Spectroscopic and theoretical characterisation of the v_2 band of $Ar \cdots DN_2^+$

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Received 20 July 2000

Abstract

The rotationally resolved infrared spectrum of the v_2 stretching vibration of $Ar \cdots DN_2^+$ has been observed by means of tunable diode laser absorption spectroscopy through a supersonic planar plasma. Its band origin is found at 1593.6058(2) cm^{-1}, and a large transition moment of 0.54 D is predicted from CCSD(T) calculations. An accurate mixed experimental/theoretical equilibrium structure is established, yielding $R_{Ar \cdots H}^{(e)} = 1.8854$ Å, $R_{H \cdots N}^{(e)} = 1.0752$ Å and $R_{NN}^{(e)} = 1.0929$ Å. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years, several spectroscopic [1–5] and theoretical [4–6] studies have been reported on the linear proton-bound ionic complex $Ar \cdots HN_2^+$. Besides the microwave spectrum [1], a series of rotationally resolved infrared bands has been recorded that involve excitation of the intramolecular (v_1 and v_2) and intermolecular (v_s) stretching vibrations [2–5]. In our recent work [5], the v_1 and v_2 vibrations were located at 2505.5000(2) and 2041.1802(3) cm^{-1}, respectively, and were found to be mixed modes, both with large anharmonicity contributions. Large transition moments of $|\mu(v_1)| = 0.434$ D and $|\mu(v_2)| = 0.611$ D were calculated.

A different situation was predicted for $Ar \cdots DN_2^+$ (see Ref. [5], Fig. 2). The intramolecular

stretching vibration with highest wave number (v_1) is considerably less anharmonic than the v_2 fundamental and corresponds to an almost local NN stretching mode with calculated origin at 2441 cm^{-1}. The origin of the v_2 vibration, mainly ND stretching in character, was predicted at 1559 cm^{-1}. Compared to the wave numbers of the NN and ND fundamentals in free DN_2^+ (2024.04 cm^{-1} [8,9] and 2636.98 cm^{-1} [7]), large differences arise upon complexation.

The present work reports on the first detection of the v_2 band of $Ar \cdots DN_2^+$. The experimental search was greatly facilitated by the results of coupled cluster calculations that are described in detail as well.

2. Methods

Rotationally resolved infrared spectra of $Ar \cdots DN_2^+$ were obtained in direct absorption, using a tunable diode laser spectrometer. The ions

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are generated by electron impact ionisation of an Ar, N_2 and D_2 mixture (90:5:5 mixing ratio) that is expanded supersonically through a 32 mm × 50 μm slit. An efficient production modulation is obtained by changing the field gradients of the electron gun which makes phase sensitive detection possible. An absolute accuracy of better than 0.002 cm^{-1} is obtained by simultaneously recording marker étalons and NO_2 as a reference gas. Online information of the mass distribution in the plasma is obtained by sampling the expansion in a quadrupole mass spectrometer. Further details are available from Ref. [10].

Ab initio calculations were carried out by the coupled cluster variant CCSD(T) [11]. Basis sets of 219 and 368 contracted Gaussian-type orbitals (cGTO) were employed as described in our previous work on Ar$\cdots$HN$_2^+$ [5]. Valence electrons were correlated in the CCSD(T) calculations which were carried out with the MOLPRO98 suite of programs.[1]

3. Results and discussion

Guided by our previous ab initio calculations [5], a total of 44 vibration–rotation lines around 1594 cm^{-1} have been assigned to the v_2 stretching mode of Ar$\cdots$DN$_2^+$. Apart from the R(9) to R(13) transitions that coincide with a diode frequency gap, a complete set of adjacent transitions has been recorded (Table 1). In Fig. 1, the corresponding stick diagram is shown, assuming a rotational temperature of 25 K [10]. The inset shows transitions around the Boltzmann maximum. The Ar$\cdots$DN$_2^+$ spectrum has a P- and R-branch and a band gap of approximately $4B$, which is consistent with a linear deuteron-bound geometry, as expected from the experiments and calculations on Ar$\cdots$HN$_2^+$. The rotational and centrifugal dis-

Table 1

Observed line positions (cm^{-1}) of rotational transitions involving excitation of the v_2 stretching vibration of Ar$\cdots$DN$_2^+$

J	P branch	o − c[a]	R branch	o − c[a]
0			1593.7680	−2
1	1593.4447	−2	1593.9321	−1
2	1593.2841	−14	1594.0976	0
3	1593.1281	5	1594.2642	−4
4	1592.9723	11	1594.4328	−2
5	1592.8178	14	1594.6021	−8
6	1592.6636	6	1594.7755	13
7	1592.5114	2	1594.9466	−3
8	1592.3615	8	1595.1208	−2
9	1592.2124	7	−	
10	1592.0643	2	−	
11	1591.9171	−7	−	
12	1591.7708	21	−	
13	1591.6288	−4	−	
14	1591.4865	−3	1596.1911	−8
15	1591.3455	0	1596.3734	−9
16	1591.2048	6	1596.5578	2
17	1591.0660	−4	1596.7421	3
18	1590.9290	7	1596.9268	−1
19	1590.7922	10	1597.1129	2
20	1590.6542	−8	1597.2995	3
21	1590.5207	12	1597.4868	6
22	1590.3845	−4	1597.6753	16
23	1590.2506	−2	1597.8616	−1
24			1598.0493	−6
25			1598.2375	−8

[a] Observed – calculated (in 10^{-4} cm^{-1}) using the constants of Table 2.

tortion constants for both ground and excited states are calculated using a standard expression for a Σ–Σ-type transition (Table 2). The v_2 band origin is found at 1593.6058(2) cm^{-1}. The difference in rotational constants for the ground and vibrationally excited state ($B_0 − B_1 = −0.76 \times 10^{-3}$ cm^{-1}) has a negative value which is typical for a proton (deuteron) stretching vibration in a hydrogen-bonded system. Although inclusion of the distortion constants is necessary to obtain a rms deviation below the experimental uncertainty, the resulting D-values ($D_0 = 6(1) \times 10^{-8}$ cm^{-1} and $D_1 = 23(1) \times 10^{-8}$ cm^{-1}) should be regarded mainly as effective parameters; higher J levels are necessary for a more accurate determination.

Calculated harmonic and anharmonic wave numbers of vibrational transitions of Ar$\cdots$DN$_2^+$ as well as the corresponding transition moments are listed in Tables 3 and 4. The CCSD(T)

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[1] MOLPRO98 is a package of ab initio programs written by H.-J. Werner and P.J. Knowles, with contributions from R.D. Amos, A. Berning, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, C. Hampel, T. Leininger, R. Lindh, A.W. Lloyd, W. Meyer, M.E. Mura, A. Nicklass, P. Palmieri, K. Peterson, R. Pitzer, P. Pulay, G. Rauhut, M. Schütz, H. Stoll, A.J. Stone, and T. Thorsteinsson.
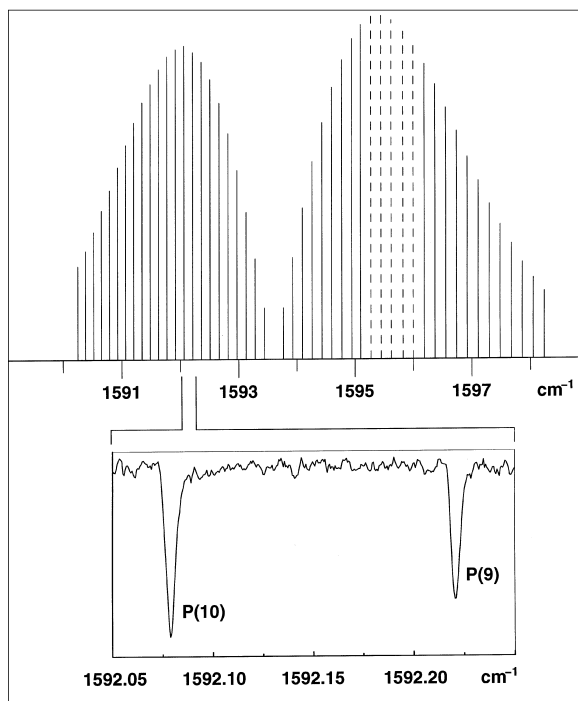
Fig. 1. A stick diagram representing the observed $Ar \cdots DN_2^+$ transitions involving v_2 excitation for $T_{rot} = 25$ K. The inset shows the P(9) and P(10) transition recorded in direct absorption through a supersonic planar plasma applying production modulation.

Table 2
Spectroscopic constants (cm^{-1}) for the ground and v_2 excited stretching vibration of $Ar \cdots DN_2^{+a}$

v_0	1593.6058(2)
B_0	0.080456(11)
B_1	0.081218(11)

[a] Values in parentheses correspond to 1σ deviations in terms of the last significant digit.

anharmonic wave number for v_2 differs by only 35 cm^{-1} from the experimentally determined value. The v_1 band is predicted at 2441 cm^{-1}, but due to a lack of diodes in this range it was not possible to record the transition in absorption. The intermolecular stretching vibration (v_3 or v_s) is predicted at 195 cm^{-1}, a few cm^{-1} above the corresponding harmonic value. This unusual anharmonicity effect results from coupling with the intramolecular stretching modes. In particular, the anharmonicity

Table 3
CCSD(T) harmonic wave numbers for the bending and stretching modes (cm^{-1}) of $Ar \cdots DN_2^{+a}$

	219 cGTO	368 cGTO
ω_1 ($\sim$ NN stretch)	2526	2527
ω_2 ($\sim$ ND stretch)	1748	1743
ω_3 (inter stretch)	188	189
ω_4 (DNN bend)	666	661
ω_5 (inter bend)	149	148

[a] CCSD(T) harmonic vibrational wave numbers for free DN_2^+ are $\omega_1 = 2722$ (2724) cm^{-1}, $\omega_2 = 555$ (552) cm^{-1} and $\omega_3 = 2065$ (2067) cm^{-1}, where the values obtained with the larger basis set are given in parentheses.

Table 4
Wave numbers and transition moments of the most intense stretching vibrations in $Ar \cdots DN_2^+$ from three-dimensional variational calculations (CCSD(T) /219 cGTO)[a]

Band	$Ar \cdots DN_2^+$	
	v (cm^{-1})	$\mid\mu\mid$ (D)
v_s	195	0.384
$2v_s$	383	0.047
v_2	1559	0.541
$v_2 + v_s$	1787	0.094
v_1	2441	0.234
$v_1 + v_s$	2645	0.024
$2v_2$	2945	0.085

[a] See Ref. [5] for further details.

constant X_{23} has a rather large positive value. A rough calculation by means of the formula $X_{23} \approx (v_2 + v_3) - v_2 - v_3$ yields 32 cm^{-1}. The v_2 band is calculated to be most intense, with a transition moment as large as 0.541 D. The first overtone with calculated origin at 2945 cm^{-1} [2] still has a rather large transition moment of 0.085 D. For the nearly local NN stretching mode $\mid\mu(v_1)\mid$ is calculated as 0.234 D. This is much larger than in free HN_2^+ and about comparable to the transition moments of the anti-symmetric NN stretching vibration of $N_2 \cdots H^+ \cdots N_2$ and $N_2 \cdots D^+ \cdots N_2$ [12]. The corresponding value for the NN stretching vibration of free DN_2^+ is 0.115 D (CCSD(T)/cc-pVQZ).

The CCSD(T) rotational, centrifugal distortion, vibration–rotation coupling (α_r) and 1-type dou-

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[2] This value is underestimated by ca. 70 cm^{-1}.

bling (q_t^e and q_t^J) constants for $Ar \cdots DN_2^+$ are listed in Table 5. The constants are calculated by means of conventional second-order perturbation theory in normal coordinate space. A B_e value of 0.07965 cm^{-1} is found, and the equilibrium centrifugal distortion constant D_e is predicted to be 5.29×10^{-8} cm^{-1}. The value of α_2 (approximately given by the experimental value for $B_0 - B_1$, see Table 2) is calculated to be -1.60×10^{-3} cm^{-1} (219 cGTO) and -1.68×10^{-3} cm^{-1} (368 cGTO). Not unexpectedly, second-order perturbation theory performs only reasonably well for the highly anharmonic system. For the ν_1 band, a much smaller value of -0.34×10^{-3} cm^{-1} is predicted. Upon excitation of the intermolecular stretching vibration (ν_3) a decrease in the rotational constant is predicted. This corresponds to the usual situation in a hydrogen-bonded complex and may be traced back to the anharmonic nature of the intermolecular stretching potential. The α values for the intramolecular (ν_4) and intermolecular (ν_5) bending vibrations are fairly small and of opposite sign.

The CCSD(T) vibration–rotation coupling constants are employed in an approximate calculation of the difference $\Delta B_0 = B_e - B_0$, according to

$$\Delta B_0 \approx \frac{1}{2} \Sigma_r \alpha_r d_r,$$

where d_r is a degeneracy factor (1 for stretching and 2 for bending modes). The results are -0.000570 cm^{-1} (CCSD(T)/219 cGTO) and -0.000662 cm^{-1} (CCSD(T)/368 cGTO). Combining the latter value with the experimental ground state rotational constant from Table 2 results in $B_e = 0.079794$ cm^{-1}, which differs from the CCSD(T) value as obtained with the larger basis set by only 0.2%. The changes in the intramolecular equilibrium bond lengths that occur upon complex formation are 0.0416 Å for the NH or ND bonds and 0.0001 Å for the NN bond (CCSD(T)/368 cGTO). Using the available experimental equilibrium bond lengths of the free cation [9] this yields values for the complex of $R_{NH}^{(e)} = 1.0752$ Å and $R_{NN}^{(e)} = 1.0929$ Å. These values should be accurate to 0.0005 Å. The equilibrium separation between the argon nucleus and deuteron is then calculated from the above value for B_e as 1.8854 Å. The uncertainty of this value is of the order of 0.001–0.002 Å and is mainly due to the use of second-order perturbation theory in the calculation of ΔB_0. The mixed experimental/theoretical equilibrium structure for $Ar \cdots HN_2^+$ and its isotopomers as well as the results of the uncorrected CCSD(T) calculations are shown in Fig. 2. The former is probably the most accurate equilibrium structure which has been established so far for a cluster ion with more than three nuclei.

A check of the present mixed experimental/theoretical structure is possible in the following way. The B_e value for $Ar \cdots HN_2^+$ calculated from this structure is 0.079863 cm^{-1}. Subtraction of the ground state vibrational contribution ΔB_0 as obtained by CCSD(T)/368 cGTO yields $B_0 = 0.080858$ cm^{-1}, which is in excellent agreement with the previously determined experimental value of $0.080868(6)$ cm^{-1} [5].
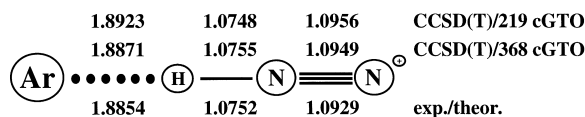
Table 5
CCSD(T) spectroscopic constants for $Ar \cdots DN_2^+$ (cm^{-1})

	219 cGTO	368 cGTO[a]
B_e	0.07943	0.07965
D_e (10^{-8})	5.28	5.29
α_1 (10^{-3})	-0.34	-0.34
α_2 (10^{-3})[b]	-1.60	-1.68
α_3 (10^{-3})	1.08	0.99
α_4 (10^{-3})	0.13	0.13
α_5 (10^{-3})	-0.27	-0.28
q_4^e (10^{-4})	0.28	0.28
q_5^e (10^{-4})	1.23	1.23
q_4^J (10^{-10})	-0.95	-0.96
q_5^J (10^{-10})	8.48	6.80

[a] Off-diagonal cubic force constants are taken from CCSD(T) calculations with the smaller basis set.
[b] Experimental value (this work): $\alpha_2 = -0.76 \times 10^{-3}$ cm^{-1}.

Fig. 2. Ab initio and mixed experimental/theoretical equilibrium structures for $Ar \cdots HN_2^+$.

Acknowledgements

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