LETTERS TO THE EDITOR

COMMUNICATIONS

Infrared absorption spectrum of Ar–HN$_2^+$ in a supersonic slit expansion

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The first direct measurement of a high resolution infrared absorption spectrum of an ionic complex, Ar–HN$_2^+$, is presented. The complex is generated in a continuous supersonic slit jet expansion with electron impact ionization. There have been observed 28 rotationally resolved transitions of the $\nu_1 + \nu_s$ combination band in the $2501-2510$ cm^{-1} region using a tunable diode laser. The band origin is determined at $\nu_0 = 2505.4998(4)$ cm^{-1}. © *1997 American Institute of Physics.* [S0021-9606(97)04044-0]

INTRODUCTION

Ionic complexes form important intermediates in many chemical processes. An understanding of these species yields information of chemical reactions at the fundamental level of molecular motions. However, only little spectroscopic information is available, presumably because of lack of a technique that generates ionic complexes in high abundances. In the last years there have been many efforts to develop approaches that combine the advantages of a two-dimensional supersonic expansion through a small slit (high densities, adiabatic cooling, and complexation)[1] and plasmas (ion and radical production). Several experimental techniques have been proposed, based either on laser flash photolysis,[2] ablation,[3] discharge,[4–9] or electron impact ionization.[10,11] Although low rotational temperatures have generally been obtained (typically <30 K), until now no weakly bound ionic complexes have been observed with these setups.

Most of the available information on ionic complexes to date is based on laser spectroscopy combined with mass spectrometry: an ionic cluster is mass selected, resonantly excited, and the spectrum is observed by monitoring the predissociation process.[12,13] This background free technique is mass selective, but has the disadvantage that for one-photon experiments only levels above the dissociation limit can be observed, which intrinsically limits the accessible spectroscopic information. These problems can be overcome by direct absorption spectroscopic techniques, but the low particle densities have limited applications to only two ionic complexes up to now. In the submillimeter range Ar–H$_3^+$ was observed in a negative glow discharge[14] and, recently, pure rotational transitions of Ar–HCO$^+$ were detected, using a Fourier transform (FT) microwave spectrometer in a jet cooled condition.[15]

EXPERIMENT

The experimental setup has been described.[10] The apparatus was used to observe the infrared gas phase spectrum of

N$_4^{+}$[11] and it was shown that low rotational temperatures can be achieved (15 ± 5 K).[16] The spectrometer consists of a tunable lead salt diode laser and a slit jet apparatus. The plasma is formed by electron impact ionization of a gas mixture that is expanded through a 32 mm$\times 50$ μm slit into a vacuum chamber that is maintained at low pressure by a 2150 m^3/h roots blower system. The planar jet is crossed by the laser beam and subsequently sampled by a quadrupole mass spectrometer. The effective pathlength of the laser beam through the expansion, using a multipass configuration, is approximately 50 cm. The radiation is focused onto an InSb detector and is phase-sensitively detected by production modulation at 5 kHz. In front of the detector a band pass filter is mounted to suppress background radiation that is generated by the plasma. An absolute accuracy of about 0.002 cm^{-1} can be obtained by simultaneously recording marker étalons and using N$_2$O as a reference gas.

The Ar–HN$_2^+$ complex is produced by expanding a mixture of Ar, H$_2$, and N$_2$ (100:20:1, stagnation pressure of 2.5 bar) and subsequent electron impact ionization. The production is optimized by monitoring the plasma with the quadrupole mass spectrometer. Besides Ar–HN$_2^+$, also protonated Ar and N$_2$-ions, as well as the N$_4$H$^+$ or N$_2$–HN$_2^+$ complex are seen in the mass spectrum.

RESULTS AND DISCUSSION

Figure 1 shows part of the infrared absorption spectrum of Ar–HN$_2^+$. The observed transitions are nearly Doppler free, because the expansion has almost no velocity component in the direction of the laser beam. The full width half maximum of the lines is ≈ 120 MHz. The signal-to-noise ratio of the strongest signals is better than 30. In total, 28 rotational transitions have been observed, most of them in the P branch. Due to the mode structure of the diode the lower rotational transitions in the R branch were not detected. The exact determination of the $R(0)$ transition is hampered by a partial overlap with an Ar atomic line. The
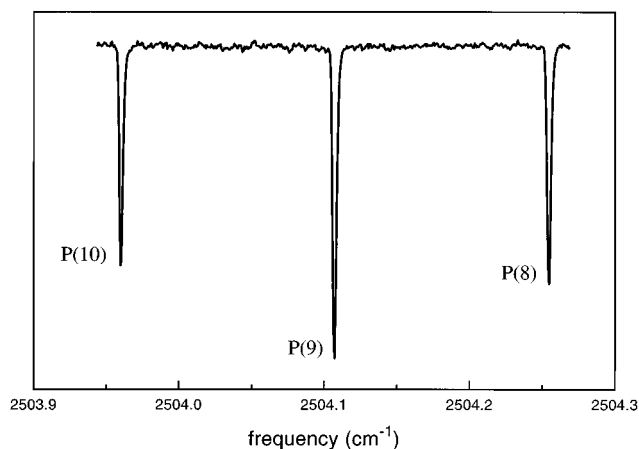
FIG. 1. The $P(8)$, $P(9)$, and $P(10)$ transitions for the $\nu_1 + \nu_s$ band of Ar–HN$_2^+$ observed in a slit nozzle expansion and electron impact ionization.

spectrum shows the ordered structure of a Σ–Σ type transition of a linear molecule, with P and R branches and a band gap of 4B. In Table I the observed transitions and the rotational assignment are listed.

The vibrational assignment follows from the outcome of a photodissociation experiment on Ar–HN$_2^+$.[17] In this experiment several combination bands of the ν_1 fundamental involving inter- and intramolecular vibrations have been observed. Guided by *ab initio* results[18] bands around 2505 and 2756 cm^{-1} were assigned as the $\nu_1 + \nu_s$ and $\nu_1 + 2\nu_s$ combinations, respectively, where ν_s is the intermolecular stretch mode. Low J levels could not be observed for these bands, because their transition energy lies below the dissociation limit. As a consequence it is hard to determine the exact positions of the band origins. For the band around 2505 cm^{-1}, which is of interest here, only rotational levels with $J \geqslant 60$ were found.[17]

The line positions were fitted to the standard expression for a Σ–Σ type transition. In order to get accurate values also for the distortion constants, high rotational levels found in the dissociation experiment [$J = 62$–71 (Ref. 19)] were included, after appropriate weighting. The resulting constants

are listed in Table I. The differences between observed and calculated frequencies are given as well. The quality of the least-squares fit is of the same order as or better than the estimated experimental uncertainty. The ground state constants compare well with the values found in Ref. 17, where a combination difference analysis yielded values of $B_0 = 0.080862(15)$ cm^{-1} and $D_0 = 5.25(20) \cdot 10^{-8}$ cm^{-1}. The present value for the band origin is two orders of magnitude more accurate than the value obtained from the dissociation experiment ($\nu_0 = 2505.40(10)$ cm^{-1}).[19]

The center-of-mass intermolecular distance is calculated from the rotational constants in Table I to be 3.428 Å for the vibrational ground state, assuming that the complex is rigid. The latter assumption is justified by the large dissociation energy that was found for Ar–HN$_2^+$ ($D_0 = 2781.5$ cm^{-1}).[17] Upon excitation the bond length decreases by about 0.02 Å.

In previous studies on Rg–HCO$^+$ complexes (Rg=He, Ne, or Ar) a linear dependence was found for the difference in proton affinities of the bases and the complexation induced redshift.[20] If the same dependence exists for the Rg–HN$_2^+$ complexes, the NH stretch is expected to be around 2280 cm^{-1} in Ar–HN$_2^+$. This value is in agreement with a rough estimate obtained from the dissociation experiments that predict ν_1 at 2255 cm^{-1}.[17] With the present setup this range has been scanned, without success, even though the fundamental is expected to be considerably stronger than the $\nu_1 + \nu_s$ combination band. This means either that the absorption lines were missed because of diode laser mode gaps, or that they lie outside the range scanned. Further dissociation results of Ar$_n$–HN$_2^+$ with $n = 2$–13 suggest that due to Fermi resonances the redshift may be smaller than what was expected.[19] Work to locate the fundamental is in progress.

It is not possible to determine the density of the Ar–HN$_2^+$ species, because absolute absorptions have not been measured. However, a rough estimate is possible. A complexation factor of around 10% is obtained when comparing the N$_2$H$^+$ and Ar–HN$_2^+$ mass signals. This is slightly larger than the typical value for neutral complexes which is due to the higher binding energy in ionic complexes. N$_2$H$^+$

TABLE I. Observed transition frequencies and molecular constants of Ar–HN$_2^+$ (in cm^{-1}).

J	P branch	Obs.-calc. (10^{-4})	J	P branch	Obs.-calc. (10^{-4})	J	R branch	Obs.-calc. (10^{-4})
1	2505.3373	−9	13	2503.5324	0	0	2505.6627	−6
2	2505.1780	−1	14	2503.3932	0	21	2509.4942	8
3	2505.0184	−14	15	2503.2549	−9	22	2509.6952	5
4	2504.8632	0	16	2503.1202	0	23	2509.8968	−10
5	2504.7089	5	17	2502.9873	10			
6	2504.5564	11	18	2502.8559	17			
7	2504.4048	8	20	2502.5938	−5			
8	2504.2530	−14	21	2502.4669	−7			
9	2504.1056	−9	22	2502.3425	−9			
10	2503.9596	−7	25	2501.9755	−23			
11	2503.8181	22	26	2501.8608	9			
12	2503.6753	20	27	2501.7480	7			

$\nu_0 = 2505.4998(4)$ cm^{-1} $B_0 = 0.080867(11)$ cm^{-1} $D_0 = 5.41(30) \cdot 10^{-8}$ cm^{-1}

$B_1 = 0.081729(11)$ cm^{-1} $D_1 = 4.85(30) \cdot 10^{-8}$ cm^{-1}

is easily formed in N_2/H_2 mixtures and densities of the order 10^{12} ions/cm^3 are attainable at the orifice of the nozzle.[9] In the current experiment the laser beam multipasses the expansion between 1 and 5 mm downstream from the slit. Based on a linear drop-off in concentration with the distance downstream, a mean density of at least 10^{10} ionic complexes per cm^3 is estimated in the infrared probe zone.

In conclusion, the first high resolution direct absorption spectrum of an ionic complex in the infrared is presented. As most infrared and submillimeter studies are based on direct absorption, this approach will be generally applicable. Whereas to date mainly the dynamics of weak intermolecular interactions in neutral complexes have been studied, this interesting field of molecular spectroscopy is now becoming accessible for charged complexes as well.

ACKNOWLEDGMENTS

[1] D. J. Nesbitt, Annu. Rev. Phys. Chem. **45**, 367 (1994).
[2] R. F. Curl, K. K. Murray, M. Petri, M. L. Richnow, and F. K. Tittel, Chem. Phys. Lett. **161**, 98 (1989).
[3] J. R. Heath and R. J. Saykally, in *On Clusters and Clustering, from Atoms to Fractals*, edited by P. J. Reynolds (Elsevier, New York, 1993), pp. 7–21.
[4] K. R. Comer and S. C. Foster, Chem. Phys. Lett. **202**, 216 (1993).
[5] G. Hilpert, H. Linnartz, M. Havenith, J. J. ter Meulen, and W. L. Meerts, Chem. Phys. Lett. **219**, 384 (1994).
[6] M. Fukushima, M. Chan, Y. Xu, A. Taleb-Bendiab, and T. Amano, Chem. Phys. Lett. **230**, 561 (1994).
[7] Y. Xu, M. Fukushima, T. Amano, and A. R. W. McKellar, Chem. Phys. Lett. **242**, 126 (1995).
[8] K. Harada and T. Tanaka, Chem. Phys. Lett. **227**, 651 (1994).
[9] D. T. Anderson, S. Davis, T. S. Zwier, and D. J. Nesbitt, Chem. Phys. Lett. **258**, 207 (1996).
[10] T. Ruchti, A. Rohrbacher, T. Speck, J. P. Connelly, E. J. Bieske, and J. P. Maier, Chem. Phys. **209**, 169 (1996).
[11] T. Ruchti, T. Speck, J. P. Connelly, E. J. Bieske, H. Linnartz, and J. P. Maier, J. Chem. Phys. **105**, 2591 (1996).
[12] E. J. Bieske and J. P. Maier, Chem. Rev. **93**, 2603 (1993).
[13] M. W. Crofton, M. M. Price, and Y. T. Lee, in *Clusters of Atoms and Molecules II*, edited by H. Haberland (Springer, Berlin, 1994).
[14] M. Bogey, H. Bolvin, C. Demuynck, J. L. Destombes, and B. P. van Eijck, J. Chem. Phys. **88**, 4120 (1988).
[15] Y. Ohshima, Y. Sumiyoshi, and Y. Endo, J. Chem. Phys. **106**, 2977 (1997).
[16] T. Speck, T. Ruchti, H. Linnartz, and J. P. Maier, J. Mol. Spectrosc. (in press).
[17] S. A. Nizkorodov, Y. Spinelli, E. J. Bieske, J. P. Maier, and O. Dopfer, Chem. Phys. Lett. **265**, 303 (1997).
[18] M. Kolbuszewski, Chem. Phys. Lett. **244**, 39 (1995).
[19] Unpublished results from this laboratory. A list with transitions is available on request.
[20] S. A. Nizkorodov, O. Dopfer, M. Meuwly, J. P. Maier, and E. J. Bieske, J. Chem. Phys. **105**, 1770 (1995).