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Short Communication

Molecular Constants for the ${}^1\Sigma^+$ Ground State of the ArH^+ Ion*

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From the near equilibrium PNO-CEPA potential and dipole moment curves the following molecular constants for the ${}^1\Sigma^+$ ground state of the ArH^+ ion have been calculated: $r_e = 1.286$ Å, $\omega_e = 2723\ \mathrm{cm}^{-1}$, $\omega_e x_e = 56\ \mathrm{cm}^{-1}$, $D_0 = 3.89$ eV and $\mu_0 = 2.384$ D. The rotationless radiative lifetimes of the five lowest vibrational states are predicted to be 2.28, 1.2, 0.85, 0.64, 0.46 for ArH^+ and 9.09, 4.71, 3.27, 2.55 and 2.11 for ArD^+, respectively (all values are in milliseconds and in ascending order of the vibrational levels).

Key words: ArH^+ ion, ground state of ~

For the interpretation of various ion-molecule reactions involving the ArH^+ ion [1–3] its molecular constants are needed which, however, are not yet reliably established from experiments. Previously, we have shown for the first- and second-row diatomic hydrides [4] that the quantum chemical calculations using correlated PNO-CEPA wavefunctions [5, 6] are capable of producing equilibrium distances to about ± 0.003 Å and ω_e values to about $\pm 20\ \mathrm{cm}^{-1}$. The near equilibrium PNO-CEPA dipole moment curves [4a] proved to yield râther reliable Einstein coefficients for low-lying vibrational transitions [7]. The overall agreement can be demonstrated in terms of rotationless radiative lifetimes, which have been calculated for the HF molecule to be 5.2, 2.8, 2.1 and 1.7 as compared to the corresponding experimental values of Sileo and Cool [8] of 5.3, 2.9, 2.1 and 1.8 and for the HCl molecule to be 33.6, 18.5, 13.5 and 9.5 as compared to the values given by Herbelin and Emanuel [9] of 28.9, 15.9, 11.6 and 9.6 (all values are in milliseconds in ascending order of the vibrational levels and are not thermally averaged). Our wavefunctions for the ${}^1\Sigma^+$ ground state of the ArH^+ ion have been

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* Dedicated to Prof. Hermann Hartmann on the occasion of his 65th birthday.

determined by the same computational procedure as used for the AH systems; therefore, similar accuracy of the calculated molecular constants is expected as for other diatomic hydrides [4].

In Table 1 the total energies and dipole moments as calculated from the SCF, PNO-CI and CEPA methods are listed. Table 2 exhibits the spectroscopic constants, the proton affinity of argon and the dipole moment. So far there are no accurate experimental values to be compared with. Our CEPA equilibrium distance is distinctly shorter than the value derived from the scattering data by Henglein [3] (1.31 Å) and the SCF value calculated by Roach and Kuntz [10] (1.38 Å) using an optimized expansion of three Gaussians for a single-zeta STO basis set plus additional polarization functions. Our r_e value is smaller and the ω_e value larger than in the HCl^+ ground state as expected from the regularities of these parameters in AH^+ systems [4b]. Futrell [11] adopted for the interpretation of the tandem-ion cyclotron resonance experiments of the reaction $D_3^+ + Ar \rightarrow ArD^+ + D_2$ a $\Delta G_{1/2}^{ArD} = 1855\ cm^{-1}$ which compares well with our CEPA value of 1890 cm^{-1} calculated for the ArD^+ ion, but the potential curve is not as anharmonic as would result from the data given in his work. Our second vibrational term lies already higher by about 100 cm^{-1}. The proton affinity of argon is calculated to be 3.89 eV with an expected accuracy of about ±0.05 eV (cf. results for proton affinities of the first- and second-row atoms in Ref. [4b]). The SCF value of Roach and Kuntz [10] of 3.92 eV

Table 1. The potential and the dipole moment curves of the ArH^+ ground state (in a.u.)

R	Total energy[a] SCF	PNO-CI (upper bound)	CEPA	Dipole moment[b] SCF	CEPA
1.9	−526.882299	−527.094803	−527.108225	0.5755	0.5655
2.1	−526.930776	−527.144255	−527.158058	0.7010	0.6823
2.2	−526.942452	−527.156419	−527.170427	0.7708	0.7464
2.35	−526.949937	−527.164581	−527.178910	0.8846	0.8492
2.5	−526.949363	−527.164601	−527.179256	1.0090	0.9595
2.7	−526.941245	−527.157121	−527.172213	1.1912	1.1174
3.0	−526.921860	−527.138323	−527.154036	1.4979	1.3763
3.3	−526.900566	−527.117123	−527.133359	1.8409	1.6607
∞	−526.806983	−527.016839	−527.03019[c]		

[a] The Gaussian basis set derived from Huzinaga's [12] 12*s*, 9*p* set for Ar and 6*s* set for H was of the size 14*s*, 10*p*, 3*d*, 1*f* for Ar and 6*s*, 2*p*, 1*d* for H, respectively, with the following exponents for the diffuse functions: Ar *s* 0.074, 0.185, 0.463, 1.163; *p* 0.093, 0.224, 0.537, 1.29; *d* 0.12, 0.35, 1.24; *f* 0.75; H *p* 0.25, 1.0; *d* 0.65. Only the innermost five *s* functions and two *p* functions on argon and three *s* functions on hydrogen were contracted. Apart from the most diffuse functions the basis set parallels that of Reinsch and Meyer [13] used in the calculation of Ar polarisability. All valence electrons were correlated and the most important single substitutions have been included in the CI expansion.

[b] With respect to argon nucleus as origin.

[c] The calculated valence correlation energy of 0.2233 a.u. lies close to the value of Ahlrichs *et al.* [14] of 0.2277 a.u. obtained with the same method; see this reference for the discussion of the correlation energy for the Ar atom.

Table 2. Molecular constants for the $^1\Sigma^+$ ground state of the ArH^+ ion

Method	r_e(Å)	B_e(cm^{-1})	α_e(cm^{-1})	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	D_0(eV)[a]	μ_0(D)
SCF	1.274	10.55	0.371	2800	59	3.74	
PNO-CI	1.282	10.43	0.362	2758	56	3.87	
CEPA	1.286	10.36	0.364	2723	56	3.89	2.229[b]

[a] All values are corrected for zero point energies $[G(0) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e]$.

[b] $\mu_1 - \mu_0 = 0.157$ D, $\mu_0^{ArH^+} - \mu_0^{ArD^+} = 0.162$ D. All values are given with respect to the center of mass as origin.

(corrected for zero-point energy) is higher by 0.2 eV than our SCF value which, however, should lie close to the SCF limit. In the literature one finds various rather uncertain values for this quantity, e.g. 3.4 to 4.2 eV [1], 3.56 eV [2] or 3.84 eV [3]. According to the present calculation the latter value of Henglein [3] is seen to be the correct one. Using the experimental and our recommended values [4] for dissociation and ionization energies, the proton affinity of argon allows for derivation of the heat of reaction for reactions like:

$$Ar + HX^+ \rightarrow ArH^+ + X \text{ or } Ar^+ + HX \rightarrow ArH^+ + X.$$

For X = H both reactions are exothermic, with heats of reaction of 120 kJ/mole and 150 kJ/mole being in good agreement with the values derived by Henglein [3]. Assuming small activation energies this energy is sufficient in both reactions to populate the rotational–vibrational levels up to $v = 4$ of ArH^+. From the CEPA dipole moment curve the Einstein coefficients and the radiative lifetimes have also been calculated, which are of interest, e.g., for the internal energy distribution in the ArH^+ product. These data are given for the five lowest vibrational states in Table 3. The very good agreement with the experimental data defined in a similar way for the HF and HCl molecules allows for estimates of the error bounds of about 15 to 20 per cent with possibly somewhat higher uncertainties in small Einstein coefficients (cf.

Table 3. Einstein "A" coefficients[a] for the ArH^+ (lower triangle) and ArD^+ (upper triangle) ions

τ (msec)[b]		"$A_{v',v''}$" (sec^{-1})						τ (msec)
ArH^+		0	1	2	3	4	5	ArD^+
	0	0.0000	0.1100+3	0.2454+1	0.6729−1	0.1532−2	0.1898−5	
2.28	1	0.4384+3	0.0000	0.2097+3	0.7410+1	0.2779+0	0.8056−2	9.09
1.20	2	0.1458+2	0.8156+3	0.0000	0.2983+3	0.1481+2	0.7539+0	4.71
0.85	3	0.6178+0	0.4333+2	0.1139+4	0.0000	0.3764+3	0.2389+2	3.27
0.64	4	0.2284−1	0.2671+1	0.7837+2	0.1486+4	0.0000	0.4497+3	2.55
0.46	5	0.3992−3	0.7157−1	0.7499+1	0.8174+2	0.2068+4	0.0000	2.11

[a] Defined in terms of rotationless dipole moment matrix elements; the vibrational spacings and eigenfunctions have been obtained from the solution of the radial Schrödinger equation with the fitted CEPA curve as an input. For the dipole moment curves the center of mass has been taken as origin.

[b] $\tau(v') = \left(\sum_{v''<v'} A_{v',v''}\right)^{-1}$

Table 3). If compared with the HF and HCl molecules, the radiative lifetimes in the vibrational states of ArH^+ are smaller by about a factor of 10 than in the isoelectronic HCl and even smaller than in the HF molecule.

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