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Model Potential Calculations for the Ground and Various Excited States of LiNa$^+$

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A theoretical investigation of the electronic structure of the molecular ion LiNa$^+$ (adiabatic potential energy curves, rovibrational energies, spectroscopic constants and dipole moments) has been performed in the framework of a model potential method. Such information, not yet available to the best of our knowledge except for the ground state, constitutes the input data for simulations of above threshold dissociation of LiNa$^+$. Although most of the energy curves are found to be dissociative, some present potential wells located at intermediate internuclear distances. A long-range extrapolation is proposed for the lowest states.

1. Introduction

During the past decade, an important effort has been devoted to the development of ultra-short and intense laser pulse generation, opening a new research domain in molecular dynamics. In particular, photodissociation and photoionization of small molecules such as H_2^+ [1] and Na_2,[2] have been observed and their interpretations appear rather complicated since many processes can occur simultaneously.

Recently, we have performed simulations based on quantum wave packet propagation[3] of the above threshold dissociation (ATD) for Na_2^+ and Li_2^+,[4,5] where the alkali dimer cation, even after reaching the lowest continuum, can absorb photons and make continuum-continuum transitions. Such simulations for Na_2^+ and Li_2^+ suggest the feasibility of one- or two-color experiments with moderately high intense laser pulses. These previous works established for the first time, the occurrence of Rabi's oscillations between continuum states and that of radiation−molecule interference[6] under peculiar conditions as a function of intensity and duration of laser pulses.

We are now extending our work on ATD simulations to heteronuclear alkali molecular ions such as LiNa$^+$, for which the necessary data: energies and dipole transition moments are not yet available for excited states. So, we report here adiabatic potential energy curves and relevant dipole moments for LiNa$^+$ calculated over a rather large range of internuclear distances in the framework of a model potentiel method applied recently to describe Na_2^+ [7] and Li_2^+.[8] Long-range extensions are considered.

2. Model Potential Method for a Heteronuclear Alkali Ion

The alkali dimer cation is treated as a monoelectronic sytem with the one-active electron moving in the field of two ionic cores. Under this model, three types of interaction have to be considered and each one is described by effective potentials.

The interaction between the active electron and each ionic core (Li$^+$ and Na$^+$ respectively), is represented by a Klapisch model potential:[9]

$$\begin{Bmatrix} V_{\mathrm{Li}^+}(r) = -\dfrac{1}{\mathrm{r}} - \dfrac{Z_{\mathrm{Li}}-1}{r}(\mathrm{e}^{-7.90875r} + 5.1605r\mathrm{e}^{-3.90006r}) \\ V_{\mathrm{Na}^+}(r) = -\dfrac{1}{\mathrm{r}} - \dfrac{Z_{\mathrm{Na}}-1}{r}(\mathrm{e}^{-7.88747r} + 2.354102r\mathrm{e}^{-2.69155r}) \end{Bmatrix} \tag{1}$$

where $Z_{a(b)}$ is the nuclear charge.

The interaction due to core polarization effects is described by an effective potential, first proposed by Bottcher and Dalgarno[10] and later by Valiron et al.:[11]

$$V_{\mathrm{pol}}(r_a,r_b,R) = \frac{\alpha_d^a}{r_a^{\,2}R^2}\cos\theta_a f_6\left(\frac{r_a}{\rho_a}\right) + \frac{\alpha_d^b}{r_b^{\,2}R^2}\cos\theta_b f_6\left(\frac{r_b}{\rho_b}\right) + ... \tag{2}$$

where $f_n(x) = \sqrt{1-\mathrm{e}^{-x^n}}$ is a cutoff function introduced in order to avoid divergence at short electron−core distance. $\alpha_d^{a(b)}$ is the static dipole polarizability of the ionic cores. We used the following values: $0.1915a_0^3$ for Li$^+$ [12] and $0.9965a_0^3$ for Na$^+$.[13] $\theta_{a(b)}$ is the angle between the position vector $\vec{r}_{a(b)}$ and the internuclear axis. Two cutoff radii ρ_a and ρ_b are required and as done previously[7,8] they are adjusted in order to reproduce the dissociation energy of the ground state, calculated for an internuclear equilibrium distance R fixed at the experimental value. The experimental equilibrium position being unknown for LiNa$^+$, we used the ab initio data of Müller and Meyer.[14]

The core−core interaction is described as in our previous work on Na_2^+ [7] as a sum of long-range-type Coulombic and polarization terms:

$$V_{cc}(R) = \frac{1}{R} - \frac{\alpha_d^a + \alpha_d^b}{2R^4} - \frac{\alpha_q^a + \alpha_q^b}{2R^6} \tag{3}$$

where $\alpha_q^{a(b)}$ is the static quadrupolar polarizability for the ionic cores a and b, respectively.We used the values $0.0156a_0^5$ for Li$^+$ [15] and $0.376a_0^5$ for Na$^+$.[13]

Molecular ion energies and relevant wave functions are obtained by solving the following Schrödinger equation for each value Λ of the projection of the total orbital angular momentum

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TABLE 1: Couples (n_k, β_k) Defining the Basis Sets Used for Σ, Π, and Δ Molecular Symmetries

Σ States																				
Li																				
n_k	2	3	3	3	3	3	3	3	3	4	5	5	6	6	8	8	8			
β_k	4.70	2.48	1.73	0.80	0.66	0.51	0.45	0.38	0.34	0.28	0.25	0.22	0.20	0.16	0.12	0.10	0.08			
Π and Δ States																				
Li																				
n_k	2	3	3	3	3	3	3	3	3	4	5	5	6	6	8	8	8			
β_k	4.700	2.48	1.73	0.80	0.66	0.45	0.38	0.34	0.33	0.28	0.25	0.22	0.20	0.16	0.12	0.09	0.08			
Σ and Π States																				
Na																				
n_k	2	2	3	3	3	3	3	4	3	3	3	3	3	4	5	7	8	8	8	8
β_k	12.66	11.01	8.36	5.74	3.61	2.25	1.11	0.71	0.61	0.47	0.37	0.31	0.27	0.25	0.20	0.16	0.12	0.09	0.08	0.06
Δ States																				
Na																				
n_k	2	2	3	3	3	3	3	4	4	5	7	8	8	8	8					
β_k	12.66	11.01	8.36	5.74	3.61	2.25	1.11	0.71	0.22	0.20	0.16	0.12	0.09	0.08	0.06					

on the internuclear axis:

$$[T + V(r_\mathrm{a}) + V(r_\mathrm{b}) + V_\mathrm{cc}(R) + V_\mathrm{pol}(r_\mathrm{a},r_\mathrm{b},R)]\Phi_\Lambda(r_\mathrm{a},r_\mathrm{b},R) = E\Phi_\Lambda(r_\mathrm{a},r_\mathrm{b},R) \quad (4)$$

The wave functions Φ_Λ are expanded on a set of generalized Slater-type orbitals expressed in prolate spheroïdal coordinates ($\lambda = (r_\mathrm{a} + r_\mathrm{b})/R$, $\mu = (r_\mathrm{a} - r_\mathrm{b})/R$, $0 \le \varphi \le 2\pi$):

$$\Phi_\Lambda(r_\mathrm{a},r_\mathrm{b},R) = \sum_{\mathrm{i=a,b}} \sum_{k=1}^{n_\mathrm{couple}} \sum_{j=1}^{N_k} C_{ij}[(\lambda^2 - 1)(1 - \mu^2)]^{|\Lambda|/2} \lambda^{\mathrm{p_j}}\mu^{\mathrm{q_j}} \exp\left(-\left[\frac{R\beta_k}{2}(\lambda + \epsilon_\mathrm{i}\mu)\right]\right) \exp(\mathrm{i}\Lambda\varphi) \quad (5)$$

with $\epsilon_\mathrm{a} = +1$ and $\epsilon_\mathrm{b} = -1$. For each center a and b exponents p_j and q_j vary from 0 to N_k, with $N_k = n_k - |\Lambda| + 1$ and n_k is the atomic principal quantum number for an atomic level k. The exponential parameter β_k is defined by $\beta_k = \sqrt{-E_{n_kl_k}}$ where $E_{n_kl_k}$ are experimental atomic energies.[16] n_couple represents the number of couple (β_k, n_k) for one center and then defines the basis size. The basis set is fully determined by reproducing experimental atomic energies[16] from the solution of the one center Schrödinger equation:

$$[T + V(r_\mathrm{a})]\Phi_{n_kl_k}(r_\mathrm{a},r_\mathrm{b},R) = E_{n_kl_k}\Phi_{n_kl_k}(r_\mathrm{a},r_\mathrm{b},R) \quad (6)$$

In that way, atomic energies of the 20 lowest levels of Li and of Na are reproduced with an average error of 3×10^{-5} au (~7 cm^{-1}).

In our previous work,[7,8] we have noted that practically the same energy was obtained whether different basis sets were used or not to describe different symmetries Λ. Here, we have chosen to determine for lithium different basis sets for Σ and (Π, Δ) molecular symmetries while for sodium we determined different basis sets for (Σ,Π) and Δ symmetries. Couples of (β_k, n_k) for both atoms are given in Table 1. We have adjusted the cutoff parameters involved in eq 2 in order to reproduce the experimental dissociation energy of the ground-state equal to 7985 cm^{-1} [17] at the ab initio equilibrium position $R = 6.35a_0$.[14] Values of ρ_a and ρ_b are $1.38a_0$ and $0.74a_0$, respectively and the computed dissociation energy is then equal to 7988 cm^{-1}.

We have performed molecular calculations including the chosen basis sets and cutoff parameters at $R = 200a_0$. The 10 lowest experimental dissociation limits of LiNa$^+$ are described with a largest discrepancy of 10^{-4} au (~26 cm^{-1}). Differences between relevant experimental and computed energies are displayed in Table 2.

TABLE 2: Comparison between Calculated Energy Values at R = 200 a_0 and Corresponding Experimental Dissociation Energies[16]

dissociation limit	$E_\mathrm{experimental}$ (au)	E_computed (au)	ΔE (au)
Li(2s) + Na$^+$	−0.198142	−0.198113	3×10^{-5}
Li$^+$ + Na(3s)	−0.188858	−0.188836	2×10^{-5}
Li(2p) + Na$^+$	−0.130235	−0.130204	3×10^{-5}
Li$^+$ + Na(3p)	−0.111548	−0.111592	4×10^{-5}
Li(3s) + Na$^+$	−0.074182	−0.074302	10^{-4}
Li$^+$ + Na(4s)	−0.071579	−0.071670	9×10^{-5}
Li(3p) + Na$^+$	−0.057236	−0.057308	7×10^{-5}
Li$^+$ + Na(3d)	−0.055937	−0.055961	2×10^{-5}
Li(3d) + Na$^+$	−0.055606	−0.055567	4×10^{-5}
Li$^+$ + Na(4p)	−0.050935	−0.051013	8×10^{-5}

3. Potential Energy Curves, Spectroscopic Constants, and Permanent Dipole Moments

Molecular potential energies of all electronic states correlated from Li(2s) + Na$^+$ up to Li$^+$ + Na(4p) have been computed for $R = 2.5a_0$ to $40a_0$.We have also calculated permanent and transition dipole moments for all electronic states considered.

Potential energy curves for the $^2\Sigma^+$ states are drawn in Figure 1 while those for the $^2\Pi$ and $^2\Delta$ electronic states are drawn in Figure 2. As previously observed for Na$_2^+$ [7] and Li$_2^+$,[8] most of the potential curves are purely dissociative, which is favorable for the interpretation of multiphoton dissociation. Moreover, Rydberg series may be easily identified. Numerous avoided crossings are shown on the potential curves of the higher states. Among Σ states avoided crossings can be recorded at the following distances R_c corresponding to the nearest approach between two states, i.e., $R_\mathrm{c} = 7.75a_0$ for the $^4/_5$ states, $R_\mathrm{c} = 4.25a_0$ for the $^5/_6$ states, $R_\mathrm{c} = 16.5a_0$ for the $^6/_7$ states, and $R_\mathrm{c} = 7.5a_0$ and $R_\mathrm{c} = 25a_0$ for the $^8/_9$ states. For Π states the positions of the avoided crossings are $R_\mathrm{c} = 8.25a_0$ for the $^3/_4$ states, $R_\mathrm{c} = 20a_0$ for the $^4/_5$ states and $R_\mathrm{c} = 18.25a_0$ for the $^5/_6$ states. Such avoided crossings should play an important role in subsequent dynamical investigations. For instance at the position of the avoided crossing between the potential energy curves of the $4^2\Sigma^+$ and the $5^2\Sigma^+$ states at $R = 7.75a_0$ it occurs a crossing of the permanent dipole moment curves of the two states as displayed in Figure 3. This indicates that this avoided crossing is expected to play a crucial role in the determination of photodissociation probabilities and in the identification of the final products.

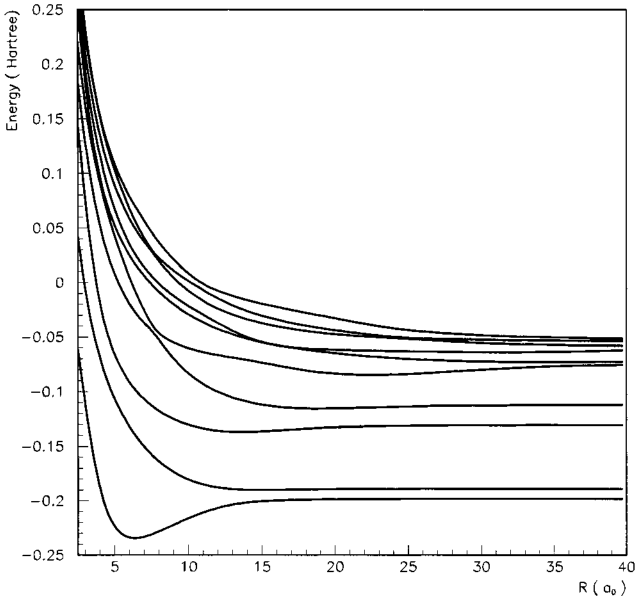

Figure 1. Potential energy curves of the $^2\Sigma^+$ electronic states correlated to the dissociation limits from Li(2s) + Na$^+$ up to Li$^+$ + Na(4p).

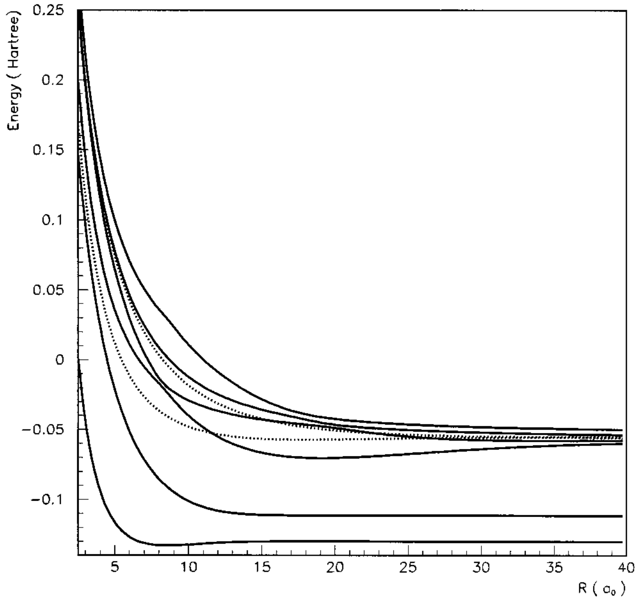

Figure 2. Potential energy curves of the $^2\Pi$ (full lines) and of the $^2\Delta$ (dashed lines) electronic states correlated to the dissociation limits from Li(2p) + Na$^+$ up to Li$^+$ + Na(4p).

Some potential curves present wells located at intermediate or rather long-range internuclear distances. For the ground state and these bound excited states, vibrational and rotational energies have been computed from Hutson's code[18] and spectroscopic constants have been deduced. They are reported in Table 3 together with values of the permanent dipole moments calculated at the equilibrium distance. Available experimental[17] and previous theoretical data[14] for the ground state are also reported in Table 3. It should be noted that, due to our process of determination of the cutoff parameters involved in eq 2, the good agreement with the ab initio value of R_e[14] as well as with the experimental value of D_e[17] is artificial. Comparison for the permanent dipole moment shows a relative difference of 10%.

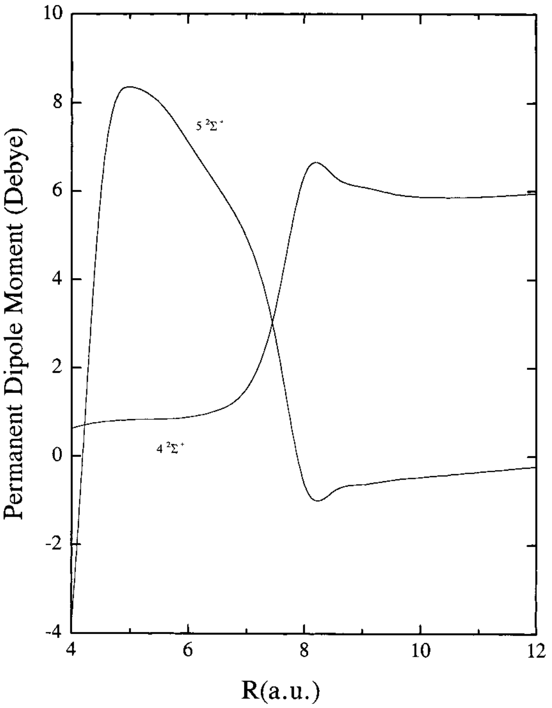

Figure 3. Variation with R of the permanent dipole moment of the $4^2\Sigma^+$ and $5^2\Sigma^+$ states.

TABLE 3: Spectroscopic Constants for the Lowest Bound States of LiNa$^+$ (R_e in Å, ω_e, T_e, and D_e in cm^{-1}, and μ in Debye)

molecular state	R_e	ω_e	T_e	D_e	μ	limit
$1^2\Sigma^+$						Li(2s) + Na$^+$
exp[17]			0	7985 ± 242		
theory[14]	3.36	193.00	0	8114	0.517	
present work	3.36	192.04	0	7988	0.465	
$3^2\Sigma^+$						Li(2p)+ Na$^+$
present work	7.22	58.24	21401	1495	9.586	
$1^2\Pi$						
present work	4.53	66.47	22282	614	4.773	
$5^2\Sigma^+$						Li(3s) + Na$^+$
present work	11.87	40	32879	2300	0.56	
$3^2\Pi$						Li(3p) + Na$^+$
present work	10.10	38.34	36020	2863	0.387	
$1^2\Delta$						Li$^+$ + Na(3d)
Present work	9.5	22	38900	340	0.820	

4. Long-Range Extrapolations

For further uses of potential energy data it may be interesting to know the curves for values of R larger than that considered in the present model potential calculations. In such ranges of R the energy can be calculated quite accurately as a sum of the energy of the separated products a + b$^+$ or a$^+$ + b and of their Coulombic interaction varying as R^{-n}. When calculating the interaction between Li$^+$ and Na(nl) and between Li(n′l′) and Na$^+$ in a perturbative way we have considered the ions Li$^+$ and Na$^+$ as species only characterized by their charge, their static dipole polarizability[12] and their ionization potential.[19] We have performed calculations for the six lowest states (4 states Σ and 2 states Π) correlating adiabatically to the three lowest dissociation limits. First-order electrostatic terms as well as induction and dispersion terms have been computed up to R^{-6} using for Li and Na the atomic functions of Patil and Tang.[20] For the energies of the separated atoms we used the experimental values.[16]

Results are visualized in Figure 4, which shows present model potential curves and calculated energy points from the long-range approach in the range 20−30a_0. At the scale of the figure the agreement is very good for the six states, demonstrating that correct long-range extrapolations can be derived in that way.

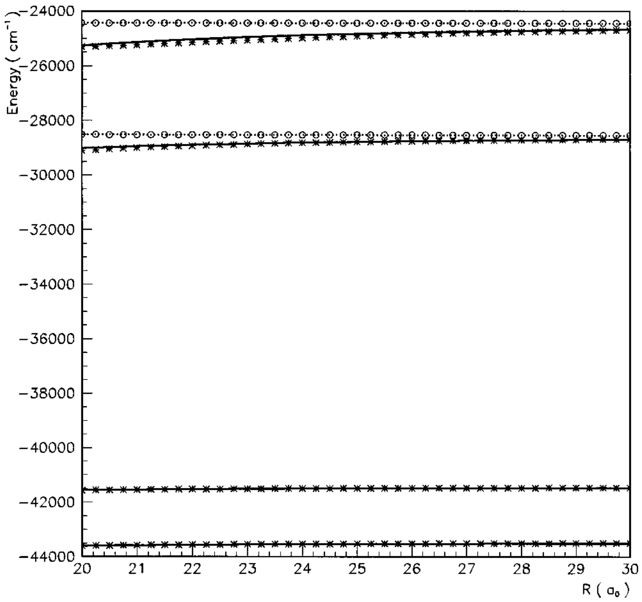

Figure 4. Comparison between model potential energy curves for the 4 lowest $^2\Sigma^+$ states (full lines) and for the 2 lowest $^2\Pi$ states (dotted lines) with long-range predictions: * for Σ states and ° for Π states.

5. Conclusion

Model potential calculations including potential energies and dipole moments have been performed for the 10 lowest Σ, the 6 lowest Π, and the 2 lowest Δ states of the heteronuclear alkali cation $LiNa^+$. Present results have already been used in the simulation of multiphoton dissociation experiments.[21] Information contained in this paper will also be used in the determination of adiabatic potential curves of LiNa.

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