Channel Interaction in Alkali-Halide Photodissociation: Interferometric Lineshapes and Dynamic Switching

H. R. SADEGHPOUR

Institute for Theoretical Atomic and Molecular Physics, Harvard–Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, Massachusetts 02138

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ABSTRACT: Photodissociation of alkali–halides is studied using a hybrid close-coupling and multichannel quantum defect theory approach. A novel class of interferometry that arises from the coherent interference of alternative pathways to bond breaking is identified. Interferometric resonances that live for hundreds of picoseconds are analyzed in the spirit of channel interaction. Interfering patterns that form in the interaction zone due to collision of nuclear wavepackets are revealed. © 2000 John Wiley & Sons, Inc. Int J Quantum Chem 80: 958–965, 2000

Key words: photodissociation; channel interaction; quantum defect theory; wavepacket dispersion; coherent interference

Introductory Remarks

A lkali-halides are the prototypical systems for study and control of chemical reactions on a femtosecond time scale [1, 2]. There has been a preponderance of studies that have explored nuclear motion in alkali-halides [3–5]. There are several traits that distinguish alkali-halide molecules. In their normal configurations, alkali-halides have ionic characteristics, i.e., the electrons have a ten-

International Journal of Quantum Chemistry, Vol. 80, 958–965 (2000) © 2000 John Wiley & Sons, Inc. dency to leave the alkali-metal atom and attach to the halogen atom. Because of an energy gap between the ionization potential of the alkali-metal and the electron affinity of the halogen atom, the ion pair dissociation threshold lies above the neutral fragmentation limit. The first excited electronic curve in alkali-halides has a covalent character that manifests in repulsive interaction between the atoms at short distances. When the electronic curves have similar molecular symmetry, such as in the case to be considered here, ${}^{1}\Sigma^{+}$, they interact and nearly cross. In alkali-haldies, the typical avoided crossing region lies around 6.5 Å. Second, because the molecules interact via an attractive Coulomb potential in the ground state, the rovibrational levels follow a Rydberg progression, with energies propor-

Correspondence to: H. R. Sadeghpour; e-mail: hrs@cfa.harvard. edu.

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tional to (μ/n^{*2}) , where n^* is a principal quantum number and μ is the reduced mass. It also means that the density of rovibrational levels is infinite. Indeed, the J = 0 vibrational series in LiF follows the form,

$$E_{v''} = \frac{-\mu}{2(v''+1-\delta/\pi)}$$

where $\delta = -126\pi$, δ/π is the quantum defect for the J = 0 series, and $n^* = v'' + 1 - \delta/\pi$. Third, the large permanent electric dipole produces a ripe environment for photoexcitation of the molecule.

In this study, a method for calculating the predissociating resonant profiles and energies is described. The feature-rich photodissociation spectrum is calculated with a multichannel quantum defect technique. The temporal evolution of the vibrational motion is depicted with an ab initio wavepacket calculation. Lithium fluoride is used as a specific example.

Predissociation

The energy gap between the two dissociation thresholds supports a large number of vibrational levels that owing to nonadiabatic interaction between the ionic and covalent electronic channels are no longer true bound states. These quasibound rovibrational levels provide the environment for temporary entrapment of the molecule in a transient state with a finite lifetime, subject to the uncertainty principle. These so-called predissociating resonances are therefore a stark realization of nonadiabaticity and multichannel phenomena. Because they occur near a dissociation threshold, these weakly bound molecules live for most of their life, like their free brethren, just above the dissociation limit. The delicate channel interaction between bound and continuum series can significantly alter the photochemistry in alkali-halides.

It is therefore plausible to treat the physics of interaction near a threshold, just below and just above, on equal footing. Such a mathematical construct exists and goes by the name of multichannel quantum defect theory (MQDT) [6–8]. MQDT has been used extensively to formulate photoabsorption and scattering reactions in atomic systems and has met remarkable success. (The reader is referred to a comprehensive review of the subject with examples in atomic physics by Aymar et al. [8].) Here, MQDT is tailored to describe predissociation in alkali–halides.

Channel Interaction and Dynamic Switching

The interaction between the ${}^{1}\Sigma^{+}$ electronic states in alkali–halides is regulated by the radial nonadiabatic coupling matrix elements. Because the electronic wave functions change abruptly near an avoided crossing between two potential energy curves, the associated radial coupling matrix element peaks to compensate for the sudden change in the electronic property and is typically Lorentzian in shape. If the avoided crossing region is narrow and the separation between the adiabatic potential curves is small, the nonadiabatic matrix element becomes sharply peaked.

DIABATIC DEFINITION

For computational efficiency and at times for physical reasons, it is best to work in a *diabatic* representation. The similarity transformation that brings an adiabatic representation to a diabatic one is, of course, unitary. In a diabatic representation, the electronic wave functions vary smoothly at crossings between potential curves, and the coupling matrix elements also smoothly vary with distance. Whereas in the adiabatic representation, the potential energy matrix is diagonal, it contains offdiagonal elements in the diabatic representation.

A rigorous transformation between the adiabatic and diabatic sets can be defined from [9]

$$\frac{d\mathbf{C}}{dR} + \mathbf{A}\mathbf{C} = 0,\tag{1}$$

where **C** is a unitary matrix that transforms the adiabatic wave function $\psi^a(\mathbf{r}; R)$ into the diabatic wave function $\psi^d(\mathbf{r}; R)$, i.e., $\psi^d(\mathbf{r}; R) = \mathbf{C}^T \psi^a(\mathbf{r}; R)$, and **A** is the non-Hermitian first-derivative radial coupling matrix, i.e., $A_{ij} = \langle \psi_i^a | \partial / \partial R | \psi_j^a \rangle$. The above expression ensures that the nonadiabatic matrix **A** is removed from the nuclear motion. However, numerical implementation of the above transformation becomes exceedingly difficult if and when the number of coupled channels is large and the interaction between these channels becomes sharply peaked. Furthermore, ab initio calculation of the radial coupling matrix elements is not a trivial task with quantum chemistry codes.

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The coupled equations in the adiabatic representation is then

$$\left[\mathbf{I}\nabla_{R}^{2}+2\mu\left(\mathbf{I}E-\mathbf{V}^{d}(R)\right)+\mathbf{C}^{T}\left(\mathbf{B}-\frac{d\mathbf{A}}{dR}-|\mathbf{A}|^{2}\right)\mathbf{C}\right]\times\mathbf{F}^{d}(R)=0,$$
 (2)

where $\mathbf{F}^{d}(R)$ are the expansion coefficients of the diabatic wave function, $\psi_{i}^{d}(\mathbf{r}; R) = \sum_{i} \phi^{d}(\mathbf{r}; R) F_{i}^{d}(R)$. For the last term in the above equation to be zero requires that the adiabatic electronic basis forms a complete set, or equivalently,

$$\mathbf{B} = \frac{d\mathbf{A}}{dR} + |\mathbf{A}|^2,\tag{3}$$

where $B_{ij} = \langle \psi_i^a | \partial^2 / \partial R^2 | \psi_j^a \rangle$ are the second-order coupling matrix elements. In alkali–halides, and specifically in LiF, the other ${}^{1}\Sigma^{+}$ electronic states lie far away in energy such that by invoking the Hellmann–Feynman theorem, their contributions to **B** are negligible and the preceding assumption holds valid.

An alternative method that circumvents the entire issue of calculating \mathbf{A} in the first place is to define a unitary transformation that diagonalizes an *R*-dependent electronic operator, such as the transition dipole operator:

$$\mathbf{V}^d = \mathbf{C}^T \mathbf{V}^a \mathbf{C},\tag{4}$$

where **C** is now the matrix of the eigenvectors of the dipole operator and V^d and V^a are, respectively, the adiabatic and diabatic potential energy matrices [10]. It should be emphasized that this transformation is not unique. The resultant *diabaticdipole* potential energies are smooth as a function of *R* and the offdiagonal energies are also smooth. Figure 1 displays the diabatic potential energy curves and the coupling matrix element. The initial vibrational wave function is also shown.

Interestingly, the same argument that leads to the definition of the adiabatic transformation in Eqs. (1) and (3) also prevails here. In other words, the error in truncating the adiabatic basis set leads to the same error in the new diabatic-dipole transformation when the number of adiabatic dipole moments is restricted to a finite set [11].

The coupled diabatic set of equations now reads

$$\left[\mathbf{I}\nabla_{R}^{2}+2\mu\left(\mathbf{I}E-\mathbf{V}^{d}(R)\right)\right]\mathbf{F}^{d}(R)=0,$$
(5)

where $\mathbf{F}^{d}(R)$ are the nuclear wave functions subject to the boundary conditions at the origin and at infinity. In what follows, regular boundary conditions at origin are enforced.



FIGURE 1. LIF ${}^{1}\Sigma^{+}$ diabatic potentila energy curves and the coupling between them. The initial vibrational wave function is also shown; from Ref. [22].

MQDT TREATMENT

MQDT has been a widely successful theory of atomic and molecular processes [7, 8]. MQDT differs from the usual scattering formalism in how the energy is partitioned. Whereas the space partitioning allows for a proper treatment of the full interaction in a close-coupling formalism for $R < R_m$, followed by matching to *uncoupled* solutions for $R \ge R_m$, the energy partitioning in MQDT is accomplished so as to reveal the interaction energy at short ranges. In alkali-halides this energy scale is determined by the diabatic coupling. It is therefore required to relax the physical boundary conditions on $\mathbf{F}^{d}(R)$. To be precise, at energies in the predissociation gap in LiF, the covalent channel is open at large *R*, but the ionic channel is energetically inaccessible, i.e., the ionic wave function decays exponentially as $F_2^d(R) \sim e^{-\kappa R}$, where κ is the wave vector in the closed ionic channel, $\kappa = \sqrt{2\mu(V_{22}(\infty) - E)}$. This is, of course, the condition necessary for obtaining discrete levels in the gap. By not immediately enforcing this boundary condition in the physically closed channels, while treating them as if they were open (weakly closed) channels, MQDT provides a prescription for studying short-range strong interactions without contamination from long-range effects.

The short-range MQDT reaction and scattering matrices are smooth functions of energy and do not exhibit resonant behavior. The solutions in the interaction region are superimposed and matched to a linear combination of asymptotic functions in the outer region,

$$\sum_{i} \phi_{i}(\mathbf{r}; R) F_{ij}(R) = \sum_{i} \phi_{i}(\mathbf{r}; R) [f_{i}(R)\delta_{ij} - K_{ij}^{s}g_{i}(R)],$$

for $R \ge R_{m}$, (6)

at each energy E [12]. The N (j = 1, 2, ..., N, where N is the number of coupled channels) independent solutions, $\mathbf{F}_i(R)$ are propagated from the origin at $R \sim 0$, subject to regular boundary conditions, to the matching radius $R = R_m$, with the aid of the renormalized Numerov method [13]. The above equation looks deceptively similar to any scattering equation, but note that the reaction matrix K_{ii}^s , is only the short-range reaction matrix. The size of K_{ii}^s is the number of open and weakly closed channels, and hence does not correspond to the number of physical channels. Here, K_{ii}^{s} is a 2 × 2 matrix, even though there is only one physically open channel, and $f_i(R)$ and $g_i(R)$ in each channel *i* are calculated relative to the long-range form of the adiabatic (or diabatic) potentials. The base pair (f_1, g_1) are the Riccati–Bessel functions of order *j* at energy $\epsilon_1 = E - V_{11}(\infty)$ and (f_2, g_2) are the Coulomb functions at energy $\epsilon_2 = E - V_{22}(\infty)$. Both base pairs are normalized with respect to energy and the regular and irregular Coulomb functions, f_2 and g_2 , contain exponential divergence.

The short-range reaction matrix is given by its eigenvalues and eigenvectors, $K_{ij}^{s} = \sum_{\alpha} U_{i\alpha}^{T} \tan \pi \mu_{\alpha} U_{j\alpha}$. The physical phase shift in the covalent channel is determined as:

$$\tan \delta = K_{11}^s - K_{12}^s \frac{1}{\tan \pi \nu + K_{22}^s} K_{21}^s, \tag{7}$$

where $v = (-2\epsilon_2/\mu)^{-1/2}$. The procedure by which δ is obtained is known as the "closed-channel elimination" in MQDT and amounts to the application of physical boundary conditions. The phase shift(s) are common to all α eigenchannels, and eigenquantum defects, μ_{α} . The eigenquantum defects (μ_1 , μ_2) vary smoothly with energy, whereas δ varies considerably and widely with energy, as resonances appear in the closed channel. The smooth short-range scattering probability, S_{12}^s , which can be obtained from **K**^{*s*}, can be written down for the 2 × 2 case as:

$$\left|S_{12}^{s}\right|^{2} = \sin^{2} 2\theta \sin^{2} \pi (\mu_{1} - \mu_{2}), \qquad (8)$$

where θ is the angle that defines the mixing between the eigenchannels and the fragmentation channels and is defined as $\theta = \cos^{-1} U_{11}$. When $\theta = 0$ or $\pi/2$, the transition probability vanishes and when $\theta = \pi/4$, strong coupling of the ionic and covalent channels results.



FIGURE 2. (a) The short-range scattering probability; the solid line is the MQDT calculation, and the symbols are the semiclassical results; (b) the eigenquantum defects. (The discontinuities simply reflect quadrant changes in the eigenvalues of K^{s} .); from Ref. [14]

The short-range transition probability $|S_{12}^s|^2$ is shown in Figure 2(a) with the eigenquantum defects in Figure 2(b). Notice the regular modulations in $|S_{12}^s|^2$. The dots and the dashed line are from a semiclassical calculation in which the probability for transition between two levels is given as the Landau–Zener probability:

$$P_{12} = 4p(1-p)\sin^2 \Delta\phi,$$
 (9)

where $\Delta \phi$ is the difference in the accumulated phases along adiabatic and diabatic paths and where $p = e^{-2\pi \gamma_{LZ}}$ is the single-pass Landau–Zener diabatic transition probability at the crossing, $R_c =$ 13.3 a.u., and $\gamma_{LZ} = |V_c|^2/|\Delta F|v_c$ [15]. All the parameters are defined at the crossing radius, with $V_c = V_{12}^d(R_c)$, $v_c = \sqrt{2(E - V_{avg})/\mu}$ the radial velocity at the crossing, and ΔF is the difference in slopes of the potential curves. The relative velocity is defined with respect to an average value of the potentials at the crossing. An immediate observation, based on a comparison of the semiclassical and MQDT results, is that the modulation of the proba-

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bility is caused by a coherent phase interference of nuclear wave functions. It can be expected that at or near $\theta = 0$ or $\pi/2$, where there is destructive interference, the interaction between the channels disappears and the predissociating resonances that form at these energies become stable against bond breaking. Those resonances that form at energies where $|S_{12}^{s}|^{2}$ reaches its maximum, i.e., constructive interference, are expected to be highly unstable.

In order to obtain the photoabsorption cross section, the dipole matrix elements must first be calculated. A set of eigensolutions $F_{i\alpha}(R)$ is constructed as:

$$F_{i\alpha}(R) = \sum_{j} F_{ij}(R) U_{j\alpha}.$$
 (10)

Recall that the eigenchannel solutions $F_{i\alpha}(R)$ share the same phase shifts in all α channels. We can now define the dipole matrix elements $D_{j\alpha} = \langle F_{j\alpha} | D_{jj}^d | F_{00} \rangle$ for each eigenchannel. These dipole matrix elements are smoothly varying with energy. Since the initial vibrational wave function $F_{00}(R)$ is calculated in the uncoupled representation, i.e., in the ionic channel, the only allowed dipole excitations are within the ionic channel—in the diabatic representation, the dipole moment matrix is diagonal. Hence, the only dipole moment that contributes to the photoexcitation of the initial state is $D_{22}^d(R)$. If, however, the initial wave function is obtained in a coupledchannel representation, electric dipole coupling to both ionic and covalent channels are allowed.

Finally, the cross section can be defined as:

$$\sigma_{\rm tot}(\omega) = \frac{4\pi^2}{3(137)} \omega |D_{2\alpha} A_{\alpha}|^2, \qquad (11)$$

where the coefficients A_{α} are obtained such that

$$\sum_{\alpha} U_{i\alpha} \begin{pmatrix} \cos \pi \, \mu_{\alpha} \\ \sin \pi \, \mu_{\alpha} \end{pmatrix} A_{\alpha} = \begin{pmatrix} \cos \delta \\ \sin \delta \end{pmatrix} \qquad \begin{array}{c} i \text{ open} \\ i \text{ closed} \\ \end{array}$$
(12)

Figure 3(a) gives the calculated photodissociation cross section of LiF in the energy region in the predissociation gap. Three prominent features are evident: the broad envelope peaking around $57,000 \text{ cm}^{-1}$, a single series of Rydberg resonances, and a systematic variation of widths and profiles of the resonances that result in a periodic modulation of the intensity. Figure 3(b) shows an expanded photoabsorption window revealing the complexity of the lineshapes. The configuration interaction formulation of Fano [16] describes the behavior of cross section as:

$$\sigma(\epsilon) \propto \frac{(q+\epsilon)^2}{1+\epsilon^2},$$
 (13)

where ϵ is a scaled dimensionless energy parameter that vanishes at the center of the resonance and the parameter *q* defines the profile of a resonance. A large *q* means a symmetric Lorentzian profile, while a *q* = 0 resonance appears as a symmetric dip. The sign of *q* also determines the asymmetry of the resonant profile. A positive (negative) value of *q* means that the intensity of the line rises (falls) as the energy is swept away from $\epsilon = 0$.

It is evident from Figure 3 that both the magnitude and the sign of q change as a function of energy. Furthermore, the sign of q varies periodically throughout the spectrum—q changes sign twice per cycle. It is well known that two-channel atomic spectra in which a bound series interacts with a single continuum are characterized by Eq. (13) with a single slowly varying q parameter that retains the same sign. Although reversal in the sign of qare common in atomic physics, where they indicate



FIGURE 3. Photopredissociation spectrum from the ground rovibrational level of LiF; (b) shows an expanded view of a typical energy region demonstrating the q reversal of the lineshapes; from Ref. [14].

the presence of interloping states within a Rydberg series [8, 17-19], no such perturbers are present in LiF. It is therefore concluded that alkali–halides photoabsorption is a novel process in which the reversal of *q* occurs periodically as a consequence of interference between alternating pathways to bond breaking.

The extremely long-lived predissociating resonances in Figure 3 appear at energies very near the zeros of $|S_{12}^s|^2$ in Figure 2—the zeros of $|S_{12}^s|^2$ do not occur precisely on resonance; such an accidental degeneracy would result in a true bound state in the continuum with infinite value of the Fano parameter (and corresponding infinite cross section). The symmetric window resonances in Figure 3(b) appear at energies very near the peaks of $|S_{12}^s|^2$ and signal a rapid dissociation process.

The lifetimes (widths) of the resonances is obtained from the largest eigenvalue of the delay-time matrix, $\mathbf{Q} = -i\mathbf{S}^{s\dagger}(d\mathbf{S}^s/dE)$ [20]; for a single open channel, $Q_{\text{max}} = 2(d\delta/dE)$ or $\Gamma = 4/Q_{\text{max}}$. It was found that the longest-lived resonances have lifetimes of the order of hundreds of picoseconds [21].

That these extremely stable resonances appear near the zeros of the transition probability suggests that the ionic and covalent channels become effectively *decoupled* at these energies. Such *dynamic switching* of the interaction between electronic channels with laser frequency is significant as it allows a degree of control over the rate of reaction—in this case the dissociation yield. This is a remarkable manifestation of coherent interference effect in molecules.

TEMPORAL ANALYSIS

To better understand the underlying time scales that conspire to produce such rich and complex interferometric features in alkali-halide spectra, a long-time nuclear wavepacket propagation was carried out [22, 26]. The recurring tendency for the vibrational motion to be stable at well-defined energies in the predissociation gap suggests that the vibrational wavepackets must coherently act to set up interfering waves in the interaction region between the inner turning point and the crossing point. Pioneering work by Zewail and co-workers [1, 2] on sodium iodide with femtosecond laser pulses significantly advanced the understanding of molecular phenomena on vibrational time scale. By arresting and imaging the vibrational motion, they detected NaI molecules in transition states and at moments right after bond breaking. Later, time delay pulse measurements observed wavepacket recurrences (phasing and dephasing) that persisted for tens of vibrational periods. Such long-time survival of vibrational wavepackets is perhaps an indirect signature of the interferometric resonances in alkali–halides.

The two-channel Schrödinger equation $i \partial \Psi / \partial t = \mathbf{H}\Psi$, where the Hamiltonian is comprised of the kinetic energy and the diabatic potential energy operators, is solved using the split-operator method [22, 23], which employs a symmetric splitting of the kinetic and potential energy operators:

$$\Psi(t + \Delta t) = e^{-i\Delta t \mathbf{V}/2} e^{-i\Delta t \mathbf{T}/2} e^{-i\Delta t \mathbf{V}/2} \Psi(t) + O(\Delta t^3).$$
(14)

The residual error results from the temporal noncommutivity of the kinetic and potential energy operators. At each step in time, the kinetic energy operator acts in the momentum space, where it is diagonal, and the potential energy operator acts in the coordinate space. Different schemes for the calculation of the exponential of the potential energy matrix are employed [22, 26], but the one used here involves Pauli spinors [24]. The photoabsorption cross section is obtained from the time-dependent wave function using the Heller [25] formulation:

$$\sigma(\omega) \propto \omega \int_{-T}^{T} dt \, w(t) C(t) e^{iEt}, \qquad (15)$$

where the energy $E = E_{v''j'} + \omega$, with $E_{v'j'}$ the rovibrational energy of the initial state. The window function w(t) is included in the Fourier transform because the autocorrelation function, $C(t) = \langle \Psi(R, t = 0) | \Psi(R, t) \rangle$, is calculated only in a finite time interval [0:*T*]. The use of the filter w(t) prevents sidebands from appearing in the Fourier transform. The initial wavepacket is defined as:

$$\Psi(t=0) = \begin{pmatrix} 0\\ F_{00}(R)D_{22}(R) \end{pmatrix}$$

Figure 4 shows the absorption spectrum at different times by truncating the upper limit in the integral in Eq. (15) to the time indicated in each panel in Figure 4. The broad frequency scale appears in a short time (10–20 fs), but it is shown here after 500 fs for time sampling reasons. The interferometric modulation of the spectrum appears after about 1 ps, which is roughly the orbital period for nuclear motion in the ionic channel. The third time scale, i.e., the Rydberg time scale, appears after about 3–5 ps, when the wavepacket has evolved long enough for the Rydberg spacing to emerge.

The spatial spread of the wavepacket is shown in Figure 5 in both the ionic and covalent poten-



FIGURE 4. Appearance of three distinct frequency scales in LiF. The upper time limits of the Fourier transform are shown in each panel; from Ref. [22].

tials. Because the potentials are anharmonic, one would expect the wavepacket to disperse and build up amplitude in the coupled potentials with time. The snapshots of the probability density in each diabatic channel, $|\psi_i(t, R)|^2$, at different time intervals is shown. Due to the coupling between the potential curves at short distances, the initial wavepacket in the ionic channel instantaneously obtains a component in the covalent channel.

After 48 fs, the covalent pulse is about five times as large as the ionic pulse; see Figure 5(a). The two wavepackets reach the crossing point at the same time at 91 fs, but their subsequent time evolution is distinctly different. At about 357 fs, the covalent pulse has escaped to dissociation, whereas the ionic pulse has just reflected from the outer turning point. At about 689 fs, the first indication of an interfering wave in the ionic channel due to dispersion is evident. The more deeply bound components in the wavepacket reflect sooner from the attractive Coulomb potential and, on being reflected again from the inner turning point, interfere with more slowly moving components of the wavepacket that are also weakly bound and are now returning from the outer turning point. Of course, because the ionic and covalent curves are coupled to each other, interfering waves also form in the covalent channel, but outside the crossing radius, there is only outgoing traveling waves. The interfering wave formation in the ionic channel begins to become prominent at times longer than 1500 fs; see Figure 5(d) when complete constructive or destructive interference takes hold. The interfering waves form within a radius of about 20 a.u. The ripple oscillations in the co-



FIGURE 5. Snapshots of the wavepacket on the ionic and covalent potentials at different times, revealing the interfering wave formation; from Ref. [22].

valent channel outside the crossing radius appear because the higher frequency components of the wavepacket that are more deeply bound (shorter classical orbital periods) emerge faster from the reaction zone; the low-frequency outgoing waves are amplitude-modulated with higher frequency waves in Figure 5(d).

Summary

Photodissociation of alkali-haldies demonstrates lineshape modulations that result from a novel class of interferometry between nuclear wave functions. Coherent interference of alternative pathways to bond breaking form extremely long-lived predissociating resonances that recur with specific period in the spectrum. These resonances are calculated with the aid of MQDT and analyzed in detail in the spirit of channel interaction. By tuning the laser frequency to these interferometric resonances, the interaction between the channels is effectively turned off. Such dynamic switching of the interaction provides a level of control over the dissociation yield. The extremely long time nature of these resonances are revealed as interfering waves, confined to the interaction zone, in a temporal evolution of wavepackets on the coupled potential curves.

ALKALI-HALIDE PHOTODISSOCIATION

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