# Quantum wave-packet dynamics of the photodissociation of LiF

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A nuclear wave-packet description of the photodissociation of LiF is described, with emphasis on the dynamics associated with the formation of long-lived resonances. The predissociation is described using *ab initio* potential-energy curves and transition dipole matrix elements. The split operator method is used to propagate time-dependent coupled-channel wave functions in a *diabatic* representation. Dissociation is incorporated using absorbing potentials at large internuclear separations to prevent the return of flux from asymptotic regions. Extremely narrow resonances and broad window resonances are found atop a broad absorption envelope, in agreement with a recent stationary-state calculation. The lifetimes of the narrow resonances extend to hundreds of picoseconds, indicating the very slow nature of the dissociation dynamics. The features of the absorption spectrum are connected to specific aspects of the wave-packet motion on the ionic and covalent potential curves through a detailed study of the autocorrelation function. [S1050-2947(99)08108-1]

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## I. INTRODUCTION

Alkali-metal-halide photodissociation has been a prototype for the study of chemical reactions on femtosecond time scales as illustrated in a number of experiments [1,2] and theoretical investigations [3–6]. In the femtosecond pumpprobe experiments, an initial wave packet is pumped onto an excited surface using an ultrashort laser pulse and is probed with another femtosecond laser. The experiments in all cases monitor the laser-induced fluorescence (LIF) signal as a function of the delay time between the pump and probe laser firings. The LIF signal shows a periodic variation with the delay time and is a function of the probe-pulse frequency.

Theoretical treatments based on time-dependent wavepacket methods [7] have been extremely valuable in the interpretation of femtosecond pump-probe experiments and also in the study of molecular photofragmentation [8,9], multiphoton dissociation of molecules in intense laser fields [10,11], and light scattering [12,13]. In the femtosecond pump-probe studies [3,4], by calculating the bound and free populations of the molecular complex during and after predissociation, these studies have been able to show qualitatively that the periodic variations of the LIF signal with the delay time are due to resonant and nonresonant atomic excitations and that the locations of the peaks in the LIF signal indicate predissociation due to interactions at the crossing between the diabatic potential-energy curves. All such calculations reported thus far have been concerned with the shorttime dynamics of nuclear motion.

In its simplest manifestation, alkali-metal-halide photodissociation involves two electronic states, the ground ionic state and the lowest excited covalent state, which cross at a certain value of internuclear distance. In Fig. 1, we show the potential energy curves of LiF, the subject of the present paper. These curves are from the *ab initio* calculations of Werner and Meyer [14]. The gap separating the two dissociation limits arises from the difference between the ionization potential of the alkali-metal atom and the electron affinity of the halogen atom. Asymptotically, the energy of the ionic species lies above the energy of the neutral species, and the interaction potential takes the Coulombic form. The long-range, attractive Coulomb interaction between Li<sup>+</sup> and F<sup>-</sup> gives rise to the crossing of the diabatic curves. The location of the crossing between the ionic and covalent curves varies



FIG. 1. Diabatic ionic and covalent potential curves and coupling elements of LiF, from Ref. [14]. The initial bound wave function is also shown in the ionic channel. Note that it is localized near  $R \sim 3$  a.u.

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for different alkali-metal halides, resulting in different time scales for the dissociation process.

The purpose of this paper is to present a time-dependent quantum-mechanical treatment of the photoabsorption of LiF and to provide a physically intuitive picture of the dissociation dynamics. Realistic ab initio potential energy curves and transition dipole matrix elements are employed in the calculations. The emphasis will be on long-time wave-packet dynamics and dissociation through the avoided crossing region. This study complements a recent time-independent quantummechanical investigation [15] of the same system, which revealed many interesting spectral features not previously discussed. In particular, the spectrum exhibits a broad envelope composed of many resonances with characteristic Fano line shapes [16]. The shapes of the resonances and their lifetimes vary systematically from very narrow resonances, whose lifetimes exceed hundreds of picoseconds, to broad window resonances with negligible oscillator strength. The resonances arise from the interaction between the bound states supported by the ionic diabatic curve and the continuum of the covalent configuration. The predissociating Feshbach resonances follow a Rydberg series [17] and exhibit a periodic double reversal of the Fano line-shape parameter. Here, we provide additional physical insight into the dissociation process by examining the details of the wave-packet formation, dispersion, and fragmentation. We demonstrate the robustness of the numerical technique by reproducing many narrow features of the photoabsorption spectrum.

## **II. THEORY**

Methods of solution of the time-dependent Schrödinger equation with two or more coupled electronic states are well documented in the literature [7,18]. One may use either an adiabatic representation or a diabatic representation to carry out the calculations. In the diabatic representation, the kinetic-energy operator is diagonal and the coupling elements are contained in the off-diagonal potential-energy matrix. In contrast, in the adiabatic representation the potentialenergy matrix is diagonal and the kinetic-energy operator couples different adiabatic curves. Both provide an equivalent description, but for computational simplicity, the diabatic representation is used here.

The two-channel Schrödinger equation in this representation is

$$i\hbar \frac{\partial \Psi}{\partial t} = \mathbf{H}\Psi,\tag{1}$$

where

$$\boldsymbol{\Psi} = \begin{pmatrix} \boldsymbol{\psi}_1(t) \\ \boldsymbol{\psi}_2(t) \end{pmatrix}. \tag{2}$$

The wave functions  $\psi_1$  and  $\psi_2$  are the components on the ground (ionic) and excited (covalent) diabatic electronic states, respectively. The Hamiltonian is given by

$$H = T + V$$

$$= -\frac{\hbar^2}{2m}\mathbf{I}\frac{d^2}{dR^2} + \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix},$$
 (3)

where **I** is the 2×2 identity matrix and *m* is the reduced mass of the molecule. The diagonal elements  $V_{11}$  and  $V_{22}$ are, respectively, the ionic and covalent diabatic potential curves corresponding to  $\psi_1(t)$  and  $\psi_2(t)$ . The diabatic coupling elements  $V_{12}$  and  $V_{21}$  result from the interaction between the two potentials. The split-operator method [19] used to solve the Schrödinger equation employs a symmetric splitting of the kinetic- and potential-energy operators:

$$\Psi(t+\Delta t) = e^{-i\Delta t \mathbf{V}/2\hbar} e^{-i\Delta t \mathbf{T}/\hbar} e^{-i\Delta t \mathbf{V}/2\hbar} \Psi(t) + O(\Delta t^3).$$
(4)

The action of the potential-energy operator is carried out in coordinate space and that of the kinetic-energy operator in momentum space where it is diagonal. The fast-Fouriertransform algorithm is used to efficiently switch between the coordinate and momentum spaces following the application of each exponential operator.

Different methods are available for the calculation of the exponential of the potential-energy matrix. One usual procedure is to diagonalize the diabatic potential-energy matrix (transform to the adiabatic representation) for the evaluation of the exponential and then return to the diabatic representation for the evaluation of the kinetic-energy operator. Here, however, we use the algorithm suggested by Broeckhove *et al.* [20], which enables the evaluation of the 2×2 exponential of the potential-energy matrix directly in the diabatic representation. This is done by rewriting the potential-energy matrix using the Pauli spinor matrices  $\sigma_i$ , *i*=1,2,3,

$$\mathbf{V} = \sum_{i=0}^{3} \nu_i \boldsymbol{\sigma}_i, \qquad (5)$$

where

$$\nu_0 = \frac{V_{11} + V_{22}}{2},\tag{6a}$$

$$\nu_1 = V_{12},$$
 (6b)

$$\nu_2 = 0, \tag{6c}$$

$$\nu_3 = \frac{V_{11} - V_{22}}{2}.$$
 (6d)

The exponential matrix is evaluated as

$$e^{i\mathbf{V}} = e^{i\nu_0} \left( \boldsymbol{\sigma}_0 \, \cos|\nu| + i \, \frac{\sin|\nu|}{|\nu|} \, \sum_{i=1}^3 \, \nu_i \boldsymbol{\sigma}_i \right), \tag{7}$$

with

$$|\nu| = \left(\sum_{i=1}^{3} \nu_i^2\right)^{1/2}$$
. (8)

The nuclear wave functions in the adiabatic and diabatic representations are related to each other by the  $2 \times 2$  unitary matrix, which diagonalizes the diabatic potential-energy matrix. Thus, if desired, we may evaluate the adiabatic wave functions from the diabatic ones by a simple rotation,

$$\boldsymbol{\Phi}(t) = \mathbf{U}\boldsymbol{\Psi}(t), \tag{9}$$

where

$$\mathbf{U} = \begin{pmatrix} \cos \theta(R) & -\sin \theta(R) \\ \sin \theta(R) & \cos \theta(R) \end{pmatrix}$$
(10)

and

$$\tan 2\,\theta(R) = \frac{2\,V_{12}}{V_{11} - V_{22}}.\tag{11}$$

Heller [21] has shown that in the Fermi golden-rule approximation the photoabsorption spectrum may be computed from the time-dependent wave function by taking a Fourier transform of the autocorrelation function,

$$\sigma(\omega) \propto \omega \int_{-T}^{T} dt \ w(t) C(t) \ e^{iEt/\hbar}.$$
 (12)

The energy E is  $E_{v''j''} + \hbar \omega$ , with  $E_{v''j''}$  the rovibrational energy of the initial state and  $\hbar \omega$ , the photon energy. The window function w(t) is included in the Fourier transform because the correlation function is calculated only in a finite time interval [0:T]. We used a Hanning window,  $w(t)=1 + \cos(\pi t/T)$ , which vanishes at the integration limits. The integral is evaluated by a trapezoidal rule. The details of the dynamics are contained in the autocorrelation function, which is defined as the overlap of the propagated and the initial state wave functions,

$$C(t) = \langle \Psi(R, t=0) | \Psi(R, t) \rangle.$$
(13)

In order for Eq. (12) to represent the photoabsorption spectrum, the initial state in Eq. (13) must be taken to be the product of the initial rovibrational wave function and the transition dipole moment. In the diabatic representation utilized here, the dipole moment matrix is diagonal [14] so that the initial wave packet is given by

$$\psi_1(R,t=0) = \phi_{v''j''}(R)\mu_1(R),$$
  
$$\psi_2(R,t=0) = 0.$$
(14)

The wave function  $\phi_{v''j''}(R)$  is a bound rovibronic state in the ionic potential. The subscripts v'' and j'' denote vibrational and rotational quantum numbers, respectively.

## **III. RESULTS AND DISCUSSION**

We consider excitation from the ground rovibrational level of LiF, with v''=0 and j''=0. Other rotational levels are readily populated in a thermal sample but are not discussed here. The bound state wave function  $\phi_{00}(R)$  is computed using the Fourier-grid Hamiltonian method [22]. The transition dipole moment function  $\mu_1(R)$ , which connects dipole-allowed rotational levels within the diabatic ionic



FIG. 2. Photoabsorption spectrum of LiF as a function of frequency.

curve, is from [14]. Accordingly, the initial wave packet Eq. (14) is accurately known.

The diabatic potential curves and the diabatic coupling element for the present system are shown in Fig. 1. The two diabatic potentials cross at an internuclear distance of about R = 13.3 a.u.

Due to the long-range Coulomb potential in the ionic channel, accurate propagation requires a relatively large spatial grid. Initial test calculations with restricted grids were unable to recover the resonances seen in the time-independent calculation. An absorbing potential was used to attenuate the dissociating wave packet in the asymptotic region of both channels, and its location was found to significantly affect the computed spectrum. The cause for this strong dependence can be traced to the premature removal of nondissociating flux in the ionic channel, which has a long-range potential. Based on a series of convergence tests, the absorbing potential was placed at R = 60 a.u., and the total number of grid points was set at 2048 with a spacing of 0.03 a.u. The time step for the propagation was taken to be 5 a.u.

The wave packet is propagated in the diabatic representation with the initial conditions given by Eq. (14). The absorption spectrum obtained from Eq. (12) is shown in Fig. 2 after substracting the background contribution. Three characteristic frequency scales are identifiable: a broad envelope, a Rydberg vibrational spacing that occurs over a fine frequency scale, and a periodic modulation over a coarse, intermediate energy scale. The total propagation time needed to resolve the narrow resonances to the degree shown is about 240 ps. The computed spectrum is in good agreement, in resonance positions and profiles, with that obtained from the time-independent quantum-mechanical calculation of Cornett *et al.* [15].

In Fig. 3, we show an expanded view of the spectrum in a typical energy range to illustrate the two distinct types of resonances: extremely narrow resonances with long lifetimes and broad window resonances with short lifetimes. The time-independent quantum-mechanical result is also given for comparison; it coincides with the present result in nearly all details, except for the widths of some of the sharp resonances. This is due to the fact that the time propagation is performed only up to 242 ps whereas the lifetimes of some of the narrow resonances are longer than one nanosecond.



FIG. 3. Expanded view of the photoabsorption spectrum illustrating the two distinct types of resonances. The upper panel shows the result of time-independent quantum-mechanical calculations and the lower panel shows the present result. The vertical lines labeled a and b in the lower panel show positions of the quantized energy levels of the diabatic ionic potential corresponding to the sharp and window resonances described in the text and whose time evolution is shown in Fig. 7.

In the following, we provide a detailed study of the origin of these resonances in terms of the autocorrelation function and the spatial and temporal evolution of the wave packet on the ionic and covalent potential-energy curves.

The photoabsorption spectrum given by Eq. (12) is determined by the autocorrelation with the localized initial wave packet, in accordance with Eq. (13). We provide here a description of the primary features of the autocorrelation function that is shown in the panels of Fig. 4 for the first 2 ps of the dynamics. Note that what is plotted is the squared modulus of the autocorrelation function, while the photoabsorption spectrum depends linearly on C(t). As a result, Fig. 4 shows additional quantum beats that have no influence on the spectrum, but which facilitate interpretation of the dynamics.

Figure 4(a) displays the part of the autocorrelation function relevant to the initial excitation of the wave packet. The



FIG. 4. Squared modulus of the autocorrelation function versus time; see Sec. III for details.

departure of the wave packet from the vicinity of the initial state results in a smooth Gaussian-like falloff corresponding to the removal of about 0.6% of the probability from the initial wave packet in roughly 10 femtoseconds. This "departure" time correlates to an energy uncertainty equal to the envelope of the photoabsorption spectrum, in agreement with the Franck-Condon principle. The rapid short-time oscillations in Fig. 4 occur on a time scale of about 0.6 femtoseconds, corresponding to an energy of about 0.25 a.u (~56 000 cm<sup>-1</sup>). This is roughly equal to the energy difference between the initial state and the maximum of the broad envelope of the predissociation spectrum. That this quantum beat is nearly monochromatic results from the fact that the energy spread of the broad envelope is small compared to the average excitation energy.

Between 15 and 650 femtoseconds, the squared modulus of the autocorrelation function in Fig. 4(b) has only a small variation corresponding to a quantum beat between the ground and first-excited vibrational components of that part of the wave packet deeply bound in the ionic potential. This time scale is  $\tau \sim 2 \pi/(E_{v''=1} - E_{v''=0}) \sim 35$  fs. During this time, the wave packet has departed from the initial state volume and so has no effect on the autocorrelation function. The observed quantum beat will remain *ad infinitum* if the off-diagonal coupling is neglected.

The first return of the wave packet to the initial Frank-Condon region occurs near  $t \sim 700$  fs. Note that this return, superimposed upon the vibrational quantum beat, is gradual and of small amplitude; only a small percentage of the dissociating wave packet returns due to dispersion in the ionic channel. The components of the wave packet, which reflect first from the outer wall of the ionic potential, move into and then out of the initial-state volume between  $t \sim 700$  fs and  $t \sim 1400$  fs. Beyond 1400 fs, higher-order recurrences of the wave packet become apparent, and the autocorrelation function grows in complexity.

The complicated frequency domain features in Fig. 2 contain different characteristic time scales, as discussed above. To reveal how the time evolution manifests itself in the spectrum, we have calculated the absorption spectrum by truncating the upper limit in the integral in Eq. (12) to the time indicated in each panel in Fig. 5. The broad frequency scale appears in a short time (10-20 fs), but is shown here after 500 fs for sampling reasons. The interferometric modulation of the spectrum described in Ref. [15] is visible after about 1 ps, corresponding roughly to a full traversal of a classical orbit in the ionic channel. This is due to the decay of those components of the wave packet corresponding to the broad window resonances in the absorption spectrum, which require only a single pass of the crossing to dissociate. Additional time scales become apparent after about 3-5 ps when the wave packet has evolved long enough for the Rydberg spacing to emerge.

The spatial spread of the wave packet mentioned above has important consequences on the computed spectrum, and it provides a complementary picture of the dissociation dynamics to that given by the autocorrelation function. For this reason, we provide a detailed analysis of the spatial evolution of the wave packet following the initial excitation and attribute details of the photoabsorption spectrum to specific aspects of the wave-packet motion.



FIG. 5. Fourier transforms of the autocorrelation function at different times. The upper limit of the integral in Eq. (12) is shown in each panel label. Note the appearance of three different frequency scales: the broad spectral envelope, the interferometric modulations, and the Rydberg frequency spacing.

The initial excitation within the ionic channel covers a broad range of energy, spanning both bound vibrational states and the region between the dissociation thresholds. Because the wave packet is not an eigenstate of the coupled Hamiltonian in Eq. (3), it disperses and builds up amplitude in the covalent channel during the propagation. This is illustrated in Fig. 6 in the form of snapshots of the probability density in each diabatic channel at different time intervals. Due to the large diabatic coupling at short distances, the buildup in the covalent channel is almost instantaneous. After 48 femtoseconds, for example, Fig. 6 shows that the covalent pulse is nearly five times as large as the ionic pulse.



FIG. 6. Snapshots of the wave packet on the diabatic ionic and covalent potentials at different time intervals shown in the panels.

The covalent and the ionic pieces reach the crossing point at the same time as shown by the snapshots at 91 fs, but their subsequent evolution is quite different. The snapshots at 357 fs show that the covalent wave packet continues to move to large internuclear separation dissociating to neutral fragments, whereas the ionic counterpart moves slowly and reflects from the outer wall of the potential curve.

We note in passing that in the adiabatic representation, since the nonadiabatic coupling is small far from the crossing, there will be no corresponding wave packet in the lower adiabatic channel at t=48 fs. By t=91 fs, however, the wavepacket will have arrived at the avoided crossing and sheared into two fragments upon traversing the crossing. This has been explicitly verified by transforming the wave packet to the adiabatic representation according to Eq. (9). The diabatic transition probability is roughly 0.8, so that only about 20% of the wave travels adiabatically through the crossing. Quantization of the levels in the ionic diabatic potential more closely reproduces the resonance positions than does quantization in the upper adiabatic potential. Accordingly, the diabatic representation will be used to describe the remaining evolution of the wave packet.

Figure 6(b) shows the diabatic representation of the wave packet at t = 689 fs. Dispersion within the ionic channel has led to the formation of a standing wave in less than one "round trip" of the centroid of the packet; the more deeply bound components reflect sooner from the Coulomb potential and, having been reflected again from the inner turning point, interfere with more weakly bound components of the same wave packet that are only just returning from the outer turning point. The resultant "standing wave," clearly localized within 20 a.u. in Fig. 6(b), moves slowly outward in Figs. 6(c) and 6(d) as the dispersion continues.

Coupling of the diabatic states likewise results in a standing wave in the covalent channel inside the crossing radius. Outside the crossing radius, there is no incident wave in the covalent channel so that only an outgoing traveling wave can be seen. This is most apparent in Fig. 6(c) where the wave in the covalent channel at t=1185 fs displays nearly perfect constructive and destructive interference. Note how the wavelength of the traveling wave increases with decreasing internuclear separation. This is not due to the repulsive potential in the covalent channel, which is too flat beyond the crossing radius to explain a variation of this magnitude. Instead, the variation is due to dispersion within the ionic channel; the more deeply bound (or higher-frequency) components of the packet correspond to orbits with shorter classical periods, and are, accordingly, the first to emerge from the reaction zone in the open channel [23].

This trend continues in Fig. 6(d) where the wavelength has now grown to roughly 20 a.u. at time t=1651 fs. Now, however, the low-frequency outgoing wave is amplitude modulated with higher-frequency waves resulting from multiple "orbits" of the high-frequency components.

If the coupling of the two channels were weaker, then the dynamics of the predissociation could be viewed, within the *diabatic representation*, as a dispersing Rydberg wave packet within the ionic channel, weakly coupled to a nearly free covalent continuum whose outgoing flux "detects" revivals of the packet. This simple picture must be modified, however, since the coupling between channels is here large



FIG. 7. Probability as a function of time in the ionic channel for a sharp and window resonance labeled a and b in Fig. 3.

enough that standing wave formation in the covalent channel impedes the emission of some frequency components from the interaction zone, giving rise to long-lived resonant states. The standing waves form due to constructive interference of traveling waves in the ionic and covalent channels. In short, the outgoing covalent flux serves both as a "detector" and as a "filter" that passes only those components of the packet that are not in resonance. Remarkably, this can be seen even at times as short as t=1651 fs in the ionic component of Fig. 6(d), where a simple modulation of the "noisy" Rydberg wave packet is emerging at small internuclear separations. This simplification results from the removal from the wave packet of all frequency components corresponding to the broad window resonances of the photoabsorption spectrum.

In Fig. 7 we show the time dependence of the probability in the ionic channel for a typical window and a sharp resonance in the diabatic representation. They are obtained by propagating eigenfunctions  $\phi_{v''i''}(R)$  of the uncoupled diabatic ionic potential whose energy eigenvalues correspond approximately to the energies of the sharp and window resonances labeled "a" and "b," respectively in Fig. 3. The time evolution is carried out with the Hamiltonian in Eq. (3). For the sharp resonance, after the initial fast exponential decay ( $\sim 100$  fs), the probability settles to an almost constant value, actually an exponential with a small decay constant, for long periods. For the window resonance, the decay is exponential for the first 3 ps ( $\sim$ 3 lifetimes) and thereafter nonexponential  $[P(t) \propto t^{-n}]$ , where  $n = \frac{1}{2}$ . From a fit to the exponential decay part of the probability, we deduced a lifetime of about 0.80 ps for the window resonance. The probabilities are modulated on time scales of about 500 fs. The oscillations represent the coherent superposition of nearby stationary states that are populated due to the energy spread of the initial wave function, which is not an eigenstate of the Hamiltonian in Eq. (3). This was confirmed by a spectral decomposition of the autocorrelation function similar to the calculation of the absorption spectrum [Eqs. (12)-(14)] with the initial condition  $\psi_1(R,t=0) = \phi_{v''i''}(R)$  in Eq. (14), which revealed the presence of a few additional eigenstates with small amplitudes corresponding to the narrow and window Feshbach resonances. The narrow resonances, upon the decay of the short-lived window resonances (after  $\sim 3$  ps), interfere and produce the observed power-law behavior of the survival probability. The survival probability after 24 ps is about 72% for the eigenstate corresponding to the sharp resonance whereas it is only about 0.5% for the window resonances. We became aware of a pump-probe experiment [24] of IBr photodissociation and an accompanying wave packet calculation [25], which discuss some aspects of the dissociation dynamics similar to those presented here.

#### **IV. CONCLUSION**

The photodissociation dynamics of LiF has been investigated using time-dependent wave packets. Realistic *ab initio* potential energy curves, transition dipole matrix elements, and coupling potentials were used. Time evolution has been described in the diabatic representations, with emphasis on the long-time dynamics responsible for resonance formation and decay.

The dissociation dynamics is found to be mainly governed by two effects: dispersion of the Rydberg wave packet in the ionic channel and the constructive interference of traveling waves in both ionic and covalent diabatic potentials. The time-dependent calculation is sufficiently robust to reproduce the dominant frequency domain features, in excellent agreement with the results of a recent time-independent quantummechanical calculation.

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- T.S. Rose, M.J. Rosker, and A.H. Zewail, J. Chem. Phys. 88, 6672 (1988); M.J. Rosker, T.S. Rose, and A.H. Zewail, Chem. Phys. Lett. 146, 175 (1988).
- [4] V. Engel and H. Metiu, J. Chem. Phys. 90, 6116 (1989); 91,

wail, Chem. Phys. Lett. 152, 1 (1988).

- 1596 (1989). [5] S.E. Choi and J.C. Light, J. Chem. Phys. **90**, 2593 (1989).
- [2] T.S. Rose, M.J. Rosker, and A.H. Zewail, J. Chem. Phys. 91, 7415 (1989); P. Cong, A. Mokhtari, and A.H. Zewail, Chem. Phys. Lett. 172, 109 (1990).
- [3] V. Engel, H. Metiu, R. Almeida, R.A. Marcus, and A.H. Ze-
- [6] M. Grønager and N.E. Henriksen, J. Chem. Phys. 109, 4335 (1998).
- [7] N. Balakrishnan, C. Kalyanaraman, and N. Sathyamurthy,

Phys. Rep. 280, 79 (1997).

- [8] K.C. Kulander and E.J. Heller, J. Chem. Phys. 69, 2439 (1978).
- [9] N. Balakrishnan and G.D. Billing, J. Chem. Phys. 101, 2968 (1994).
- [10] G. Jolicard and O. Atabek, Phys. Rev. A 46, 5845 (1992).
- [11] R. Numico, A. Keller, and O. Atabek, Phys. Rev. A 56, 772 (1997).
- [12] S.O. Williams and D.G. Imre, J. Phys. Chem. 92, 6648 (1988).
- [13] B. Hartke, W. Kiefer, E. Kolba, J. Manz, and J. Strempel, J. Chem. Phys. 96, 5636 (1992).
- [14] H.J. Werner and W. Meyer, J. Chem. Phys. 74, 5802 (1981).
- [15] S.T. Cornett, H.R. Sadeghpour, and M.J. Cavagnero, Phys. Rev. Lett. 82, 2488 (1999).
- [16] U. Fano, Phys. Rev. 124, 1866 (1961).

- [17] C. Asaro and A. Dalgarno, Chem. Phys. Lett. 118, 64 (1985).
- [18] J. Alvarellos and H. Metiu, J. Chem. Phys. 88, 4957 (1988).
- [19] M.D. Feit, J. Fleck, Jr., and A. Steiger, J. Comput. Phys. 47, 412 (1982).
- [20] J. Broeckhove, B. Feyen, L. Lathouwers, F. Arickx, and P. Van Leuven, Chem. Phys. Lett. 174, 504 (1990).
- [21] E.J. Heller, Acc. Chem. Res. 14, 368 (1981).
- [22] C.C. Marston and G.G. Balint-Kurti, J. Chem. Phys. 91, 3571 (1989).
- [23] F. Robicheaux and W.T. Hill III, Phys. Rev. A 54, 3276 (1996).
- [24] M. Shapiro, M.J.J. Vrakking, and A. Stolow, J. Chem. Phys. 110, 2465 (1999).
- [25] A.N. Hussain and G. Roberts, J. Chem. Phys. **110**, 2474 (1999).