

Interferometric Line Shape Modulation in Alkali-Halide Photoabsorption

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An *ab initio* calculation of the photoabsorption spectrum of ground state LiF below the ionic $\text{Li}^+ + \text{F}^-$ threshold predicts a periodic modulation of the predissociation line shapes. Specifically, we predict a periodic reversal of Fano's line shape asymmetry parameter q . In this case, reversal of the q parameter occurs because of the interference of vibrational wave functions propagating alternatively along diabatic and adiabatic potentials. The interference modulates the predissociation spectrum giving rise to both extremely long-lived resonances and broad window resonances. These anomalous resonances occur periodically on an energy scale greater than the Rydberg energy spacing and are finite in number. [S0031-9007(99)08649-4]

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A simple and intuitive picture of vibrational predissociation in molecular systems emerges when a repulsive Born-Oppenheimer electronic potential energy curve crosses a second electronic energy curve that supports bound vibrational levels. A curve crossing of this type occurs for the lowest $^1\Sigma^+$ states of the alkali-halides, as depicted in Fig. 1 for the specific case of lithium fluoride (LiF) [1,2]. The ground electronic state of LiF has an ionic configuration, resulting in a potential curve that tends (diabatically) to Li^+ and F^- at infinite separations. The covalent configuration, on the other hand, is insufficient to bind the molecule, and yields a relatively flat potential curve that tends to the energy of the neutral ground state atoms at infinite separation. The gap (of roughly 2 eV) between the ionic and covalent energy thresholds results from the energy difference between the ionization potential of Li and the electron affinity of F.

The long-range, attractive Coulomb potential in the ionic channel results in a single Rydberg series of vibrationally bound levels that follows the usual Rydberg progression with energies proportional to $(n^*)^{-2}$, where n^* is the effective principal quantum number [3]. Those members of the series ($247 < n^* < \infty$) which lie above the $\text{Li} + \text{F}$ threshold predissociate through coupling to the covalent channel. This situation is similar to the autoionizing *electronic* Rydberg series common in atomic spectra. Here, however, the large reduced mass (9265 a.u.) associated with vibrational motion results in striking departures of the photoabsorption spectrum from more familiar two-channel atomic autoionization spectra.

In this Letter we (a) report on a quantum mechanical calculation of predissociation in LiF, (b) demonstrate that this two-channel system possesses a rich spectroscopy reminiscent of interloper effects in atomic autoionization spectra, and (c) show that the complex spectrum results from an interference between alternative pathways to dissociation. Interferences in the production of neutral atomic fragments as a function of photon energy result

from phase differences accumulated along various dissociation pathways. This interferometric periodicity gives rise, for energies corresponding to destructive interference, to very long-lived vibrationally hot and rotationally cold molecules [4].

Our calculated photoabsorption spectrum of the ground rovibrational level of LiF is plotted in Fig. 2(a) in an energy range between the covalent and ionic thresholds. To obtain this cross section, we have developed a multi-channel algorithm which treats separately the long-range and short-range physics. It relies on propagating solutions of the coupled-channel Schrödinger equation through the short and intermediate internuclear regions [5] where most of the complicated interactions occur. For large internuclear distances, where the potentials take on simple forms, highly accurate, analytic multichannel quantum-defect theory (MQDT) [6–8] wave functions that describe either ionic or covalent dissociation are employed. The spectrum in Fig. 2(a) is obtained upon calculating

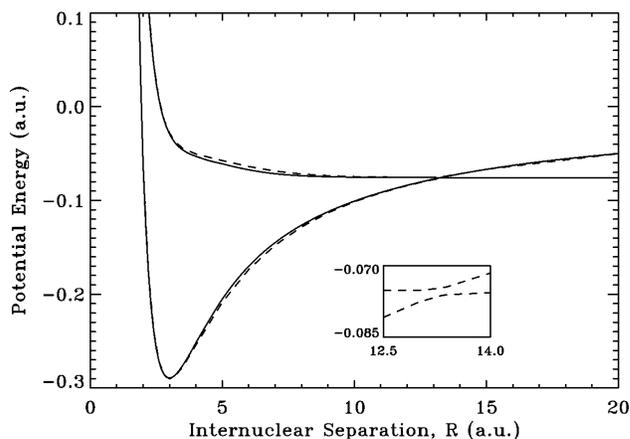


FIG. 1. $\text{LiF } ^1\Sigma^+$ molecular potential energy curves: solid line, diabatic representation; dashed line, adiabatic representation. The inset shows an enlargement of the adiabatic avoided crossing region.

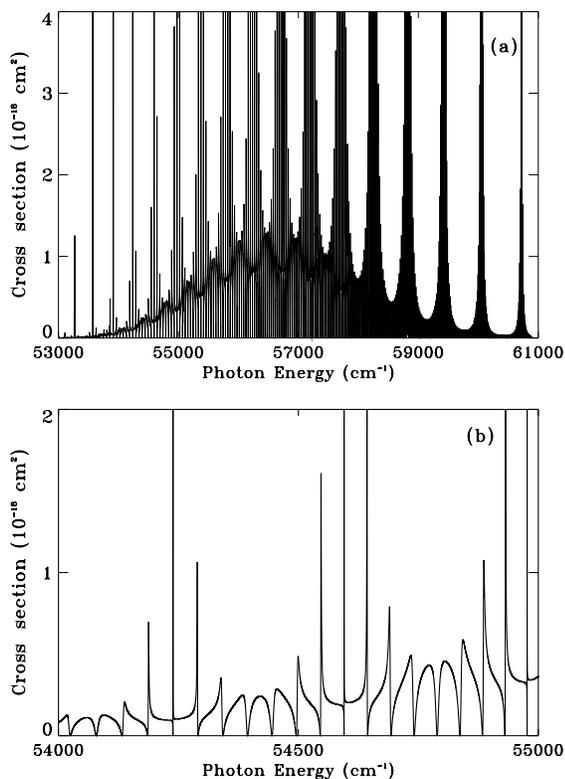


FIG. 2. Photopredissociation spectrum from the ground rovibrational level of LiF; (a) shows the envelope of the spectrum, while (b) shows an expanded view of a typical energy region demonstrating the q reversal of the line shapes.

dipole transition matrix elements between the initial ground state wave function in the diabatic ionic potential curve and the final dipole-allowed, coupled-channel wave function. The electronic part of the transition dipole matrix element is taken from Ref. [1]. We will describe an outline of the theory below; details will be presented elsewhere [9].

Three features of the spectrum are apparent. On average, the spectrum gently rises and falls over the energy range shown, a feature that can be attributed to the overlap of initial and final vibrational wave functions. Second, this broad background is comprised of a single series of resonances [10] whose energies approximately follow the expected $(n^*)^{-2}$ Rydberg progression. Third, the shapes and widths of the individual resonance profiles vary systematically, resulting in a periodic modulation of the average intensity. The line shape variations are more apparent in the narrower energy range of Fig. 2(b).

The profiles of the individual resonances are expected, within the configuration interaction picture [11], to have the Fano line shape,

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

where ϵ is a scaled dimensionless energy parameter that vanishes at the center of the resonance. A large q reso-

nance has a Lorentzian profile, while a $q = 0$ “window” resonance appears as a symmetric dip. A positive (negative) value of q indicates that the intensity of the line rises (falls) as the energy is increased from $\epsilon = 0$. The parametrization of resonance profiles with a single q parameter is also well known in solid-state physics [12], in scattering from semiconductor surfaces, and for the interpretation of giant resonances in nuclei [13].

Typically, two-channel atomic spectra, in which a bound series interacts with a single continuum, are characterized by a series of resonances with slowly varying q values. In contrast, the sign of q in Fig. 2 varies periodically through the spectrum. Close examination of the figures shows that q changes sign twice per cycle; one sign change occurs at each of the extremely narrow lines, and these are interspersed with zeros of q that occur at symmetric dips (window resonances).

The periodicity of the spectrum is also apparent when the delay time, shown in Fig. 3, is plotted in the same energy range as in Fig. 2(b). (The delay time is proportional to the derivative of the phase shift in the covalent channel with respect to energy [14].) The peak of each Lorentzian profile gives twice the predissociative lifetime of the resonance. Although not shown, the narrowest resonances, appearing as vertical lines, have lifetimes of hundreds of picoseconds.

Reversals in the sign of q are common in atomic spectra, where they indicate the presence of interloping (or perturbing) states within a Rydberg series [15–17]. Examples of interloper interactions in atomic spectra are found in the comprehensive review by Aymar *et al.* [18]. Giusti-Suzor and Lefebvre-Brion [17] examined the coupling of two discrete series of levels with a continuum and showed that the q parameter contains both a pole and a zero as a function of energy [19]. At the pole, the width of the resonance vanishes and a bound state is created in

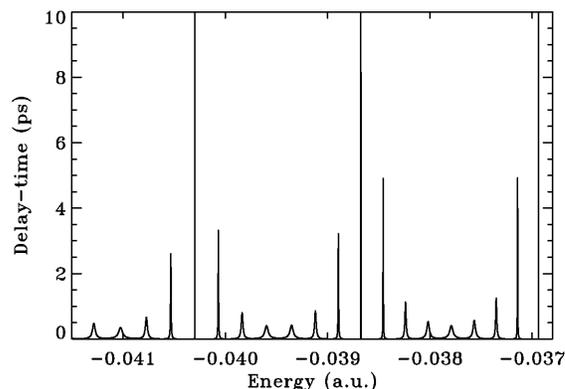


FIG. 3. Delay time of the predissociating states in picoseconds over the same energy region as Fig. 2(b). The energy in atomic units is measured relative to the ion-pair formation threshold. The ionic dissociation energy is 0.28743 a.u. The sharp resonances are truncated in the figure, but have lifetimes of the order of tenths of nanoseconds.

the continuum. At the zero, the resonance appears as a dip or window in the spectrum.

Alkali-halide photoabsorption is a novel process in which q reversal occurs *periodically* and *in the absence of perturbing levels* as a consequence of interference between alternative pathways to dissociation. The emergence of the periodicity is here traced to coupling between the ionic and covalent channels at distances less than the crossing of the diabatic curves shown in Fig. 1. To this end, a short-range scattering matrix S^s , unique to MQDT, is determined without imposing long-range boundary conditions on the solutions. As shown below, S^s is smooth on the energy scale of the Rydberg spacing but has the same periodicity as the line shape asymmetry parameter q .

Linear superpositions of analytical solutions of Schrödinger's equation, $f_j(R)$ and $g_j(R)$, in the covalent ($j = 1$) and ionic ($j = 2$) channels are matched to the multichannel solutions Ψ_i , to determine a short-range reaction matrix K^s defined by

$$\Psi_i = \sum_j \Phi_j [f_j(R)\delta_{ij} - K_{ij}^s g_j(R)], \quad R > R_0, \quad (2)$$

where Φ_j is the electronic wave function in channel j . The matching is done at an internuclear separation R_0 that lies between the crossing of the potential curves at $R = 13.3$ a.u. and the outer turning point in the ionic channel over the energy range of interest. Here, K^s is represented by its eigenvalues $\tan \pi \mu_\alpha$ and eigenvectors U . For a two-channel system, U is parametrized by a mixing angle θ ,

$$U = \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix}. \quad (3)$$

The short-range matrix K^s is related to the phase shift δ in the covalent channel by

$$\tan \delta = K_{11}^s - K_{12}^s \frac{1}{\tan \pi \nu + K_{22}^s} K_{21}^s, \quad (4)$$

where ν is related to the binding energy E and the reduced mass M by the Rydberg formula $E = -M/2(\nu)^2$.

The eigenquantum defects (μ_1, μ_2) and the mixing angle θ vary smoothly with energy on the scale of the Rydberg spacing $M/(n^*)^3$, unlike the physical phase shift δ . These smooth parameters can be used to define a short-range scattering matrix,

$$S^s = [I + iK^s][I - iK^s]^{-1}, \quad (5)$$

where I is the identity matrix, so that the short-range scattering probability between covalent and ionic channels is

$$|S_{12}^s|^2 = \sin^2 2\theta \sin^2 \pi(\mu_1 - \mu_2). \quad (6)$$

The short-range scattering probability of Eq. (6) is shown as the solid line in Fig. 4(a), while the two eigenquantum defects are shown in Fig. 4(b). These short

range parameters show regular modulations with the same periodicity as the spectrum discussed above. Note, in particular, that the very narrow resonances occur in the vicinity of the zeros of $|S_{12}^s|^2$. At energies for which the mixing angle tends to 0 or $\pi/2$ the channels become effectively decoupled, and Rydberg states in the ionic potential are stabilized against predissociation. The zeros of $|S_{12}^s|^2$ do not occur precisely on resonance; such an accidental degeneracy would result in a true bound state of zero width and infinite cross section (and correspondingly infinite q). We note that the two terms in Eq. (6) oscillate nearly in phase, but it is the first term that actually passes through zero on each cycle.

A simple interpretation of $|S_{12}^s|^2$ emerges from a semiclassical analysis of propagation in the two potentials of Fig. 1, based on a Landau-Zener analysis [20] of the curve crossing. Standard texts [21] show that the probability of a transition between the two adiabatic states, evaluated inside the turning point of the ionic channel, is given by

$$P_{12} = 4p(1 - p) \sin^2 \Delta\phi, \quad (7)$$

where $\Delta\phi$ is related to the difference in phases accumulated along adiabatic and diabatic paths and where p is the single-pass Landau-Zener diabatic transition probability at the crossing. P_{12} is the semiclassical equivalent of $|S_{12}^s|^2$ as is demonstrated in Fig. 4(a), where the semiclassical result is represented by open diamonds. The envelope of

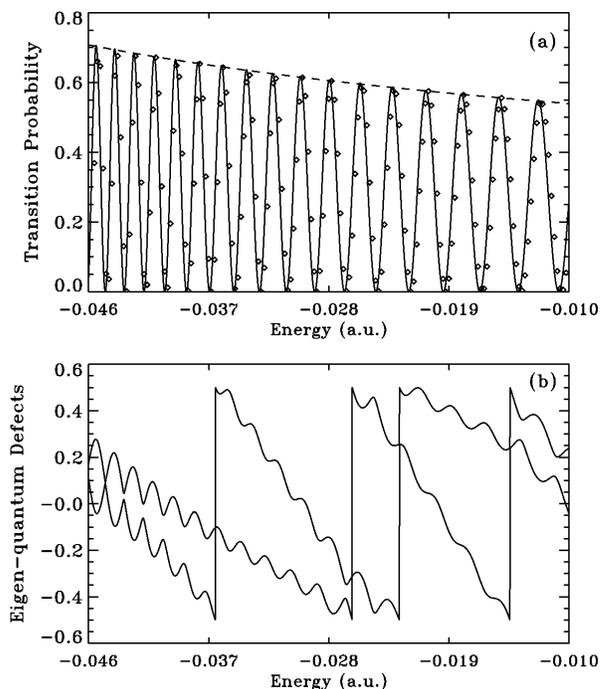


FIG. 4. (a) The short-range scattering probability; the solid line is the MQDT calculation, and the open diamonds are the semiclassical form. The dashed line is twice the average Landau-Zener probability. (b) The eigenquantum defects (the discontinuities simply reflect quadrant changes in the eigenvalues of K^s).

$|S_{12}^s|^2$ (dashed curve) is seen to agree precisely with twice the average Landau-Zener probability, $4p(1-p)$, since it represents complete constructive interference of the two pathways. A semiclassical interpretation of predissociation was first advanced by Child [4,22], who employed a mixed adiabatic and diabatic representation to first predict the occurrence of long-lived predissociating states.

The fact that the sharp resonances in Fig. 2 have predissociative lifetimes that compete with radiative lifetimes provides an opportunity for observing them in femtosecond laser spectroscopy. There is some evidence of these extremely long-lived states in the femtosecond probe of NaI [23], where recurrences on the order of 10 ps were observed. To observe the modulation directly in the absorption spectrum, the molecules need to be rotationally cooled.

We mention briefly that an electronic state of $^1\Sigma^+$ symmetry which correlates to the ground state of the F atom and the first excited state of the Li atom is expected to cross the ionic potential energy curve at about 200 a.u. [2]. This potential curve is repulsive and lies nearly 2 eV above the crossing in Fig. 1. This alternative electronic state, which lies outside the region of the spectrum shown in Fig. 2, will influence the Rydberg states lying close to the ion-pair formation threshold. The dipole coupling to this closed channel is weak, and so it plays little role in the dynamics described in this Letter.

In summary, an *ab initio* quantal calculation of the photoabsorption of ground state LiF displays a rich spectroscopy reminiscent of atomic autoionization spectra, perturbed by interlopers. The Fano q parameter is shown to reverse sign periodically, due to an interference between two alternative paths to dissociation. The interference results in novel vibrationally hot, rotationally cold molecules with long lifetimes.

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