

Liquid-Phase Hydrogen Bonding and Raman Spectrometry

II—Primary and Secondary Amines

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Structure, intensity and depolarization ratio of NH or NH₂ Raman bands of some primary and secondary amines have been studied in pure liquid state at different temperatures and in dilute CCl₄ solutions. The depolarization ratio and scattering activity, as in the case of alcohols previously studied, increase with self-association. It confirms the change of the XH bond polarizability derivatives with hydrogen bond formation.

INTRODUCTION

As part of a study of weak hydrogen bonds by Raman spectrometry, we present here results obtained on the NH...N system relating to simple primary or secondary amines. In previous work¹ on the ν OH band of the O—H...O liquid alcohol system, two noteworthy results were obtained: a two-compound structure due to the molecules' chain association, and a significant increase in the scattering activity ($45\alpha^2 + 7\gamma^2$) and in the depolarization ratio through self-association.

Our study is divided into two parts, the first of which relates to a description of the liquid-phase ν NH or ν NH₂ bands from the triple point to the vicinity of the critical point, and the second to intensity measurements on those same bands.

The primary amines studied are methylamine and ethylamine; the secondary amines, dimethylamine, diethylamine (and the corresponding ND-deuterated species) and pyrrole.

EXPERIMENTAL PART

The hydrogenated species come from Rhône-Poulenc. The compounds are introduced by vacuum distillation into the measuring cell. The deuterated species were prepared through successive exchanges of hydrochloride in heavy water. The isotopic rate, controlled spectroscopically, is over 90%.

The spectra recording technique has been described previously.¹ All amines are perfectly stable in the laser beam with the exception of the pyrrole, which requires working at low power (50 mW) and renewing the contents of the cell approximately every hour.

† Part I: see Ref. 1.

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DESCRIPTION OF THE ν NH AND ν NH₂ BANDS

Secondary amines

Dimethylamine. The change in the I_{VV} and I_{VH} spectra is presented in Fig. 1. At high temperatures, the I_{VV} compound is symmetrical and small in width, characteristic of free NH vibrators. At a lower temperature, a second wide band appears in the shoulders of the previous one around the low frequencies and gradually replaces it as it cools; it corresponds to the NH...N vibrators disrupted by hydrogen bond formation. In the vicinity of the melting point, the monomeric band has almost completely disappeared, while the I_{VV} and I_{VH} compounds have maximum values of 3247 cm⁻¹ and 3258 cm⁻¹ respectively. In the transition to the crystalline phase, the two-compound structure remains, with the respective maximum values of 3215 and 3238 cm⁻¹ at 170 K. These results may be interpreted as follows: as has already been observed in infrared,² the degree of self-association is much lower for amines than for alcohols of an equivalent formula. The monomeric band (or potentially chain end) is observed at a much lower temperature for dimethylamine than for isopropyl alcohol and only disappears at about 190 K instead of 360 K for alcohol. The discrepancy between I_{VV} and I_{VH} observed then for the self-associated band may be interpreted, as in the case of alcohol, by a coupling effect between NH vibrators; as the interaction between NH vibrators is weaker than it is between OH vibrators, the rupture observed here is much smaller and only really appears in the vicinity of the melting point. The continuity observed in the bands' structure in the transition to the crystalline state is evidence of a short-range order in liquid phase. Because of the absence of crystallographic data, we cannot specify whether this is a chain association or not.

Similar measurements were made on the deuterated species (CH₃)₂ND, but analysis of the results was complicated by a Fermi resonance between the ν ND vibration and a combination around 2500 cm⁻¹ observed in both the liquid phase and in the gaseous state.³ The change in liquid spectra is shown in Fig. 2; at high temperature, as in the gaseous state, the high-frequency

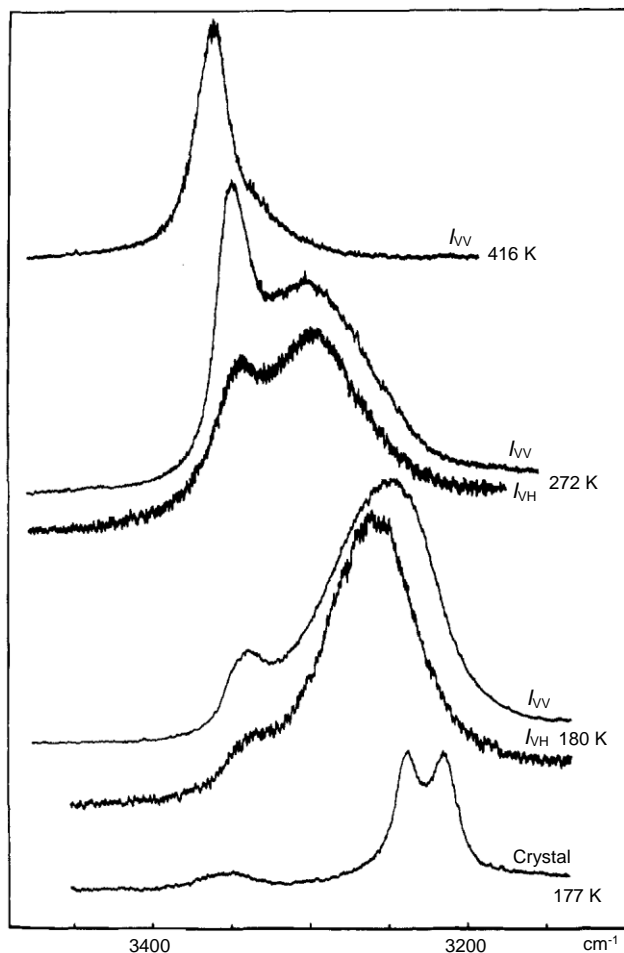


Figure 1. $(\text{CH}_3)_2\text{NH}$. Spectra I_{VV} and I_{VH} at different temperatures. The intensity of the I_{VH} compounds has increased fivefold. Spectral slit width 1.5 cm^{-1} .

compound is the most intense, indicating that the fundamental νND largely contributes to the intensity of this band. Through cooling, the frequency of the fundamental decreases and the intensity of the high-frequency band gradually weakens, becoming negligible in the crystal spectrum at 170 K. Because of the complexity, it appears difficult to discuss the relative positions of the I_{VV} and I_{VH} compounds. It should be noted, however, that in the vicinity of the melting point, the I_{VH} compound shifts to high frequencies by some 10 cm^{-1} compared to the I_{VV} compound.

Diethylamide. The change in the spectra of the νNH band of the liquid diethylamine differs significantly from that observed for the dimethylamine. On the one hand, the band corresponding to the free NH vibrator splits at high temperatures (Fig. 3) as a result of the existence of rotational isomers 4: at 416 K, the two compounds were measured at 3340 and 3327 cm^{-1} , the high-frequency band gradually weakening as the temperature was lowered. From this observation, we therefore conclude that the most stable thermodynamic isomer must be associated with the low-frequency band. Moreover, in the vicinity of the melting point, the free band is still large and the associated band appears at 3263 cm^{-1} . On the crystal spectrum, only one compound strongly shifted to the low frequencies appears (3205 cm^{-1} at 220 K), while

an NH/ND isotopic dilution effect at the same temperature indicates a shift towards high frequencies (3216 cm^{-1}).

For this compound, we therefore conclude that the effects of self-association are weak in the liquid phase, as the polymerization stage barely exceeds the dimer stage. Spectrum analysis of the corresponding ND compound appears more complex due to a resonance comparable to the one mentioned for dimethylamine. However, we find the main characters of the NH solid (Fig. 4): conformational equilibrium characterized by a duplication of the monomer band and a very pronounced shift of the polymer band in the transition to the crystalline state (2365 cm^{-1} 2391 cm^{-1}).

Pyrrrole. For the pyrrrole, we find results already discussed by Lautié.⁵ Between 300 and 200 K, the spectra of the liquid or glassy compounds have wide bands, replaced in the crystalline state by two fine lines due to an intermolecular coupling effect.

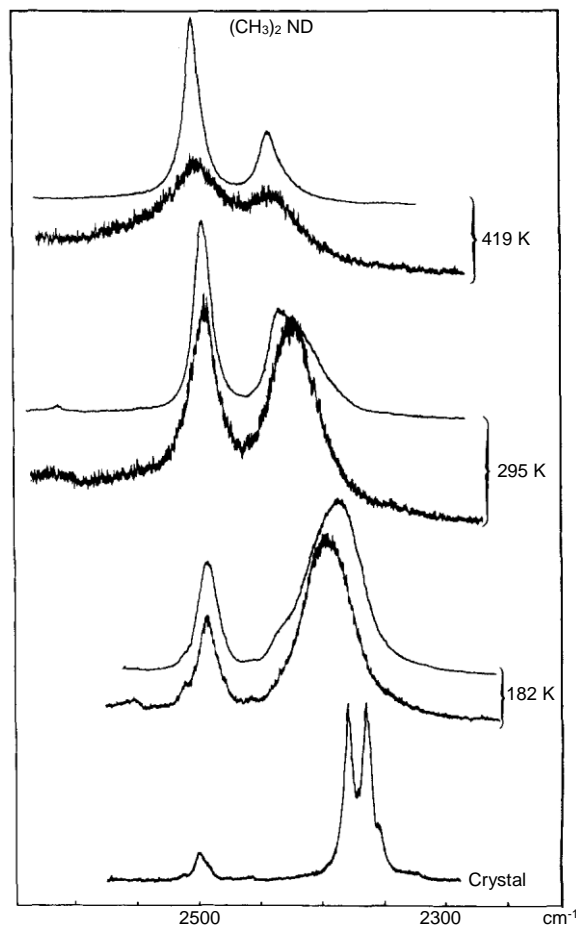


Figure 2. $(\text{CH}_3)_2\text{ND}$. Spectra I_{VV} and I_{VH} at different temperatures. The intensity of the I_{VH} compounds has increased fivefold. Spectral slit width 1.7 cm^{-1} .

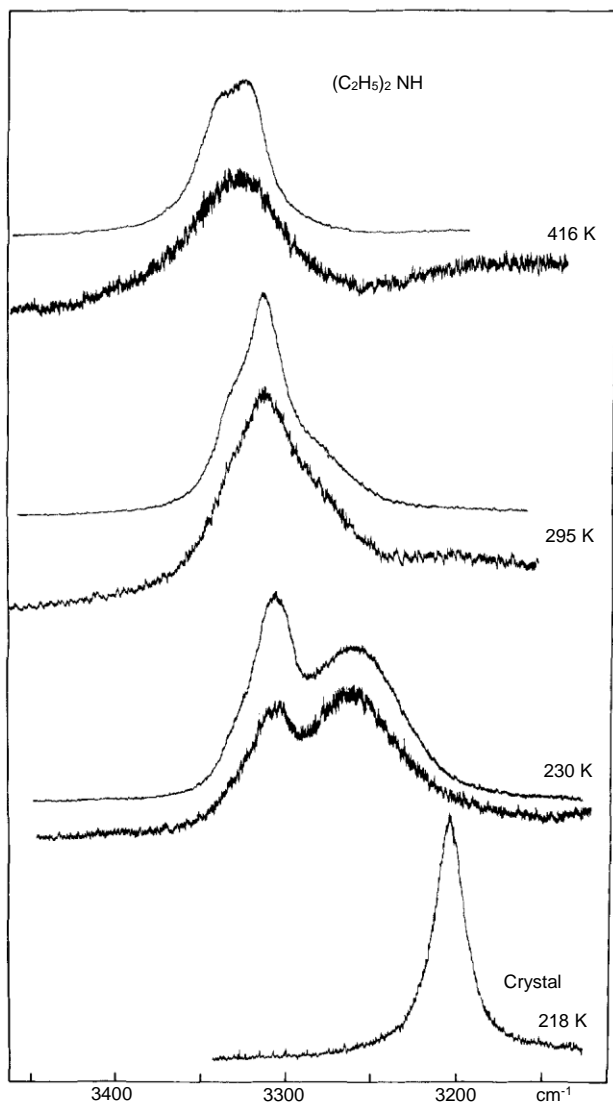


Figure 3. $(\text{C}_2\text{H}_5)_2\text{NH}$. Spectra I_{VV} and I_{VH} at different temperatures. The intensity of the I_{VH} compounds has been multiplied by 10 for the spectra at 416 and 295 K and by five for the spectrum at 230 K. Spectral slit width 3.0 cm^{-1} .

In our Raman study, we also observe that in the liquid or glassy state, the I_{VH} compound has shifted by 8 cm^{-1} at the maximum around the high frequencies in comparison to the I_{VV} compound (Fig. 5). As with the crystal, we associate this phenomenon with the existence of couplings between NH vibrators, associated with a short-range order in the so-called disordered phases.

Primary amines

The combination of methylamine and ethylamine and the structure of the corresponding νNH_2 bands have already been discussed at length by Wolff *et al.*⁶ based on infrared and Raman results.

Ethylamine. At high temperature (414 K), the two ν_a and ν_s bands are observed respectively at around 3387 and 3334 cm^{-1} (Fig. 6), and correspond to the NH_2 vibrators not engaged in hydrogen bonding. When the temperature drops to 196 K, the maximums of the two bands decrease, respectively, by 30 cm^{-1} for ν_a and 50 cm^{-1} for ν_s ; the band

corresponding to ν_s widens considerably and becomes dissymmetrical, due to a greater sensitivity to molecule association. In addition, a band appears around 3180 cm^{-1} , already observed by Wolff⁶ in absorption, and probably attributable to the harmonic of the vibration δNH_2 exalted by Fermi resonance with the vibration ν_s . In the crystalline state, four compounds appear at 3325 , 3265 , 3237 and 3179 cm^{-1} .

Methylamine. Similar spectra were obtained for methylamine in both the liquid and solid states. The crystal spectrum was interpreted⁶ taking into account the existence, proven by a crystallographic study,⁷ of two types of hydrogen bond and a Fermi resonance at level $2\delta\text{NH}_2$.

INTENSITY MEASUREMENTS OF THE νNH BANDS

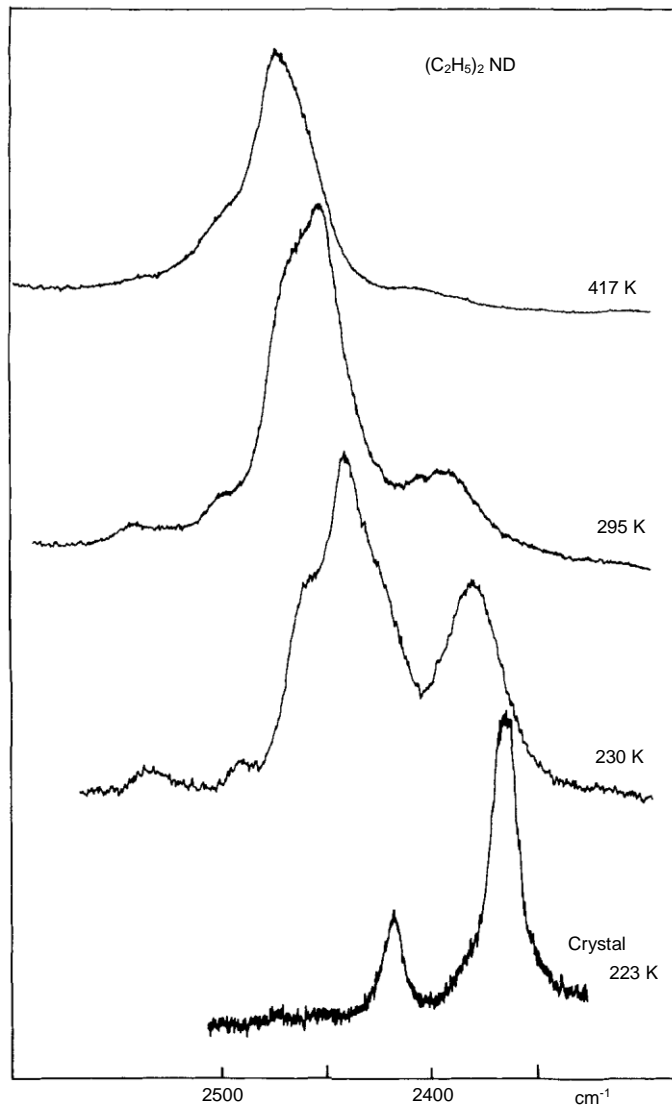


Figure 4. $(\text{C}_2\text{H}_5)_2\text{ND}$. Spectra I_{VV} at different temperatures. Spectral slit width 3.3 cm^{-1} .

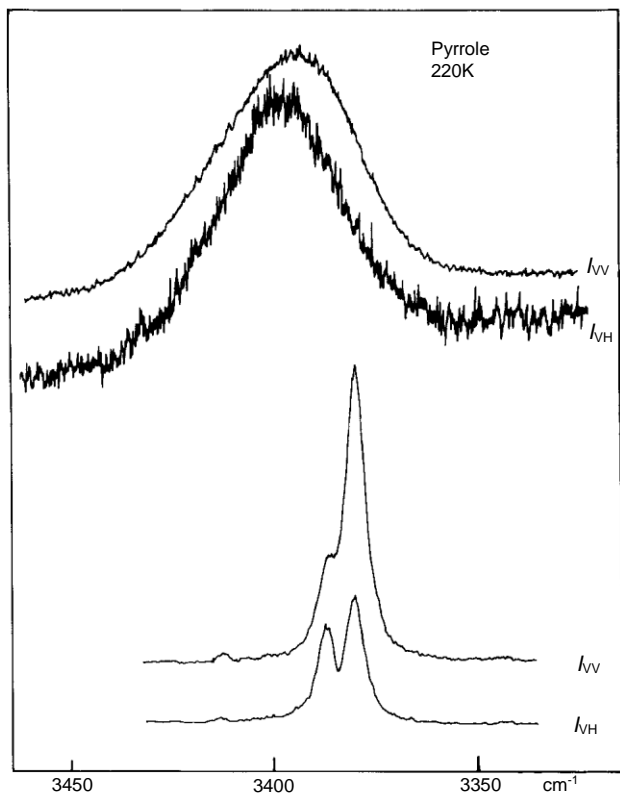


Figure 5. Comparison of the Raman spectra (I_{VV} and I_{VH}) of pyrrole in the glassy state and the crystal state at 220 K. For the glassy state, the intensity of the compound I_{VH} has increased fivefold. Spectral slit width 5.3 cm^{-1} .

As we did with the alcohols, here we studied the change in the depolarization ratio and the intensity of the amines' νNH bands according to their physical condition and, as a result, the state of self-association by hydrogen bond. Two types of measurements were carried out: on the one hand, cross-section and scattering activity measurements, with the compounds taken at ordinary temperature in the gaseous state, the liquid state or dissolved in CCl_4 , and, on the other, measurements of the relative intensity of the νNH bands in comparison to the νCH bands, according to temperature, with the compounds in a liquid state.

Relative intensity measurements on the liquid

Relative intensity measurements were carried out on the NH and ND dimethylamines and the NH diethylamine from the triple point to the vicinity of the critical point. For the dimethylamine, the CH band chosen for comparison was the low-frequency band ($\nu_5\text{C}_3$) located around 2780 cm^{-1} ; for the diethylamine, the comparison was made with the νCH solid as a whole between 2700 and 3000 cm^{-1} . Measurements of the νNH band's depolarization ratio were also carried out.

All the results are presented in Figs. 7 and 8. It is clear in all cases that the ratio of the $I_{\text{NH}}/I_{\text{CH}_3}$ intensities increases significantly from the critical point (low-density liquid, with the molecules not self-associated) to the triple point (self-associated molecules); at the same time, the depolarization ratio of the νNH bands increases from 0.13 to 0.19.

These results are very similar to those obtained for tert-Butyl alcohol.¹ They suggest that, assuming the intensity of the νCH bands is independent from the molecules' state of association, the intensity of the νNH bands increases through self-association.

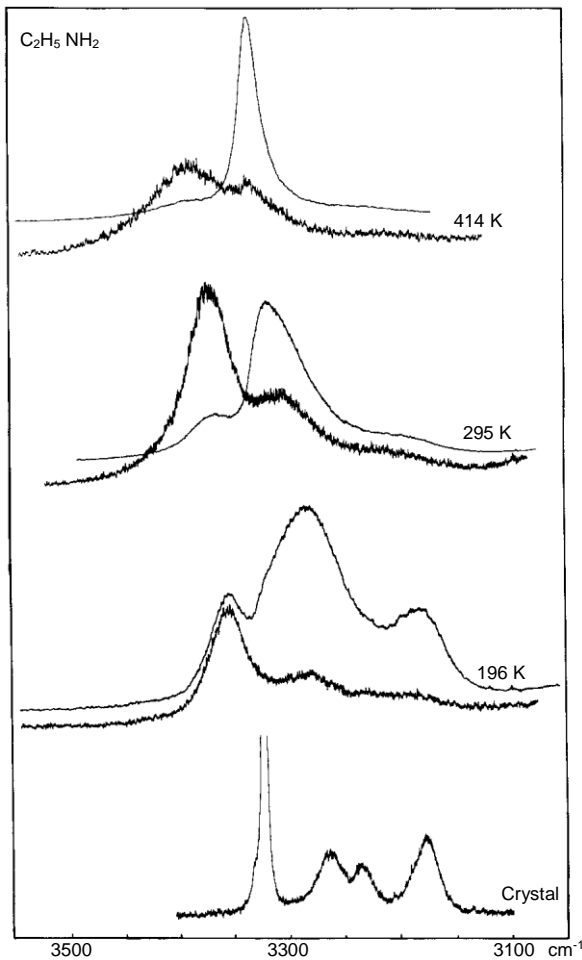


Figure 6. $\text{C}_2\text{H}_5\text{NH}_2$. Spectra I_{VV} and I_{VH} at different temperatures. The intensity of the I_{VV} compounds was multiplied by 10 at 414 K, by five at 295 K and by 2.5 at 196 K. Spectral slit width 3.0 cm^{-1} .

Scattering activity measurements

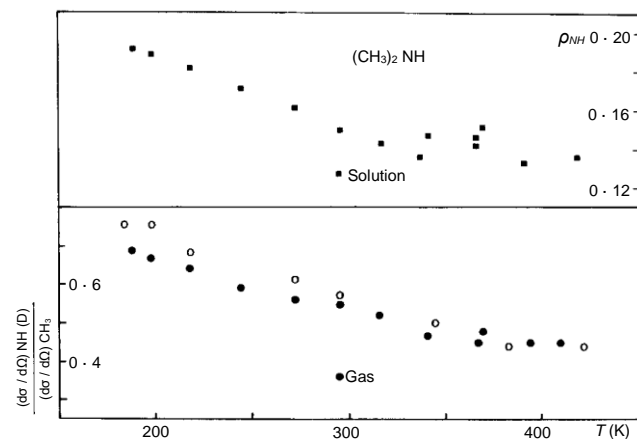


Figure 7. $(\text{CH}_3)_2\text{NH}(\text{D})$. Change according to the temperature of the depolarization ratio ρ_{NH} of the $\nu(\text{NH})$ band, and of the scattering cross-section ratio of the $\nu(\text{NH})$ [●] or $\nu(\text{ND})$ band [○] and of the $\nu_5\text{CH}_3$ BAND.

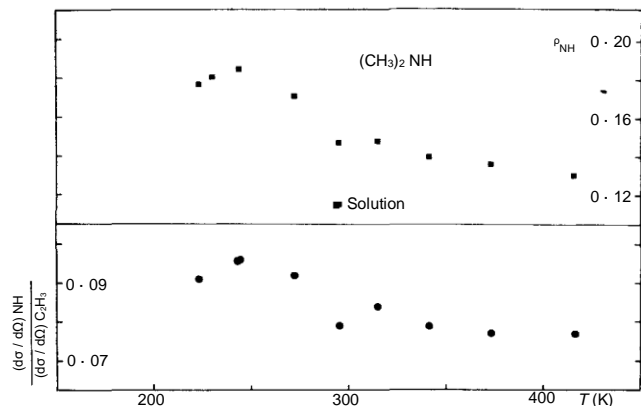


Figure 8. $(\text{C}_2\text{H}_5)_2\text{NH}$. Change according to the temperature of the depolarization ratio ρ_{NH} of the $\nu(\text{NH})$ band, and of the scattering cross-section ratio of the $\nu(\text{NH})$ band and of the $\nu(\text{C}_2\text{H}_5)$ solid.

The measurements of cross-section ($d\sigma/d\Omega$) and scattering activity (SA), already defined in reference 1, were carried out according to both internal and external reference techniques for the liquids and the solutions and according to the external reference technique for the gas. In the internal reference technique, we chose as a reference the band at 991 cm^{-1} of benzene introduced in small quantities into the sample and, in the external reference method, the same band of benzene or the ν_I band of CCl_4 . For the gas, the external reference band is the ν_I band of methane, whose intensity was determined beforehand by comparing it with the intensity of nitrogen.⁸

The internal reference measurement technique has been described previously.¹ The external reference technique is the same as the one described by Nestor and Lippincott.⁹ In both cases, to make any corrections, it is necessary to know the index of the medium. For the dilute CCl_4 solutions, the index chosen was the one for solvents; for the liquid methylamine, the index was not known at the temperature at which the experiment was conducted (295 K). We calculated it from the known values of the specific mass using the molecular refraction method.¹⁰ We were

able to verify, on cases in which the index was known (e.g., ethylamine), that this method enabled us to attain the liquid index quite accurately.

The intensity measurements were carried out not only on the νNH bands, but on the νCH bands as well, for comparison. In the case of the methylamine and the dimethylamine, the νCH bands considered were located around 2820 and $2,780\text{ cm}^{-1}$, respectively; except in the gaseous state, these bands were not perfectly insulated but were slightly overlapped with other, higher-frequency bands. To determine their surface, we made a graphic breakdown of the high-frequency wing, resulting in an error of a few percentage points. For the other amines (ethyl and diethylamine, pyrrole), we measured the intensity of the νCH solid as a whole.

All of the results are presented in Table 1, into which we have carried over the depolarization ratios, the cross-sections and the scattering activities, as well as the cross-section ratios in the liquid state and the dissolved state. The results presented are an average of 4-6 measurements, half of which were carried out in the internal reference and half in the external reference.

On reading this table, it appears that the intensities of the νCH bands vary little according to the physical state, while the intensities of the νNH bands change more significantly, except in the case of diethylamine, which in fact is hardly associated at 295 K. The most significant example is that of the pyrrole, highly self-associated in the liquid state, whose scattering activity increases by 50% through self-association. For the other amines, partially self-associated in the liquid state at 295 K, the increased intensity of NH or NH_2 bands is less marked from the solution to the liquid. However, the general trend of the results seems to confirm those obtained for the alcohols,¹ namely, that the intensity of the νXH Raman bands increases when $\text{X}-\text{H}\cdots\text{X}$ hydrogen bonds are formed.

This variation, which is accompanied by a large increase in the depolarization ratio, had been associated with a marked increase in the α'_1/α'_ρ ratio as a result of hydrogen bond formation,¹ α'_1 being the derivative of the polarizability of the XH bond along the axis of this bond

Table 1. Changes in the depolarization ratio intensity of the νNH band of some amines according to physical state at 295 K

		^a $(\text{CH}_3)_2\text{NH}$		$(\text{C}_2\text{H}_5)_2\text{NH}$		Pyrrole		C_3NH_2		$\text{C}_2\text{H}_5\text{NH}_2$	
		νNH	νCH_3	νNH	νCH	νNH	νCH	νNH_2	νCH_3	νNH_2	νCH
Gas	$\frac{d\sigma}{d\Omega} \times \frac{1}{L}$	1.0	3.0					1.6	0.74	1.6	8.1
	SA	3.9	8.8					6.5	2.2	6.3	25.3
CCl_4 solution	$\frac{\rho}{d\sigma} \times \frac{1}{L}$	0.13	0.03	0.12	0.17	0.12	0.25	0.14	0.01	0.13	0.17
	SA	1.15	2.2	1.2	14.7	1.2	4.4	1.7	1.0	2.0	7.7
Liquid	$\frac{\rho}{d\sigma} \times \frac{1}{L}$	0.15	0.03	0.15	0.17	0.20	0.28	0.13	0.01	0.16	0.17
	SA	1.5	2.7	1.3	16.7	1.9	4.5	2.4	1.1	2.8	9.3
(SA) liquid / (SA) solution		1.3	1.2	1.1	1.1	1.5	1.0	1.4	1.1	1.4	1.2

^a L refers to the internal field factor corresponding to each medium.¹ The scattering cross-sections $d\sigma/d\Omega$ are expressed in $10^{-30}\text{ cm}^2\text{ mol}^{-1}\text{ sr}^{-1}$ and the scattering activities SA in $10^{-7}\text{ cm}^4\text{ g}^{-1}\text{ mol}^{-1}$.

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