Prompt solvent-induced electronic predissociation of femtosecond pumped iodine. A computational study

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Received 8 August 1995

Abstract

Solvent-induced electronic predissociation (X → B → a1g(2Π) state) of molecular iodine is discussed using a classical ensemble representation of Heisenberg's equations of motion. Excitation of the intermediate B state by an ultrafast pulse creates a coherent vibrational motion in this bound state. The localized solvent-induced coupling to the a state results in the spawning of dissociation products which occur in bursts, twice per vibrational period. Equations of motion for both the electronic and nuclear degrees of freedom in each electronic state are derived from a quantum mechanical Hamiltonian. These equations are coupled whenever two electronic states are interacting. The formalism includes coupling to the surrounding classical solvent. Comparison with a pump-probe experiment is provided.

1. Introduction

Molecular iodine has been the subject of many ultrafast pump–probe experiments both in the gas phase [1] and in solution [2]. In a typical gas phase experiment a fs laser pulse is used to electronically excite the ground state iodine molecule to the bound region of the electronically excited B state, Fig. 1. The localized nature of the Franck–Condon limited initial state that can be accessed by the ultrashort excitation results in an experimentally observed vibrational coherence on the excited B state [3]. Gas phase experiments observed this excited state coherent nuclear motion (whose time period reflects an oscillation between the two classical turning points) which persists for a few picoseconds and decays due to the intrinsic anharmonicity of the excited state potential. (On a longer timescale the wavepacket rephases [4].)

Unlike the well-understood gas phase dynamics, the situation in condensed phases is much richer, for a number of reasons. The most important one is the possibility of a solvent-induced predissociation of the bound B state into the dissociative a1g(2Π) and possibly also into the a0g*(2Σ−) state [5]. Furthermore, the dynamics on the B state also manifest the interaction with the liquid, causing a loss of coherence through vibrational dephasing and energy transfer. These processes can be particularly important in the B state because [6] of the long range of the potential, Fig. 1. Another feature is that in solution the atoms moving out on the repulsive potential can be slowed down or even turned around by the solvent. For molecular iodine both in organic solvents
the B state is contracting, the atoms are launched on the repulsive a state with their momentum favoring their approach. The atoms will first move towards the inner turning point of the a state, turn around and move out. The dissociation dynamics are further discussed in Section 3 below.

The delayed dissociation has been observed experimentally and the outgoing population has been shown to be localized both in space and in time [2], for the first couple of exits. It was concluded that (for the 580 nm excitation) the crossing point is close to the middle of the B state but even so only one distinct exit per period is observed. The simulations reproduce this behavior. On a somewhat longer timescale (=2 ps) predissociation should be followed by caging and possibly geminate recombination. The liquid phase experiments on iodine have not yet probed a far enough distances and/or times to directly monitor these effects.

The above description implies that any realistic attempt to theoretically model the short timescale dynamics of the excited B state must include at least three (and possibly also four) surfaces: the ground X state, the excited B state and the dissociative a1g (3Π) state. As the problem at hand involves also the solvent degrees of freedom, a fully quantum mechanical calculation is not realistic.

In this Letter we discuss and apply a new computationally tractable formalism for computing both interstate and intrastate dynamics. The proposed method involves the solution of the correlated equations of motion for both the electronic and the nuclear parts. Unlike previously suggested methods [8] we obtain separate (yet coupled) equations of motion for the nuclear dynamics (position and momentum) for each electronic state. When the electronic states are interacting, the equations for the motion of the nuclei are coupled so that the dynamics on one state are influenced by the motion on the others. This formulation of the nuclear dynamics enables us to distinguish between the position (and momentum) on different states. We consider this distinction to be vital as it enables us to monitor the step-like decrease in the excited B state population which results in a spike-like appearance of population on the dissociative a state.

In Section 2 we outline the theory. A detailed derivation for the case of a two electronic state
Hamiltonian has been accepted for publication [6]. In discussing the results we center attention on the depletion of the excited B state population as a function of solvent density, and on the temporal and spatial profiles of the dissociation products. A more detailed report that discusses other aspects, such as the effect of solvent polarizability, is in preparation.

2. Theory

The essence of the derivation is as follows. Using an \( N \) (electronic) state quantum mechanical Hamiltonian, Heisenberg’s equations of motion are derived for the various electronic and nuclear operators. By taking the expectation value of these operators over the total (electronic and nuclear) wavefunction, one obtains equations of motion for electronic and nuclear observables. Hence, the final result is a set of coupled electronic and nuclear equations for each of the electronic states. This implies that in mathematical terms we are working in a direct product space where each electronic state has its own variables for nuclear motion. The resulting electronic equations are coupled to the nuclear motion via Franck–Condon overlap integrals between each of the two coupled states that result from the localized nature of the coupling between each of the two surfaces.

The three electronic surface problem is modeled using an \( N \) electronic state Hamiltonian,

\[
\hat{H} = |1\rangle \hat{E}_1(t) |1\rangle + |2\rangle \hat{E}_2(t) |2\rangle + \sum_{i=1}^{N} |i\rangle \hat{E}_i(t) |i\rangle + |1\rangle \hat{\mu}_{12}(t) |2\rangle + |2\rangle \hat{\mu}_{21}(t) |1\rangle + \sum_{i=3}^{N} \left[ |i\rangle \hat{\mu}_{i2}(t) |2\rangle + |2\rangle \hat{\mu}_{2i}(t) |i\rangle \right].
\]  

In Eq. (1) \( \hat{H} \) is the molecular Hamiltonian including the coupling to the solvent (cf. Eq. (2) below) and throughout the Letter we use a carat to denote an operator. The numbers 1 and 2 refer to the ground state electronic surface and to the excited B state, respectively. The third state involved in the computation is the dissociative a state and the summation over the electronic index \( i \) is a summation on identical a ‘states’. This representation of the a state is motivated by the nature of the dynamics: each time the excited B state wavefunction approaches the crossing region some of it predissociates into the repulsive a state. We consider each of these predissociation events to open a new a ‘state’, and hence the summation in the third term of Eq. (1) is over all the predissociation events. All these a ‘states’ are identical in the sense that they involve the same intramolecular potential energy function. This distinction which is analogous to previous pure classical forking algorithms [9] is essential as it allows us to compute classical like dynamics on each of these a state potentials (we note, however, that such a distinction between a ‘states’ is realistic only when the predissociation events are well separated in time). The energy operators on each electronic surface (X, B and all the a) are a sum of two potential and a single kinetic energy operators,

\[
\hat{E}_j(t) = \hat{V}_j(R) + \hat{U}_j(R, X) + (2m)^{-1} \hat{P}^2.
\]  

Here \( \hat{V}_j(R) \) is the intramolecular potential energy curve of the \( j \)th electronic surface, \( \hat{U}_j(R, X) \) is the intermolecular solvent–jth solute interaction potential that depends on the intramolecular separation, \( R \), and on the positions of all the liquid atoms (denoted by the vector \( X \)) and \( m \) is the reduced mass.

Eq. (1) does not include the Hamiltonian of the pure solvent. This Hamiltonian has the usual form employed in classical molecular dynamics simulations.

The coupling between the X and B surfaces (\( \hat{\mu}_{12} \) and/or \( \hat{\mu}_{21} \) in Eq. (1)) involves an ultrashort laser pulse which is modeled as the product of a cosinusoidal oscillation at the carrier frequency, a Gaussian envelope centered at \( t_0 \) and a vector dot product of the transition dipole with the electric field. The surrounding solvent atoms subsequently induce a transition from the B state to the a state (\( \hat{\mu}_{12} \) and/or \( \hat{\mu}_{21} \) in Eq. (1)) which is believed to be analogous to the gas-phase collision induced electronic predissociation [5,10]. The nature of the solvent-induced coupling between the B and a states has not been fully determined [5,11] but to leading order the off-diagonal matrix element (\( \hat{\mu}_{12} \) and/or \( \hat{\mu}_{21} \) integrated over the initial and final wavefunctions, \( \langle \mu_{12} \rangle = \langle \mu_{21} \rangle \)) coupling the B and a states has a \( 1/R^5 \) dependence on the iodine–quencher distance and is proportional.
to the quencher's polarizability \((\alpha_Q)\) and to the vibrational overlap integral \(F_{12}\),

\[
\langle \mu_{12} \rangle = -\alpha_{Q}^{12} F_{12} \alpha_Q / (\text{iodine–quencher distance})^6.
\]

(3)

Since the actual value of the proportionality constant is not known, we report here results for \(a_{\mu}^2 = 6 \text{ eV} \AA^3\). In the computational example the quenching is due to the surrounding Ar atoms and we sum over all the quencher–molecule distances.

The Heisenberg representation is used to compute the time evolution of the electronic \(\hat{\rho}(t) = |j\rangle\langle k|, j, k = 1, 2, \ldots, N\) and nuclear \(\hat{\Omega}_{ij} = |j\rangle\langle j|\hat{\Omega}_{ij}, j = 1, 2, \ldots, N\) operators. \(\hat{\Omega}\) can be either the position or momentum operator, and we note that the expectation value of the diagonal operator \(\hat{\rho}_{jj}\) is the electronic population in the \(j\)th electronic state whereas the off-diagonal elements measure the coherence.

The operator equations of motion are converted into equations of motion for expectation values by taking their expectation value over the wavefunction \(^1\). The latter is written as a linear combination of \(N\) product wavefunctions, each term being itself a product of an electronic times a nuclear part,

\[
\psi(t) = C_1(t) \phi_1(r) \chi_1(R) + C_2(t) \phi_2(r) \chi_2(R)
+ \sum_{i=3}^{N} C_i(t) \phi_i(r) \chi_i(R).
\]

(4)

In Eq. (4) \(\phi_j(r)\) is the \(j\)th orthonormal electronic wavefunction, and the summation over \(i\) is over the sequence of a states, each term representing a different \(B\) to a transition at a different time. \(\chi_j(R)\) is the time dependent nuclear wavefunction in the \(j\)th electronic state. The use of a time dependent nuclear wavefunction is dictated by the localized nature of the coupling (both \(X-B\) and \(B-a\)) that results in a non stationary nuclear wavefunction.

The equations of motion for the elements of the density matrix \(\langle \hat{\rho}_{jk} \rangle = C_j^* C_k\) are similar to the Feynman–Vernon–Hellworth \([12]\) equations. The only difference is that all the expectation values that appear in these equations involve an additional integration over the nuclear coordinates. As a result, any coupling term in the equations involves an appropriate Franck–Condon overlap integral. It is this Franck–Condon overlap factor that correctly couples the nuclear and electronic motion whenever two surfaces are interacting. Once the interaction is turned off (the laser is turned off or the B state wavefunction is away from the crossing region to the a state) the electronic states evolve independently.

For the nuclear dynamics one obtains, for each surface, equations for average momentum and position times the population: \(n_j \langle R \rangle\) and \(n_j \langle P \rangle\), where \(n_j = |C_j(t)|^2\). Whenever two surfaces are interacting the nuclear equations are coupled so that the motion on one surface affects the other one. As for the electronic equations, the solution of the nuclear equations involves the computation of Franck–Condon overlap integrals. In addition one must compute the expectation value of the force on each surface and in the present computation a simple approximation was made: the averaged value of the derivative of the \(j\)th potential was replaced by the derivative computed at the average value of the position on the \(j\)th potential. Details on many points are available elsewhere \([6]\).

The iodine nuclear equations of motion include the interaction with the surrounding solvent, \(U_i(R, X)\) of Eq. (2), which may be different for each electronic state. This implies that the solvent equations of motion include in addition to the pure solvent–solvent interaction a solvent–solute interaction which is of a mean-field form: the solvent interacts with all the iodine's electronic states and the importance of the interaction with the \(j\)th electronic state is determined by its population, \(n_j\).

3. Methodology

Three electronic surfaces, see Fig. 1, are included in the computation and the iodine molecule is embedded in liquid Ar at different densities and temperatures. A Morse potential function is used for the iodine X and B interatomic potential energy func-
tions and a modified Morse potential function was used to fit the a state potential. The different potential energy parameters are summarized in Table 1. No attempt is being made to numerically fit any experimental results and for this reason the solvent–solute interaction potential is modeled, as is often done, using a pairwise Lennard-Jones (12–6) potential (LJ). The same LJ potential parameters were used for all three electronic surfaces, as given in Table 1. Different values were tested for the non-diagonal polarizability matrix element, $\alpha_{\rho}^{(2)}$, of Eq. (3). As the actual value is not known and can only be estimated (unless one performs high quality quantum mechanical computations) we report here results for $\alpha_{\rho}^{(2)} = 6$ eV Å$^2$.

Prior to the initiation of the actual dynamics, equilibrated configurations of a single ground state iodine molecule embedded in rare gas Ar atoms were computed using the actual procedures. For the actual dynamics, the following equations of motion were integrated: for the solvent atoms – the usual Hamilton equations of motion, including the mean field coupling to the molecule. For the iodine molecule we solve for the electronic and nuclear degrees of freedom for the X, B and any a state that is already populated. The number of a ‘states’ increases by one whenever the motion on the B state returns to the crossing region. In the integration of the electronic equations of motion an interaction picture representation [13] is used, and as in the experiment we limit the duration of propagation to a short period of about 2 ps. Thus, only a small number of a ‘states’ is involved in the computation.

Both for the B state and for all the a ‘states’ the initial conditions for the nuclear dynamics are sampled from the Franck–Condon region that can be accessed by classical mechanics. For the B state this implies a narrow region between the inner classical turning point on the B surface (the energy on the B state is sampled from a Gaussian distribution determined by the uncertainty in energy which is induced by the limited duration of the pulse) and the outer turning point on the ground electronic surface. The initial energy for each a ‘state’ is determined by the instantaneous value of energy on the B state (from which the dissociative population is spawned). Once we determine the a state energy the position and momentum are sampled between the inner classical

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>Potential parameters used in the molecular dynamics simulations</td>
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<tr>
<td><strong>Lennard–Jones parameters</strong></td>
</tr>
<tr>
<td><strong>$\epsilon$ (kJ/mol)</strong></td>
</tr>
<tr>
<td>Ar–Ar</td>
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<tr>
<td>Ar–I</td>
</tr>
</tbody>
</table>

Morse parameters:

$$V = D_0[1 - \exp(-\beta(r - r_e))]^2 + T_e$$

<table>
<thead>
<tr>
<th>$D_0$ (cm$^{-1}$)</th>
<th>$\beta_e$ (Å$^{-1}$)</th>
<th>$r_e$ (Å)</th>
<th>$T_e$ (cm$^{-1}$)</th>
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<tbody>
<tr>
<td>X</td>
<td>12440</td>
<td>1.875</td>
<td>2.656</td>
</tr>
<tr>
<td>B</td>
<td>5169</td>
<td>1.696</td>
<td>3.025</td>
</tr>
</tbody>
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$$V = D_e^{(1)} \exp(-2\beta^{(1)}(r - r_e^{(1)})) - 2D_e^{(2)} \exp(-\beta^{(2)}(r - r_e^{(2)})) + T_e$$

<table>
<thead>
<tr>
<th>$D_e^{(1)}$ (cm$^{-1}$)</th>
<th>$D_e^{(2)}$ (cm$^{-1}$)</th>
<th>$\beta_e^{(1)}$ (Å$^{-1}$)</th>
<th>$\beta_e^{(2)}$ (Å$^{-1}$)</th>
<th>$r_e^{(1)}$ (Å)</th>
<th>$r_e^{(2)}$ (Å)</th>
<th>$T_e$ (cm$^{-1}$)</th>
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<tr>
<td>a$_1g$ (11)</td>
<td>281.73</td>
<td>63.729</td>
<td>1.5498</td>
<td>0.6853</td>
<td>4.0262</td>
<td>5.812</td>
</tr>
</tbody>
</table>
turning point of the a state and the B—a surface crossing point for the case of predissociation that occurs when the B state molecule stretches and between the crossing point and a point to its right where the Franck-Condon factor between the two surfaces is practically zero for the case of predissociation in the opposite direction, i.e. the B state molecule contracts. The a state trajectories are placed in this asymmetric form around the crossing point (to the left of it for forward spawning and to the right of it for backward spawning) for the following reason. Suppose we examine a forward spawning event (the reasoning for backward spawning will follow the same lines) and we decide to put some ‘virtual trajectories’ also to the right of the crossing point. (We refer to these trajectories as ‘virtual’ because they are still not populated.) These trajectories will remain in their initial position for a long time and start moving only when the B state trajectory overlaps with them so that the a state population increases from zero. (Since we are propagating the position and/or momentum of an electronic state times its population, any new state starts to propagate only when its population begins to differ from zero. This will occur only when the overlap with the parent state starts to differ from zero.) On the other hand, suppose that we follow the dynamics of a ‘virtual trajectory’ that was placed to the left of the crossing point. It starts to propagate earlier for the very simple reason that it’s overlap with the parent B state started to vary from zero at an earlier point in time (remember that we are examining a forward spawning event). Hence, if we look on two ‘virtual’ trajectories that are placed to the right and to the left of the crossing point, the only difference between them is the point in time in which they start to propagate. At this point one may argue that this will make a big difference because these two trajectories will enter the probing window (which is placed at an intramolecular distance of \( \approx 4 \) Å on the dissociative a state, see below) at very different times. This is not true and has been checked. The reason is that the extra time which the trajectory to the left of the crossing point has propagated is similar to the time that it takes the B state trajectory to reach the region at which its overlap with the trajectory which is placed to the right of the crossing point varies from zero. In other words the ‘extra’ time of propagation by the left placed trajectory coincides with the time that the right placed trajectory stands and waits so that if we consider that \( t = 0 \) is the time that the right placed trajectory started to move then the left one would reach the position of the right one at \( t = 0 \). From this point on, their propagation is the same. All these arguments apply also (in an inverse way) to the backward spawning. To conclude, what our procedure does is to ensure that for our ensemble of trajectories there is, on average, a continuous non-zero overlap between the parent B state and the newly spawned a state, throughout the coupling region so that the dynamics and hence the population transfer are correctly weighted by Franck-Condon overlap factors.

4. Results

In this section we present results for a model simulation of the experimental scheme of Scherer, Jonas and Fleming [2]. Fig. 2 shows a typical profile of the ground state population when a Gaussian shaped pulse with a width of 30 fs (centered at \( t_0 = 60 \) fs) and with a carrier frequency of 550 nm interacts with the molecule. At all densities and temperatures about 5%–6% of the population is being excited. This small excitation is similar to the experimental estimate of less than 10% [2].

The excited B state population as a function of time for different liquid Ar densities is shown in the
Consider a localized excited state that is formed by the ultrashort excitation. The excited molecules (about 5% of the total population) start to evolve on the excited state potential surface while the majority of molecules (about 95%) continue to evolve on the ground state. As the excited molecules approach the crossing of the dissociative a state, see Fig. 1, the B–a coupling changes from zero and some of the excited states predissociate. The predissociation generates population on the first a 'state' that evolves with positive momentum to larger interatomic separations. Once the B state 'molecule' passes through the crossing region, the coupling between the B and a states gradually decreases to zero as this coupling depends on the Franck–Condon overlap between the two states. The B state molecule reverses the sign of its momentum either when it reaches its classical outer turning point or when a neighboring solvent Ar atom prevents it from fully stretching. Once the molecule begins to contract the predissociation is again possible, i.e. as the molecule approaches the B–a crossing region the solvent induced coupling gradually changes from zero and population is being transferred to the a state. This time the predissociation occurs as the molecule is moving in the inward direction. Thus, every B state vibrational period involves two predissociation events: one when the molecule is stretching and the second when the molecule is contracting. For each classical like trajectory in the initially localized ensemble the predissociation events are limited to such short time durations when the excited B state molecule is within the Franck–Condon overlap region between the B and a states. We therefore expect to see a step-like decline for each trajectory that crosses. Upon averaging over the ensemble, the step-like form will persist only if the ensemble is localized, i.e. if different members in the ensemble predissociate at similar times. In a previous computation we have observed the B state coherence to be a strong function of both solvent density and temperature [6]. In the absence of population decay, the spreading has been shown to be a direct result of the unusual form of the B state potential energy curve that is shallow with a large anharmonicity and with a large equilibrium distance, see Fig. 1. As a result of this shape, it is often the case that the repulsive interaction with the surrounding solvent atoms prevents the excited iodine
molecule from fully stretching itself. In an ensemble of excited state molecules this results in a somewhat different vibrational period for each molecule and hence the rapid loss of vibrational coherence at high densities. However, even at high densities the delocalization is not instantaneous and hence one does observe a step-like behavior at short times even at the higher densities. At moderate to lower densities (and specifically so at lower temperatures) the repulsive interaction with the solvent is less pronounced (as the average molecule-solvent separation is larger) so that the vibrational coherence, and thus the step-like depletion of excited B state population, persists for longer periods.

As a final point in the discussion of the excited B state dynamics we consider the asymmetry in time in the occurrence of predissociation. The onset of a drop in the population is determined by two factors: the excited state vibrational period and the position of the B—a curve crossing. For an excitation at 550 nm, the excited B state molecule has a large excess of vibrational energy (almost half of the excited state well depth). At this energy the excited state is asymmetric in the sense that the molecule spends longer to the right of the equilibrium point than to the left. Because of the location of the curve crossing it takes longer to complete a cycle from the curve crossing region to the outer turning point and back than it does to the inner turning point and back. Thus, after the first predissociation (first bleach in lower panel of Fig. 3) there is a long period during which the population is constant as the excited molecule completes the long duration motion to the outer turning point and then back to the crossing region. Once it is back there is a second bleach (second predissociation) which is followed by a third bleach after a definitely shorter time span (the short duration of the second step). This second short time interval reflects the shorter time duration of cycling into (and back from) the inner turning point. A sequence of a long step followed by a short one completes a single localized vibrational motion on the excited state and it will periodically repeat itself in this asymmetric form as long as the excited state vibrational motion remains localized.

Note that the result of the slow motion in the region near the outer turning point of the B state is that time intervals between the different exits to the a

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Fig. 4. Histograms of the \(a_1g(\Sigma^+I)\) population versus atom–atom separation at four time points. Different shadings are used to represent the different exits from the B to the \(a_1g(\Sigma^+I)\) state. (In binning the results each trajectory is weighted by its population.) Shown are the first three exits (black, gray and blank) which correspond to the first three steps in the lower panel of Fig. 3. The time periods at which the first, third and fourth panels are drawn is such that the first, second and third dissociative populations have reached an average intramolecular separation of \(4\ \text{Å}\). (This distance is about the upper limit of the experimental probing window [2].) The initial localized nature of the dissociative population is a direct result of the vibrational localization on the parent B state. Evidence for the spreading of the population on the \(a_1g(\Sigma^+I)\) state is apparent already 60 fs after the first appearance of population at a distance of \(4\ \text{Å}\) (second panel). This is due both to the repulsive anharmonic shape of the \(a_1g(\Sigma^+I)\) potential and to the cage of the surrounding liquid atoms. As time evolves the spreading in the population becomes more pronounced and in the third and fourth panels one observes trajectories that reversed the sign of their momentum. The time instances (190, 480 and 540 fs) at which the dissociative populations appear at a distance of \(4\ \text{Å}\) are not equally spaced. This is due both to the asymmetry of the B state dynamics with respect to the B–a curve crossing point and due to the negative momentum with which even numbered \(a_1g(\Sigma^+I)\) states are being spawned (see text for more detail).
state do not reflect the distance covered. Even though
the crossing region is to the right of the equilibrium
position of iodine, it takes longer to go from the
crossing region to the outer turning point and back
than to the inner turning point and back. The point is
that during most of the first route the velocity is
much lower.

The step-like depletion of the B state population
shows up in a spike-like appearance of population on
the unbound state, Fig. 4. The first appearance of
dissociation products at large intramolecular separa-
tion (larger than the outer turning point of the ex-
icted B state) is around 200 fs, lower panel of Fig. 4.
This delayed appearance reflects both the B state
dynamics and the subsequent a state dynamics and it
is basically a sum of two time intervals. The first is
the duration during which the B state molecule prop-
gagates from the optically accessed Franck-Condon
region (close to the B state inner turning point) to the
crossing region, and the second is the time that it
takes the a state molecule to travel from the B—a
Franck-Condon overlap region to the sampling point
which is at about 4 Å in this case. The localized
nature of the dissociation products is a direct result
of the localized initial population on the B state and
the exits will remain localized in time and space as
long as the B state population is localized. As the a
state population continues to propagate on the repul-
sive potential it starts to delocalize (second panel of
Fig. 4) due to both the repulsive form of the potential
and to the interaction with the surrounding solvent.
(Note that the latter is of importance as the distances
shown are large.) The appearance of the second
spike of population on the a state (gray sticks in the
third panel) is delayed to a much longer time period
for two reasons: the first is the above mentioned
asymmetry of the B state dynamics with respect to
the B—a crossing point which shows up as a se-
quence of long and short steps in the B state popula-
tion. To this delay one has to add a second delay
which is due to the initial direction of momentum of
predissociation in the backward direction: the a state
population is spawned with negative momentum since
the excited molecule is predissociating when it is
contracting. Hence, any even a state population first
travels toward the inner turning point of the a state
after which it traverses the sign of its momentum and
moves toward larger intramolecular separations of
about 4 Å where it is probed. These two delays
combined with the above-mentioned shorter time
duration of cycling from the crossing point to the
inner B state turning point result in a rapid appear-
ance of the third dissociative population (blank stick
in upper panel). Like its two former partners this
population is also localized. As for the depletion of
population, this sequence of asymmetric appearances
of localized dissociative populations continues as
long as there is an excited B state coherent vibra-
tional motion. Once this motion begins to delocalize,
the dissociative population would be less localized.
Apart from the shot like fashion by which any newly
spawned dissociative population appears the snap-
shots in Fig. 4 reflect also the strong and almost
immediate interaction of the a state with the liquid. If
we examine the first a state (i.e. the population
generated by the first exit from B to a shown as
black sticks in Fig. 4) we see that after only half a
picosecond it is already highly delocalized and some
of it has already been caged by the surrounding
liquid atoms. We note that experimentally one has
not, so far, distinguished between the new dissociat-
ive population and the one resulting from previous
older populations that collided with the liquid, re-
versed the sign of the momentum and entered the
probing window for the second time. The timescale
for such a cage effect is strongly dependent on the
solvent density and to a lesser extent on the B state
energy. In view of the present results it may be
interesting to discriminate between new and caged a
state molecules using polarized light.

5. Concluding remarks

The condensed phase dynamics of molecular io-
dine on three electronic states were examined using a
new method for computing the multi-state correlated
electronic and nuclear dynamics. The equations of
motion were derived from a quantum mechanical
Hamiltonian and their form was simplified using the
localized nature of the coupling between each of the
two surfaces.

The computation followed the experimental
scheme of an ultrafast electronic excitation of ground
state molecular iodine into the bound region of the
excited B state. The fast excitation generates a local-
ized population on the upper state. Due to solvent
induced predissociation, the excited state localized vibrational motion results in a step-like depletion of the population, twice in every vibrational period. The sharpness of the steps (or the lack of them) is a probe of the excited B state vibrational motion, which is strongly influenced by changes in the density of the solvent. The B state localization is also reflected in the spike-like appearance of the dissociative a state population.

Acknowledgement

We thank Dr. T.J. Martinez for many useful discussions. MBN is a Clore Foundation scholar. The theoretical computations were supported by the Air Force Office of Scientific Research (AFOSR).

References


