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Theoretical Description of the Electronic Structure of the Alkali Hydride Cation NaH$^+$

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A theoretical determination of the electronic structure of NaH$^+$ is presented. Potential energy curves and dipole moments have been computed for 48$^2\Lambda^{(+)}$ electronic states (i.e., correlated adiabatically up to Na(6s) + H$^+$) through a model-potential-type method over a wide range of R. Equilibrium distances, transition energies, depths of wells, and/or heights of humps predicted at short and large interatomic separations are reported and compared with available experimental and theoretical values. Variations of the static dipole polarizabilities versus internuclear distance have been determined for the two lowest states.

I. Introduction

Experiments involving ultracold plasmas[1−3] or ultracold Rydberg atoms in which many-body effects may be important,[4] have illustrated recently the need of studying molecular systems in which dications are present. For instance, mechanisms of their formation have been established in a Bose−Einstein condensate,[5] and in the past few years, the alkali molecular ion NaCs$^+$ [6] has been observed for the first time.

Although several experimental schemes have been proposed to create a Bose−Einstein condensate of alkali hydride molecules,[7] present theoretical and experimental investigations in the ultracold energy regime are mainly done on alkali molecular systems (ionic and neutral). In contrast, those on alkali hydride molecular ions are practically nonexistent. No spectroscopy experiments have been achieved presently despite their importance in astrophysics,[8] and their electronic structure is mainly known theoretically via the interpretation of charge transfer processes.[9−16]

So to encourage similar studies on alkali hydride compounds, we present here a complete description of the electronic structure of NaH$^+$, including a determination of dipole moments and molecular polarizabilities. The present calculations have been achieved in the framework of a model potential-type method that has been developed previously for alkali molecular ions[17−20] and recently used with success to describe the electronic structure of LiH$^+$,[21] for which various experimental and theoretical data are available.[22−29]

II. Theoretical Approach

The alkali hydride cation NaH$^+$ is treated as a one-active electron system in which the valence electron is moving in the field of the ionic core, Na$^+$, and a proton separated by a distance, R. The interaction between the outermost electron and the alkali ion Na$^+$ is modeled by a model potential[30]

$$V(r_{\mathrm{Na}^+}) = \frac{-1}{r_{\mathrm{Na}^+}} - \frac{10}{r_{\mathrm{Na}^+}}(\mathrm{e}^{-7.887\,47 r_{\mathrm{Na}^+}} + 2.354\,102 r_{\mathrm{Na}^+}\,\mathrm{e}^{-2.6988 r_{\mathrm{Na}^+}}) \quad (1)$$

whereas that between the external electron and the proton is represented by the Coulomb potential

$$V(r_{\mathrm{H}^+}) = \frac{-1}{r_{\mathrm{H}^+}} \quad (2)$$

Polarization effects are taken into account through a core polarization potential[31]

$$V(r_{\mathrm{Na}^+}, R) = \frac{\alpha^{\mathrm{d}}_{\mathrm{Na}^+}\vec{r}_{\mathrm{Na}^+}.\vec{R}}{r^3_{\mathrm{Na}^+}R^3}\sqrt{1 - \exp-\left(\frac{r_{\mathrm{Na}^+}}{\rho}\right)^6} \quad (3)$$

where $\alpha^{\mathrm{d}}_{\mathrm{Na}^+}$ is the static dipole polarizability of the ionic core Na$^+$. We used the value $\alpha^{\mathrm{d}}_{\mathrm{Na}^+} = 0.9965 a_0^3$.[32] The cutoff parameter ρ needed to avoid a divergence at short range is obtained through a variational calculation of the ground-state energy at the computed equilibrium position $R_{\mathrm{e}}^{\mathrm{computed}}$. Repulsion between the ionic core Na$^+$ and the proton is represented by a long-range model limited to Coulombic and polarization interactions in which overlap and exchange effects have been neglected

$$V(R) = \frac{1}{R} - \frac{\alpha^{\mathrm{d}}_{\mathrm{Na}^+}}{2R^4} \quad (4)$$

The energy and wave function of a molecular state $^2\Lambda^{(+)}$ are determined by solving in prolate spheroidal coordinates the one-electron model Schrödinger equation

$$[T + V(r_{\mathrm{H}^+}) + V(r_{\mathrm{Na}^+}) + V(r_{\mathrm{Na}^+}, R) + V(R)]\Psi^{2\Lambda(+)}(r_{\mathrm{Na}^+}, r_{\mathrm{H}^+}, R) = E^{2\Lambda(+)}\Psi^{2\Lambda(+)}(r_{\mathrm{Na}^+}, r_{\mathrm{H}^+}, R) \quad (5)$$

where T is the one-electron kinetic energy operator. The wave

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TABLE 1: Comparison between Molecular Energies Computed at $R = 500a_0$ and Relevant Experimental Data Averaged over J Values[33] [a]

dissociation limit	E_{exptl} (cm^{-1})	E_{computed} (cm^{-1})	ΔE (cm^{-1})
$Na^+ + H(1s)$	109 737.31	109 737.29	0.02
$Na(3s) + H^+$	41 449.65	41 444.69	4.95
$Na^+ + H(2s)$	27 434.33	27 436.87	2.54
$Na^+ + H(2p)$	27 434.33	27 434.32	0.01
$Na(3p) + H^+$	24 482.00	24 474.06	7.94
$Na(4s) + H^+$	17 709.79	15 729.60	19.82
$Na(3d) + H^+$	12 276.78	12 284.95	8.17
$Na^+ + H(3s)$	12 193.03	12 186.52	6.51
$Na^+ + H(3p)$	12 193.03	12 196.21	3.18
$Na^+ + H(3d)$	12 193.03	12 192.96	0.07
$Na(4p) + H^+$	11 179.02	11 197.43	18.41
$Na(5s) + H^+$	8 248.95	8 258.39	9.44
$Na(4d) + H^+$	6 900.89	6 912.81	11.92
$Na(4f) + H^+$	6 861.05	6 860.78	0.27
$Na^+ + H(4s)$	6 858.58	6 820.29	38.29
$Na^+ + H(4p)$	6 858.58	6 847.70	10.88
$Na^+ + H(4d)$	6 858.58	6 848.14	10.44
$Na^+ + H(4f)$	6 858.58	6 846.92	11.66
$Na(5p) + H^+$	6 407.70	6 402.23	5.47
$Na(6s) + H^+$	5 077.00	5 081.61	4.61

[a] in reciprocal centimeters.

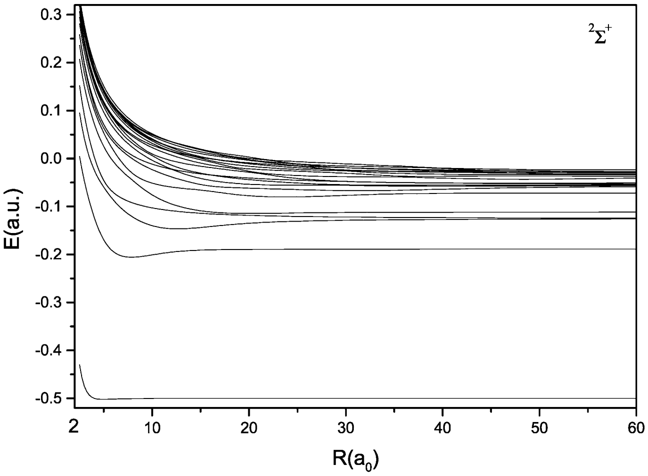

Figure 1. Potential energy curves (in atomic units) for $^2\Sigma^+$ electronic states adiabatically correlated up to the $Na(6s) + H^+$ asymptote. R is given in a_0.

function $\Psi^{2\Lambda(+)}$ is expanded on a set of generalized Slater-type functions

$$\Psi^{2\Lambda(+)}(r_{Na^+}, r_{H^+}, R) = \sum_{n=1}^{2}\sum_{k=1}^{N_{\mathrm{couple}}}\sum_{j=1}^{n_k} c_{ij}[(\lambda^2 - 1)(1 - \mu^2)]^{|\Lambda|/2}\lambda^{p_j}\mu^{q_j}\exp-\left[\frac{R}{2}\beta_k(\lambda + \epsilon_n\mu)\right]e^{i\Lambda\varphi} \quad (6)$$

with $\epsilon_1 = 1$ and $\epsilon_2 = -1$. With n_k being the principal quantum number, integer exponents p and q vary from 0 to $N_k = n_k - |\Lambda| + 1$. Exponential parameters β_k are given by $\sqrt{-E(n_k,l_k)}$ where $E(n_k, l_k)$ corresponds to the experimental energy of a given state (n_k, l_k).[33] N_{couple} corresponds to the number of couples (n_k, β_k).

For each atom Na and H, a basis set is determined by solving the model one-electron Schrödinger equation (eq 5) in which only the electron−core interaction $V(r_{Na^+/H^+})$ is considered, with $V(r_{Na^+}, R)$ and $V(R)$ being excluded. An averaged discrepancy of 12 cm^{-1} is obtained for the 20 lowest states of each atom. As a check of the accuracy of the atomic calculations, the atomic static dipole polarizability $\alpha_d(ns)$ is estimated afterwards for the ground state of each atom. We obtained $\alpha_d(Na(3s)) = 165\ a_0^3$ and $\alpha_d(H(1s)) = 4.50a_0^3$; these estimations are in excellent agreement with the experimental value $\alpha_d(Na(3s)) = 165 \pm 11a_0^3$ [34] and with the exact data $\alpha_d(H(1s)) = 4.5a_0^3$.[35]

With the atomic basis sets defined, the equilibrium distance R_e^{computed} is then searched for the ground state of NaH$^+$ without including polarization effects, followed by the determination of ρ (eq 3). We found $R_e^{\mathrm{computed}} = 4.90a_0$ and $\rho = 2.82a_0$. As a check of our overall procedure (length of basis sets, value of ρ), molecular energies have been computed at large R ($R = 500a_0$). A comparison to experimental energies of separated species[33] is listed in Table 1 for the 20 lowest asymptotes (i.e., up to $Na(6s) + H^+$). The average discrepancy is found to be equal to ~9 cm^{-1}, with the largest one equaling ~38 cm^{-1}.

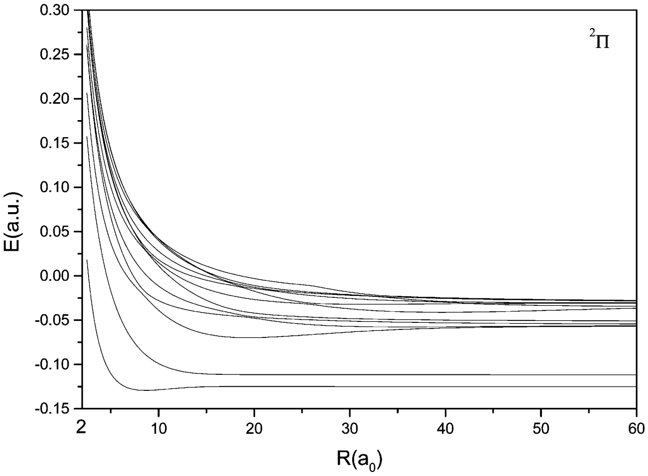

Figure 2. Potential energy curves (in atomic units) for $^2\Pi$ electronic states adiabatically correlated up to the $Na(5p) + H^+$ asymptote. R is given in a_0.

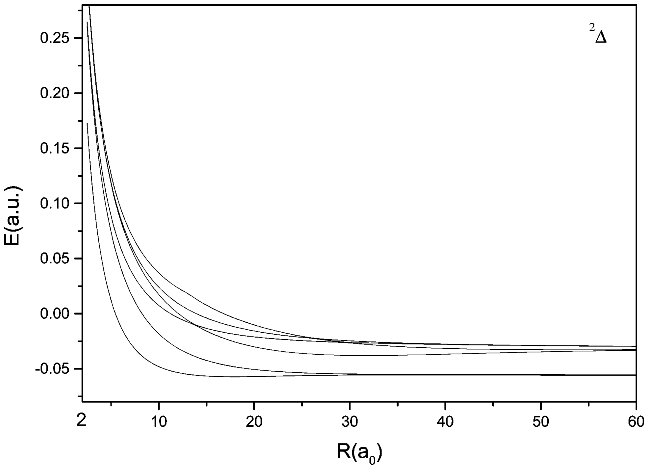

Figure 3. Potential energy curves (in atomic units) for $^2\Delta$ electronic states adiabatically correlated up to the $Na^+ + H(4f)$ asymptote. R is given in a_0.

III. Potential Energy Curves, Spectroscopic Constants, and Electronic Properties

Energy and dipole moment calculations have been performed for molecular states $^2\Lambda^{(+)}$ corresponding to the 20 lowest dissociation limits (i.e., up to $Na(6s) + H^+$) over a large range of R ($2.5a_0 \le R \le 60a_0$). Potential energy curves (PECs) of $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ states are displayed in Figures 1−3, respec-

TABLE 2: Spectroscopic Constants for the Bound Electronic States of NaH^+ [a]

molecular state	R_e	ω_e	T_e	D_e
$X^2\Sigma^+$ [$Na^+ + H(1s)$]				
theory (a)	5.80			161
theory (b)	5.10			492
theory (c)	4.90	302.30		480
theory (d)	5.1 ± 0.2			492 ± 121
theory (e)	4.86	330		645
theory (f)	4.65			834
present work	4.90	266.70		496
$2^2\Sigma^+$ [$Na(3s) + H^+$]				
theory (a)	8.20			2742
theory (d)	7.98 ± 0.10	320		3791 ± 403
theory (g)	8.70			3146
theory (h)	7.87			3710
theory (f)	7.80			3511
present work	7.86	345	65 026	3712
$3^2\Sigma^+$ [$Na^+ + H(2s)$]				
theory (a)	13.00			2952
theory (i)	13.00			4383
theory (g)	15.00			2577
present work	12.63	196.00	78 071	4725
$5^2\Sigma^+$ [$Na(3p) + H^+)$]				
theory (a)	22.00			282
theory (i)	20.00			~380
theory (g)	22.50			77
present work	20.12	75.90	85 104	653
$6^2\Sigma^+$ ($Na(4s) + H^+$)				
present work	23.70	92.30	92 659	1844
$7^2\Sigma^+$ [$Na(3d) + H^+$]				
present work	31.53	53.70	95 556	2478
$1^2\Pi$[$Na+ + H(2p)$]				
present work	8.64	169.90	81 870	929
$3^2\Pi$[$Na(3d) + H^+$]				
present work	19.31	89.40	94 926	3019
$8^2\Pi$[$Na(4f) + H^+$]				
present work	31.33	26.55	103 214	154
$1^2\Delta$[$Na(3d) + H^+$]				
present work	17.91	51.60	97 676	272
$3^2\Delta$[$Na(4d) + H^+$]				
present work	31.73	38.60	101 900	1420

[a] R_e is given in a_0, and ω_e, T_e, and D_e in reciprocal centimeters. Available theoretical data are also listed: a = ref 23, b = ref 9, c = ref 22, d = ref 13, e = ref 24, f = ref 16, g= ref 10, h = ref 12, and i = ref 11.

tively. As for LiH^+,[21] structures rich in avoided crossings and large-range potential wells are observed. The PEC of the ground state is found to be practically flat, indicating that no significant interaction with other PECs is found. Three molecular states (the ground state $1^2\Sigma^+$ ($Na^+ + H(1s)$) and the lowest excited states $2^2\Sigma^+$ ($Na(3s) + H^+$) and $1^2\Pi$ ($Na^+ + H(2p)$) present a well at short interatomic separations ($R < 10a_0$), while several long-range potential wells are found in PECs of highly excited states. The corresponding vibrational and rotational energies have been determined from Hutson's code[36] in which all bound vibrational levels have been considered for each potential well. The deduced spectroscopic constants (equilibrium distance R_e, vibrational constant ω_e, excitation energy T_e, and dissociation energy D_e) are listed in Table 2, in which available data[9−13,16,23−25] have been also reported.

Because the electronic structure of NaH^+ is mainly known through calculations on collisional processes as collisional charge transfer involving H^+ and Na atoms in the ground state,[9−13,16] PECs have then been determined for few electronic states (i.e., the five lowest states) over a limited range of internuclear distances ($R < 30a_0$). Relevant spectroscopic constants are included in Table 2. A satisfying agreement is obtained for the ground state between the present and the many previous theoretical determinations[9,13,16,23−25] for the equilibrium position R_e ($\delta R_e \leq 0.20a_0$) and the dissociation energy D_e ($\delta D_e \leq 16$ cm^{-1}). Large discrepancies are found with the predictions of Valance[23] ($\delta R_e = 0.90a_0$ and $\delta D_e = 331$ cm^{-1}) and with the recent calculations of Watanabe et al.[16] ($\delta R_e = 0.25a_0$ and $\delta D_e = 338$ cm^{-1}). The determinations of ref 16 are based on the use of a pseudopotential proposed by Bardsley[37] including core polarization effects, which is seen to be less accurate than that usually used for alkali atoms.[28,38] So, these disagreements may be partly explained by an inaccurate description of core polarization effects and of the interaction between the alkali core and the valence electron. They are also due to the use of a limited atomic basis set restricted to the lowest atomic states for H and Na. For excited states, the present equilibrium distances, R_e, are generally seen to be shorter than other values, and large discrepancies are also found for the dissociation energy as, for instance, for $3^2\Sigma^+$ ($Na^+ + H(2s)$) and $5^2\Sigma^+$ ($Na(3p) + H^+$) ($\delta D_e = 2148$ cm^{-1} and $\delta D_e = 576$ cm^{-1} to be compared with calculations of ref 11, respectively). In the case of PECs, a comparison between present and previous CI PECs

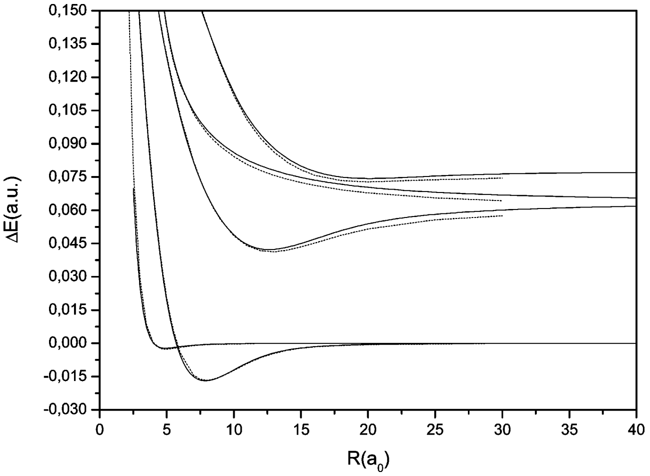

Figure 4. Comparison (in atomic units) between present and previous CI potential energy curves for the ground state and various excited states (solid line, present calculations; dashed lines, previous data[9]). R is given in a_0. Energy values are relative to the asymptotic energy of the ground state.

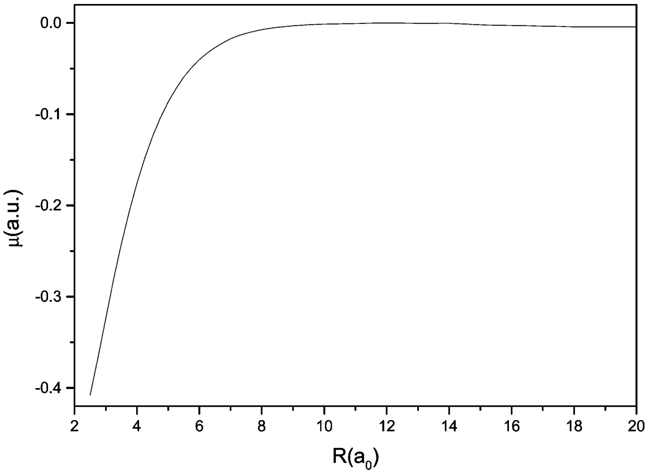

Figure 5. Transition dipole moments vs R, between $1^2\Sigma^+$ ($Na^+ + H(1s)$) and $2^2\Sigma^+$ ($Na(3s) + H^+$) electronic states. R is given in a_0 and μ in atomic units.

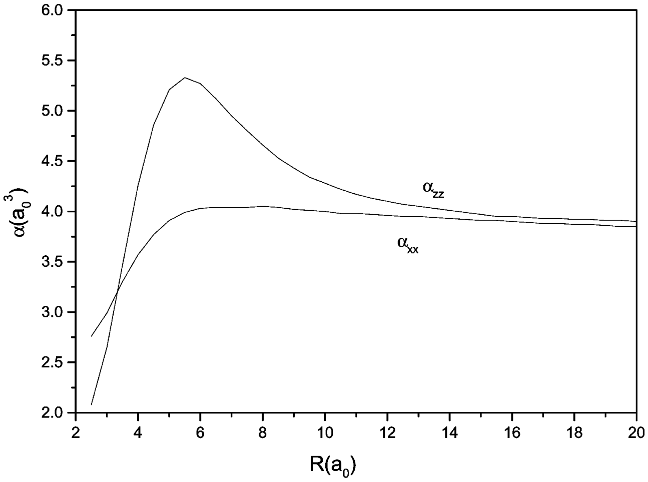

Figure 6. Variations of molecular dipole polarizabilities $\alpha_{zz=(\|)}$ and $\alpha_{xx=(\perp)}$ of the ground state $1^2\Sigma^+$ (Na$^+$ + H(1s)) vs *R*. *R* is given in a_0 and α in a_0^3.

of ref 9 is displayed in Figure 4. The PECs are seen to be in satisfying agreement for the lowest states at short and intermediate *R* values, while the present curves are found to be deeper for the most excited ones. Only spectroscopic experiments could confirm or invalidate the accuracy of the present calculations.

For dipole moments, comparisons with previous determinations appear to be more difficult, because only the recent pseudopotential calculations of Watanabe et al.[16] are available for the transition between $1^2\Sigma^+$ (Na$^+$ + H(1s)) and $2^2\Sigma^+$ (Na(3s) + H$^+$) electronic states. Because of the large discrepancies observed with spectroscopic constants, variations of the dipole moment as a function of *R* are seen to be different: In ref 16, the dipole moment is seen to increase up to $\sim 5a_0$ and to tend slowly toward 0 at $R \geq 12a_0$, whereas present calculations are found to increase and to tend also toward 0 at $R \geq 10a_0$ as drawn in Figure 5. Given their importance in the description of long-range interactions between a molecular ion and other compounds such as an atom and a neutral molecule, dipole molecular polarizabilities $\alpha_{zz(=\|)}$ and $\alpha_{xx(=\perp)}$ have been estimated through a sum-over-states approach. Variations as a function of interatomic separation are displayed in Figure 6 for the ground state, for instance. They appear to be similar to those observed for the ground state of LiH$^+$.[21]

IV. Conclusion

Potential energies and dipole moments have been computed for numerous molecular states of NaH$^+$ over a large range of *R*. Various potential wells have been predicted at short and large internuclear separations. The present calculations are seen to be in satisfying agreement with previous determinations[9−13] for the five lowest states.

As the large amount of numerical data could not be fully reported here, a supplementary database is available upon request. Both results will be used in the determination of the electronic structure of the neutral molecule NaH.

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