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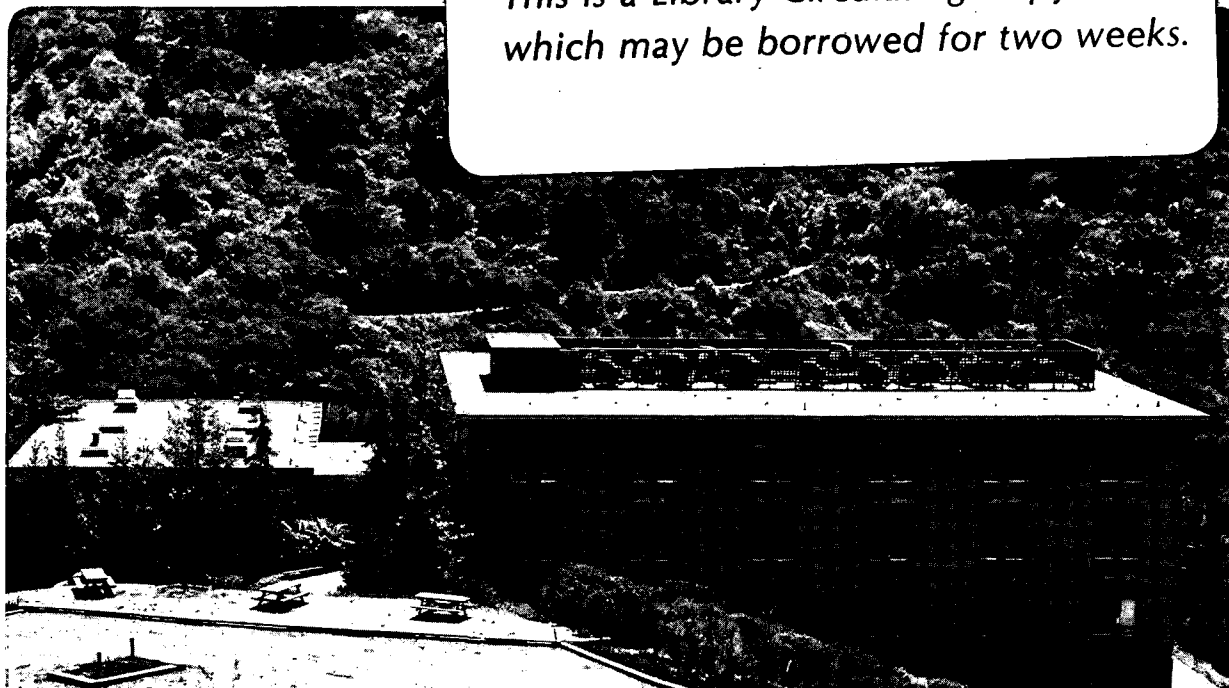
### Observation of Internal Rotation in the $N_4^+(NH_3)_4$ Ionic Cluster

J.M. Price, M.W. Crofton, and Y.T. Lee

April 1989

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OBSERVATION OF INTERNAL ROTATION IN THE  
 $\text{NH}_4^+(\text{NH}_3)_4$  IONIC CLUSTER

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Although there has been considerable progress in the spectroscopic study of molecular ions, the study of gas phase ionic clusters has been rather limited.<sup>1</sup> Pioneering work in this area was carried out by Schwarz in a series of low resolution ( $\approx 25 \text{ cm}^{-1}$ ) direct absorption experiments on the hydrated hydronium  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  ( $n=3$  to  $5$ )<sup>2</sup> and ammoniated ammonium  $\text{NH}_4^+(\text{NH}_3)_n$  ( $n=0$  to  $4$ )<sup>3</sup> clusters, using pulsed radiolysis. More recently, mass-selected ion beams have been employed to study the absorption spectra of ionic clusters either through vibrational predissociation or by using infrared multiphoton dissociation to detect the vibrational excitation. The hydrogen cluster ions  $\text{H}_3^+(\text{H}_2)_n$  ( $n=1$  to  $6$ )<sup>4</sup> as well as the hydrated hydronium ions ( $n=1$  to  $3$ )<sup>5</sup> were studied by these methods in our laboratory, using a tunable infrared laser source alone, or in conjunction with a high power  $\text{CO}_2$  laser. Liu and Lisy using a similar technique have recently obtained vibrational predissociation spectra for the  $\text{Cs}^+$  ion

solvated by 4-10 methanol molecules in the  $9.6\mu$  region using a cw  $\text{CO}_2$  laser.<sup>6</sup>

In this paper we present the infrared vibrational predissociation spectrum for the  $\text{NH}_4^+(\text{NH}_3)_4$  ionic cluster from 2600 to  $3500\text{ cm}^{-1}$ . Of the more interesting features observed in the spectrum are rotation-vibration transitions due to the nearly free internal rotation of the solvent ammonia molecules attached to the  $\text{NH}_4^+$  core. Internal rotation within an ionic cluster has never been observed before.

The experimental apparatus used in this work has been described previously.<sup>7</sup> Briefly, the solvated ammonium ions are produced in a molecular beam apparatus from a high pressure corona discharge ion source and subsequent supersonic expansion. The ion beam is skimmed at near thermal energies and passes through two regions of differential pumping with a kinetic energy of  $\approx 300\text{ eV}$  before being mass analyzed by a  $60^\circ$  sector magnet. The mass-selected beam is decelerated to about  $1\text{ eV}$ , and is directed into a radio frequency octopole ion trap whose axis is collinear with that of a pulsed infrared laser beam.

The tunable infrared laser pulses (Quanta Ray IR WEX,  $\approx 1\text{ cm}^{-1}$  spectral linewidth) induce vibrational excitation and subsequent predissociation by a two photon process. One photon excites the cluster to a discrete level, and a second photon of the same frequency excites the cluster over its dissociation limit. After  $1\text{ msec}$  trapping time from

excitation, the ions are allowed to leave the trap and are focused into a quadrupole mass spectrometer tuned to pass the cluster ion smaller than the parent by one solvent molecule. Standard ion counting techniques are used to monitor the number of daughter ions produced for each laser shot. By monitoring the predissociation products as a function of laser frequency the absorption spectrum of the parent ionic cluster is obtained. It should be noted that the intensity of the product signal need not accurately reflect the absorption cross section of the ion, but previous work shows no difference in the spectral profile when either a one or two color excitation scheme is used.

An infrared predissociation spectrum of the  $n=4$  ammoniated ammonium ion taken with  $\approx 1 \text{ cm}^{-1}$  resolution appears in figure 1a. In this spectrum four main features are observed, two which can be assigned to vibrations involving the  $\text{NH}_4^+$  core and two which can be assigned to the solvent  $\text{NH}_3$  molecules.

Both of the transitions involving the core species have been observed previously by Schwarz.<sup>3</sup> The structure of the  $\text{NH}_4^+(\text{NH}_3)_4$  cluster was shown to have  $T_d$  symmetry with each of the nitrogen atoms of the solvent molecules associated with one of the hydrogens of the  $\text{NH}_4^+$  ion core.<sup>3</sup> The dominant feature in the spectrum is a strong absorption centered at  $2867 \text{ cm}^{-1}$  which Schwarz assigned to the fundamental of the triply degenerate asymmetric stretch  $\nu_3$  of the  $\text{NH}_4^+$  ion.

Schwarz also observed a second core transition at  $3087 \text{ cm}^{-1}$  which he assigned to  $2\nu_4$ , the first overtone of the degenerate bending mode of the ion. The values obtained in this work ( $\nu_3 = 2868 \text{ cm}^{-1}$  and  $2\nu_4 = 3094 \text{ cm}^{-1}$ ) are in good agreement with those obtained by Schwarz and further support his conclusion that the structure of the cluster is tetrahedral.

Two previously unobserved transitions, due to the solvent  $\text{NH}_3$  molecules are seen in this study. The first at  $3243 \text{ cm}^{-1}$  is tentatively assigned to the overtone  $2\nu_4'$ , corresponding to the degenerate bending motion,  $2\nu_4$ , of free ammonia weakly perturbed from its equilibrium value of  $3219 \text{ cm}^{-1}$  <sup>8-10</sup> by association with the cluster. The second transition, whose central maximum occurs at  $3420 \text{ cm}^{-1}$  has been well assigned to the  $\nu_3'$  fundamental, analogous to  $\nu_3$ , the antisymmetric stretch of free ammonia which originates at  $3444 \text{ cm}^{-1}$ . <sup>8,9,10</sup> Due to the superior spectral resolution of the excitation source and the fact that the ions are rotationally colder ( $\approx 45 \text{ K}$  with respect to  $\text{K}$  and  $\approx 20 \text{ K}$  with respect to  $\text{J}$ ) than previous studies, these weaker transitions have been observed.

An expanded view of the spectrum for the  $\nu_3'$  band appears in figure 1b. The observed subbands for this transition have a characteristic spacing of  $\approx 12.5 \text{ cm}^{-1}$ , or roughly twice the  $A'$  rotational constant of ammonia about its  $C_3$  molecular axis ( $A_e = 6.32 \text{ cm}^{-1}$ ). <sup>10</sup> Since any rotation

involving the cluster as a whole would have a rotational spacing of  $< 0.2 \text{ cm}^{-1}$  based on the expected geometry of the cluster, it is clear that these features are due to an internal rotation of the  $\text{NH}_3$  subgroups. We assign this structure to a progression of Q-branches in the  $\nu_3'$  rotation-vibration transition resulting from a rotation of the ammonia subgroups about their local  $C_3$  axes. Further support for this assignment comes from the enhanced intensity of the  $^P Q_3$  and  $^R Q_3$  branches, resulting from the threefold symmetry of the solvent ammonias.

Assignments of the subbands appear in figure 1b. and employ the usual notation for a perpendicular band of a symmetric top.<sup>10</sup> (While not strictly correct for this case of internal rotation within a spherical top, the notation is convenient. The present situation may be approximately described as that of an ammonia attached perpendicularly to a wall along its  $C_3$  axis.) The apparent splitting of the subbands, most evident in the  $^P Q_1$  subband in this spectrum, may be due to vibrational coupling between the  $\text{NH}_3$  rotors. Vibrational coupling of this kind has been described by others in the analysis of the infrared spectrum of dimethylacetylene.<sup>11,12</sup> These workers have employed a formalism to generate theoretical spectra for this molecule which takes into account torsional barriers and vibrational coupling in its vibration-rotation spectrum.

In the case of dimethyl acetylene, the band contour of



the asymmetric stretch of the substituent methyl groups showed little variation from the spectrum calculated for freely rotating methyls. The spectrum for the n=4 ammoniated ammonium ion can also be modeled by freely rotating substituent groups nearly to the limit of experimental resolution. It is assumed that the barrier to internal rotation is comparable to that for dimethyl acetylene ( $< 10 \text{ cm}^{-1}$ )<sup>13</sup>. The splittings observed in the Q-branches resulting from vibration-vibration coupling in dimethyl acetylene are significantly larger than those observed in this work.

Systematic studies are now underway of the infrared spectroscopy of the series of ammoniated ammonium ions for n=1 to 10 solvent molecules.

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Figure Caption

Fig. 1. Infrared vibrational predissociation spectrum of  $\text{NH}_4^+(\text{NH}_3)_4$ . Signal is product  $\text{NH}_4^+(\text{NH}_3)_3$  counts.  
(a) Medium resolution spectrum. (b) Finer detail of the region around  $3420 \text{ cm}^{-1}$ .

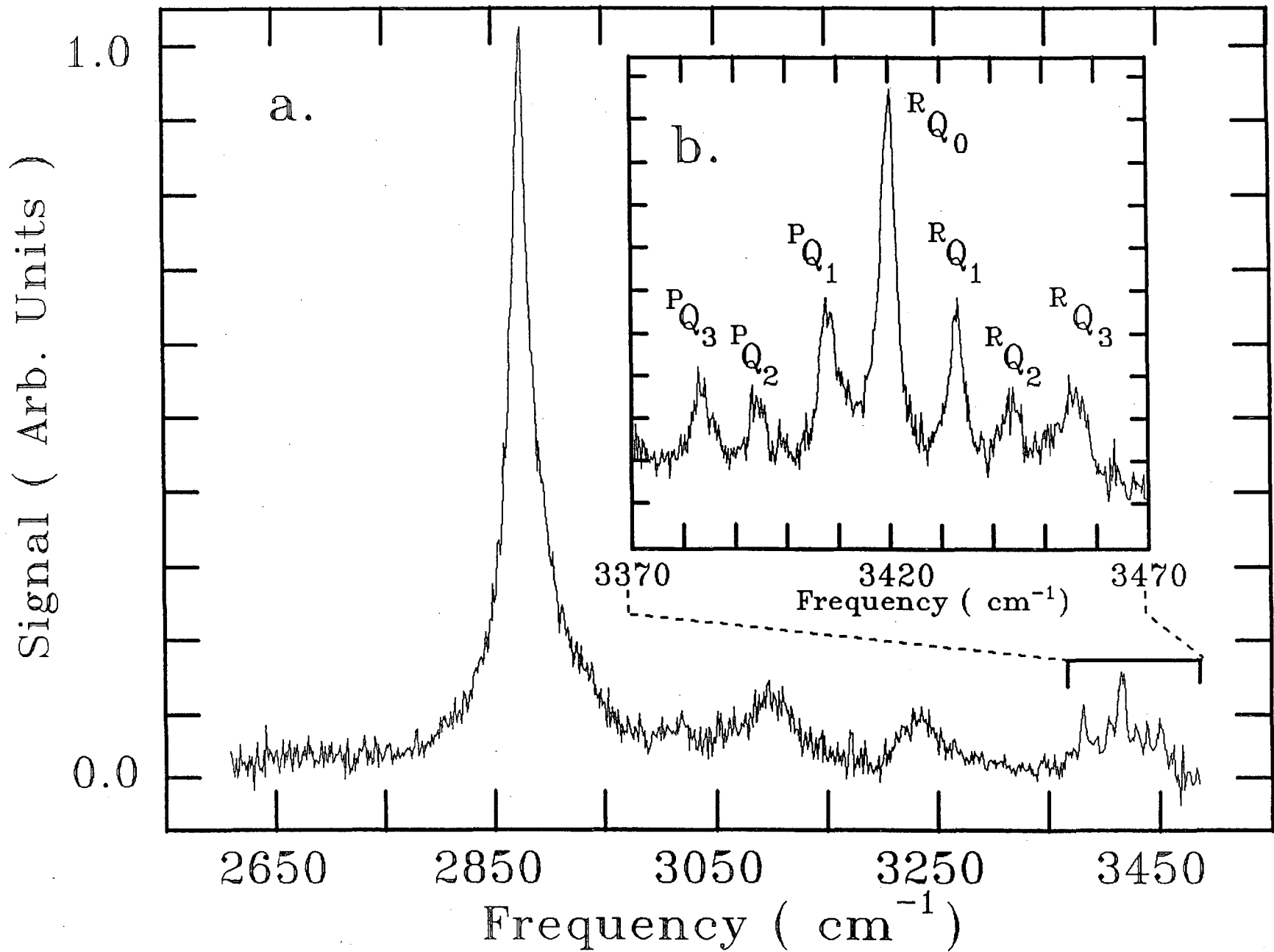


Fig. 1

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