

Dissociation energy of the Ar–HN₂⁺ complex

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Abstract

The Ar–HN₂⁺ ionic complex has been studied by means of infrared photodissociation spectroscopy in the region between 2470 and 6000 cm⁻¹. The rotational constants for the ground state of the complex extracted from combination differences are $B'' = 0.080862(15)$ cm⁻¹ and $D'' = 5.25(20) \times 10^{-8}$ cm⁻¹. For the transitions lying in the range 2470–2800 cm⁻¹ predissociation could only be observed for rotational levels above a certain J' value. This observation allows the binding energy of the complex to be determined as $D_0 = 2781.5 \pm 1.5$ cm⁻¹.

Vibrational predissociation spectroscopy coupled to tandem mass spectrometry, since its first implementation in 1985 [1], has provided a wealth of experimental information about the structure and dynamics of ionic complexes and clusters [2–4]. Species that would otherwise be difficult if not impossible to study by other spectroscopic methods have been successfully isolated and investigated in low energy guided ion beams. The power of the method is demonstrated by the fact that for certain systems rotational resolution has been achieved [5]. In our laboratory, the focus has been on rovibrational spectroscopy of proton-bound dimers consisting of two neutral bases A and B linked together via a central proton (e.g. He–HCO⁺ [6], Ne–HCO⁺ [7], Ar–HCO⁺ [8], He–HN₂⁺ [9,10] and Ne–HN₂⁺ [11]).

In the case of a large disparity in the proton affinities of the two bases ($\Delta PA = PA_A - PA_B$)

these complexes can be considered as a stable covalently bound AH⁺ ion that is only slightly perturbed by the weak intermolecular bond to the other base B. Complexes of HCO⁺ or HN₂⁺ with the rare gases (Rg) He, Ne and Ar appear to fall in this category (PA = 594, 495, 371, 201 and 178 kJ/mol for CO, N₂, Ar, Ne and He, respectively [12]). The correlation between ΔPA and the intermolecular bond strength of the complex has long been known from thermochemical experiments [13]. In previous studies of the Rg–HCO⁺ series (Rg = He, Ne, Ar) a linear dependence between $\Delta PA (= PA_{CO} - PA_{Rg})$ and the complexation induced red-shift of the CH stretching vibration of the HCO⁺ ion has been found [7]. Assuming a similar relationship exists for the isoelectronic Rg–HN₂⁺ series, a red-shift of around 950 cm⁻¹ is calculated for the ν_1 vibration (NH stretch) of Ar–HN₂⁺ ($\Delta PA = 124$ kJ/mol) from known experimental values for He–HN₂⁺ ($\Delta PA = 317$ kJ/mol, $\Delta \nu_1 = 75.5$ cm⁻¹) and Ne–HN₂⁺ ($\Delta PA = 294$ kJ/mol, $\Delta \nu_1 = 180.5$ cm⁻¹). A shift of this order is consistent with a recent ab initio calculation [14] predicting the ν_1 frequency to drop from

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3233.95 cm^{-1} [15] in the free monomer to $2330 \pm 100 \text{ cm}^{-1}$ in the complex. Though this frequency falls outside the range covered by our IR laser ($\nu > 2470 \text{ cm}^{-1}$), combination bands of ν_1 involving intermolecular and intramolecular vibrations should be accessible.

The comparatively low ΔPA value for Ar-HN_2^+ implies a relatively high dissociation energy for this complex. The ab initio calculation predicts it to be as high as $\approx 3000 \text{ cm}^{-1}$ with respect to HN_2^+ and Ar fragments [14]. This value is larger than any intramolecular fundamental but it falls in the range of the numerous combination bands of the complex which allows the observation of photodissociation thresholds in the spectrum. The determination of the complex's binding energy from such thresholds forms the main subject of this Letter.

The experimental procedure has been described previously [16,17] and only details related to the Ar-HN_2^+ formation are reported here. The complexes are synthesized in a pulsed supersonic expansion of Ar, H_2 and N_2 (ratio 100:20:1, 3–5 bar stagnation pressure) crossed by two electron beams. Mass-selected Ar-HN_2^+ ions are photodissociated in an octopole ion guide with a pulsed tunable IR laser ($\approx 0.02 \text{ cm}^{-1}$ bandwidth). Resulting HN_2^+ fragments are subsequently separated from the parent ions by a second quadrupole and sensed with a Daly detector. Photodissociation spectra were recorded between 2470 and 6000 cm^{-1} and calibrated against optoacoustic absorptions of N_2O , C_2H_2 , HDO, OCS, NH_3 and H_2O [18,19].

In total, more than 25 bands with widely different intensities have been observed in the scanned frequency range, 14 of them being at least partly rotationally resolved. Except for one transition of $\Pi \leftarrow \Sigma$ type, all bands had structures appropriate for a $\Sigma \leftarrow \Sigma$ transition of a linear molecule. A linear Ar-HN_2^+ equilibrium geometry was predicted by ab initio calculation [14] which is consistent with experimental results obtained for similar proton-bound species. An analysis of combination differences showed that within the experimental uncertainty almost all of the rotationally resolved bands shared the same lower state. We presume that this state is the vibrationless ground state of the complex because hot bands have not dominated the spectra of other proton-bound complexes generated in our cluster ion source. Lower

state combination differences were weighted according to the respective band intensities and averaged. This procedure provided data for J ranging from 1 to 70 and fitting them to a standard linear molecule expression gave the rotational constants $B'' = 0.080862(15) \text{ cm}^{-1}$ and $D'' = 5.25(20) \times 10^{-8} \text{ cm}^{-1}$. The error in brackets represent 2σ limits in the last two significant digits. As Ar-HN_2^+ is strongly bound it may be possible to detect it using microwave spectroscopy in order to obtain more accurate values. The presented constants should provide useful guidance for such searches.

Four bands observed at lower energy have an unusual structure, with transitions into levels below certain J' (different for each band) being completely absent. The bands lack Q branch transitions for the observed J ranges and are probably of parallel type ($\Sigma - \Sigma$). Three of the bands, denoted A–C, apparently originate from the ground state of the complex, and are shown in Fig. 1. Their origins are derived

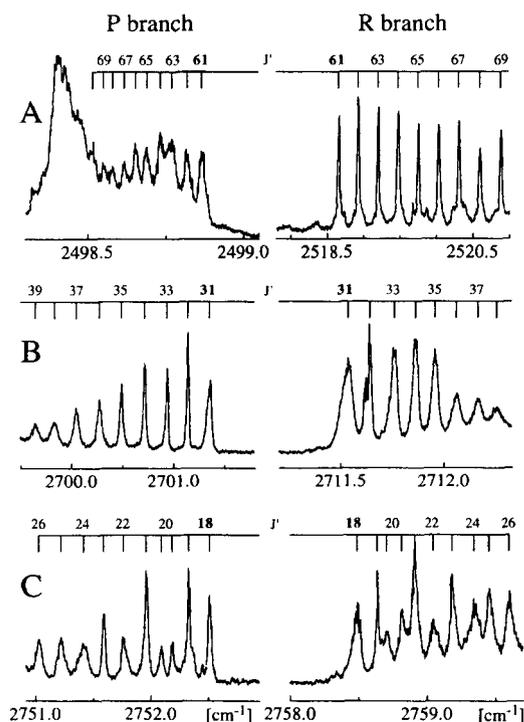


Fig. 1. Three selected bands in the IR vibrational predissociation spectrum of Ar-HN_2^+ showing the onset of dissociation at $J' = 61, 31$ and 18 for bands A ($\nu_1 + \nu_5$), B (unassigned) and C ($\nu_1 + 2\nu_5$), respectively. Upper state rotational levels of B and C are heterogeneously perturbed.

from fitting the line positions to a linear molecule Hamiltonian keeping the lower state constants fixed: $\nu_0 = 2505.40 \pm 0.10$ (band A), 2707.34 ± 0.05 (B) and $2755.62 \pm 0.05 \text{ cm}^{-1}$ (C). Large uncertainties in the origin values result from the fact that they are most sensitive to transitions involving low J' levels which were not observed experimentally. Bands A and C are the strongest ones observed in the examined spectral range. Comparison with the ab initio calculation [14] suggests an assignment to the combination bands $\nu_1 + \nu_s$ and $\nu_1 + 2\nu_s$ respectively, where ν_s is the intermolecular stretch mode. This gives rough estimates for the fundamental frequencies of $\nu_1 \approx 2255 \text{ cm}^{-1}$ and $\nu_s \approx 250 \text{ cm}^{-1}$ in reasonable agreement with the theoretical predictions of 2330 ± 100 and $\approx 210 \text{ cm}^{-1}$. Combination differences and additional evidence given below are consistent with the assumption that the less intense band B ($\leq 10\%$ of band C) originates from the vibrational ground state as well. Though its upper state assignment is not definitive at the present stage, it does not influence the outcome of the analysis presented here. The fourth band with missing low J' levels (not shown here, $\nu_0 \approx 2496.5 \text{ cm}^{-1}$) has a different set of lower state combination differences and may be a sequence band associated with band A. The relative positions of the upper state rotational energy levels of the bands A–C are shown in Fig. 2. Although their vibrational origins are quite different, the first J' levels subject to photodissociation are roughly at the same total energy, being almost coincident for bands B and C. This observation is attributed to vibrational predissociation of the upper rovibrational levels of the complex leading to cold HN_2^+ fragments.

The detection of photofragment ions relies on the vibrational predissociation of photoexcited molecules. Individual rotational lines in bands A–C as well as in most of the other rotationally resolved bands of the Ar-HN_2^+ spectrum have laser limited bandwidths indicating upper state lifetimes larger than 250 ps. In addition, certain bands in the spectrum display a quite irregular pattern of linewidths and intensities most likely caused by heterogeneous perturbations. Examples of such perturbations are the splitting of the $J' = 20$ level and the anomalous intensity distribution in band C and line broadening observed for $J' = 36\text{--}41$ in band B (Fig. 1).

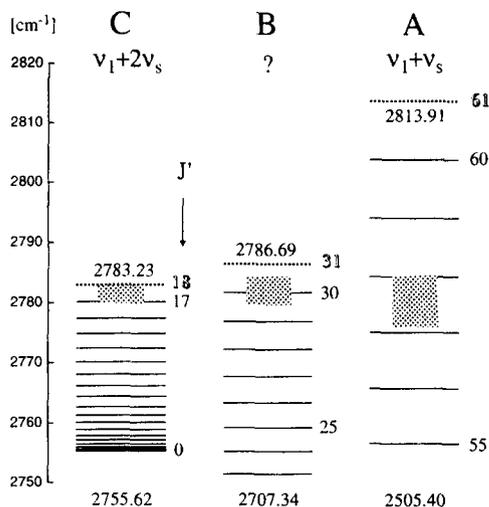


Fig. 2. Rovibrational energies of the upper vibrational states accessed in transitions A, B and C presented in Fig. 1. Energy levels shown by solid lines do not predissociate: these include levels up to $J' = 17, 30$ and 60 for C, B and A respectively. Predissociation starts from levels represented by dotted lines (i.e. $J' = 18, 31, 61$). The dissociation threshold is believed to be located somewhere within the shaded areas which represent differences in energy levels of $J' = 17$ and $18, 30$ and $31, 60$ and 61 for bands C, B and A corrected by the respective centrifugal barrier heights. The numbers below each manifold are the bands' vibrational origins in cm^{-1} .

Upper rovibrational levels with $J' \leq 60, 30$ and 17 for bands A, B and C respectively do not appear in the corresponding photodissociation spectra. This indicates predissociation lifetimes for these levels of at least 0.1 ms, a typical flight-time through the octopole ion guide. Slowing the ions down in order to increase the residence time in the octopole region above 1 ms did not affect the photodissociation spectra. The most probable conclusion is that these J' levels are *intrinsically stable* with respect to dissociation. This observation provides an upper limit for the binding energy of the Ar-HN_2^+ complex based on the energy of the lowest observed rovibrational level capable of predissociation, $D_0 < 2783.23 \pm 0.03 \text{ cm}^{-1}$ (Fig. 2). If the resulting HN_2^+ fragments were rotationally and vibrationally cold and the relative kinetic energies of the recoiling particles were small then the quoted value would be quite close to the real dissociation energy.

The fact that the energy intervals bracketed by the first dissociating J' level and last non-dissociating

J' level for bands A–C do not overlap (Fig. 2) is indicative of the different degrees of internal and kinetic energy in the photofragments. This difference is explicable from a mechanistic viewpoint where the fragment kinetic energy release is related to the initial angular momentum of the rotating complex by classical conservation laws. Predissociation of Ar–HN₂⁺ arises from coupling of the initially prepared quasibound levels with continuum states. Neglecting tunneling, the first available continuum channel occurs at the top of the J dependent centrifugal barrier of the vibrational ground state. Assuming for the moment that the HN₂⁺ fragments possess no vibrational and rotational energy, one can estimate the energy necessary to surmount the rotational barrier by considering the long-range part of the intermolecular potential (V_{LR}). To a first approximation this contribution is given by the sum of the rotational and charge induced dipole potential terms

$$V_{LR} = \frac{h^2 J(J+1)}{8\pi^2 \mu R^2} - \frac{\alpha q^2}{2(4\pi\epsilon_0)^2 R^4}$$

where μ is the reduced mass of the Ar–HN₂⁺ pseudodiatom, R is the intermolecular centre of mass displacement and α is the polarizability of the Ar atom ($1.83 \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$). Here we have assumed that the centre of charge coincides with the HN₂⁺ centre of mass.

According to this approximation, the rotational barriers occur at $R \approx 23.6, 13.8$ and 7.1 \AA for $J = 18, 31$ and 61 , with respective heights of $0.3, 2.6$ and 37.8 cm^{-1} . Adjustment of the dissociation thresholds for the pseudodiatom kinetic energy releases in all three cases leads to excellent agreement for the intervals calculated from bands B and C. On the other hand, the agreement is not so good for band A. However, because of the high angular momentum involved here, the rotational barrier is much closer in and the long-range approximation to the potential is less likely to be valid. It is worth noting, however, that if the centre of charge is placed anywhere between the midpoint of the NH bond and the central N atom (this position is expected from the Mulliken analysis), better agreement between all three energetic limits is obtained. Fig. 2 demonstrates perfect overlap of the energy intervals between $J' = 17$ – 18 ,

30 – 31 and 60 – 61 for bands C, B and A, corrected by the centrifugal barrier heights calculated with the charge located on the central nitrogen (2776.3 – $2784.5, 2779.8$ – 2784.4 and 2780.0 – 2782.9 cm^{-1}). Practically the same result is obtained when the charge distribution is taken from the distributed multipole analysis over the atomic centres ($0.244 e$ on the terminal N, $0.389 e$ on the central N and $0.366 e$ on H [10]). Overlap of the three energy intervals is consistent with the previous assumption that these band share the same lower state and dissociate in the same vibrational state of the HN₂⁺ fragment.

Finally, the possibility is considered that the HN₂⁺ fragment is formed in a vibrationally excited state. It appears unlikely that the fragment can be in the ν_3 state (2258 cm^{-1} [20]), because this would lead to a binding energy of less than 530 cm^{-1} , a value far from the ab initio estimate of 3000 cm^{-1} [14], and also inconsistent with the binding energies for related proton-bound species He–HN₂⁺ ($\approx 380 \text{ cm}^{-1}$ [10]) and Ar–HCO⁺ ($\approx 1000 \text{ cm}^{-1}$ [8]) which are expected to be significantly less strongly bound. Excitation of ν_2 (685 cm^{-1} [21]) in the fragment also appears to be somewhat unlikely given the observations of a sharp cut-off at particular J' values and the spectra's unchanging appearance when the complexes are trapped for up to 1 ms. Closing of the HN₂⁺ (010) channel below a particular J' value would still allow the complex to dissociate to HN₂⁺ (000). The absence of lower J' lines (even for 1 ms trapping times) would imply that this process must be much slower than dissociation into HN₂⁺ (010). Excitation of ν_2 in the fragment HN₂⁺ for all three bands (A–C) would shift the binding energy interval by roughly 685 cm^{-1} down to 2100 cm^{-1} which is again less consistent with the theoretical prediction.

In conclusion, under the presumptions outlined above we can confine the range for D_0 to the interval between the $J' = 0$ level (2783.2 cm^{-1}), which has no angular momentum restriction for the dissociation into rovibrationally and translationally cold fragments, and $J' = 18$ (2755.6 cm^{-1}) of the C band (Fig. 2). If centrifugal barrier corrections are taken into account we arrive at an even narrower interval for the dissociation energy of the Ar–HN₂⁺ complex, $D_0 = 2781.5 \pm 1.5 \text{ cm}^{-1}$, again taken from the C band. This value is comparable to binding energies obtained for other proton-bound het-

erodimers of similar composition, for example, Ar–H₃⁺ where D_0 is of the order of 2700 cm⁻¹ [22]). The presented experimental values for the rotational constants and dissociation energy suggest Ar–HN₂⁺ to be a suitable system for testing quantum chemical methods applied to charged complexes.

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