High-Resolution Rotational Spectroscopy of Weakly Bound Ionic Clusters: $ArH_3{}^+$, $ArD_3{}^+$

M. Bogey, H. Bolvin, C. Demuynck, and J. L. Destombes
Laboratoire de Spectroscopie Hertzienne, Université de Lille 1, 59655 Villeneuve d'Ascq Cédex, France

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The first high-resolution study of weakly bound cluster ions is reported. The millimeter- and submillimeter-wave rotational spectra of $ArH_3{}^+$ and $ArD_3{}^+$ have been observed in a magnetically confined, liquid-nitrogen–cooled glow discharge and a partial molecular structure has been derived from their analysis. $ArH_3{}^+$ appears to be planar, with the Ar atom lying on a symmetry axis of the $H_3{}^+$ equilateral triangle, 2.38 Å from the $H_3{}^+$ centroid. Splitting of some of the lines is strong evidence for tunneling motion.

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Cluster ions form a class of molecules which play a key role in a number of natural and laboratory processes.[1] Though they are weakly bound, a number of these clusters are now well characterized by mass spectrometry, and there is presently a growing interest in the kinetics and photodissociation dynamics of these species.[1,2] However, very little is known about the spectroscopic properties of these molecules in the gas phase. Nevertheless, such measurements are necessary to obtain accurate geometries and potential functions, and to interpret dynamical behavior should, for example, fine structure resulting from tunneling motions be observed. For the time being, only very low-resolution (several inverse centimeters) ir spectra are known for cluster ions such as $H_3O^+(H_2O)_n$ [3] and $H_3{}^+(H_2)_n$.[4]

In this Letter, we report the first high-resolution spectroscopic study of a weakly bound cluster ion, $ArH_3{}^+$, which we have detected through its rotational spectrum in the submillimeter-wave range, and we present a preliminary determination of its molecular structure.

$ArH_3{}^+$ is well known in mass spectrometry[5] and its binding energy is estimated to be about 0.36 eV.[6] To our knowledge, no *ab initio* calculation has been performed on this molecule, although results are available for some rare-gas–hydrogen clusters.[7] In particular, its analog $HeH_3{}^+$ has been studied extensively and found to be weakly bound[6,8] though it has not yet been detected by mass spectrometry.

The millimeter-wave spectrometer used in this study has been described elsewhere.[9] In the submillimeter-wave range (330–407 GHz), the source was a Carcinotron which could be phase locked if required.[10] The detector was a liquid-helium–cooled InSb bolometer. The whole spectrometer was controlled by a microprocessor system which ensured accurate frequency control, data acquisition, and signal processing. The ions were produced and observed in a negative-glow discharge ($L=80$ cm, i.d. $=5$ cm) extended by a longitudinal magnetic field, as initially developed by De Lucia *et al.*[11] and used in the study of a number of molecular ions.[10,12]

The first line was observed at 390 272 MHz on discharging a mixture of high-purity grade Ar and D_2, cooled with liquid nitrogen. From the characteristic change of its intensity with strength of the confining magnetic field B, namely, a sharp increase with B and the existence of an optimum magnetic field ($\cong 110$ G), this line was definitively attributed to an ionic species.[12] Under optimum conditions [$p(D_2)=8$ mTorr; $p(Ar)=14$ mTorr; discharge current $=4$ mA], the line could be observed with a signal-to-noise ratio of 10 with a 1-s scan time and a lock-in time constant of 10 ms. This is about 2 orders of magnitude weaker than the optimum $HN_2{}^+$ signal intensity observed in the same apparatus. Addition of traces ($\cong 5\times 10^{-4}$ Torr) of air, O_2, N_2, CO, CH_4, C_2H_2, or Kr immediately led to the disappearance of the line. In contrast, addition of H_2, Ne, or He, at partial pressures comparable to that of D_2, led to a decrease of the line by only about a factor 2. Replacing the stainless steel with brass electrodes had no effect on the line intensity. Since ArD^+ can be ruled out in view of the line frequency,[13] the identity of the absorber, formed with only Ar and D atoms, became of considerable interest.

An exhaustive frequency scan of ±2.5 GHz led to the detection of only four additional lines, which showed the characteristic K pattern expected for a $J\geq 2$ ${}^aR$ type rotational transition of a slightly asymmetric prolate rotor.[14] With the use of the Carcinotron in free-running mode, an extended frequency range of about 40 GHz was carefully explored and this led to the discovery of two further very weak lines (readily identified as H_2O and $DN_2{}^+$), and of another characteristic set of five lines. A fit of these ten lines reported in Table I led to the determination of the rotational and centrifugal distortion constants given in Table II. The inertial defect $\Delta=0.118$ amu Å^2 is similar to that of SO_2, O_3, etc.,[14] and suggested strongly that the molecule was planar. This was confirmed by the magnitude of the quartic defect $\delta=7.5\times 10^{-3}$ GHz^2, much smaller than, for example, in the deuterated water molecule (0.743 GHz^2).[14] The relative intensities of the $K=1$ and $K=0$ lines, though difficult to measure accurately, also appeared to be consistent with spin statistics involving two equivalent D atoms.

TABLE I. Observed transitions of ArD_3^+. The transitions are assigned as $J',K_a',K_c'-J'',K_a'',K_c''$.

Transition	ν_{obs} (MHz)
11,1,11-10,1,10	355 453.705(40)
11,2,10-10,2,9	357 105.961(40)
11,2,9-10,2,8	357 141.252(40)
11,0,11-10,0,10	357 915.910(50)
	357 915.207(50)
11,1,10-10,1,9	360 019.410(40)
12,1,12-11,1,11	387 595.942(40)
12,2,11-11,2,10	389 395.436(40)
12,2,10-11,2,9	389 441.402(40)
12,0,12-11,0,11	390 272.378(50)
	390 271.576(50)
12,1,11-11,1,10	392 569.456(40)

TABLE II. Molecular constants for the ground vibrational state of ArD_3^+ with the use of Watson's A-reduced Hamiltonian in the I^r representation.

	ArD_3^+
A (MHz)	655 137(4615)
B (MHz)	16 541.08(82)
C (MHz)	16 076.43(83)
Δ_J (kHz)	158.08(12)
Δ_{JK} (kHz)	9605.2(38)
Δ_K	0 (fixed value)
δ_J (kHz)	3.29(19)
δ_K (kHz)	11 600(408)
Δ (amu Å^2)	0.118

The relatively low B and C values clearly showed that one heavy atom, most likely Ar in view of the chemical composition of the discharge, was present in the molecule. Moreover, the A value is very close to the corresponding molecular constant in D_3^+ [654 266(10) MHz],[15] and quite different from the rotational constant of D_2 (896 600 MHz).[16] This strongly suggested that the molecule contained a D_3^+ triangle.

The evidence pointed then to a planar diamagnetic molecule with C_{2v} symmetry, very probably formed with a D_3^+ ion and one Ar atom. By analogy with the structure of the related molecules HeH_3^+ [6,8] and $H_2H_3^+$,[17] the molecular structure was first assumed to contain the Ar atom lying on a symmetry axis of D_3^+. If one assumes that the D_3^+ triangle remains equilateral, and derives the D—D bond length from the A value (d=0.876 Å), it is possible to adjust the distance of the Ar atom from the D_3^+ centroid to derive the ArD_3^+ molecular constants B and C to within 3×10^{-3}. This structure was used to predict the rotational spectrum of ArH_3^+, which was subsequently searched for in the negative glow by replacing D_2 by H_2, under the optimum experimental conditions required for ArD_3^+. Two sets of lines were found, remarkably close to the frequencies predicted for the $K=0$ and $K=1$ components of the $J=2\rightarrow3$ and $5\rightarrow6$ rotational lines (Table III). These results strongly support the identification of the observed ion and of its molecular structure. The apparent absence of the $K=2$ components does not negate this conclusion: They are predicted to be 15 times weaker than the $K=0$ line because of statistical and Boltzmann factors, and lie below the sensitivity threshold of our spectrometer.

Two further factors corroborate this conclusion: (i) With such a structure, the center of mass is well displaced from the center of charge which remains at the center of the H_3^+ triangle as the weakly bound Ar does not seriously disturb the charge distribution in H_3^+. A large dipole moment, of the order of 9 D, is then anticipated, which explains why the lines were observed under relatively unfavorable experimental conditions for the formation of clusters. From comparison with HN_2^+ signals an ArH_3^+ concentration of about 3×10^8 cm^{-3} was estimated. If we assume that the ArH_3^+ ions are produced by the three-body reaction

$$H_3^+ + 2Ar \xrightarrow{k_{3B}} ArH_3^+ + Ar$$

(Ref. 5), and take a conservative value $\tau\cong50$ μs for their lifetime (which is limited mainly by ambipolar diffusion to the wall and by volume reactions with electrons and Ar atoms), a value for the rate constant k_{3B} can be estimated, $k_{3B}\cong8\times10^{-29}$ cm^6 s^{-1} at about 100 K. This value compares with two values measured for the reaction $H_3^+ + 2H_2 \rightarrow H_5^+ + H_2$: 1.5×10^{-28} cm^6 s^{-1} at 130 K [18] and 1.2×10^{-29} cm^6 s^{-1} at 156 K.[19] (ii) Since the Ar atom is weakly bound, an in-plane tunneling motion can occur, which would explain the splitting observed on some transitions. Table IV gives a summary of the splitting $\Delta\nu$ and of the intensity ratio α of the two components, showing an unusual evolution of $\Delta\nu$ as a function of K. Such behavior can be understood in terms

TABLE III. Observed transitions of ArH_3^+ and comparison with predictions. The transitions are assigned as $J',K_a',K_c'-J'',K_a'',K_c''$.

Transition	ν_{pred} [a]	ν_{obs} (MHz)
3,1,3-2,1,2	182 184	181 871.745(100)
		181 846.579(150)
3,0,3-2,0,2	183 237	183 234.594(100)
3,1,2-2,1,1	184 175	184 198.883(100)
		184 201.462(100)
6,1,6-5,1,5	364 268	363 395.763(40)
		363 345.902(40)
6,0,6-5,0,5	366 366	366 108.959(40)
6,1,5-5,1,4	368 246	368 036.116(40)
		368 041.152(40)

[a] Predicted with the rotational constants derived from the ArD_3^+ structure (see text) and with the centrifugal distortion constants of ArD_3^+.

TABLE IV. Tunneling motion splittings $\Delta\nu$ and intensity ratio α of the two resolved components of a line.

	$\Delta\nu$ (MHz)	α_{meas}	α_{pred}[a]
	ArD_3^+		
11,0,11–10,0,10	0.700(100)	0.8(1)	8:10
11,1,11–10,1,10	Not observed		1:8
11,1,10–10,1,9	Not observed		1:8
12,0,12–11,0,11	0.800(100)	0.7(1)	8:10
12,1,12–11,1,11	Not observed		1:8
12,1,11–11,1,10	Not observed		1:8
	ArH_3^+		
3,0,3–2,0,2	Not observed		0:1
3,1,2–2,1,1	2.579(200)	Not measured	2:4
3,1,3–2,1,2	25.166(250)	Not measured	2:4
6,0,6–5,0,5	Not observed		0:1
6,1,5–5,1,4	5.036(80)	0.5(1)	2:4
6,1,6–5,1,5	49.861(80)	0.5(1)	2:4

[a] Statistical weight ratios of the two components.

of conventional group theory,[20] which also predicts spin statistics which agree with our observation, as shown in Table IV.

In the case of ArH_3^+, the splitting $\Delta\nu$, which has not yet been quantitatively analyzed, is large enough to complicate accurate determination of the molecular parameters. Moreover, as only a limited data set is available, the A rotational constant is poorly determined. Nevertheless, a rough estimate of A can be obtained by scaling of the ArD_3^+ A value according to the H and D atomic masses, yielding $A = 1\,309\,230$ MHz. Fixing A at this value leads to a preliminary determination of B and C: $B = 30\,962.29(81)$ MHz, $C = 30\,137.67(81)$ MHz.

The most probable Ar-H_3^+ centroid distance which best reproduces the molecular constants of both ArD_3^+ and ArH_3^+ is then $d = 2.384$ Å. This distance, which is similar to that calculated for HeH_3^+ (2.64 Å),[8] is, as expected from the bond energy of ArH_3^+ (0.36 eV),[6] intermediate between the bond lengths in a bound molecule such as ArH^+ ($d = 1.288$ Å)[13] and in a true van der Waals molecule like Ar--HCl ($d = 4.006$ Å).[21] Figure 1 presents the two possible planar structures, with the Ar at the vertex of the triangle (structure I) or opposite to it (structure II). By analogy with HeH_3^+ [6,8] and $H_2H_3^+$,[17] structure I seems energetically the more likely. However, since Ar possesses p electrons, structure II cannot be ruled out at this stage. For moderate bond lengths, when we take into account interactions between occupied Ar orbitals and vacant symmetry-adapted orbitals of H_3^+, the σ-bonding structure (I) is more stable and more likely than a π-bond structure (structure II). However, for a relatively long bond length, as in ArH_3^+, this argument weakens, and the energy difference between the two configurations might be small.

A complete determination of the molecular structure will need data on the "mixed" isotopic forms ArH_2D^+ and ArD_2H^+. This study is currently in progress but is experimentally difficult since signals are very weak and at the detection threshold of the spectrometer. Moreover, a detailed analysis of the tunneling motion will probably need new theoretical developments,[22] which will, in turn, lead to a new approach to the dynamics of these ion clusters.

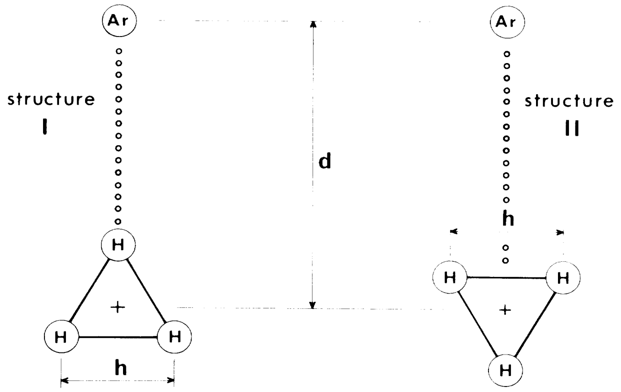

FIG. 1. Molecular structures of ArH_3^+: $h = 0.876$ Å; $d = 2.384$ Å.

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