Collinear Quantum Calculation of Transition-State Spectrum for the K+NaCl Reaction

Toshiyuki Takayanagi

Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki 319-11

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The laser-induced reaction, $K+NaCl+h\nu \rightarrow KCl+Na^*$, has been studied quantum-mechanically, with consideration of only collinear geometries. Laser-dressed equations are numerically solved by the R-matrix propagation method. Quantum reaction probabilities are dominated by many resonances corresponding to the vibrational states of the reaction complex formed in the reaction. The results obtained are compared with surface hopping trajectory calculations. The trajectory surface hopping model fails in predicting the translational energy dependence of the reaction probabilities but a Landau–Zener model is qualitatively correct in the calculation of the laser wavelength dependence of the reaction probabilities. These results suggest that the dynamics of the laser-induced reaction can be divided into two independent processes; the ground state reaction $K+NaCl \rightarrow KCl+Na$ and the non-adiabatic transition from the laser-dressed ground state to the excited state.

Recent developments in molecular beam techniques and laser spectroscopy have opened a new field of "transition-state spectroscopy". The first attempt at spectroscopic probing of the transition-states was carried out by Polanyi and his co-workers.[1] They have studied the $F+Na_2$ reaction and observed a broad "wing" emission around the Na D-line, which they ascribed to the emission from the FNa_2 transition-states. Brooks and his co-workers[2,3] have reported evidence for absorption from the intermediate configurations in the K+NaX (X=Cl, Br, I) reactions. Neumark and his co-workers[4—6] have utilized photodetachment processes of negative ions XHY^- to study the transition-states for the neutral X+HY reactions, where X and Y are halogen atoms. Zewail and his co-workers[7,8] have succeeded in real-time probing of transition-states by using a femtosecond pump-probe technique. Although the experimental spectra observed by using these techniques give important information about the transition regions in potential energy surfaces, it is generally difficult to obtain the potential energy surfaces directly from the spectra. Therefore, a theoretical simulation of the experimental spectra is a very important step for understanding the characteristics of the potential energy surfaces.

In this paper, we address the transition-state spectrum for the K+NaCl reaction system which have been experimentally obtained by Maguire et al.[2] They have obtained the excitation spectrum by monitoring emission from Na^*. The spectrum obtained possesses a higher energy shoulder that increases in the direction of the Na D-line and a broad peak around 640 nm. The origin of this spectrum is attributed to the following laser-induced reaction:

$$K + NaCl + h\nu \rightarrow KCl + Na^*.$$

Several theoretical studies have been carried out to simulate the experimental spectrum. Yamashita and Morokuma[9,10] have carried out ab initio calculations for the ground and first two excited states of the KClNa molecule. They have constructed global analytical potential surfaces only for the ground and the second excited states, since the absorption to the first excited state was found to be negligible in the wavelength region of the experiments. They carried out surface hopping trajectory calculations where the non-adiabatic transition probability between two potential surfaces is estimated by the Landau–Zener approximation. Later, Barnes et al.[3] have performed similar calculations on slightly modified potential surfaces of Yamashita and Morokuma. The agreement between the theoretical calculations and the experimental results was found to be poor. Barnes et al.[3] could not confirm if the surface hopping trajectory model is inadequate or the potential energy surfaces employed are inadequate. Thus, an exact quantum calculation is clearly desirable. Johnson[11] has carried out collinear quantum calculations on the potential surfaces of Yamashita and Morokuma using a time-dependent formalism. However, converging results could not be obtained because of the small number of grid points and the short propagation times.

Motivated by these studies, we here compare accurate quantum calculations with the surface hopping trajec-

tory calculations. Three-dimensional calculations are of course desirable. However, the masses of the K+NaCl system are too large to perform three-dimensional quantum calculations because of the huge number of ro-vibrational states. For this reason, only collinear geometries are considered in the present investigation. Although we cannot confirm whether the conclusions obtained from the reduced dimensionality calculations are still valid in higher dimensionality ones, the theoretical calculations presented here will still provide valuable insight into spectral studies of transition-states.

Computational Procedure

A. Quantum Calculations. In order to calculate the transition state spectra, a laser-dressed picture[12,13] is introduced. In this formalism, both photoabsorption and photoemission processes are treated as non-adiabatic transitions between the laser-dressed ground and excited states. The equation to be solved can be written as

$$-\frac{1}{2\mu}\left(\frac{\partial^2}{\partial R^2}+\frac{\partial^2}{\partial r^2}\right)\begin{pmatrix}\phi_1\\ \phi_2\end{pmatrix} + \begin{pmatrix} V_1+\hbar\omega & \mu_{12}E \\ \mu_{12}E & V_2\end{pmatrix}\begin{pmatrix}\phi_1\\ \phi_2\end{pmatrix} = E\begin{pmatrix}\phi_1\\ \phi_2\end{pmatrix}. \quad (1)$$

Here ϕ_1 and ϕ_2 are the scattering wave functions in the dressed ground and excited state, respectively. V_1 and V_2 are the ground and excited potential energy surfaces, respectively. R is the scaled distance between the K atom and the center of mass of the NaCl molecule. r is the scaled internuclear distance of NaCl. μ is the reduced mass of the system. $\mu_{12}E$ is the laser coupling matrix element between two surfaces and is set at a constant value of 0.1 kcal mol^{-1}. This value is the same as that used by Yamashita and Morokuma.[10] Equation 1 is similar to those for ordinary non-adiabatic reactions. In the present study the hyperspherical coordinates (ρ, θ) are employed in order to solve Eq. 1 numerically. Standard R-matrix propagation method is used for scattering calculations. In the R-matrix propagation method, it is necessary to solve an eigenvalue problem on a grid of fixed values of hyperradius ρ. This was done by adopting a standard finite-difference method. The number of grid points used was 5000, which has been determined from convergence tests. The deep well in the potential energy surfaces for the KNaCl system implies that a large number of basis functions in the coupled-channel expansion is needed to converge the reaction probabilities. The calculation was carried out with 30 channels for each potential surface and well converged results were obtained in the energy range considered here.

Our computational code was checked by comparing with the results for the collinear $F(^2P_{3/2,1/2}) + H_2$ reaction in Ref. 15. An excellent agreement was obtained.

B. Surface Hopping Trajectory Calculations. The surface hopping trajectory model is based on a classical trajectory calculation performed on a single potential surface. The difference is that the non-adiabatic transition is incorporated with this model. Two methods have been developed to calculate surface hopping trajectories. One has been proposed by Stine and Muckerman[16] and the other by Blais and Truhlar.[17] Although it is still unsettled which method is more accurate, the method by Stine and Muckerman is more frequently employed in practical calculations. This is because their method is very simple and the modifications from a computer program for a single surface calculation may be straightforward. Recent calculations by Yamashita and Morokuma[10] and by Barnes et al.[3] also employed their method. Thus, we here adopt the same method, although our calculations are within collinear configurations.

The non-adiabatic transition probability was estimated using a standard Landau–Zener equation.[3,10] Typically, 500 trajectories were sampled for a specific laser wavelength and a specific translational energy. Integration of the classical equations of motion was carried out by a variable step-size Runge–Kutta–Fehrberg method.

C. Potential Energy Surfaces. As mentioned in the Introduction, the analytical potential surfaces based on ab initio results are available.[10] At first, we employed the potential surfaces. However, well converged results could not be obtained. This is probably because the surfaces have small potential wells in the asymptotic region for both entrance and exit arrangement channels. Since only collinear geometries were considered in the present study, we employed simple LEPS (London–Eyring–Polanyi–Sato) potentials[18] for both the ground and the excited states. For the excited states, a one body term were also added to the LEPS potential so as to reproduce the experimental endothermicity. The explicit expression and the parameters are described in the paper of Yamashita and Morokuma.[10]

The parameters for the LEPS potentials are summarized in Table 1. The adjustable Sato parameters are determined so as to reproduce roughly the characteristics of the reaction complex, such as the location of complex and the depth of the well, which have been

Table 1. LEPS Parameters Used in the Present Calculations

Molecule	KCl	NaCl	NaK
$De^{a)}$/eV	4.3570	4.2530	0.6277
$Re^{a)}$/Å	2.6667	2.3608	3.5890
$b^{a)}$/Å^{-1}	0.7842	0.8969	0.8084
$\Delta^{b)}$	0.3500	0.3500	0.3500
$\Delta^{c)}$	0.5000	0.5000	0.5000

a) The same values are used for both the ground and excited states. b) Sato parameters for the ground state potential. c) Sato parameters for the excited state potential.

calculated by Yamashita and Morokuma.[9,10] Figure 1 shows the contour plots for both the ground and excited state potentials employed in the present calculations.

Results

Figure 2 shows the total reaction probabilities for the K+NaCl (v=0) $+h\nu \rightarrow$KCl+Na* reaction at the laser wavelength of 593.3 nm. The reactant NaCl molecule is in the ground vibrational state and the probabilities were summed over all open vibrational states of the product KCl molecule. The solid line stands for the quantum calculations and the solid circles stand for the surface hopping trajectory calculations. The quantum calculations clearly show oscillatory structures, i.e., about sixty resonances are observed in this energy range. These resonances correspond to the vibrational states of the reaction complex formed in the reaction, since the potential energy surfaces of this reaction have deep wells. On the other hand, the probabilities calculated using the surface hopping trajectory are nearly constant in this energy range, and the values are found to be about 0.4. It is also interesting to compare the lifetimes of the reaction complex calculated by the two methods. From the resonance linewidth in Fig. 2, we can roughly estimate the quantum lifetime of the reaction complex. The resonance linewidth observed lies in the range of about 0.0001 to 0.001 eV and these values correspond to the lifetime of about 1 to 10 ps. On the other hand, the classical lifetimes can roughly be estimated from the total integration time for the reactive trajectories. The orders of the classical lifetimes were found to be almost the same as the quantum results.

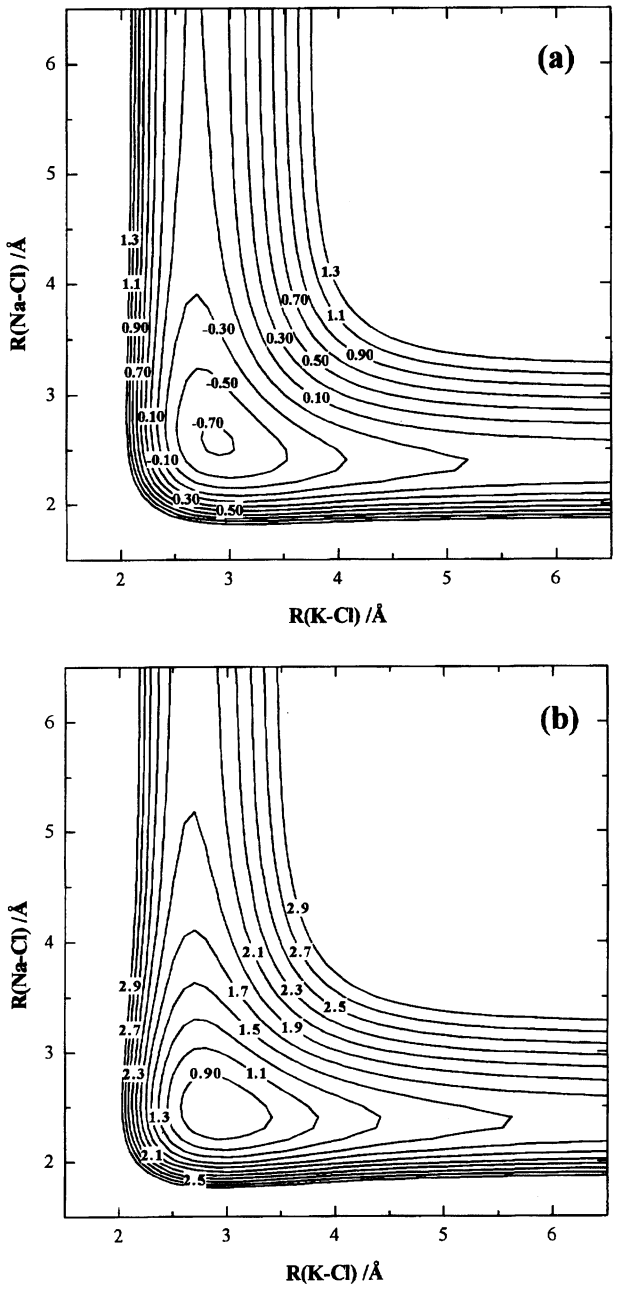

Fig. 1. Contour plots of potential energy surfaces used in the present calculations. (a) is for the ground state and (b) for the excited state. Numbers in the figures indicate the height of contours in unit of eV.

Figure 3 shows the laser wavelength dependence of the total reaction probabilities for the K+NaCl (v=0) $+h\nu \rightarrow$KCl+Na* reaction. The same result is shown in Fig. 4 in the three-dimensional perspective plots. Although small differences are seen at some translational energies, the figures show that the probabilities decrease with the increase of laser wavelength. In addition, Figs. 3 and 4 also show that the shape of probability curve does not depend on the laser wavelength and only the magnitude of the probability is different. These behaviors suggest that the reaction dynamics may be determined by a single potential surface. In order to check the validity of this suggestion, we calculated the total reaction probabilities for the K+NaCl (v=0) $\rightarrow$KCl+Na reaction on the ground-state potential energy surface. In Fig. 5, the results for the single surface calculations are shown. Although the detailed structures of resonance are slightly different, the figure clearly shows that the probability curve obtained by the single surface calculations agrees very well with the results obtained by the two surface calculations.

Figure 6 shows the laser wavelength dependence of quantum reaction probabilities for the K+NaCl (v=0) $+h\nu \rightarrow$KCl+Na* process at several translational energies. The figure also includes the probabilities calculated from the following one-dimensional Landau–Zener approximation:

$$p = 1 - \exp\left[-2\pi d_{12}^2/(\hbar v|\Delta F|)\right], \qquad (2)$$

where $d_{12}=\mu_{12}E$ and ΔF is a slope difference between the dressed ground and excited potentials. v is the translational velocity. In order to calculate ΔF, we employed one-dimensional potentials which were obtained from the vibronic curve of the ground and excited potential surfaces. The laser wavelength dependence of

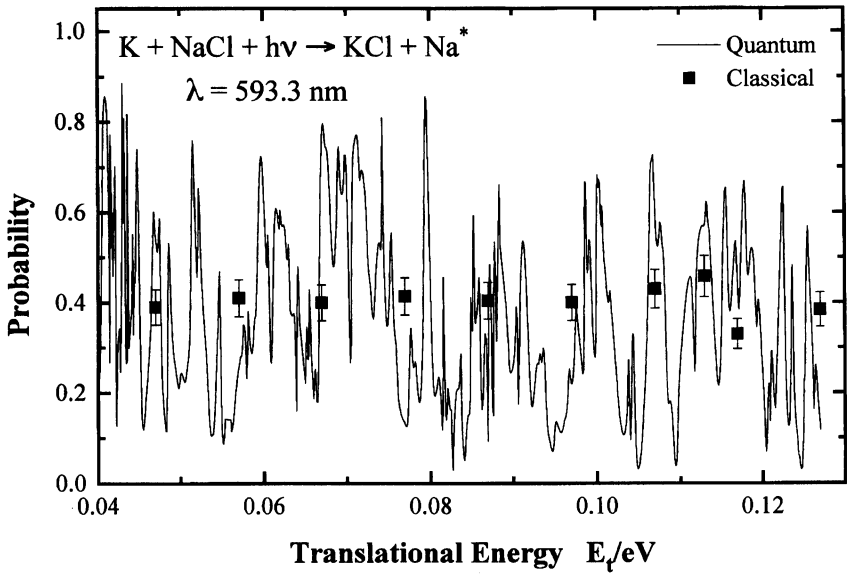

Fig. 2. Translational energy dependence of the total reaction probabilities for the K+NaCl (v=0) +$h\nu$→KCl+Na* reaction at the laser wavelength of 593.3 nm. Solid lines show the results from quantum calculations and the solid squares the results from the surface hopping trajectory calculations.

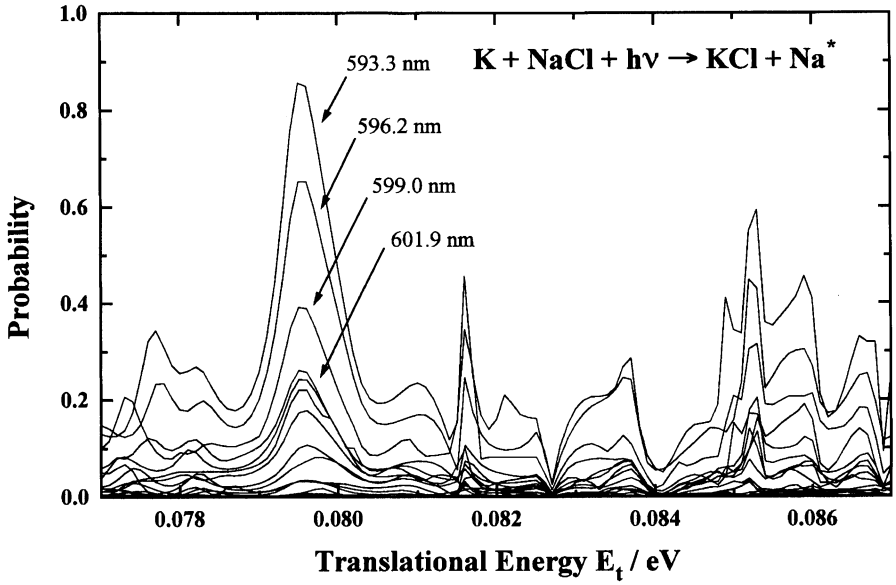

Fig. 3. Translational energy dependence of the total reaction probabilities for the K+NaCl (v=0) +$h\nu$→KCl+Na* reaction at several laser wavelengths.

probabilities calculated using the surface hopping trajectory method is also given in Fig. 6. For both the Landau–Zener and surface hopping trajectory calculations, the results were found to be almost independent of the translational energy considered here (0.04—0.13 eV). All the probabilities monotonously decrease with the increase in the laser wavelength. It is not important to compare the absolute values of the quantum probabilities with those of other methods, because the quantum probabilities are strongly dependent on the translational energy, as shown in Fig. 2.

Discussion

The quantum results described in the previous section suggest that the reaction probabilities $P_{K\rightarrow Na^*}(E_t, \lambda)$ for the laser-induced K+NaCl+$h\nu$→KCl+Na* process can be approximated as a simple product of two probabilities:

$$P_{K\rightarrow Na^*}(E_t,\lambda) \sim P_{K\rightarrow Na}(E_t)P_{Na\rightarrow Na^*}(E_t,\lambda), \quad (3)$$

where E_t is the translational energy and λ is the laser wavelength. Equation 3 clearly shows that the K+

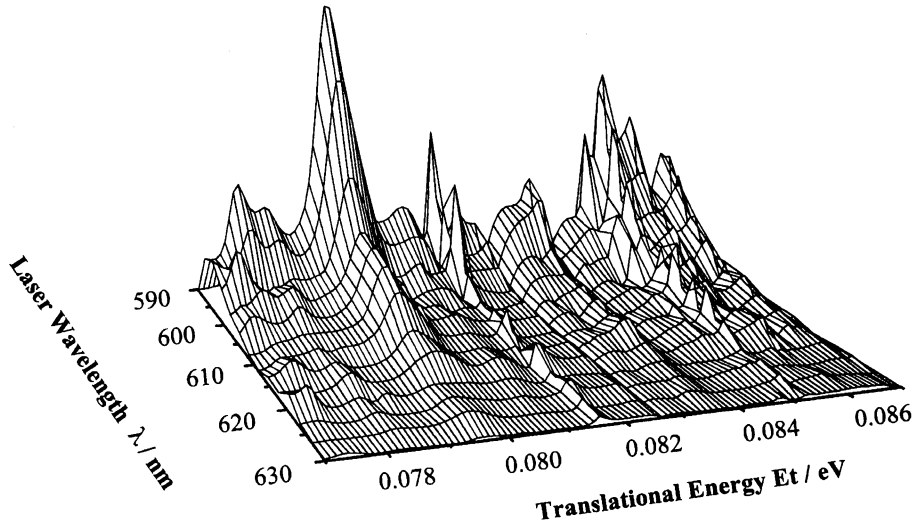

Fig. 4. Three-dimensional perspective plots of Fig. 3.

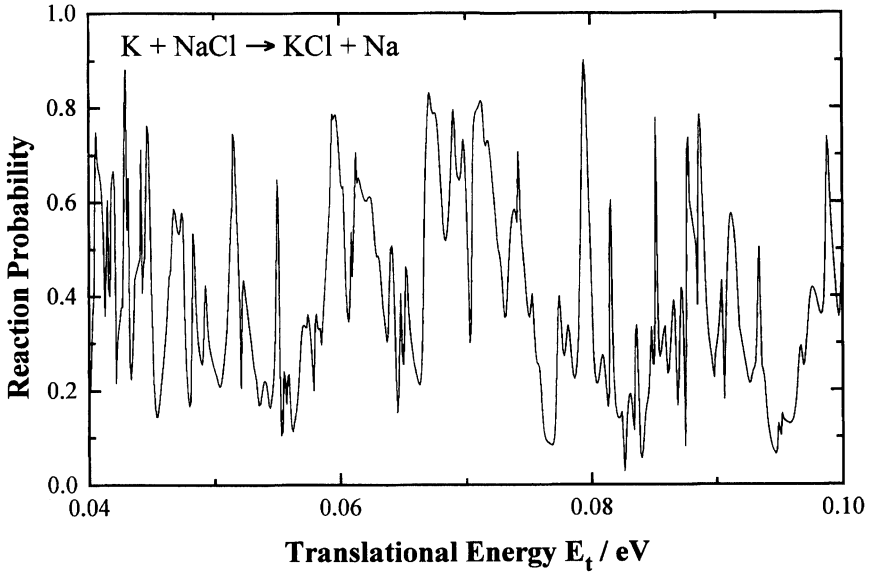

Fig. 5. Translational energy dependence of the total reaction probabilities for the K+NaCl (v=0) →KCl+Na reaction on the ground state potential energy surface.

NaCl+$h\nu$→KCl+Na* process can be divided into two steps. The first step is the K+NaCl→KCl+Na reaction on the ground-state potential and the reaction probability for this process is denoted as $P_{K\rightarrow Na}$ (E_t). Of course, this process does not depend on the laser wavelength and the reaction dynamics is governed by the many resonances, since the potential surface for the ground state has a complex well, as shown in Fig. 5. The second step is the non-adiabatic transition from the laser-dressed ground state to the excited state. The transition probability for this process is denoted as $P_{Na\rightarrow Na^*}$ (E_t, λ). This transition is caused by the strong laser field and is strongly dependent on the laser wavelength. Consequently, the reaction dynamics for the laser-induced K+NaCl+$h\nu$→KCl+Na* process can be treated as a combination of two independent processes.

Figure 6 indicates that $P_{Na\rightarrow Na^*}$ (E_t, λ) in Eq. 3 can be qualitatively approximated by the Landau–Zener probability. This suggests that the non-adiabatic transition probability is determined at the restricted regions of the potential energy surfaces, viz., around the crossing seam. In other words, the reaction on the ground state and the non-adiabatic transition between two surfaces occur in different regions of the potential energy surface. Figure 7 shows the crossing seams for several laser wavelengths. The crossing seams are located in the direction of the exit channel of the K+NaCl→KCl+Na reaction. As the laser wavelength becomes shorter, the crossing seam moves toward the product channel away from the interaction region. The transition probability between the dressed ground and excited states becomes large because the slope difference in Eq. 2 becomes small. On the other hand, as the laser wavelength increases, the crossing seam moves to the inter-

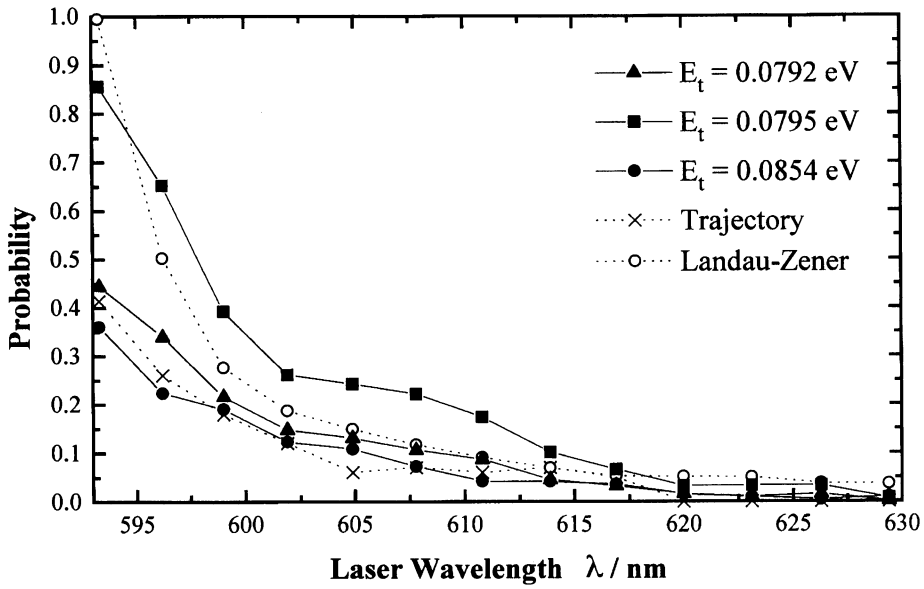

Fig. 6. The laser wavelength dependence of reaction probabilities for the K+NaCl (v=0) +$h\nu$→KCl+Na* process. Solid triangles, squares, and circles stand for the quantum results and the numbers in the figure indicate the translational energy. Open circles represent the Landau-Zener results and crosses represent the surface hopping trajectory results.

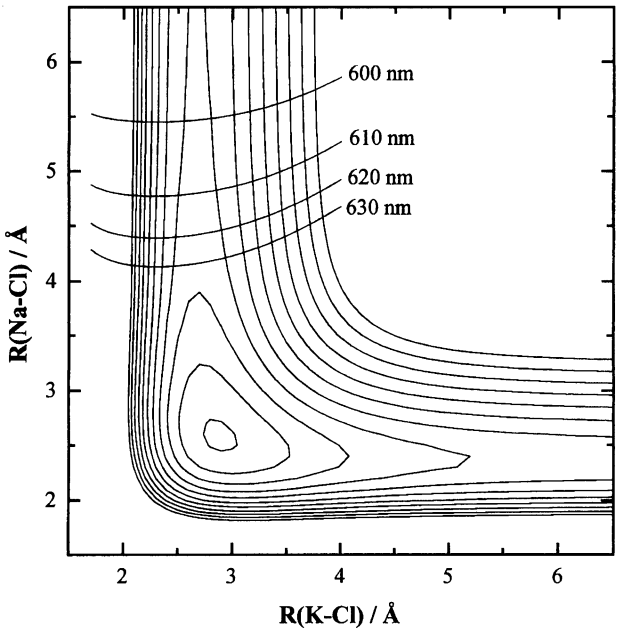

Fig. 7. The crossing seams for several laser wavelengths. Contours are drawn for the ground state potential energy surface.

action region; however, the transition probability decreases because of the large crossing angle between two surfaces. Thus, the laser wavelength dependence of the reaction probabilities does not reflect the dynamics on the ground-state surface nor the dynamics on the excited state surface. The main factor determining the laser wavelength dependence of the reaction probabilities is the non-adiabatic transition between the two surfaces. Jiang and Hutchinson[19] have also studied the transition-state spectrum of the K+NaCl reaction by a time-dependent wave packet calculation in one dimension. They concluded that the Landau–Zener model is quantitatively incorrect but a Franck–Condon model is valid in predicting the transition-state spectrum. However, the laser wavelength region investigated in their study was very different; they have studied the longer wavelength region in which the absorption is mainly due to the free-bound transitions.

Although only collinear collisions were considered in the present calculations, it is still informative to compare our results with the experimental spectrum[2,3] and with the three-dimensional surface hopping trajectory results.[3,10] The experimental spectrum shows that the intensity at 595 nm is about three times as large as that at 600 nm. On the other hand, the three-dimensional surface hopping trajectory calculations on the potential surfaces of Yamashita and Morokuma did not show such a sharp variation; the calculated difference between 595 and 600 nm is only 5%. As shown in Fig. 6, our quantum results qualitatively reproduce the experimental results although the probabilities depend on the translational energy. These results suggest that the model potential energy surfaces employed in the present study have a reasonable crossing behavior on the exit channel. Barnes et al.[3] have already pointed out that the potential surfaces of Yamashita and Morokuma have no such crossing behavior. Nevertheless, the qualitative agreement is probably, in part, fortuitous since our quantum results were not averaged over initial translational energies, initial impact parameters, or initial internal states of the reactants. In addition, the origin of the broad peak around 640 nm observed in the experiments is still unknown. Barnes et al.[3] have reported that such a feature is well resolved for other reaction

systems: K+NaBr and K+NaI. They have suggested that other excited states may play an important role. However, there are no ab initio studies concerning the excited potential energy surfaces for the K+NaBr and K+NaI reactions.

It is important to study the effect of non-collinear collisions on the reaction probabilities. In fact, for a non-linear configuration, Yamashita and Morokuma[10] have reported that the crossing seams move toward the reactant side, on the basis of ab initio calculations. In order to study the non-linear effect, one must use the analytical potential surfaces developed by Yamashita and Morokuma, because the LEPS potentials employed in the present study are constructed only for collinear calculations. Such calculations are currently under investigation.

In summary, the quantum reaction probabilities have been calculated for the laser-induced K+NaCl+$h\nu$→KCl+Na* process within collinear geometries. It has been found that the surface hopping trajectory model does not reproduce the quantum results, but the Landau–Zener approximation is qualitatively valid in predicting the laser wavelength dependence of reaction probabilities. This behavior suggests that the non-adiabatic transition between the dressed ground and excited surfaces occurs predominantly at the crossing seam of these surfaces.

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