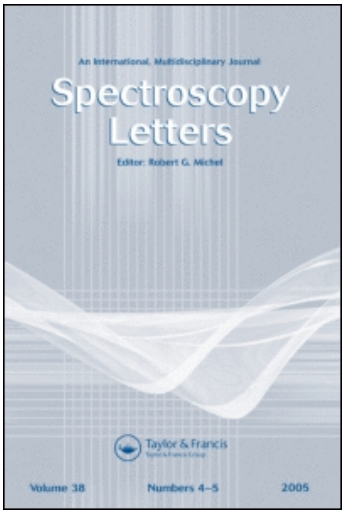

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RAMAN SPECTRUM OF n-PROPYLAMINE IN CYCLOHEXANE

Key Words: Raman Spectra, Amines, Hydrogen Bonding

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ABSTRACT

Polarized (Isotropic) Raman spectra of the N-H valence region of n-propylamine have been recorded as a function of concentration in cyclohexane. Statistical analysis of the data using non-linear least squares techniques revealed the presence of a fourth spectral band in this region, not observed in an earlier IR study. This latter peak has been assigned to vibrations of monomers in the liquid. The resolved spectral parameters are consistent with a picture of diminishing molecular association upon dilution of the amine in this non-polar solvent.

INTRODUCTION

The primary amines form an interesting class of compounds in that they possess the potential to form either 1:1 or 1:2 complexes with themselves or other bases in solution.

Wolff and coworkers[1-4] have performed extensive investigations on the hydrogen bonding properties of these molecules utilizing infrared spectroscopy. They have been able to show that, at least in the aliphatic amines, intermolecular hydrogen bonds are of the 1:1 type. That is, an associated molecule contains one bonded N-H

group, with the second one remaining 'free' in solution. In particular, one IR study[1] of various amines as a function of concentration in carbon tetrachloride shows clearly the presence of two distinct N-H symmetric stretching vibrations (Fig. 3 of ref. 1), assigned to monomeric and hydrogen bonded molecules, respectively. As expected, the former peak predominates at the highest dilutions (Table 2 of ref. 1). The spectra of the neat liquids, however, reveal only a single symmetric stretching mode at the frequency of the complexed amine (Fig. 4 and Table 2 of ref. 1). This implies that all molecules are hydrogen bonded in the pure liquid state. The result is in contrast with that of a later IR study on aniline,[3] which revealed the presence of monomers in the neat liquid.

In order to pursue this question further, we have recorded the Raman spectra of n-propylamine in the neat liquid and at various concentrations in the non-polar solvent, cyclohexane. The data were then analyzed using non-linear curve fitting techniques to resolve the band structure in the N-H valence region of the Raman spectrum.

EXPERIMENTAL

n-Propylamine and cyclohexane were obtained commercially and distilled prior to use. Solutions were prepared gravimetrically. We note that attempts to use the same solvent employed in the earlier study,[1] carbon tetrachloride, were unsuccessful, apparently due to the known tendency of amines to react with it.[5]

The details of laser excitation, spectrometer operation and signal detection have been presented elsewhere.[6,7]

Initially, both polarized and depolarized spectra were recorded in order to obtain the isotropic spectra ($I_{iso}(\omega)=I_{pol}(\omega)-(4/3)I_{dep}(\omega)$), which avoids reorientational linebroadening.[8] However, the depolarization ratios of all modes with the exception of the antisymmetric stretch, ν_a, were quite low ($\rho<0.1$). Therefore, $I_{iso}\simeq I_{pol}$, and only the polarized spectra were used.

After digitization of the experimental spectra, at 5 cm^{-1} increments, non-linear least squares curve fitting techniques were used to test models incorporating varying numbers of Gaussian/Lorentzian summation bands. The calculated spectra were convoluted with a triangular slit function (SW=10 cm^{-1}(FWHM)) in order to avoid instrumental contributions to the calculated linewidths. We note that, in principle, the fraction Lorentzian, f_{Lor}, may differ for the various peaks in the spectrum. However, a common fraction was employed for all bands in each model in order to maintain a tractable number of variable parameters.

RESULTS AND DISCUSSION

Shown in the Figure are the polarized spectra of n-propylamine in the neat liquid (Fig. A) and at 20 mole percent in cyclohexane (Fig. B). Three peaks are immediately apparent in the liquid's spectrum, including a weak, very broad band centered around 3250 cm^{-1}, and two stronger peaks at approximately 3320 cm^{-1} and 3380 cm^{-1}. The first of these, which is seen to disappear upon dilution in cyclohexane, arises from the Fermi resonance enhanced first overtone of the symmetric deformation mode, $\nu_{2\delta}$.[9] The latter two are assigned to the NH_2 symmetric (ν_s) and antisymmetric (ν_a) stretching modes respectively.[9]

Careful inspection of Fig. A reveals a definite asymmetry in the central peak, with an apparent shoulder on its low frequency side. This suggests the possibility of a fourth band in this region.

In order to test further the hypothesis of an additional vibrational mode, the spectrum was fit with both three and four band Gaussian/Lorentzian summation functions (vide supra). Of course, one expects to observe a decrease in the residual squared error using the latter model due to the presence of the three additional parameters. However, the improvement was quite substantial, leading to a reduction of more than a factor of 3. Furthermore, employing Hamilton's R-factor ratio test,[10] the fourth band was found to be statistically significant to a

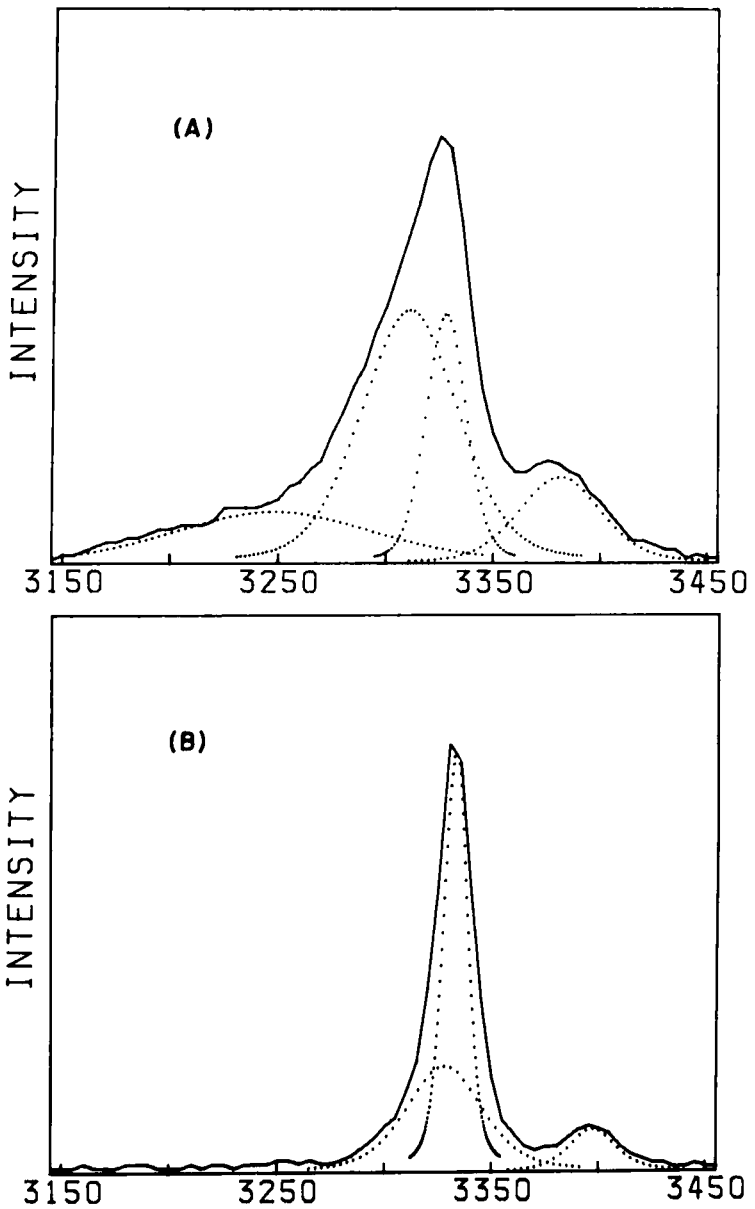

Fig. - Polarized Raman spectrum of n-propylamine: (A) neat liquid; (B) 20 mole percent in cyclohexane.

The solid curves are the experimental spectra.
The dotted lines represent the individual component bands determined from non-linear least squares regression.

confidence level, α=0.005 . That is, there is a 99.5% probability that the band is real and not simply an artifact of the data. The test was also passed at the same confidence level in each of the solutions studied.

We also tested models including a fifth peak in the regions of $\nu_{2\delta}$ and ν_a, but could not obtain definitive evidence for splitting of either of these two bands. This result is not surprising, since one expects the Fermi resonance to be much weaker for non-hydrogen bonded molecules (Fig. B and ref. 1), which explains the absence of a corresponding band in the $\nu_{2\delta}$ region. In addition, it has been shown that in 1:1 complexes, ν_a is not expected to be split significantly.[2,3]

As noted above, the IR spectrum of neat n-propylamine revealed only a single symmetric stretching vibration. However, it is believed that the splitting of this mode is likely to have been obscured by the reorientational broadening of infrared bands, not present in the polarized (isotropic) Raman spectrum.[8]

Presented in Table 1 are the resultant parameters of the four band fits as a function of concentration. It is seen that the intensity of the Fermi resonance band, $\nu_{2\delta}$, diminishes to zero at the two lowest concentrations.

of the two symmetric stretching modes, ν_{s_1} and ν_{s_2}, the former can be assigned unambiguously to associated species, due both to its lower frequency and also its greater linewidth, each factor indicative of hydrogen bonded species.[11] Additionally, it is seen that the peak frequency, ν_{s_2} remains approximately independent of concentration, which is to be expected for free NH_2 groups.

Further analysis of ν_{s_1} requires determination of the unperturbed peak frequency, ${}^{o}\nu_{s_1}$, and intensity, ${}^{o}I_{s_1}$, which can be accomplished using the standard Fermi resonance perturbation treatment.[12,13] The results of this calculation are presented in Table 2.

One sees that, in contrast to ν_{s_2}, the peak frequency, ${}^{o}\nu_{s_1}$, rises steadily upon dilution, indicative of a decreased state of

TABLE 1

Resolved Band Parameters of n-Propylamine in Cyclohexane

M.F.	$\upsilon_{2\delta}$ *	$\Delta_{2\delta}$ **	$I_{2\delta}$ ≠	υ_{s_1} *	Δ_{s_1} **	I_{s_1} ≠	υ_{s_2} *	Δ_{s_2} **	I_{s_2} ≠	υ_a *	Δ_a **	I_a ≠	f_{Lor}
1.00	3248	111	0.60	3311	53	2.95	3328	22	2.90	3381	45	1.00	0.26
0.80	3256	112	0.44	3314	54	2.94	3329	19	3.56	3383	40	1.00	0.29
0.60	3250	82	0.33	3317	53	2.93	3330	16	4.93	3387	38	1.00	0.33
0.40	--	--	0	3321	50	2.46	3332	15	6.77	3392	33	1.00	0.34
0.20	--	--	0	3328	42	2.50	3333	13	9.90	3397	26	1.00	0.41

* Peak Frequencies are given in cm^{-1}
** Δ represents full-width at half-maximum (FWHM), in cm^{-1}
≠ Integrated intensities are presented relative to that of the antisymmetric stretching mode.

TABLE 2

Fermi Resonance Analysis

M.F.	$I_{2\delta}/I_{s_1}$	${}^{o}\nu_{2\delta}$ *	${}^{o}\nu_{s_1}$ *	W_{ni} **	$I_{s_2}/{}^{o}I_{s_1}$
1.00	0.20_3	3259	3300	23.6	0.82
0.80	0.15_1	3264	3306	19.6	1.05
0.60	0.11_4	3257	3310	20.3	1.51
0.40	0.00	--	3321	0.00	2.75
0.20	0.00	--	3328	0.00	3.96

* Unperturbed peak frequencies, in cm^{-1}

** Fermi resonance matrix element, in cm^{-1}

aggregation. Additionally, the ratio, $I_{s_2}/{}^{o}I_{s_1}$, proportional to the relative number of free to hydrogen bonded NH_2 groups, is found to increase substantially, from somewhat less than unity in the neat liquid to nearly 4:1 at the lowest concentration studied. This is evident from inspection of both Table 2 and the Figure.

In summary, it has been found that, in contrast to earlier infrared spectra,[1] the Raman spectrum of liquid n-propylamine shows clearly the presence of two N-H symmetric stretching vibrations. The results are consistent with the model first proposed by Wolff,[1] in which primary aliphatic amines are assumed to associate via 1:1 complexes. The various parameters of the resolved bands in the spectra are in agreement with the concept of decreasing molecular association upon dilution in cyclohexane. This is intuitively quite reasonable in this non-polar hydrocarbon solvent.

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