

Raman Spectroscopy of Alkali Metal-Ammonia Solutions

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A laser Raman spectrometer has been constructed which readily accepts a specially designed dewar assembly. After the resolution and polarization performance characteristics of the spectrometer were determined, polarization studies on liquid ammonia were undertaken. Depolarization ratios for the fundamental modes of ammonia are reported, and a doublet has been observed for the ν_2 band. Alkali metal-ammonia solutions in the concentration range $0-50 \times 10^{-4} M$ were studied. No scattering center attributed to the solvated electron was found, nor were the positions of the bands altered by the presence of the solute in this concentration region. The intensity of the scattered radiation was found to decrease with increasing metal concentration and has been attributed to the absorbance of these solutions. The Raman effect in F centers is discussed and compared to alkali metal-ammonia solutions.

Introduction

The nature of the species present in a very dilute metal-ammonia solution continues to be a matter of speculation. Numerous models have been proposed, but as yet no single theory is clearly superior. A discussion of the various models will not be attempted in this work because numerous review articles are available.¹ Copeland, Kestner, and Jortner² have proposed a model for localized excess electron states in ammonia, and this model has a particular bearing on the present work. According to Copeland, *et al.*, very dilute solutions may be described in terms of unassociated solvated cations and electrons. The electron is envisioned as existing in a cavity created by some number of preferentially oriented ammonia molecules.

The proposed model predicts a totally symmetric vibration in the ground state with a frequency given by

$$\nu = (1/2\pi)[K/\mu]^{1/2}$$

where K is $\frac{1}{2}(\partial^2 E_t / \partial R^2)_{R=R_0}$, and $\mu = Nm_{\text{NH}_3}$. E_t is the total energy of the ground state, R is the cavity radius, N is the number of solvent molecules in the primary solvation shell, and m_{NH_3} is the reduced mass of the ammonia molecule. Depending on the value of N and V_0 , the electronic energy of the quasifree electron state, the totally symmetric vibration is predicted to be between 25 and 60 cm^{-1} .

Rusch,³ applying the treatment of Klick and Schulman⁴ to metal-ammonia solutions, has suggested that the symmetric "breathing" mode may be in the 400- to 700- cm^{-1} region. These results were obtained using the formulation for the frequency of the "breathing" mode which is given by

$$\nu_g = (2kT/h)[W_{h/2}(\text{LT})/W_{h/2}(\text{HT})]^2$$

where ν_g is the frequency of the ground-state vibration, $W_{h/2}$ is the width at half-height of the absorption band, and LT and HT refer to the low- and high-temperature limits, respectively.

Regardless of the model used to explain the observed properties of these solutions, the effect of the metal on the solvent structure is of primary importance. Several investigators have addressed themselves to this problem, but at

present the results are incomplete and appear contradictory. Beckman and Pitzer,⁵ using external reflection techniques, studied the intermediate and concentrated solutions in the infrared. Burow and Lagowski,⁶ using internal reflection techniques, addressed themselves to much the same problem. Rusch,⁷ using transmission techniques, studied the effect of metal concentration on the 3300- cm^{-1} envelope of ammonia. The results of the aforementioned investigations are summarized in Table I.

In addition to the effect of metal on the solvent structure, the assignment of the Raman bands of liquid ammonia is contradictory and still speculative. It is not the purpose of this work to review all the vibrational data reported on ammonia; however, the Raman data available on liquid ammonia are summarized in Table II.⁸⁻¹⁶

Experimental Section

A laser Raman spectrometer was constructed from three basic components: (1) Control Laser Corporation Ar⁺ laser, (2) Spex 1401 double monochromator, and (3) Solid State Research photon-counting detection system. The spectrometer utilized the conventional 90° geometry and is shown schematically in Figure 1.

Radiation of appropriate frequency and intensity was focused on the sample cell (Figure 2) and the scattered radiation collected at right angles. Both the 4880- (50-350 mW) and the 4579-Å lines (maximum power 100 mW) were used in this work. The beam was focused to a diameter of approximately 0.2 mm at the sample cell.

The scattered radiation was collected and collimated with a conventional camera lens (55 mm $f/2$), passed through an analyzer, and focused on the entrance slit with a lens compatible with the f number of the monochromator. Prior to the slit assembly, a dove prism was used to rotate the image 90° (this rendered the image compatible with the vertical entrance slit), and a calcite wedge scrambler was inserted to remove the polarization dependence of the monochromator.

An SSRI photocounting detection system was employed with the Spex 1401 monochromator. This detection system incorporates a Bendix Channeltron photomultiplier tube which has a dark count of 10 counts/sec at room temperature.