

Observation of the infrared spectrum of the ν_3 band of the argon–ammonium ionic complex

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Abstract

The infrared spectrum of the rare gas–tetrahedral molecule ionic complex Ar-NH_4^+ has been detected. In the region of the ν_3 (t_2) triply degenerate vibration of the NH_4^+ monomer, a parallel and a perpendicular band are observed. Tunnelling splittings of the Q branches of the latter band are attributed to substantially hindered internal rotation of the NH_4^+ unit. A recently developed model of atom-spherical top complexes is applied to estimate anisotropic terms in the intermolecular potential; both the vibrational anisotropy of the order of 90 cm^{-1} and the rotational anisotropy $\approx 220 \text{ cm}^{-1}$ are substantial.

1. Introduction

Despite their relative simplicity, atom-spherical top van der Waal's complexes have been little studied. The observation and analysis of the spectrum of the Ar-SiH_4 complex [1] in the region of the silane ν_3 (t_2) vibration represents the first complete account of such a complex. The theory of vibration–rotation states of internally rotating atom-spherical top complexes has been considered by Hutson and Thornley [2], and by Randall et al. [3]. Randall et al. developed a model for the energy levels of a rare gas–tetrahedral molecule complex bound by an anisotropic intermolecular potential. In this model,

zero rotational anisotropy corresponds to a freely internally rotating spherical top, while a high anisotropy has the effect of ‘locking’ the complex into a rigid (symmetric top) geometry. For the Ar-SiH_4 complex [1], the vibrational anisotropy, responsible for lifting the threefold degeneracy of the ν_3 (t_2) monomer vibration was observed to be small ($\approx 1 \text{ cm}^{-1}$) while the rotational anisotropy, V_3 , was larger ($\approx 90 \text{ cm}^{-1}$). However, the SiH_4 unit still undergoes two-dimensional internal rotation within the complex.

Other neutral van der Waals molecules containing spherical top molecules have also recently been observed. Infrared spectra of methane-containing complexes Ar-CH_4 , Kr-CH_4 , $\text{H}_2\text{-CH}_4$ and $\text{D}_2\text{-CH}_4$ were reported by McKellar [4] but their structure has not yet been analysed. Infrared spectra of the ν_3 mode of the complexes Ar-SiF_4 and Kr-SiF_4 have

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recently been reported [5]; no splitting due to internal motion was observed. The recently observed complex Ne–SiH₄ [6] appears to show even weaker intermolecular interaction than the Ar–SiH₄ complex. On the other hand, substantial hindering of the internal rotation can occur if the rare gas atom is replaced by a ligand capable of forming strong hydrogen bonds to the tetrahedral molecule core. Thus, microwave spectra of the CH₄–HCN [7], CH₄–HF [8], CH₄–HCl [8,9] and CH₄–HBr [10] complexes show that, while the HCl, HBr and HCN complexes apparently undergo internal rotation, the interaction in the HF complex is of the two-centre type, involving two hydrogen bonds, and the internal rotation is effectively quenched.

The Ar–NH₄⁺ complex represents the first ionic tetrahedral molecule–rare gas complex to be the object of spectroscopic attention, and analysis of its ν_3 mid-infrared spectrum within the framework of the model of Randall et al. [3] provides us with an opportunity to compare the intermolecular interactions in related neutral and ionic systems. Fortunately, our analysis is expedited by the fact that the infrared spectrum of the triply degenerate mode ν_3 of the NH₄⁺ monomer has been thoroughly studied by difference frequency [11,12] and colour centre laser spectroscopy [13,14]. While it is anticipated that, due to the charge-induced dipole interaction, the angle-averaged radial intermolecular bond in Ar–NH₄⁺ should be substantially stronger than in the corresponding neutral complexes (rare gas atoms bound to methane or silane molecules), the nature of the anisotropic part of the intermolecular potential is less certain. Perhaps significantly, analysis of the spectra of other ionic proton-bound rare-gas-containing complexes such as Ar–H₃⁺ [15], He–HN₂⁺ [16], Ar–HCO⁺ [17] and H₂–HCO⁺ [18] indicates that the minimum energy geometry is one where the excess proton is best shared by the contributing moieties, and that the intermolecular potential may be quite anisotropic.

2. Experimental

Mid-infrared spectra of mass-selected Ar–NH₄⁺ complexes were obtained in a tandem mass spectrometer by monitoring their photo-induced vibra-

tional predissociation into NH₄⁺ and Ar. The arrangement has been described in detail in several publications [17–19]. Briefly, Ar–NH₄⁺ was produced by crossing a pulsed supersonic expansion of NH₃, H₂, and Ar (mixing ratio 1:4:60, 5 bar backing pressure) with 200 eV electrons emitted from two filaments positioned near the nozzle orifice. After mass selection in a first quadrupole, the Ar–NH₄⁺ packet is overlapped in an octopole ion guide with a collinear IR pulse generated by a commercial optical parametric oscillator system (pulse length 3.5 ns, spectral resolution 0.02 cm⁻¹). Resulting photofragment NH₄⁺ ions are mass-filtered by a second quadrupole and detected by a Daly scintillation detector [20]. Calibration was accomplished by simultaneously recording optoacoustic spectra of NH₃ [21]. The parent ions pass through the octopole with a kinetic energy of 3.0 ± 0.5 eV causing a Doppler shift of roughly +0.032 cm⁻¹ and a contribution to the line width of 0.006 cm⁻¹ (at 3350 cm⁻¹).

3. Interpretation of the spectra

Fig. 1 shows the mid-infrared spectrum of the Ar–NH₄⁺ ionic complex recorded between 3280 and 3420 cm⁻¹. The ν_3 (t_2) vibrational frequency of the NH₄⁺ monomer is 3343.1399 cm⁻¹ [12]. Thus in the

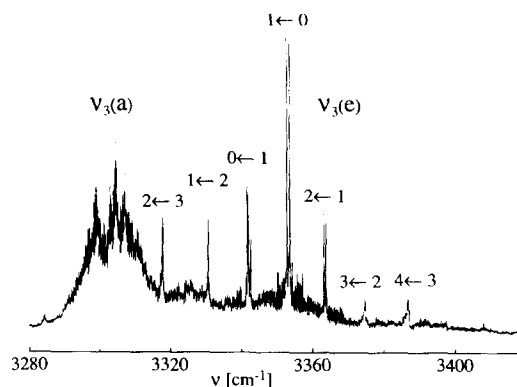


Fig. 1. The mid-infrared spectrum of the Ar–NH₄⁺ complex, in the vicinity of the ν_3 (t_2) mode of the NH₄⁺ monomer, recorded by monitoring the NH₄⁺ product of photo-induced vibrational predissociation of mass-selected Ar–NH₄⁺ ionic complexes. Parallel ($\Delta K = 0$) and perpendicular ($\Delta K = \pm 1$) features are apparent in the spectra.

region of the ν_3 mode of the monomer, the spectrum of the Ar–NH₄⁺ complex shows what is apparently a parallel (≈ 3300 cm⁻¹) and a perpendicular (≈ 3355 cm⁻¹) band system of a symmetric top molecule. This is attributed to the resolution of the triply degenerate ν_3 monomer mode into a-type and e-type vibrational modes as a result of a substantial vibrational anisotropy term V_2 in the intermolecular potential [3]. Similar behaviour was recently observed for the Ar–SiF₄ and Kr–SiF₄ complexes [5].

The parallel band system, whilst mainly unresolved, shows three features consistent with a P, Q, R branch structure. The perpendicular band system, extending from 3317 to 3410 cm⁻¹ comprises a number of Q branches separated by ≈ 11.3 cm⁻¹, surrounded by a dense, but resolved P and R branch rotational structure. It closely resembles the pattern [22] of a perpendicular band of a symmetric top molecule with the prolate symmetric top rotational constants $A \gg B$, and a vibrational angular momentum $\zeta \sim 0$. This characteristic pattern has a series of prominent $\Delta K = -1$ and $\Delta K = +1$ Q branches with a spacing $\approx 2A$. Hence, the observed spacing of 11.3 cm⁻¹ is consistent with the rotational con-

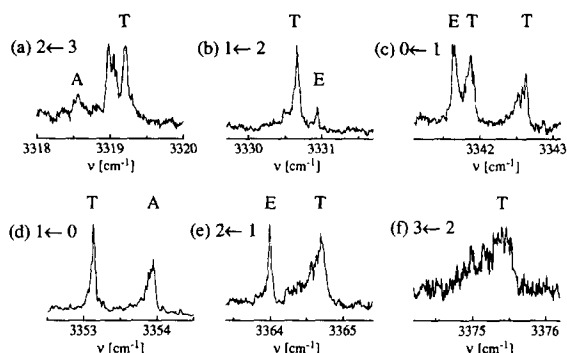


Fig. 2. The fine structure of a number of $K' \leftarrow K''$ subband Q branches of the perpendicular transition. The symmetries (in the T point group – see text) are indicated for each component: (a) $K' = 2 \leftarrow K'' = 3$, (b) $K' = 1 \leftarrow K'' = 2$, (c) $K' = 0 \leftarrow K'' = 1$, (d) $K' = 1 \leftarrow K'' = 0$, (e) $K' = 2 \leftarrow K'' = 1$, (f) $K' = 3 \leftarrow K'' = 2$.

stant of the NH₄⁺ monomer [12], $b_3 = 5.8764$ cm⁻¹. There is no zero gap between the $\Delta K = +1$ and $\Delta K = -1$ branches, and the Hönl–London factors decrease steadily with K , rather than go through a maximum, so that the overall effect is of a single branch appearance with one maximum of intensity only [22]. Hence, the strong feature at ≈ 3353 cm⁻¹ is assigned as the Q branch of the $K' = 1 \leftarrow K'' = 0$ subband; the other assignments are as given in Table 1.

Closer examination shows that each of the K subband Q branches is split into two or more components. This is shown in Fig. 2 for the three most intense $\Delta K = -1$ Q branches and the three most intense $\Delta K = +1$ Q branches. Whilst the $K = 1 \leftarrow 0$ and $2 \leftarrow 1$ Q branches show two components, the $K = 3 \leftarrow 2$ Q branch is a single, much broader feature, as are the higher K , $\Delta K = +1$ subbands. In contrast, the $K = 0 \leftarrow 1$ subband Q branch clearly shows three major components, whilst the $K = 1 \leftarrow 2$ subband has two.

This internal structure of the Q branches is interpreted as a tunnelling splitting of a substantially hindered internal rotation, between four equivalent positions, of the NH₄⁺ unit within the Ar–NH₄⁺ complex. The model derived for the energy levels of a rare gas-tetrahedral molecule complex by Howard and co-workers [3] has been applied to simulate the splittings of the K subband Q branches.

Table 1

Assignment of the sub-structure of the K subband Q branches, and results of a fit (ν_{calc}) to a hindered rotor model

Subband $K' \leftarrow K''$	Symmetry T group	ν_{obs} (cm ⁻¹)	ν_{calc} (cm ⁻¹)	Δ (cm ⁻¹)
2 ← 3	A	3318.59	3318.25	+0.34
	T	3319.25	3319.17	+0.08
1 ← 2	T	3330.66	3330.45	+0.21
	E	3330.95	3331.10	-0.15
0 ← 1	E	3341.69	3341.50	+0.19
	T	3341.90	3341.89	+0.01
	T	3342.65	3342.61	+0.04
1 ← 0	T	3353.18	3353.19	-0.01
	A	3353.98	3354.06	-0.08
2 ← 1	E	3364.07	3364.13	-0.06
	T	3364.75	3364.95	-0.20
3 ← 2	T	3375.39	3375.76	-0.37
0 ← 0 ^a	T	3305.00	3304.99	+0.04

^a As noted in the text, one $\Delta K = 0$ transition must be included in the fit.

4. Calculating the hindered rotor energy level pattern

The tetrahedral monomer is assumed to be undistorted upon complexation. Thus its energy levels, labelled by the rotational quantum numbers j and k are given by a standard spherical top Hamiltonian [23], H_{mon} . In addition, much of the original T_d point group symmetry is retained; tunnelling of the undistorted tetrahedral molecule between four equivalent geometries (which involve coordination of the rare gas atom to either the vertices or faces of the tetrahedron) in the complex leads to the adoption of the point group T, which consists of just the pure rotations belonging to the full tetrahedral point group T_d . The T point group contains the irreducible representations A, E and T.

The Hamiltonian for the whole system is [3]

$$H = \frac{\hbar^2}{2\mu} \left(\frac{(J-j)^2}{R^2} - \frac{\partial^2}{\partial R^2} \right) + H_{\text{mon}} + V, \quad (1)$$

where R is the distance from the centre of mass of the tetrahedral molecule to the rare gas atom, and μ is the reduced mass of the complex. J is the total angular momentum of the complex; its projection onto the intermolecular axis is K . Thus the first two terms of the Hamiltonian describe, respectively, the ‘end over end’ rotational motion, and the stretching motion of a pseudo-diatomic complex of bond length R . It is assumed that the rotation and intermolecular stretching motion of the complex is separable from the rest of the Hamiltonian [3]. The energy levels for end over end rotation are a simple power series [1]

$$F(J, K) = B[J(J+1) - K^2] - D_J[J(J+1) - K^2]^2 \quad (2)$$

in $J(J+1) - K^2$ rather than the more usual $J(J+1)$. The rotational constant for the complex, B , the expectation value of $\hbar^2/2\mu R^2$, will be much smaller than that of the NH_4^+ monomer, b . The selection rule $\Delta J = 0, \pm 1$ gives rise to familiar P, Q and R branches in the spectra. The $\Delta K = 0$ and $\Delta K = \pm 1$ transitions may be resolved into parallel and perpendicular band systems, as is observed for Ar-NH_4^+ (see Fig. 1), or alternatively these bands may overlap, as was observed for the Ar-SiH_4 complex [1];

this is dependent on terms in the intermolecular potential.

In Eq. (1), the term V is the intermolecular potential, a function of all the internal coordinates of the system. The potential V must possess the overall tetrahedral symmetry of the problem; its components must be invariant under all symmetry operations of the T point group. It has been shown [3] that the three leading non-zero anisotropic contributions to the intermolecular potential are:

(i) A vibrational anisotropy, V_2 , that is present only for the degenerate modes ν_3 or ν_4 of the monomer, and is responsible for lifting their three-fold degeneracy.

(ii) A rotational anisotropy, V_3 , whose effect upon the energy levels of the complex is such that only the magnitude and not the sign of V_3 can be determined. A positive V_3 term would correspond to the Ar atom coordinating to a face of the NH_4^+ tetrahedron, a negative V_3 term to coordination to a vertex of the tetrahedron.

(iii) Another rotational anisotropy, V_4 . A negative value of V_4 would correspond to coordination of the Ar atom to the midpoint of an edge of the NH_4^+ tetrahedron.

In order to simulate the splittings of the Q branches that are apparent in Fig. 2, the end-over-end rotation of the complex is for the moment neglected. Using $b_3 = 5.8764 \text{ cm}^{-1}$, $\zeta_3 = 0.06038$ and other parameters for the NH_4^+ monomer determined by Crofton and Oka [12], a number of simulations of the tetrahedral splitting pattern were made for a wide range of V_2, V_3 and V_4 parameters. It was immediately apparent that the V_2 (vibrational) parameter was not significantly correlated to the other two, and that its value of $\approx 90 \text{ cm}^{-1}$ is determined solely by the extent of separation of the parallel and perpendicular bands. A value of $V_3 \approx 200 \text{ cm}^{-1}$ gave a simulation with the general appearance of figure 1; widely spaced K subband Q branches, with a smaller, $\approx 0.5 \text{ cm}^{-1}$, splitting into the correct number of components, as shown in Fig. 2. In contrast high positive or negative values of V_4 gave totally different sets of patterns inappropriate to the observed spectra. The values $V_2 \approx 90 \text{ cm}^{-1}$ and $V_3 \approx 220 \text{ cm}^{-1}$ seem to be unique in reproducing the observed spectra. This led to the assignment of the K subband Q branch components to either A, E or T symmetry transitions, as

indicated in Table 1 and in Fig. 2. The program correctly predicts the observation of two components for the K $1 \leftarrow 0$ and $2 \leftarrow 1$ subbands, whilst the K $0 \leftarrow 1$ subband has three intense transitions, of symmetry E, T and T. The only discrepancy is in Fig. 2a, where the K $2 \leftarrow 3$ subband is predicted as having two, not three components. The transitions, of A and T symmetry, fit best with the features at 3318.59 and 3319.25 cm^{-1} , whilst the intervening feature at $\approx 3319.0 \text{ cm}^{-1}$ is assumed to be an interloper.

Using the Q branch assignments shown in Table 1, a least-squares fit to the observed maxima of the Q branches was performed, in which the anisotropy parameters V_2 and V_3 were floated. In addition, the purely vibrational origin, ν_0 , for the ν_3 mode of the complex must be floated. The results of this fit are shown in Table 1 as ν_{calc} ; the standard deviation was 0.20 cm^{-1} . The determined parameters for this fit are shown in Table 2. It should be noted that a single parallel band ($\Delta K = 0$) transition must be included in the least-squares fit, otherwise the V_2 parameter is completely correlated with ν_0 . The central parallel band feature was measured as 3305.00 cm^{-1} , and the K $0 \leftarrow 0$ T symmetry transition assigned to this frequency as shown in Table 1. This effectively fixes the separation of the parallel and perpendicular bands, and hence V_2 . Simulation of the parallel band structure showed this to be a reasonable assignment, and V_2 is not overly sensitive to the exact value of this transition. A simulation of the tunnelling splitting pattern (neglecting end over end rotational structure) using the parameters of Table 2 is shown in Fig. 3. It assumes a rotational temperature of 60 K and nuclear spin statistical weights of A = 5, E = 1 and T = 3 (T point group). Explicit calculation of the rotational partition functions indicated small deviations ($\approx 1\%$) at 60 K from the high-temperature limit of A:E:T = 5:1:3. While the overall intensities of the simulation resemble those of the observed Q branch heads,

Table 2

Parameters derived from the fit to Q branch components in Table 1

ν_3 band origin	3335.72(11) ^a cm^{-1}
V_2 anisotropy	91.80(57) cm^{-1}
V_3 anisotropy	221.03(862) cm^{-1}

^a Errors are one standard deviation, in units of the last quoted decimal place.

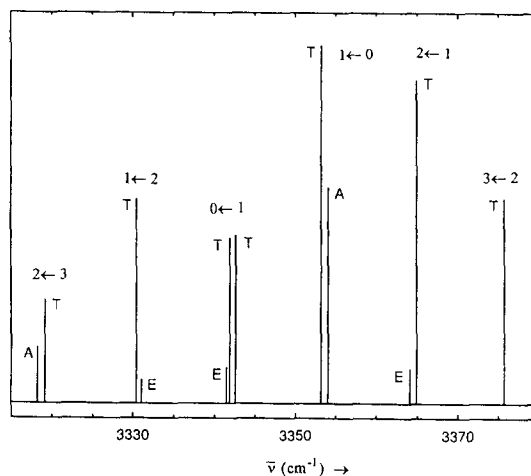


Fig. 3. A simulation of the splitting of the observed Ar-NH_4^+ $\Delta K = \pm 1$ subband origins, using the V_2 , V_3 and ν_0 parameters given in Table 2. A rotational temperature of 60 K was used. ('End over end' rotation of the complex has been omitted from this simulation.)

the correlation is less than ideal. In particular, high K $\Delta K = +1$ subbands seem to be broadened in comparison to the experimental spectrum, Fig. 1.

Alternative assignments of the Q branch components led to worse standard deviations, and a mismatch with the pattern of the spectrum. V_4 was floated as an additional parameter; it was correlated to V_3 and whilst floating V_4 improved the standard deviation of the fit slightly, the value for V_4 was small and not well determined.

5. Discussion

The values estimated for $V_3 \approx 220 \text{ cm}^{-1}$, and especially that for $V_2 \approx 90 \text{ cm}^{-1}$ are large compared to those for the ArSiH_4 complex [1], $V_3 \approx 90 \text{ cm}^{-1}$ and $V_2 \approx 1 \text{ cm}^{-1}$. The considerable increase in V_2 means that the $\Delta K = 0$ parallel and $\Delta K = \pm 1$ perpendicular spectra are clearly resolved. The value of the ν_3 band origin, 3335.72 cm^{-1} , implies a red-shift of 7.42 cm^{-1} compared to the monomer value of 3343.1399 cm^{-1} [14]. The increase in V_3 relative to Ar-SiH_4 implies a greater potential barrier to internal rotation, i.e. Ar-NH_4^+ is apparently more hindered than Ar-SiH_4 . However, whilst an ionic complex like Ar-NH_4^+ may be expected to show a

stronger radial intermolecular interaction when compared to a neutral complex like Ar–SiH₄, this does not in itself mean that the ionic complex is more rigid. There appears to be a distinction between proton-bound ionic complexes, such as Ar–H₃⁺ [15,24] and He–HN₂⁺ [16] which show strongly directional intermolecular bonding, and a few non-proton-containing ionic complexes, such as He–N₂⁺ [19] which undergo almost free internal rotation.

The geometry of the Ar–H₃⁺ complex is believed [15,24] to be an Ar atom coordinated in plane to a vertex of an H₃⁺ equilateral triangle. The experimental evidence for Ar–H₃⁺ is consistent with a barrier to internal rotation of the order of 1000 cm⁻¹. Similar strongly directional behaviour has recently been observed for the protonated He–HN₂⁺ complex [16]. The value of $V_3 \approx 220$ cm⁻¹ estimated here for the Ar–NH₄⁺ complex is intermediate between that of the Ar–SiH₄ neutral and Ar–H₃⁺ ionic complexes.

The question of the geometry of the Ar–NH₄⁺ complex remains unanswered. Since the sign of V_3 is not determined, it is uncertain whether the Ar atom prefers coordination to the face or vertex of the NH₄⁺ tetrahedron. As mentioned previously, the Ar–H₃⁺ complex is believed to involve coordination to an H₃⁺ vertex; in contrast the Ar–SiH₄ neutral complex is suspected [1] to involve coordination of Ar to a face of the SiH₄ tetrahedron.

It should be emphasised that the fit shown in Tables 1 and 2 is to the observed maxima of the Q branch components; a full analysis of the P, Q and R branch spectra of the *K* subbands of the perpendicular transition is under way. The derived values of the subband origins and rotational constants for each PQR spectrum will be used to re-fit the symmetry components, in order to refine the values of ν_0 , V_2 and V_3 estimated here.

6. Conclusion

The spectrum of the Ar–NH₄⁺ complex has been observed for the first time. The ν_3 mode of the monomer gives rise to well separated parallel and perpendicular bands. The latter has been interpreted

in terms of a hindered rotor model to estimate vibrational and rotational anisotropies in the intermolecular potential. It would appear that the Ar–NH₄⁺ ionic complex is substantially more rigid than the Ar–SiH₄ or Ne–SiH₄ neutral complexes.

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