Calculation of Molecular Constants for the $^1\Sigma^+$ Ground States of the NeH$^+$ and KrH$^+$ Ions

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Potential energy and dipole moment functions have been calculated for the ground states of the NeH$^+$ ($1.0 \leqq R \leqq 15$ a.u.) and the KrH$^+$ ($1.6 \leqq R \leqq 20$ a.u.) ion from highly correlated SCEP/VAR and SCEP/CEPA electronic wave functions. The following spectroscopic constants have been derived: Ne^{20}H$^+$ $r_e = 0.996 \pm 0.003$ Å, $\omega_e = 2896 \pm 20$ cm^{-1}, $D_0(\mathrm{Ne}+\mathrm{H}^+) = 2.10 \pm 0.05$ eV; Kr^{84}H$^+$ $r_e = 1.419 \pm 0.003$ Å, $\omega_e = 2561 \pm 20$ cm^{-1}, $D_0(\mathrm{Kr}+\mathrm{H}^+) = 4.65 \pm 0.05$ eV. The Einstein transition probability coefficients of spontaneous emission have been calculated for all transitions $v \leqq 5$ of Ne^{20}H$^+$, Ne^{20}D$^+$, Kr^{84}H$^+$ and Kr^{84}D$^+$, respectively.

1. Introduction

Scattering [1 – 4], associative ionization [5], ion cyclotron resonance [6], mass [7, 8] and infrared [9] spectroscopic experiments on the strongly bound protonated rare gas atoms have stimulated much theoretical work concerning the potential energy functions (PEF's) for the ground states of the HeH$^+$ [10 – 13], NeH$^+$ [10, 14 – 16] and ArH$^+$ [17 – 19] ions. There is considerable interest in accurate PEF's for these ions, which have been, for instance, used to interpret the observed HeH$^+$ quasibound rovibronic states [11, 13] and the scattering experiments [1 – 4]. They also represent an interesting model system for the study of the long-range interactions [11]. Only recently, molecular parameters of the present work for NeH$^+$ and our previous results for ArH$^+$ [19] have been found to agree very well with the electron energy spectra for as-

Table 1a. The potential energy and the dipole moment functions of the $^1\Sigma^+$ ground state of NeH$^+$ (all values in a.u.).

Distance	Total energy [a]			Dipole moment [b]	
	SCF	SCEP/VAR	SCEP/CEPA	SCF	SCEP/CEPA
1.0	−128.089673	−128.342347	−128.349039	.5652	.5577
1.05	.200137	.453939	.460775	.5944	.5857
1.1	.289371	.544313	.551296	.6251	.6148
1.2	.419631	.676833	.684119	.6906	.6770
1.3	.504063	.763448	.771045	.7616	.7441
1.5	.591145	.854475	.862689	.9198	.8925
1.7	.620652	.887162	.895954	1.0992	1.0591
1.9	.624393	.893185	.902477	1.2979	1.2426
2.1	.617269	.887443	.897128	1.5135	1.4419
2.3	.606358	.877121	.887075	1.7426	1.6557
2.5	.594995	.865739	.875837	1.9818	1.8826
2.7	.584665	.854983	.865112	2.2275	2.1206
2.9	.575909	.845581	.855648	2.4763	2.3672
3.1	.568799	.837746	.847689	2.7253	2.6192
3.3	.563193	.831431	.841213	2.9721	2.8733
3.5	.558863	.826466	.836076	3.2152	3.1264
4.0	.552091	.818543	.827771	3.8011	3.7405
6.0	.545762	.811030	.819782	5.9321	5.9209
9.0	.544929	.810095	.818814	8.9713	8.9676
15.0	.544772	.809923	.818639	14.9897	14.9884

[a] The following Gaussian AO basis sets have been employed: **12s, 8p, 3d, 1f** for Ne and **7s, 2p, 1d** for H; in the SCEP/VAR calculations all single and double substitutions with respect to the Hartree-Fock configuration have been included and the higher substitutions have been approximately accounted for by the CEPA scheme. Previously, the following total energies at r_e have been calculated: −128.6283 a.u. (SCF, Ref. [10]), −128.5886 a.u. (SCF, Ref. [14]), −128.6242 a.u. (SCF, Ref. [16]), −128.6818 a.u. (FO-CI, Ref. [16]).

[b] with respect to the Ne atom as origin.

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sociative ionization [5] in the collisional processes Ne*($^3P_2$), Ar*($^3P_2$) + H. These experiments yielded so far the most accurate proton affinities of the Ne and Ar atoms and the vibrational spacings for several bound vibrational states of the NeH$^+$ and ArH$^+$ ions.

In this work we report the ground state PEF's for the NeH$^+$ and KrH$^+$ ions, encompassing a large region of internuclear distances, and their infrared transition probability coefficients of spontaneous emmission as calculated from high correlated SCEP/VAR [20] (self-consistent electron pair approach yielding variational results) and SCEP/CEPA [21 – 23] (coupled electron pair approach) electronic wave functions.

2. Results

In Table 1 a the calculated SCF, SCEP/VAR, and SCEP/CEPA total energies and the dipole moments for NeH$^+$ are listed (for computational details see footnote of Table 1 a). The calculated spectroscopic constants are given in Table 2. Our SCF results closely parallel those calculated by Peyerimhoff [10], which represent near Hartree-Fock limit results for NeH$^+$. Comparison of the SCEP/VAR correlation energies at $R = 15.0$ a. u. with the so far best variational calculations for the Ne atom performed by Sazaki and Yoshimine [24] demonstrates that we have obtained about 90 per cent of their correlation energy, i. e. about 85 per cent of the valence correlation energy for the Ne atom. Thus, the SCEP/CEPA potential energy function should reproduce the "true" function quite accurately close to the equilibrium distance. In our recent calculations for the isoelectronic HF, HCl, and HBr molecules [25] we used the same size of the basis sets as in the present work and obtained spectroscopic constants which agree within about 5 to 15 cm^{-1} for ω_e and within ± 0.003 Å for r_e with the well established experimental values. We therefore expect similar accuracy also for the present values for both NeH$^+$ and KrH$^+$ ions. The SCEP/CEPA results for NeH$^+$ confirm the previously published theoretical ω_e and

Table 1b. The potential energy and the dipole moment functions of the $^1\Sigma^+$ ground state of KrH$^+$ (all values in a.u.).

Distance	Total energy [a]		Dipole moment [b]	
	SCF	SCEP/CEPA	SCF	SCEP/CEPA
1.6	−2750.887202	−2751.076708	.3374	.3174
1.7	1.023850	.213329	.3599	.3390
1.8	1.126236	.315776	.3868	.3649
1.9	1.202395	.392060	.4185	.3951
2.0	1.258473	.448306	.4549	.4297
2.2	1.328164	.518420	.5422	.5116
2.4	1.361199	.551985	.6488	.6097
2.6	1.372549	.563975	.7749	.7227
2.8	1.371131	.563287	.9202	.8487
3.0	1.362514	.555449	1.0846	.9856
3.2	1.350179	.543891	1.2674	1.1309
3.4	1.336247	.530666	1.4679	1.2825
3.6	1.321988	.51698	1.6848	1.4386
4.0	1.295221	.49070	2.1624	1.7600
4.5	1.267903	.4626	2.8244	2.178
6.0 [c]	1.224998	.4115	4.9911	3.7
10.0	1.210935	.3885	9.8959	9.847
15.0	1.210495	.387952	14.9588	14.9586
20.0	1.210427	.387889	19.9769	19.9767

[a] The following Gaussian AO basis sets have been employed: 16s, 12p 5d, 1f for Kr and 7s, 2p, 1d for H. The s and p exponents in the core region have not been fully optimized with respect to the energy, since we were only interested in valence shell properties.

[b] with respect to the Kr atom as origin.

[c] Near $r = 6$ an avoided crossing of two states causes convergence difficulties so that the results of the procedure employed are subjected to larger errors.

Table 2. Calculated molecular constants (ground state).

	r_e (Å)	B_e (cm^{-1})	α_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_0 [a] (eV)	μ_0 [b] (Debye)
NeH$^+$							
SCF	0.975	18.48	1.200	3030	134	2.00	
VAR [c]	0.992	17.86	1.097	2932	116	2.09	
CEPA [d]	0.996	17.72	1.096	2896	113	2.10	3.004
KrH$^+$							
SCF	1.411	8.50	0.248	2625	52	4.27	
CEPA [d]	1.419	8.41	0.256	2561	49	4.65	1.944

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

[b] vibrationally averaged dipole moment with respect to the center of mass as origin.

[c] SCEP/VAR.

[d] SCEP/CEPA.

D_0 values obtained from first order CI calculations by Bandybey et al. [16], in which only a small portion of the correlation energy had been accounted for. Our equilibrium distance is calculated to be somewhat larger (cf. Table 3).

In Table 1 b results obtained for the KrH^+ ion are given. For this molecule no other theoretical results for comparison are available.

Various theoretical and experimental molecular parameters for the ions HeH^+ to XeH^+ are listed in Table 3. From these data one recognizes that, though relatively small, the correlation contributions to the PEF's are not negligible. The correlation effect always increases the SCF r_e values (for instance, by about 0.02 Å for NeH^+), decreases the ω_e values (for instance, by about 130 cm^{-1} for NeH^+), and increases the values of the dissociation energies (for NeH^+ and ArH^+ by about 0.1 eV). For the KrH^+ ion a rather pronounced increase in the correlation energy has been calculated by going from the Kr atom to the KrH^+ ion, increasing the SCF proton affinity of the Kr atom by 0.38 eV. This is due to the strong penetration of the proton into the valence shell of Kr (for the R-dependency of the calculed correlation energies cf. Table 1 b).

Our calculated equilibrium distances can be compared only with those obtained from model potentials used for the interpretations of the elastic scattering experiments [1 – 4]. The agreement for NeH^+ is quite well, the theoretical value lies between the values $r_e = 0.99$ Å of Weise et al. [2] and $r_e = 1.005$ Å of Rich et al. [4]. For KrH^+ these empirical values are seen to be too long by about 0.05 Å (cf. Table 3). The ΔG values of NeH^+ has been directly measured in the associative ionization experiments of Lorenzen et al. [5]. Although the energy resolution in these experiments is smaller than our estimated error in the SCEP/CEPA value of about $\pm 20\ cm^{-1}$, both values agree nicely (cf. Table 3). The proton affinities of the rare gas atoms are of considerable interest for the calculation of the heat of reaction of a variety of ion-molecule reactions. One would therefore like to know these values rather accurately. As we have previously demonstrated in the calculations of the proton affinites for the atoms Li to F and Na to Cl, these quantities can be calculated for the atoms at the right side of the periodic system from highly correlated electronic wave functions within an accuracy of about ± 0.05 eV [26]. This is fully confirmed also by the associative ionization experiments of Lorenzen et al. [5] for NeH^+ and ArH^+, which yielded values in a very good agreement with our theoretical predictions (cf. Table 3). For KrH^+ only a value derived from model potentials is available for comparison. This value lies close to our SCF result, but the SCEP/

Table 3. Comparison of some spectroscopic data of the protonated rare gas atoms.

Molecule	Method	r_e(Å)	$\Delta G_{1/2}$(cm^{-1})	D_0(eV)	$A_{v''=0}^{v'=1}$(sec^{-1})
HeH^+	SCF[a]	0.765	2992	1.72	
	CW[b]	0.7743	2911.29	1.8441	
	Exp.[c]	0.77			
NeH^+	SCF	0.975	2762	2.00	
	FO-CI[d]	0.989	2691	2.09	
	SCEP/CEPA	0.996 ± 0.003	2670 ± 20	2.104 ± 0.05	756.0
	Exp.	0.99[e]; 1.005[f]	2653 ± 200	2.101 ± 0.03[g]	
ArH^+	SCF[h]	1.274	2682	3.74	
	PNO/CEPA[h]	1.286 ± 0.003	2611 ± 20	3.89 ± 0.05	438.0
	Exp.	1.24[f]; 1.31[e]	2564 ± 200	3.856 ± 0.03	
KrH^+	SCF	1.411	2522	4.27	
	SCEP/CEPA	1.419 ± 0.003	2463 ± 20	4.65 ± 0.05	285.0
	Exp.	1.47[e]; 1.54[f]		4.29[e]	
XeH^+	Exp.	1.74		6.75	

[a] Ref. [10].

[b] from data given in Ref. [12] as calculated from the PEF from correlated wave functions (CW) of Ref. [11].

[c] Ref. [2].

[d] first order CI calculations of Ref. [16].

[e] Ref. [1], [2] and [3]. f) Ref. [4]. g) Ref. [5]. h) Ref. [19].

Table 4. Einstein "A" transition probability coefficients[a] of spontaneous emission ($J = 0$, all values in sec^{-1}).

v'	0	1	2	3	4	5
Ne^{20}H$^+$ (lower triangle and Ne^{20}D$^+$ (upper triangle)						
0	0.	0.196/ + 3	0.130/ + 2	0.156/ + 1	0.244/ + 0	0.227/ − 1
1	0.756/ + 3	0.	0.358/ + 3	0.336/ + 2	0.386/ + 1	0.512/ + 0
2	0.672/ + 2	0.130/ + 4	0.	0.473/ + 3	0.588/ + 2	0.780/ + 1
3	0.961/ + 1	0.175/ + 3	0.162/ + 4	0.	0.551/ + 3	0.880/ + 2
4	0.196/ + 1	0.287/ + 2	0.301/ + 3	0.174/ + 4	0.	0.596/ + 3
5	0.449/ + 0	0.617/ + 1	0.622/ + 2	0.440/ + 3	0.169/ + 4	0.
Kr^{84}H$^+$ (lower triangle) and Kr^{84}D$^+$ (upper triangle)						
0	0.	0.714/ + 2	0.110/ + 1	0.384/ − 2	0.499/ − 5	0.124/ − 5
1	0.285/ + 3	0.	0.137/ + 3	0.374/ + 1	0.289/ − 1	0.865/ − 3
2	0.683/ + 1	0.536/ + 3	0.	0.198/ + 3	0.770/ + 1	0.697/ − 1
3	0.408/ − 1	0.222/ + 2	0.753/ + 3	0.	0.251/ + 3	0.126/ + 2
4	0.336/ − 2	0.304/ + 0	0.452/ + 2	0.932/ + 3	0.	0.297/ + 3
5	0.750/ − 3	0.172/ − 1	0.996/ + 0	0.762/ + 2	0.107/ + 4	0.

[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 SCEP/CEPA PEF as input. For the dipole moment curves the center of mass has been taken as origin.

CEPA proton affinity of Kr is calculated to be larger by 0.36 eV.

Very frequently the protonated rare gas atoms are produced in excited rovibronic states. Nevertheless, no emission systems could so far be detected experimentally. From our SCEP/CEPA dipole moment functions we have calculated the Einstein transition probability coefficients of spontaneous emission which are listed for all transitions $v' \leqq 5$ of Ne^{20}H$^+$, Ne^{20}D$^+$, Kr^{84}H$^+$, and Kr^{84}D$^+$ in Table 4. These data give insights into the magnitude of the radiative lifetimes of the vibronic states in this series of molecules, and they might be useful for the derivation of the infrared intensities and the populations of the particular rovibronic states in the protonated rare gas atoms. Similar calculations for the isoelectronic HF, HCl, and HBr molecules [25] demonstrated the high reliability of such theoretical values. This investigation allows to estimate an accuracy of about 5 to 10% for the fundamental sequence ($\Delta v = 1$) in the calculated probability coefficients and probably slightly larger uncertainties for the first overtone sequence. It is interesting to note that the NeH$^+$, ArH$^+$, and KrH$^+$ ions in their electronic ground states emit much better than their isoelectronic neutral counterparts HF, HCl, and HBr. The corresponding $A(v' = 1 \rightarrow v'' = 0)$ values are: HF 189 [25], NeH$^+$ 755.9; HCl 34.6 [25], ArH$^+$ 438.4; HBr 5.6 [25], KrH$^+$ 284.9 (all values in sec^{-1}).

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