{6b} fundamental. The other two fundamentals ν_{8b} and ν_{7b} in this class show appreciable gain in intensity thus, it seems are sensitive to lowering of the symmetry. The strong infrared bands at 1540 and 3040 cm^{-1} with corresponding 1535 and 3045 cm^{-1} analogous Raman lines have been assigned to these fundamentals. Both the Raman lines are depolarized in character.

The remaining two Raman active nonplanar B_{3g} fundamentals have been identified with the weak infrared bands at 745 (ν_4) and 895 cm^{-1} (ν_5). The choice of these two infrared bands is based on the corresponding Raman lines at 755 and 895 cm^{-1} and their intensities in expected region. Here, the Raman lines are polarized in character.

Although our assignments for aromatic nucleus part are generally compatible with recent publications[11,16] there are some notable differences particularly in case of vibration ν_{14}. We prefer to localize this fundamental vibration at 1350 cm^{-1} with corresponding depolarised Raman line at 1355 cm^{-1} rather than 1149 cm^{-1} as proposed for pyrazine by Sbrane et al.[11] and Zarembowitch et al.,[16] spectrum does not show any strong band in the proposed region of 1150 cm^{-1}.

It is, however, important to note that the state of polarization of some of the Raman lines do not behave as per present C_s symmetry rules. Although, the symmetry of the molecule is C_s, an analogous assignments, considering higher C_{2v} symmetry, have been proposed in few cases. Assigning the vibrations in this way will give rise to an occasional depolarized B_1 Raman lines. Some of the vibrations belongs to B_{3u} and B_{2g} species fall under such characteristic class. This induced non-behaviorable character of these vibrations may be attributed to the coupling between the various NH_2 deformation modes, which ultimately results in various combination bands, particularly in the 3000—1700 cm^{-1} spectral region.

As mentioned earlier, 2-aminopyrazine form a dimer due to intermolecular hydrogen bonding. Various spectra recorded at low and higher concentrations, show that this bonding does not make a pronounced effect on the vibrational frequencies arising out of aromatic nucleus. In general the steady shift towards higher frequency side of these various fundamental modes in comparison to 2-aminopyridine clearly indicates that the heterocyclic aromatic nucleus here is more strong electron-accepting in nature and thus conjugate more with the amino nitrogen. However, the similarity of infrared spectrum with 2-aminopyridine is instructive.

In case of ring vibrations the behavior analogy with monosubstituted benzenes is remarkable. The symmetric hexagonal breathing mode ν_1 and trigonal breathing mode ν_{12} are closely coupled with the vibrational modes of the substituent groups in substituted benzens and has been discussed in detail.[34-36] Considering amino group as a light substituent,[34] one expect vibration ν_1 to show large decrement while ν_{12} remains relatively unchanged as is actually observed in present case.

Similar is the case with the degenerate ν_6 ring distortion vibration, of which the totally symmetric component decreases while the asymmetric component is somewhat localized.

Remaining other ring vibrations which get coupled predominantly with C-H in-plane deformation rather than other C-X vibrations and so are little effected on substitution.

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