Theoretical Studies of Nonresonant Charge-Transfer Processes Using a Multistate Molecular Wave-Function Approach: Li + Na$^+$ ⟷ Li$^+$ + Na†

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The charge-transfer processes for the collisions Li + Na$^+$ → Li$^+$ + Na and Na + Li$^+$ → Na$^+$ + Li have been studied theoretically using the first six molecular states in a multistate impact-parameter approach (using the Born-Oppenheimer breakdown terms to couple the states). The results lead to a rather simple description of the charge-transfer process involving primarily transitions between the $1^2\Sigma^+$ and $2^2\Sigma^+$ states and between the $2^2\Sigma^+$ and $1^2\Pi$ states of the LiNa$^+$ quasimolecule.

Atom-atom and atom-molecule scattering processes such as electronic excitation, electron transfer, and electronic excitation energy transfer are often described formally in terms of a collisionally induced coupling between various (Born-Oppenheimer) electronic states of the quasimolecule.[1] Previous studies have generally been restricted to the coupling between two states using approximate methods[2] such as the Stueckelberg-Landau-Zener[3] or Demkov[4] approximations. While these cases generally treat states of the same symmetry, recent approximate calculations[5] have shown the importance of angular coupling between states of different symmetry (e.g., Σ and Π). However, little progress has been made in the rigorous use of the multistate molecular wave-function approach because of formidable difficulties both in the evaluation of the Born-Oppenheimer breakdown terms[6] and in the determination of the molecular wave functions for a number of excited states. Bottcher and Oppenheimer[7] attempted the two-state molecular wave-function approach for LiNa$^+$, but ignored translational invariance of the coupling terms and ignored backcoupling. The actual coupling mechanism for the molecular wave-function representation has itself been open to controversy.[2b,7,8]

Herein we report multistate calculations for the asymmetric nonresonant charge-transfer processes

$$Li + Na^+ \to Li^+ + Na, \tag{1a}$$

$$Na + Li^+ \to Na^+ + Li, \tag{1b}$$

using the first six molecular eigenstates (including the excited states of Na and Li as possible products) and rigorously evaluating the Born-Oppenheimer coupling terms and molecular eigenstates as a function of internuclear distance. High-quality experimental total charge-transfer cross sections have been reported by Daley and Perel,[9] providing a good test of the efficacy of the theoretical treatment.

We find that the calculated cross sections are in good agreement with the experimental results, both in total magnitude and in the oscillatory structure. We further find that the charge-transfer process can be described essentially in terms of two simple two-state processes, one coupling the lowest two $^2\Sigma^+$ states and the other coupling the $2^2\Sigma^+$ and $1^2\Pi$ states.

In the molecular wave-function approach using the impact parameter method,[1,8] we must solve

the set of coupled equations

$$da_i(z)/dz = -\sum_j \Gamma_{ij}(z)\exp[-iw_{ij}(z)]a_j(z), \qquad (2)$$

where z is the coordinate along the path of motion ($z = -\infty$ initially), $w_{ij}(z) = \int_{-\infty}^{z} v^{-1}(V_j - V_i)dz'$, v is the relative velocity, V_i is the potential energy of the ith molecular state, and Γ_{ij} is the dominant Born-Oppenheimer breakdown term. Γ can be expressed[10] as

$$\Gamma_{ij} = zM_{ij}/R + bN_{ij}/R, \qquad (3a)$$

where b is the impact parameter, R is the internuclear distance,

$$M_{ij} = \langle\psi_i|\partial/\partial R|\psi_j\rangle, \qquad (3b)$$

and

$$N_{ij} = \langle\psi_i|R^{-1}\partial/\partial\theta|\psi_j\rangle. \qquad (3c)$$

We calculated the charge-transfer cross sections for processes (1a) and (1b) including in Eq. (2) the lowest six molecular states of the LiNa$^+$ molecule (i.e., all the states dissociating to the $2s$ or $2p$ states on the Li and the $3s$ or $3p$ states on the Na). The potential energy curves and the important coupling terms are shown in Fig. 1.[11]
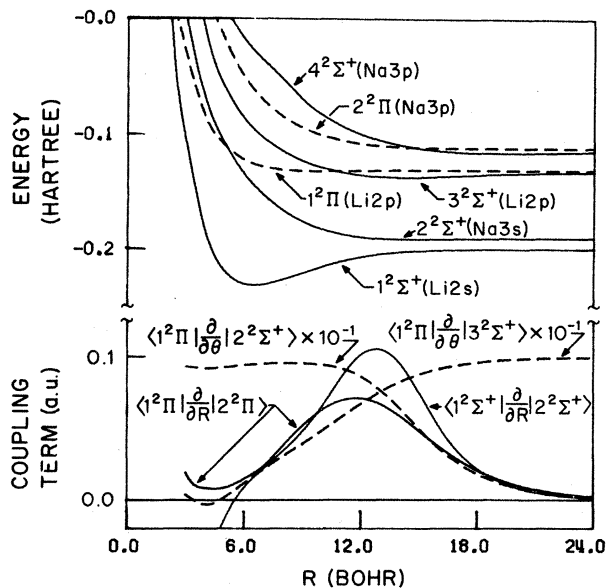

FIG. 1. The potential energy curves and coupling terms between various states of the LiNa$^+$ molecule. Energy curves for the first four $^2\Sigma^+$ states and the first two $^2\Pi$ states are included [atomic units ($\hbar = 1$, $|e|$ = 1, $m_e = 1$) are used; 1 hartree = 27.211 eV, 1 bohr = 0.529 17 Å]. The Σ-Π coupling terms $\langle\Pi_i|\partial/\partial\theta|\Sigma_j\rangle$ [see Eq. (3c)] are scaled by a factor of 1/10.

The total charge-transfer cross sections are shown in Fig. 2 where they are compared with the experimental results of Daley and Perel.[9] While the absolute magnitude for either of the experimental cross-section curves has an uncertainty of 10%,[12] the positions and amplitude of the oscillatory structure in the experimental cross sections are very accurate and provide a good test for the theoretical results. We see from Fig. 2 that there is excellent agreement in the oscillatory structure. We also see that cross sections for processes (1a) and (1b) are correctly distinguished, with the total magnitudes of the cross sections within the experimental error of the experimental results.[13]

In Fig. 3 we show the cross sections for each of the individual processes. We see that the charge exchange (including the oscillatory structure) is dominated by the transitions between the lowest two $^2\Sigma^+$ states. However, as indicated by the dotted lines in Fig. 3, it is not sufficient to include merely these two states in describing the charge exchange. The two-state approximation incorrectly predicts identical cross sections for processes (1a) and (1b), and, in addition, leads to oscillations out of phase with the experimental results.

We also carried out a set of four-state calculations including the first four $^2\Sigma^+$ states. This led
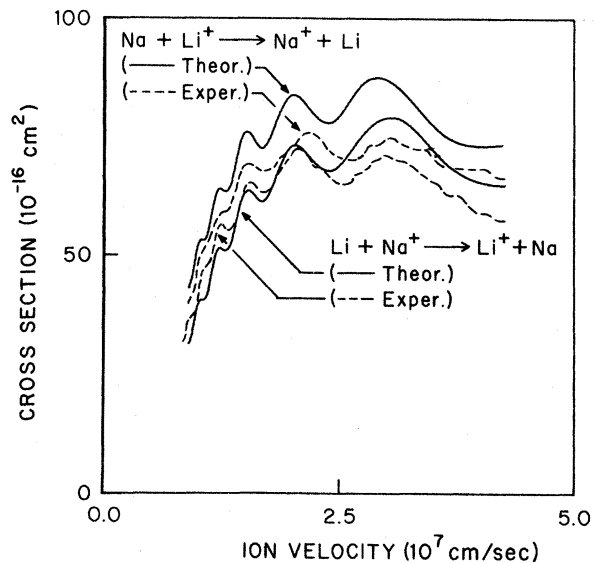

FIG. 2. Comparison of the theoretical (six-state) and experimental total charge-transfer cross sections for Li + Na$^+$ → Li$^+$ + Na and Na + Li$^+$ → Na$^+$ + Li (solid curves, theoretical; dashed curves, experimental). Estimated error in the absolute values of the experimental total cross sections is 10%.
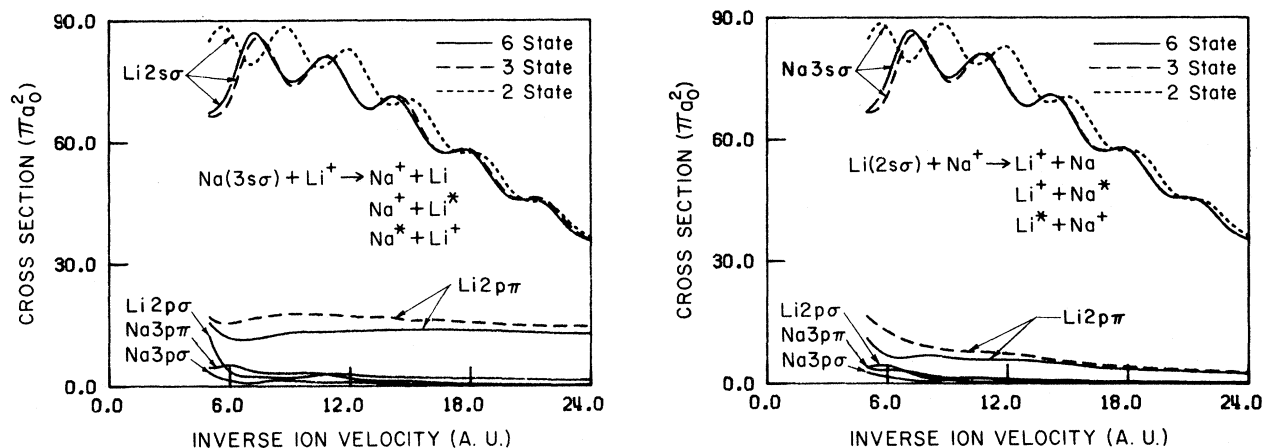
FIG. 3. Comparison of the theoretical cross sections to individual atomic states using six-state, three-state, and two-state approximations in Eq. (2) for collisions of $Na + Li^+$ and $Li + Na^+$ (1 a.u. velocity $\equiv 2.18 \times 10^8$ cm/sec; $\pi a_0^2 = 0.89 \times 10^{-16}$ cm^2).

to essentially the same results as for the two-state calculations, indicating that inclusion of higher Σ states is not important. However, including the $1^2\Pi$ state in addition to the $1^2\Sigma^+$ and $2^2\Sigma^+$ states does lead to a proper description of the charge transfer (see dashed lines in Fig. 3), both in magnitude and in the phase of the oscillations. Comparing the six-state and three-state results in Fig. 3, we see that the six-state calculation merely leads to a redistribution of the excited-state products but to almost no change in the $1^2\Sigma^+ \leftrightarrow 2^2\Sigma^+$ transitions.

The reason for this is obvious from the potential energy curves (see Fig. 1). The energy differences are too great to allow direct transitions from the $1^2\Sigma^+$ or $2^2\Sigma^+$ states to the excited $^2\Sigma^+$ states [except for very large velocities ($v > 0.2$ a.u.)]. However, because of the curve crossing between the $2^2\Sigma^+$ and $1^2\Pi$ states at $5.1a_0$, there is a significant probability of transition between the $2^2\Sigma^+$ and $1^2\Pi$ states.[14] There are strong transition probabilities between $1^2\Pi$ and $3^2\Sigma$, $1^2\Pi$ and $2^2\Pi$, and $2^2\Pi$ and $4^2\Sigma$ so that once this $1^2\Pi$ is populated, the other excited states can also be obtained.

We see therefore that the total collision process can be described essentially in terms of a coupling between the $1^2\Sigma^+$ and $2^2\Sigma^+$ states and a coupling between the $2^2\Sigma^+$ and $1^2\Pi$ states. From an examination of the a_i [see Eq. (2)] as a function of z, we find that each of the coupling processes proceeds by a three-step process involving a transition region (where the energy difference is small while the coupling term is large) and an intermediate region. First, as the atoms

approach, they enter the transition region and the two states are coupled, leading to nonzero a_1 and a_2. For closer approaches (the intermediate region) the magnitudes of a_1 and a_2 do not change because of the large ΔE. However, the relative phases of a_1 and a_2 change because of their evolution on different potential energy curves. Finally, as the atoms separate, they re-enter the transition region and decouple. However, because of the relative phase difference resulting from the second step, the decoupling leads to interference and hence to some probability for ending up on either state. Since Γ_{ij} is an odd function of z for Σ-Σ transitions while Γ_{ij} is even for Σ-Π transitions, the net transition probability for Σ-Σ coupling would be zero for a zero phase difference while the Σ-Π net transition probability would be a maximum for a zero phase difference.

We find that the transition region for the $1^2\Sigma^+$-$2^2\Sigma^+$ coupling occurs at long range ($14a_0 < R < 22a_0$) where the atomic wave functions begin to overlap. On the other hand, the $2^2\Sigma^+$-$1^2\Pi$ transition occurs at short range in the region near the curve crossing at $5.1a_0$. Thus, the entire $2^2\Sigma^+$-$1^2\Pi$ coupling process occurs while the $1^2\Sigma^+$ and $2^2\Sigma^+$ states are uncoupled and depends only on the initial probability amplitude of being in the $2^2\Sigma^+$ state for the $1^2\Sigma^+$-$2^2\Sigma^+$ intermediate region. However, because of the $2^2\Sigma \rightarrow 1^2\Pi$ transitions, the amount of $2^2\Sigma$ is reduced slightly and the phase of $2^2\Sigma$ relative to $1^2\Sigma$ is altered. As a result the decoupling step leads to a modified interference between $1^2\Sigma$ and $2^2\Sigma$. This effect is larger for (1b) because of the larger probability of being in $2^2\Sigma$ in the intermediate region. Transitions from the

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$1^2\Pi$ state to the other excited states occur only as the atoms are separating and thus involve only one transition region, with no phase interference effects occurring. At low velocities, the $2^2\Sigma \to 1^2\Pi$ transition will dominate process (1b). The Σ-Π coupling is therefore an important mechanism in charge-transfer processes (for example,[15] in $K + Li^+ \to Li + K^+$).

From the above interpretations, we see that the total collision process can be represented by a succession of simple two-state processes. One can therefore have confidence in the appropriate use of approximate two-state methods that have been developed (see Ref. 2). This should allow one to make qualitative predictions of important electronic processes occuring in a variety of other scattering systems without the necessity of extensive, rigourous calculations as reported herein. However, it *is* necessary to keep in mind the nature of the electronic states involved in order to predict correctly the particular pairs of states being coupled for each nuclear configuration.

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[10]Care must be taken to keep the M_{ij} and N_{ij} translationally invariant (see Ref. 6). A method for evaluating these quantities has been presented in Ref. 8.

[11]The potential energy curves were calculated using *ab initio* effective potentials [see C. F. Melius, W. A. Goddard, III, and L. R. Kahn, J. Chem. Phys. **56**, 3342 (1972); Ref. 8; C. F. Melius and W. A. Goddard, III, to be published; L. R. Kahn and W. A. Goddard, III, J. Chem. Phys. **56**, 2685 (1972)].

[12]J. Perel, private communication.

[13]The theoretical cross sections are too large on the higher-energy side in Fig. 2 because of neglect of the translational momentum of the electron and thus need not reflect an error in the experimental measurements. On the other hand, the theoretical cross sections on the lower-energy side in Fig. 2 should be quite accurate.

[14]Experimental measurements of the individual transitions $Na + Li^+ \to Na(3p) + Li^+$ and $Na + Li^+ \to Na^+ + Li(2p)$ have been reported by V. Aquilanti, G. Liuti, F. Vecchio-Cattivi, and G. G. Volpi, in *Proceedings of the Seventh International Conference on the Physics of Electronic and Atomic Collisions, Amsterdam, The Netherlands, 1971* (North-Holland, Amsterdam, 1971), p. 600. While the former cross section agrees with our theoretical results, the latter cross section is 2 orders of magnitude smaller than we predict. To obtain the experimental cross section, it was necessary to correct for the Li $2p$ emission resulting from the Li ion source. We believe that these corrections must be in error and that the theoretical cross sections are correct. A strong argument in favor of this is that the same experiments also measured cross sections for $Na + Na^+ \to Na^+ + Na(3p)$ in agreement with our values. This latter process should have a cross section similar to $Na + Li^+ \to Na^+ + Li(2p)$ since the latter also has a $^2\Sigma$ - $^2\Pi$ crossing at about the same R (the calculated crossing of the $1^2\Sigma_u^+$ and $1^2\Pi_u$ states for Na_2^+ is $R = 4.8a_0$).

[15]C. F. Melius and W. A. Goddard, III, to be published.