

COMMUNICATIONS

Linear and centrosymmetric $\text{N}_2 \cdots \text{Ar}^+ \cdots \text{N}_2$

H. Linnartz and D. Verdes

Institute for Physical Chemistry, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

P. J. Knowles

School of Chemistry, University of Birmingham, Birmingham, B15 2TT, United Kingdom

N. M. Lakin

Institute for Physical Chemistry, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

P. Rosmus

Theoretical Chemistry Group, Université de Marne-la-Vallée, F-77454 Champs sur Marne, France

J. P. Maier

Institute for Physical Chemistry, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

(Received 4 May 2000; accepted 18 May 2000)

A high resolution infrared absorption spectrum of the ionic complex $\text{N}_2 \cdots \text{Ar}^+ \cdots \text{N}_2$ has been observed by tunable diode laser spectroscopy through a supersonic planar plasma. Seventy-six rovibrational transitions were measured involving excitation of the antisymmetric NN (ν_3) stretching fundamental. The band origin is at $2288.7272(2) \text{ cm}^{-1}$ and the ground state rotational constant is determined as $B_0 = 0.034296(7) \text{ cm}^{-1}$. The spectrum shows a clear spin-statistical intensity alternation and is consistent with a linear and centrosymmetric equilibrium geometry and a ground state with ${}^2\Sigma_u^+$ symmetry. The charge is predominantly located on the argon atom. The assignment is supported by high level *ab initio* calculations carried out. The best estimate for the equilibrium geometry is $R_e(\text{NN}) = 1.1014 \text{ \AA}$ and $r_e(\text{Ar} \cdots \text{N}) = 2.3602 \text{ \AA}$, yielding $B_e = 0.034297 \text{ cm}^{-1}$. The equilibrium dissociation energy D_e for fragmentation into N_2 and $[\text{ArN}_2]^+$ is calculated to be $\sim 1.7 \text{ eV}$. © 2000 American Institute of Physics. [S0021-9606(00)01627-5]

In recent years many accurate experimental and theoretical methods have been developed for the study of weak intermolecular forces. Most of these have focused on *neutral* complexes in which van der Waals and hydrogen bonds dominate.¹ Charge induced interactions have been studied in less detail, because of the difficulties involved in the production and spectroscopic detection of weakly bound ionic complexes. Nevertheless, the importance of this type of molecule in chemistry is indisputable; ionic complexes are known to play a key role as intermediates in many chemical reactions and in interstellar and atmospheric environments, where many processes depend on ion–molecule interactions.^{2,3} Most of the spectroscopic information on ionic complexes available to date has been obtained in photodissociation experiments^{4–6} and particularly proton-bond rare gas complexes have been a topic of intense research.⁷ Recent progress in the generation of dense supersonic planar plasmas has made possible the detection of cluster ions in direct absorption as well.⁸ These sources offer a nearly Doppler free environment where adiabatic cooling yields rotational temperatures of $\sim 10\text{--}20 \text{ K}$. Within this context work on the linear complexes $(\text{N}_2 \cdots \text{N}_2)^+$ (Ref. 9) and $\text{N}_2 \cdots \text{H}^+ \cdots \text{N}_2$ (Ref. 10) is mentioned.

Cluster ions have binding energies that are intermediate between pure van der Waals and stable covalent bonds

($\approx 0.2\text{--}1 \text{ eV}$) and consequently they are not as floppy as many of their neutral counterparts. This is of interest particularly from a theoretical point of view; state-of-the-art *ab initio* calculations allow accurate predictions of high resolution molecular spectra and their application to ionic clusters provides insight into charge induced phenomena as well.^{10,11} The present study on $\text{N}_2 \cdots \text{Ar}^+ \cdots \text{N}_2$ offers a special case because the ionization potentials of Ar (15.76 eV) and N_2 (15.58 eV) are almost identical,¹² the resonance tending to favor a bond with covalent character. The $\text{N}_2 \cdots \text{Ar}^+ \cdots \text{N}_2$ complex is therefore expected to be strongly bound, as is the case for homonuclear cluster ions [e.g., Ar_n^+ (Ref. 4)] and the closely related $[\text{Ar} \cdots \text{N}_2]^+$.¹³

The experimental method used here is based on the absorption of tunable infrared radiation that multipasses an expansion cooled planar plasma.⁸ The plasma is generated by electron impact of a mixture of 5%–10% N_2 in Ar that is expanded supersonically through a $50 \mu\text{m} \times 32 \text{ mm}$ slit. A mass spectrometer is used to characterize the plasma conditions. An effective and fast production modulation is obtained by periodically changing the electric field gradients of the electron gun. This allows phase-sensitive detection by lock-in techniques. An absolute frequency calibration better than 0.001 cm^{-1} is obtained by simultaneously recording marker étalons and CO_2 as a reference gas. The best S/N

TABLE I. Observed frequencies (cm^{-1}) of rotational transitions involving vibrational excitation of the ν_3 antisymmetric NN stretch of $\text{N}_2 \cdots \text{Ar}^+ \cdots \text{N}_2$.

P-branch						R-branch					
J	ν	$\text{o}-\text{c}^{\text{a}}$ (10^{-4})	J	ν	$\text{o}-\text{c}^{\text{a}}$ (10^{-4})	J	ν	$\text{o}-\text{c}^{\text{a}}$ (10^{-4})	J	ν	$\text{o}-\text{c}^{\text{a}}$ (10^{-4})
0			21	2287.2616	5	0	2288.7981	24	21	2290.2040	3
1	2288.6590	4	22	2287.1910	10	1	2288.8616	-24	22	2290.2688	-6
2	2288.5931	32	23	2287.1186	-2	2	2288.9318	-5	23	2290.3350	1
3	2288.5209	-2	24	2287.0486	11	3	2289.0029	26	24	2290.3992	-11
4	2288.4532	11	25	2286.9757	-4	4	2289.0683	0	25	2290.4657	1
5	2288.3835	5	26	2286.9039	-8	5	2289.1362	1	26	2290.5314	6
6	2288.3127	-11	27	2286.8331	0	6	2289.2040	2	27	2290.5969	11
7	2288.2438	-7	28	2286.7609	-5	7	2289.2708	-6	28	2290.6617	10
8	2288.1748	-2	29	2286.6882	-14	8	2289.3384	-4	29	2290.7247	-8
9	2288.1053	-1	30	2286.6174	-3	9	2289.4054	-7	30	2290.7907	5
10	2288.0357	0	31	2286.5465	8	10	2289.4720	-13	31	2290.8547	-1
11	2287.9657	-1	32	2286.4732	-5	11	2289.5397	-6	32	2290.9189	-4
12	2287.8958	-1	33	2286.4014	-2	12	2289.6068	-4	33	2290.9843	7
13	2287.8251	-7	34	2286.3306	13	13	2289.6733	-7	34	2291.0488	9
14	2287.7540	-16				14	2289.7406	-1	35	2291.1122	2
15	2287.6862	9				15	2289.8066	-6	36	2291.1769	9
16	2287.6153	4				16	2289.8734	-2	37	2291.2395	-4
17	2287.5442	-2				17	2289.9403	4	38	2291.3033	-5
18	2287.4724	-13				18	2290.0060	0	39	2291.3668	-7
19	2287.4030	0				19	2290.0719	-2	40	2291.4304	-7
20	2287.3329	8				20	2290.1380	0	41	2291.4948	2

^aObserved-Computed.

ratios amount to ~ 30 and typical linewidths (FWHM) do not exceed 100 MHz.

In total 76 adjacent vibration-rotation lines around 2289 cm^{-1} were observed, all of which have been assigned to the ν_3 stretching mode of $\text{N}_2 \cdots \text{Ar}^+ \cdots \text{N}_2$. Transitions with rotational quantum numbers J , of up to 34 in the P branch and 41 in the R branch, were recorded (Table I). The spectrum resembles that of a $\Sigma-\Sigma$ transition of a linear molecule and exhibits a clear 5 to 4 spin-statistical alternation for odd and even rotational levels, as shown in Fig. 1 for both P - and R -branch transitions. This is consistent with a ${}^2\Sigma_u^+$ ground state symmetry, predicted from the electronic configuration $\dots 1\pi_g^4 3\pi_u^4 8\sigma_g^2 7\sigma_u$. The assignment of the

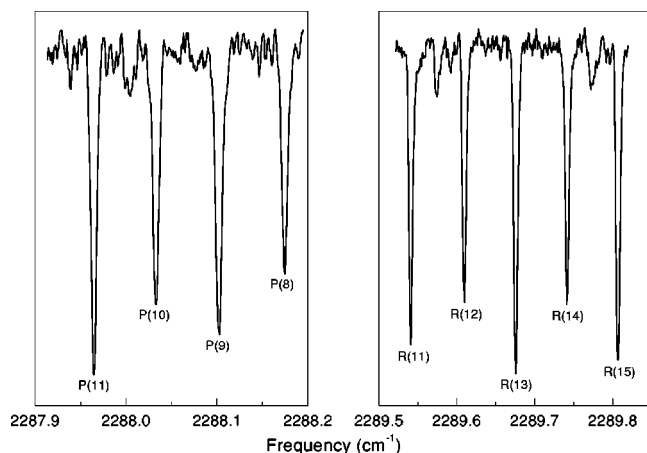


FIG. 1. Rovibrational transitions of the excited antisymmetric stretching vibration of $\text{N}_2 \cdots \text{Ar}^+ \cdots \text{N}_2$ around the Boltzmann maximum ($T_{\text{rot}} \approx 15 \text{ K}$) in the P -branch (left trace) and R -branch (right trace). A clear 5:4 spin-statistical alternation is observed for odd and even rotational levels, respectively, consistent with a linear and centrosymmetric geometry and a ground state with ${}^2\Sigma_u^+$ symmetry.

transitions to the antisymmetric NN stretching vibration of linear centrosymmetric $\text{N}_2 \cdots \text{Ar}^+ \cdots \text{N}_2$ is straightforward, even though other species (mainly $[\text{ArN}_{2n}]^+$ and pure nitrogen cluster ions $[\text{N}_{2n}]^+$) are also produced in the plasma. The absorption signals are not observed without Ar or N_2 in the expansion and scale linearly with the $[\text{ArN}_{2n}]^+$ mass signals. This excludes pure argon or nitrogen clusters. The spin-statistical alternation excludes molecules that do not have a center of symmetry, such as the ones with van der Waals like $[\text{Ar} \cdots \text{N}_2]^+$ or $[\text{Ar} \cdots \text{N}_4]^+$ geometry. Further evidence is provided by analysis of the rotational structure. Using a pseudodiatom energy level expression for the ground and vibrationally excited state and rotational energy levels given by an expansion in $J(J+1)$, an excellent fit with a standard deviation of less than 0.001 cm^{-1} is obtained. The resulting ground and vibrationally excited state constants are given in Table II. A rotational constant of the order 0.034 cm^{-1} excludes a molecule of the form $[\text{Ar} \cdots \text{N}_{2n}]^+$; for $n=1$ a much larger value ($>0.1 \text{ cm}^{-1}$) is calculated¹⁴ and, assuming that the N_4^+ unit is not seriously distorted upon complexation, B_0 will not exceed 0.02 cm^{-1} for $n=2$ and will only become smaller for larger n . For com-

TABLE II. Spectroscopic constants (cm^{-1}) of $\text{N}_2 \cdots \text{Ar}^+ \cdots \text{N}_2$ in the ${}^2\Sigma_u^+$ electronic ground state for $v=0$ and $\nu_3=1$.^a

ν_0	2288.7272(2)
B''	0.034 296(7)
D''	$1.9(4) \cdot 10^{-8}$
B'	0.034 232(6)
D'	$1.7(4) \cdot 10^{-8}$

^aThe uncertainties (in parentheses) are 1σ deviations in units of the last significant digit.

TABLE III. Calculated equilibrium structures, equilibrium dissociation energies, and rotational constants for $N_2 \cdots Ar^+ \cdots N_2$.

Method	Basis	$R_e(NN)$ (Å)	$r_e(N \cdots H)$ (Å)	B_e (cm^{-1})	D_e (eV)
MP2	aug-cc-pVDZ	1.134	2.343	0.034245	1.66
MP2	aug-cc-pVTZ	1.116	2.315	0.035139	1.68
RCCSD-T	cc-pVDZ	1.1200	2.4092	0.032956	1.740
RCCSD-T	cc-pVTZ	1.1049	2.3705	0.034004	1.668
RCCSD-T	cc-pVQZ	1.1014	2.3602	0.034297	1.725

plexes containing two or more argon atoms this value decreases even more rapidly.²¹

The assignment is supported by the outcome of high level *ab initio* calculations. These were carried out using both a restricted open shell MP2 (Ref. 15) and a partially spin-restricted coupled cluster approach (RCCSD),¹⁶ with a perturbative correction for the effects of triple excitations (RCCSD-T).¹⁷ Only valence-shell orbitals were correlated. In these calculations the correlation-consistent basis sets of Dunning and co-workers^{18,19} and augmented variants were used. The calculations at both levels converge to a linear centrosymmetric equilibrium geometry with a rotational equilibrium constant, B_e , close to the experimentally determined value for B_0 . The results are summarized in Table III.

The picture of a linear centrosymmetric molecule is also consistent with the outcome of the only other gas phase study on $N_2 \cdots Ar^+ \cdots N_2$ reported so far;²⁰ in this a symmetric isomer was proposed to explain a nearly exclusive loss of N_2 upon photodissociation of $[ArN_4]^+$.

The current study provides information on the charge delocalization in the complex. For the linear $[Ar \cdots N_2]^+$ species several calculations show that typically between 65% and 85% of the positive charge is located on the Ar-atom.^{13,14,21} Even when solvating N_2^+ ions with argon atoms a switch of the cation center is observed yielding $Ar^+ \cdots N_2$.²¹ When increasing the chain length by the addition of a second N_2 ligand the electrostatic polarization energy may become greater than the extra delocalization energy, drastically changing the bonding nature, but for $N_2 \cdots Ar^+ \cdots N_2$ this is not found to be the case. Actually, the present calculations predict an equilibrium dissociation energy D_e around 1.7 eV (Table III), clearly larger than the value calculated for $N_2 \cdots H^+ \cdots N_2$ [~ 0.7 eV (Ref. 10)] or measured in the case of N_4^+ [1.12(7) eV (Ref. 22)].

The band origin position of the antisymmetric stretch is located at 2288.7272(2) cm^{-1} , representing a shift of 41.99 cm^{-1} to the red of the N_2 fundamental, and more than 110 cm^{-1} to the blue of N_2^+ . This frequency shift is repro-

duced reasonably faithfully in the computed *harmonic* wave numbers (RCCSD-T, see Table IV), which are red-shifted by 30.65 cm^{-1} (cc-pVDZ) and 31.45 cm^{-1} (cc-pVTZ) relative to N_2 .²³ A possible interpretation of this result is that the vibration has considerably more N_2 than N_2^+ character, which means that the charge will be predominantly located at the Ar-atom. This also explains why the ν_3 stretching vibration of N_4^+ at 2234.5 cm^{-1} (Ref. 9) is closer to the N_2^+ fundamental and why that of $N_2 \cdots H^+ \cdots N_2$ at 2352.2 cm^{-1} (Ref. 10) is closer to that of N_2 . For these complexes the positive charge is expected to be respectively more and less delocalized than in $N_2 \cdots Ar^+ \cdots N_2$. A pronounced localization of the charge on the argon atom (more than 60%) is also indicated by the present MP2 calculations (aug-cc-pVTZ).

It is likely that $N_2 \cdots Ar^+ \cdots N_2$ is formed by recombination of N_2 and $Ar^+ \cdots N_2$. The latter molecule has been the subject of several reaction studies and was shown to photodissociate via two decay channels, $Ar^+ + N_2$ and $Ar + N_2^+$ in approximately 3:1 ratio.²⁴⁻²⁶ The present spectroscopic proof of an *intermolecular* bond based on an $Ar^+ \cdots N_2$ interaction may be of further help in characterizing the involved reaction dynamics.

This work has been supported by the Swiss National Science Foundation, project 20-55285.98 and by EEC Grant No. HPRN-CT-1999-00005. A grant by the French Embassy in Bern to support Swiss-French collaborations is acknowledged.

TABLE IV. Calculated (RCCSD-T) harmonic and experimental vibrational frequencies (cm^{-1}) compared to the N_2 fundamental.

Basis	ω_1	ω_2	ω_3	$\omega(N_2)$	$\omega_3 - \omega(N_2)$
cc-pVDZ	2330.21	183.7	2312.79	2343.44	-30.65
cc-pVTZ	2336.02	174.8	2318.79	2350.24	-31.45
cc-pVQZ	2360.31	...
Experiment	ν_1	ν_2	ν_3	$\nu(N_2)$	$\nu_3 - \nu(N_2)$
	2288.73	2330.72	-41.99

¹S. Novick, "Bibliography of rotational spectra of weakly bound complexes," <http://www.wesleyan.edu/chem/bios/vdw.html>.

²G. Winnewisser and E. Herbst, *Topics in Current Chemistry* (Springer-Verlag, Berlin, 1987), Vol. 139, pp. 121-172.

³R. P. Wayne, *Chemistry of Atmospheres* (Clarendon, Oxford, 1991).

⁴R. G. Keese and A. W. Castleman, Jr., in *Ion and Cluster Ion Spectroscopy and Structure*, edited by J. P. Maier (Elsevier, Amsterdam, 1989).

⁵M. W. Crofton, M. M. Price, and Y. T. Lee, in *Clusters of Atoms and Molecules II*, edited by H. Haberland (Springer-Verlag, Berlin, 1994).

⁶E. J. Bieske and J. P. Maier, *Chem. Rev.* **93**, 2603 (1993).

⁷O. Dopfer, D. Roth, R. V. Olkhov, and J. P. Maier, *J. Chem. Phys.* **110**, 11911 (1999), and references therein.

⁸H. Linnartz, D. Verdes, and T. Speck, *Rev. Sci. Instrum.* **71**, 1811 (2000).

⁹T. Ruchti, T. Speck, J. P. Connelly, E. J. Bieske, H. Linnartz, and J. P. Maier, *J. Chem. Phys.* **105**, 2591 (1996).

¹⁰D. Verdes, H. Linnartz, J. P. Maier, P. Botschwina, R. Oswald, P. Rosmus, and P. J. Knowles, *J. Chem. Phys.* **111**, 8400 (1999).

¹¹C. Léonard, P. Rosmus, S. Carter, and N. C. Handy, *J. Phys. Chem. A* **103**, 1846 (1999).

¹²G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, *J. Phys. Chem. Ref. Data* **17**, Suppl. 1 (1988).

¹³J. Mähner, H. Baumgärtel, and K.-M. Weitzel, *J. Chem. Phys.* **102**, 180 (1995).

¹⁴V. Freccer, D. C. Jain, and A. M. Sapse, *J. Phys. Chem.* **95**, 9263 (1991).

- ¹⁵D. J. Tozer, N. C. Handy, R. D. Amos, J. A. Pople, R. H. Nobes, Y. Xie, and H. F. Schaefer, *Mol. Phys.* **79**, 777 (1993).
- ¹⁶P. J. Knowles, C. Hampel, and H.-J. Werner, *J. Chem. Phys.* **99**, 5219 (1993).
- ¹⁷M. J. O. Deegan and P. J. Knowles, *Chem. Phys. Lett.* **227**, 321 (1994).
- ¹⁸T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
- ¹⁹D. E. Woon and T. H. Dunning, *J. Chem. Phys.* **98**, 1358 (1993).
- ²⁰T. F. Magnera and J. Michl, *Chem. Phys. Lett.* **192**, 99 (1992).
- ²¹K. Hiraoka, T. Mori, and S. Yamabe, *Chem. Phys. Lett.* **189**, 7 (1992).
- ²²K. Hiraoka and G. J. Nakajima, *J. Chem. Phys.* **88**, 7709 (1988).
- ²³For technical reasons the calculation of vibrational frequencies following cc-pVQZ was not possible.
- ²⁴H.-S. Kim and M. T. Bowers, *J. Chem. Phys.* **93**, 1158 (1990).
- ²⁵P. Tosi, O. Dmitrijev, and D. Bassi, *Chem. Phys. Lett.* **200**, 483 (1992).
- ²⁶S. Kato, J. A. de Gouw, C.-D. Lin, V. M. Bierbaum, and S. R. Leone, *Chem. Phys. Lett.* **256**, 305 (1996).