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The ν_3 infrared spectrum of the He–NH₄⁺ complex

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Abstract

The mid-infrared spectrum of the ionic complex He–NH₄⁺ has been recorded in the vicinity of the triply degenerate ν_3 (t_2) vibration of the free ammonium ion. Apart from a small blue shift (≈ 0.7 cm⁻¹), the spectrum of the complex closely resembles that of the monomer. Ab initio calculations predict a vertex-bound minimum structure with an intermolecular well depth $D_e \approx 150$ cm⁻¹, a center-of-mass separation of $R_c \approx 3.17$ Å and barriers for internal rotation less than 30 cm⁻¹.

1. Introduction

Complexes containing tetrahedral molecules (e.g., CH₄, SiH₄, NH₄⁺) serve as relatively simple model systems for studying the spectroscopic manifestations of anisotropic intermolecular interactions. Among them, those involving a rare gas atom as a ligand have been studied most extensively, particularly in the region of the triply degenerate ν_3 vibration of the free monomers (Ar/Kr–CH₄ [1], Ar/Ne–SiH₄ [2–4], Ar/Kr–SiF₄ [5], Ar–NH₄⁺ [6]). According to the available theoretical models [7–9], a reasonable representation of the interaction between the rare gas atom and the tetrahedral molecule is attained by employing a potential involving a few parameters relating to the anisotropy of the interaction. The basic assumptions of these models can be summarized as follows. (i) The tetrahedral geometry of the monomer is not distorted upon complexation

with the rare gas atom. This allows the application of the point group T to describe the internal rotation leading to equivalent configurations. (ii) The intramolecular vibrational degrees of freedom as well as the end-over-end rotation of the complex can be separated in an adiabatic sense from the internal rotational levels of the tetrahedron. With these assumptions the number of parameters describing the anisotropy of the potential may be considerably reduced. Most significant are: (i) a *vibrational* anisotropy parameter V_2 which is correlated with the magnitude of the splitting of the triply degenerate ν_3 vibration (species t_2 in point group T_d) of the free tetrahedral monomer into two components ($e + a_1/C_{3v}$) on forming the complex with a C_{3v} equilibrium structure; (ii) *rotational* anisotropy parameters (V_3, V_4) that characterize the anisotropy of the intermolecular potential for internal rotation along paths between possible minimum structures (vertex-bound, face-bound, and side-bound geometries) of the complex. As expected, Ar–SiH₄ demonstrates a less isotropic potential ($V_2 \approx 1$ cm⁻¹, $V_3 \approx 60$ cm⁻¹ [2]) than Ne–SiH₄ ($V_2 \approx -1$ cm⁻¹, $V_3 \approx 28$ cm⁻¹ [4]) due to the larger polarizability of the rare gas. In

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turn, the ionic Ar-NH_4^+ complex ($V_2 \approx 90 \text{ cm}^{-1}$, $V_3 \approx 220 \text{ cm}^{-1}$ [6]) appears more rigid than Ar-SiH_4 . The He-NH_4^+ complex should provide an interesting intermediate case since it combines a charged core with a slightly polarizable ligand.

Spectroscopic studies on *neutral* van der Waals complexes are often complicated by strong interferences with overlapping absorptions of the ubiquitous monomer and other complexes formed under typical experimental conditions. For *ionic* complexes, mass selection and spectroscopic methods can be combined to circumvent this problem. Photoinduced dissociation of mass selected cluster ions in a tandem mass spectrometer provides unambiguous identification of the spectral carrier and also features high sensitivity due to the efficient detection for charged particles. In the present work infrared vibrational predissociation spectroscopy was employed to probe the spectrum of the He-NH_4^+ complex.

2. Experimental

Mid-infrared photofragmentation spectra of mass selected He-NH_4^+ complexes were recorded in the ν_3 region of NH_4^+ by monitoring the intensity of the photoproduct NH_4^+ as a function of the photon frequency. The experimental setup has been described [10–12]. He-NH_4^+ complexes were produced in a pulsed and skimmed supersonic expansion of He, NH_3 , and H_2 (ratio 1000:1:1, stagnation pressure 4–6 bar) crossed by 200 eV electrons. After mass selection in a first quadrupole mass filter, the He-NH_4^+ beam was exposed in an octopole ion guide to a counterpropagating IR laser pulse (5 ns) generated by an OPO laser system (bandwidth 0.02 cm^{-1}). Resonantly photoexcited ions undergo fragmentation when the energy of the absorbed photon exceeds the binding energy of the complex. Resulting photofragments were mass selected by a second quadrupole mass filter and detected with a Daly detector [13]. Wavelength calibration was accomplished by simultaneously recording an optoacoustic spectrum of NH_3 [14] and an etalon transmission signal (FSR = 0.13 cm^{-1}). Calibrated line positions have been corrected for a Doppler shift of $\approx +0.08 \text{ cm}^{-1}$ caused by the $6.0 \pm 0.5 \text{ eV}$ kinetic energy of ions approaching the radiation source.

3. Results and discussion

3.1. Experimental spectrum

Fig. 1a shows a portion of the experimental IR photodissociation spectrum of the He-NH_4^+ complex in the region of the triply degenerate ν_3 vibration (t_2) of the free ammonium ion. Observed transition energies are summarized in Table 1. The illustrated band is the only one observed between 3100 and 3500 cm^{-1} and consists of a series of regularly spaced peaks separated by $11.12 \pm 0.07 \text{ cm}^{-1}$, with decreasing intensities on either side of the central feature at 3343.19 cm^{-1} . The spacings are very close to the value of $B_0 + B_1 - 2B_1\xi_3 = 11.10 \text{ cm}^{-1}$ of free NH_4^+ [15]. The small blue shift of the most intense peak (3343.2 cm^{-1}) with respect to the free ammonium ion ν_3 transition origin (3342.35 cm^{-1} [15]) and the similarity in the rotational spacings suggest that neither the rotational nor the vibrational motion of the NH_4^+ ion is strongly affected upon the complexation with He. Further evidence for the relatively minor influence of the He on the NH_4^+ subunit is presented below.

First, the vibrational structure of the transition is considered. For a rigid proton bound complex, the triply degenerate ν_3 vibration (t_2/T_d) of the free monomer would be split into perpendicular and parallel components ($a_1 + e/C_{3v}$), both being IR allowed. The magnitude of the e/a_1 splitting and the relative intensities of these two bands can be correlated with the degree of vibrational anisotropy of the

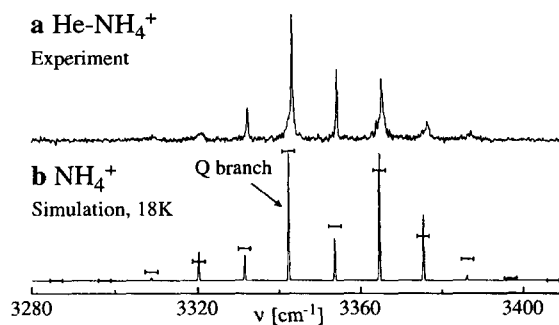


Fig. 1. (a) Vibrational predissociation spectrum of He-NH_4^+ in the region of the ν_3 vibration of free NH_4^+ . (b) Simulated IR spectrum of the ν_3 vibration of free NH_4^+ . For comparison, integrated intensities of the He-NH_4^+ transitions (from Fig. 1a) are indicated by bars.

Table 1
Assignment and line positions (in cm^{-1}) of the experimental spectrum of He-NH_4^+ (Fig. 1a). Line positions of NH_4^+ [15] are intensity-weighted averages over Coriolis splittings (Fig. 1b)

Transition	NH_4^+	He-NH_4^+
P(3)	3308.75	3309.15 ± 0.25
P(2)	20.19	20.95 ± 0.10
P(1)	31.44	32.26 ± 0.03
Q-branch	42.35	43.19 ± 0.03
R(0)	53.63	54.26 ± 0.03
R(1)	64.57	65.26 ± 0.03
R(2)	75.41	76.46 ± 0.10
R(3)	86.13	87.22 ± 0.16

intermolecular potential characterized by the parameter V_2 [7]. In the case of Ar-NH_4^+ , for which a V_2 value of $\approx 92 \text{ cm}^{-1}$ was estimated, the splitting is approximately 40 cm^{-1} , with transitions to both vibrational levels showing comparable intensities [6]. A further consequence of vibrational anisotropy is that the ν_1 (a_1/T_d) symmetric stretch vibration, which is dipole-forbidden for free NH_4^+ , becomes allowed (a_1/C_{3v}) upon attachment of the rare gas. For Ar-NH_4^+ this transition appears with appreciable intensity ($\approx 10\%$ of the allowed a_1/e components of the ν_3 vibration) reflecting the significant vibrational anisotropy [6]. Thus, for He-NH_4^+ at least three vibrational bands ($a_1 + a_1 + e/C_{3v}$) might be expected in the investigated spectral range. However, only a single perpendicular band is observed indicating a small vibrational anisotropy for the interaction.

Evidence for only slightly hindered internal rotation in He-NH_4^+ arises from examination of the band's rotational structure. For both rigid and semi-rigid atom – spherical top complexes an e-type band (C_{3v}) should be dominated by a series of prominent Q branches ($\Delta J = 0$) corresponding to $\Delta K = \pm 1$ transitions, quite similar in appearance to the structure shown in Fig. 1a. However, P and R branch transitions due to changes in the overall angular momentum ($\Delta J \pm 1$) should also be seen with appreciable intensity surrounding each of the Q-branch peaks. When the angular anisotropy of the intermolecular potential becomes much less than the rotational constant of the complex, the quantum numbers j and l (characterizing the internal rotation of NH_4^+ and the end-over-end rotation of the complex) be-

come appropriate. Transitions with $\Delta l = \pm 1$ (leading to the P and R branches) are forbidden in the free rotor limit and should be weak when the potential energy barriers for internal angular motion are small. The He-NH_4^+ spectrum lacks any discernible structure where the P and R branches might be expected, whereas in the case of Ar-NH_4^+ ($V_3 = 220 \text{ cm}^{-1}$) these branches are quite obvious [6].

A further effect of the V_3 rotational anisotropy is the splitting of the 4-fold degeneracy of each K level which, in addition to the usual 2-fold degeneracy for levels with $K \neq 0$, arises from the fact that the rare gas can be connected to the tetrahedron, either to the faces or to the vertices, in four equivalent ways. For finite anisotropy, tunneling between these equivalent positions results in splittings of the rovibrational transitions. The splitting is negligibly small for a rigid complex, does not exist in a free internal rotor system, and may follow a rather complicated pattern in intermediate cases [7]. This splitting is of the order of 1 cm^{-1} for Ar-NH_4^+ ($V_3 \approx 220 \text{ cm}^{-1}$ [6]), whereas for He-NH_4^+ no splitting is evident (Fig. 1a).

The absence of P and R branches and any resolvable Q-branch splittings indicates that not only the vibrational but also the rotational anisotropy is relatively small for the He-NH_4^+ complex. However from the widths of some of the Q branch features (around 0.5 cm^{-1}), which substantially exceed the laser resolution (0.02 cm^{-1}), it is evident that some hindrance to internal rotation may exist leading to unresolved substructure. However, the degree of anisotropy is obviously much smaller than in the case of the homologous Ar-NH_4^+ complex [6].

The resemblance of the He-NH_4^+ spectrum to that of the free ammonium ion is illustrated in Fig. 1 where the experimental spectrum of He-NH_4^+ is compared with a simulated spectrum of NH_4^+ . For the simulation the relative weights for the nuclear subpopulations corresponding to A, E, and T symmetries of the rotational levels were assumed to be 5, 2, and 9, corresponding to the high temperature limit. A Boltzmann rotational energy distribution was assumed whereby the energy of the lowest possible rotational level within each nuclear subpopulation (i.e. $j = 0, 1, 2$ levels for the states with A, T, E rotational symmetries) was taken as zero. Line strength factors were taken from Ref. [16]. The rotational temperature was varied to reproduce the

integrated intensities of the He–NH₄⁺ transitions. The best fit (Fig. 1b, convolution width 0.3 cm⁻¹) shows qualitative agreement with the experimental He–NH₄⁺ spectrum (Fig. 1a) and yields a temperature ($T = 18$ K) typical for ions formed in this ion source.

3.2. Ab initio calculations

The experimental spectrum of He–NH₄⁺ suggests that the angular anisotropy of the intermolecular potential is small. Unfortunately, the spectrum provides little information concerning other properties of the intermolecular potential, such as the equilibrium geometry and the intermolecular bond strength. To investigate these characteristics of the complex ab initio calculations were undertaken.

The calculations were conducted at the MP2 level using the Gaussian 94 package [17]. Three basis sets were employed [18]: (I) basis A (81 contracted Gaussians (cG)) consisted of a standard 6-311G** set for N, a 6-311++G(2d, 2p) set for H, and a Hunzinger 7s (4s contracted) augmented by three p functions (exponents 1.2, 0.4, 0.13) and one d function (0.25) for He; (II) basis B (117 cG) was constituted by an Ahlrich VTZP (10s,6p,1d) → [6s,3p,1d] contraction augmented with 1s (0.0576), 1p (0.0491) and 1d (0.151) functions for N, an Ahlrich VTZP (5s,1p,1d) → [3s,1p,1d] contraction augmented by 1s (0.02526) and 1p (0.102) functions on H, and the same functions for He as in basis A; (III) basis set C (161 cG) was composed of basis B plus two f functions on N (1.093, 0.364) and one 1d function

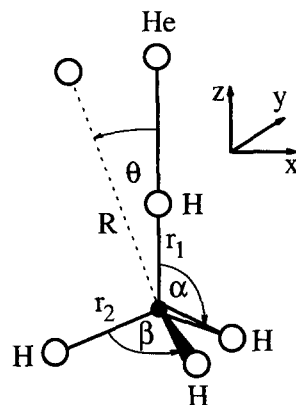


Fig. 2. Coordinate system for He–NH₄⁺.

(0.247) on H. All calculations for the complex were corrected for basis set superposition error.

First, minimum energy structures were calculated allowing all coordinates to relax (Table 2). The proton-bound structure ($\theta = 0^\circ$) was found to be the global minimum for all basis sets, with a radial well depth of $D_e \approx 150$ cm⁻¹ and an equilibrium intermolecular separation of $R = 3.17$ Å (see Fig. 2 for the coordinate system). As expected, the complexation has little effect on the monomer geometry. For the vertex-bound minimum, r_1 increases somewhat (0.0001 Å), while r_2 decreases, reflecting a slight tendency for proton transfer from NH₃ to He. The angle α increases a little, while β decreases correspondingly. Analysis of the harmonic molecular vibrational frequencies for the global minimum structure of He–NH₄⁺ indicate that the complexation

Table 2

Parameters for the global minimum structures of NH₄⁺ and He–NH₄⁺ obtained from ab initio calculations using various basis sets

	Basis A		Basis B		Basis C		Exp. ^a NH ₄ ⁺
	NH ₄ ⁺	He–NH ₄ ⁺	NH ₄ ⁺	He–NH ₄ ⁺	NH ₄ ⁺	He–NH ₄ ⁺	
R_e (Å)	–	3.20	–	3.20	–	3.17	–
θ (°)	–	0	–	0	–	0	–
α (°)	109.47	109.50	109.47	109.49	109.47	109.49	109.47
β (°)	109.47	109.44	109.47	109.45	109.47	109.45	109.47
r_1 (Å)	1.0204	1.0205	1.0186	1.0187	1.0210	1.0211	1.0208
r_2 (Å)	1.0204	1.0203	1.0186	1.0184	1.0210	1.0209	1.0208
D_e (cm ⁻¹)	–	140	–	140	–	147	–

^a Ref. [15].

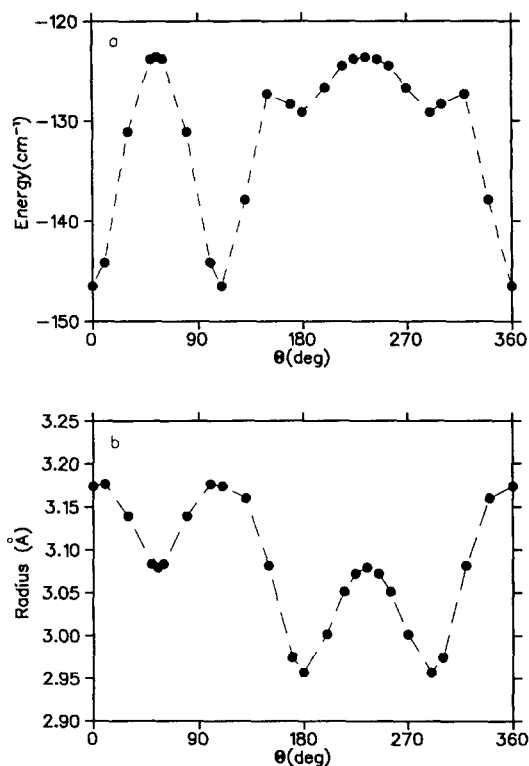


Fig. 3. Ab initio D_e (a) and R_e (b) values for the 1-D intermolecular radial potential of He-NH₄⁺ as a function of the angle θ .

induced frequency shifts and splittings are small (of the order of 1 cm⁻¹) for all normal modes.

To investigate the three-dimensional intermolecular potential energy surface in more detail, one-dimensional radial potentials were constructed for different angles θ by calculating several points (MP2, basis set C) along the intermolecular radial coordinate R whereby the NH₄⁺ structure was kept frozen. Variation of θ in the xz plane samples all important configurations. D_e and R_e values obtained for the radial potentials as a function of θ are plotted in Fig. 3. The results can be summarized as follows. The vertex-bound structure ($\theta = 0^\circ$) corresponds to the global minimum with a well depth of 147 cm⁻¹ and an intermolecular bond length of 3.17 Å. By increasing θ , the side-bound structure ($\theta = 54^\circ$, $D_e = 124$

cm⁻¹) is reached, representing the transition state into another vertex-bound geometry ($\theta = 109^\circ$). Further increase in θ leads to the face-bound structure, which is in fact a local minimum ($\theta = 180^\circ$, $D_e = 130$ cm⁻¹). Due to symmetry, the rest of the θ range is redundant, and one reaches the starting point $\theta = 0^\circ$ via another side-bound saddle and face-bound minimum. The barrier between two vertex-bound minima is less than 25 cm⁻¹, i.e. the angular anisotropy of the potential is relatively small (see Fig. 3a). The angular potential near the global minimum is very narrow, which together with the light mass of He tends to push the zero-point level of the intermolecular bending vibrations up to higher energies. Whether the zero-point energy is below or above the barrier for internal rotation is difficult to determine without solving the Schrödinger equation in all three intermolecular coordinates. In particular, angular-radial coupling seems to be important for this complex as can be seen from Fig. 3b. The ab initio results demonstrate a significant variation of R_e as a function of θ . The local minimum with the face-bound structure possesses the shortest bond length ($R_e = 2.96$ Å) whereas for the global minimum, the vertex-bound geometry, it is somewhat longer ($R_e = 3.17$ Å). While charge-induced dipole interactions would seem to favour the face-bound structure, the vertex-bound form is consistent with the preference for the proton to form linear bridges in these types of complexes [11,19,20].

Ab initio calculations performed on a similar level for Ar-NH₄⁺ show that for this complex the vertex-bound structure is also the global minimum [21]. Due to the larger polarizability of Ar, the well depth is significantly larger ($D_e = 470$ cm⁻¹) than for He-NH₄⁺. In addition, the barrier for internal motion between two vertex-bound minima via a side-bound saddle is substantially higher (about 200 cm⁻¹) with the effect of localizing the complex in a C_{3v} structure with a small probability for tunneling between vertices [6]. The weaker intermolecular interaction in He-NH₄⁺, together with the smaller van der Waals radius of He compared to Ar, leads to comparable intermolecular separations between the rare gas and NH₄⁺ in He/Ar-NH₄⁺. In contrast to the ionic He/Ar-NH₄⁺ systems, the related neutral Ar-SiH₄ complex seems to possess a face-bound global minimum [2].

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