Spin-orbit effects in photodissociation of sodium iodide

A. B. Alekseyev, H.-P. Liebermann, and R. J. Buenker

Fachbereich 9-Theoretische Chemie, Bergische Universität-Gesamthochschule Wuppertal, D-42097 Wuppertal, Germany

N. Balakrishnan^{a)} and H. R. Sadeghpour

Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138

S. T. Cornett and M. J. Cavagnero

Department of Physics and Astronomy, The University of Kentucky, Lexington, Kentucky 40506-0055

(Received 16 March 2000; accepted 26 April 2000)

Ab initio configuration interaction calculations of the electronic binding energies, spin–orbit coupling matrix elements and transition dipole moments of NaI are presented. The results are used to construct adiabatic and diabatic representations of the 0⁺ molecular states relevant to predissociation. The dynamics of photopredissociation is elucidated by multichannel time-dependent wave packet propagation in the diabatic representation. Specific features associated with the spatial and temporal evolution of the wave packet are ascribed to those observed in femtosecond pump–probe experiments. In particular, the rate of decay of the electronically excited NaI* complex is found to be in close agreement with time-resolved experimental studies. Partial photoabsorption cross sections for the production of iodine atoms in the ground (${}^{2}P_{3/2}$) and excited (${}^{2}P_{1/2}$) spin–orbit states are calculated and found to peak at excitation wavelengths of 322 and 263 nm, respectively, in accord with experimental data. © 2000 American Institute of Physics. [S0021-9606(00)01228-9]

I. INTRODUCTION

Photodissociation of a diatomic molecule constitutes one of the simplest examples of photochemistry. Since this occurs on the time scale of a vibrational period of the molecule, femtosecond transition state spectroscopy has become an ideal tool for studying real-time dynamics of chemical reactions, as illustrated in a number of elegant experiments by Zewail and co-workers.^{1–5} The dynamics of dissociation is modified if an excited-state potential curve exhibits an avoided crossing with another potential curve, giving rise to interesting features in the time-resolved dynamics. This occurs for alkali-metal halide systems, in which the lowest excited $2 \, {}^{1}\Sigma^{+}$ covalent potential curve crosses the bound ionic $X^{1}\Sigma^{+}$ potential curve at a value of the internuclear separation of about 10-15 a.u. The crossing arises because the energy required to dissociate these polar molecules into ions is higher than that required to separate into neutral atoms. This is a classic example of Landau-Zener-type curve crossing and alkali-metal halides have been prototypes for such studies.

Among alkali halides, NaI is perhaps the most extensively investigated system and is also the subject of this study. Despite an impressive number of experimental¹⁻⁶ and theoretical studies⁷⁻¹⁵ on this and other alkali halide systems, theoretical understanding of the exact nature of the excited-state potential curve(s) is far from complete. In particular, the effect of the spin–orbit interaction that give rises to $I({}^{2}P_{3/2})$ and $I({}^{2}P_{1/2})$ products has never been explicitly considered. The substantial energy difference between $I({}^{2}P_{3/2})$ and $I({}^{2}P_{1/2})$ (0.942 eV) quantitatively changes the nature of

the potential curves near the crossing region. In particular, the nature of the second crossing that occurs at a larger internuclear separation between the ionic curve and the covalent curve separating to Na+I(${}^{2}P_{1/2}$) has not been explored and its influence, if any, on the dynamics is not understood. This is important because the threshold for Na+I(${}^{2}P_{1/2}$) production lies in the midst of the Franck–Condon energy zone for excitation of the electronic state correlating to Na+I(${}^{2}P_{3/2}$).

Alkali–metal halides have been the focus of attention of a number of recent experimental and theoretical investigations of quantum control of chemical reactions,^{13,14,16} and an accurate description of the potential curves and spin–orbit coupling elements is essential for a quantitative comparison with experiments. A recent high-resolution continuous wave laser measurement of predissociating linewidths in NaI, for example, clearly demonstrated the need for more accurate potential energies and coupling elements.⁶

Here we present *ab initio* calculations of binding energies, spin–orbit couplings, dipole moments and diabatic coupling elements for NaI and investigate its photopredissociation dynamics. The diabatic potential curves and couplings are made use of in a time-dependent wave packet dynamics calculation to determine the probabilities and partial cross sections for dissociating into different fine-structure states of the iodine atom. We show that inclusion of the spin–orbit coupling nearly quantitatively reproduces the observed peaks in the absorption spectrum.

The paper is organized as follows: In Sec. II we give the details of the *ab initio* calculations of the adiabatic potential energies, spin–orbit matrix and transition dipole moments. In Sec. III, we describe a procedure for constructing diabatic

^{a)}Electronic mail: nbalakrishnan@cfa.harvard.edu

potential-energy curves and coupling elements that are suitable for the dynamics calculations from the corresponding spin-orbit Hamiltonian. The time-dependent quantummechanical approach used to investigate the predissociation dynamics is described in Sec. IV. The results are presented in Sec. V and a summary and conclusions of our findings are given in Sec. VI.

II. AB INITIO CALCULATIONS

In the present treatment, core electrons of the sodium atom are described by the relativistic electron core potential (RECP) of Pacios and Christiansen,¹⁷ with the 2s, 2p, and 3s electrons included in the valence space. A RECP of the same shape-consistent type is also employed for the iodine atom,¹⁸ for which only seven outer 5s and 5p electrons are treated explicitly via basis functions. The atomic basis set employed for Na has been taken from Ref. 10 and consists of (6s6p3d)/[5s5p3d] Gaussian orbitals. The iodine atomic basis is an uncontracted set (6s7p3d1f) and is described in more detail in our previous work.¹⁹

The first step in the present molecular calculations is a self-consistent-field (SCF) computation of the $\cdots \sigma^2 \pi^{4} \Sigma^+$ ground state. At this stage, as well as in the configuration interaction (CI) step, calculations are carried out with the spin-independent part of the RECP (AREP) and include only scalar relativistic effects, whereas the spin-orbit interaction is introduced at the last stage. The CI calculations are carried out using the conventional multireference single- and double-excitation (MRD-CI) method,²⁰ including configuration selection. The Table CI algorithm²¹ is employed for efficient handling of the various open-shell cases generated. All calculations are carried out in C_{2v} symmetry. Since the main emphasis of this study is to calculate potential-energy curves for the three lowest $\Omega = 0^+$ states for analyzing the photopredissociation process, the MRD-CI calculations have been carried out for only two ${}^{1}A_{1}({}^{1}\Sigma^{+})$ roots and one root each of the singlet or triplet symmetry. This set of states includes ${}^{1,3}\Sigma^+$ and ${}^{1,3}\Pi$ symmetries converging to the lowest $Na(^{2}S) + I(^{2}P)$ dissociation limit, as well as the ionic $^{1}\Sigma^{+}$ state dissociating to Na⁺(¹S) + I⁻(¹S) and the ^{1,3} Δ states going to the $Na(^{2}P) + I(^{2}P)$ asymptote. The calculations typically include 4–7 reference configurations for each Λ -S symmetry, generating $(5-19) \cdot 10^5$ symmetry-adapted functions, of which 38000-61000 functions have been selected by imposing an energy threshold of $0.1 \, \mu E_h$. The above set of generated and selected configurations is typical for internuclear separations in the Franck-Condon region and becomes substantially smaller at larger values of R as the correlation effects become less important. Ab initio results are obtained at internuclear distances ranging from 3.75 to 25 a.u.

The lowest $\Lambda - S$ states are shown in Fig. 1. The $X^{1}\Sigma^{+}$ state is dominated by the $\sigma^{2}\pi^{4}$ ionic configuration and is strongly bound. The lowest pair of excited states, ${}^{3}\Pi$ and ${}^{1}\Pi$, both arise from the same $\sigma^{2}\pi^{3}\sigma^{*}$ covalent configuration. The energy difference between these two states is exponentially small due to the weak exchange interaction between the π and σ^{*} electrons. These electrons are localized far from each other on the I and Na atoms, respectively. The



FIG. 1. Potential-energy curves for the low-lying $\Lambda - S$ states of the NaI molecule calculated without including spin–orbit coupling.

 $^{3}\Sigma^{+}$ and $^{1}\Sigma^{+}$ states, that have $\sigma\pi^{4}\sigma^{*}$ configuration as the dominant configuration, lie somewhat higher in the Franck-Condon region since the energy required for electron excitation from the bonding σ orbital is higher than that from the iodine π lone pair. As one can see from Fig. 1, all low-lying covalent states are repulsive. An avoided crossing between the ionic $X^{1}\Sigma^{+}$ and covalent $2^{1}\Sigma^{+}$ states, which occurs at a distance of \sim 15.5 a.u., leads to the adiabatic dissociation of the ground state to the lowest atomic limit and formation of a minimum on the 2 ${}^{1}\Sigma^{+}$ potential curve. It is interesting to note that this avoided crossing is calculated to lie at a much larger distance than the experimentally determined value of R = 13.1 a.u., between the two lowest 0⁺ states. The ground $X^{1}\Sigma^{+}$ state dissociation energy obtained at this stage of the calculation is 3.343 eV, significantly larger than 3.061²² and 3.086 eV,¹⁰ calculated earlier at an analogous level of treatment.

Inclusion of the spin-orbit interaction leads to the splitting of the ${}^{3}\Pi$ and ${}^{3}\Sigma^{+}$ states as well as to the coupling of the singlet and triplet states of the same Ω symmetry. The resulting Ω states are shown in Fig. 2. The ground $X^{1}\Sigma_{0}^{+}(X0^{+})$ state is weakly influenced by the spin-orbit interaction—its energy is lowered by $20-30 \text{ cm}^{-1}$ in the Franck-Condon region. The calculated equilibrium distance of $R_e = 2.751 \text{ Å}$ and vibrational frequency of 256 cm⁻¹ for the ground state are in good agreement with the experimental values: $R_e = 2.7115$ Å and $\omega_e = 258$ cm⁻¹.²³ The $\Omega = 2$ state is the lowest excited state and has nearly pure ${}^{3}\Pi$ character. The first $\Omega = 1$ state is characterized by a strong mixture of the ${}^{3}\Pi$ and ${}^{1}\Pi$ states and lies very close to the 2(I) state, as should be in the present case where the spin-orbit interaction is much stronger than the exchange interaction. These states are followed by the $0^{-}(I)$ and 1(II) states. The $0^{-}(I)$ state is composed of ${}^{3}\Pi$ and ${}^{3}\Sigma^{+}$ states and the 1(II) state is composed of ${}^{1}\Pi$, ${}^{3}\Pi$, and ${}^{3}\Sigma^{+}$ states. The above states are all repulsive and converge to the lowest $Na({}^{2}S) + I({}^{2}P_{3/2})$ atomic limit.

In contrast to the 0^+ ground state, the second and third-





FIG. 2. Potential-energy curves for the lowest electronic states of the NaI molecule calculated including spin–orbit coupling.

FIG. 3. Dipole moments between the ground and first excited ${}^{1}\Sigma^{+}$ states of NaI in the adiabatic and diabatic representations. The solid and dashed curves are, respectively, the dipole moments in the ionic and covalent states of NaI. The adiabatic dipole moments and the transition dipole moment are shown by the symbols: $X {}^{1}\Sigma^{+}$ (open circles); $2 {}^{1}\Sigma^{+}$ (open triangles); transition dipole moment (open squares).

 0^+ states are strongly influenced by the spin-orbit interaction. The $0^+(II)$ state (usually denoted as A), contrary to what is commonly assumed, is not of pure $2 \ ^{1}\Sigma^{+}$ character, but is a mixture of ${}^{3}\Pi$ (62.6%) and 2 ${}^{1}\Sigma^{+}$ (37.4%) at the value of R = 5.2 a.u. The third 0^+ (hereafter denoted as $B0^+$) consists of the same $\Lambda - S$ states, but with an orthogonal composition. The spin-orbit interaction also lowers the dissociation asymptote for the adiabatic $X0^+$ state by 0.29 eV (at 25.0 a.u.), which in turn leads to a significant shift of the X-A crossing point to shorter distances. Extrapolating the $B0^+$ potential curve from R = 25 a.u. to infinity with an attractive Coulomb potential, leads to an ionic dissociation limit that lies 2.079 eV above the Na(${}^{2}S$) + I(${}^{2}P_{3/2}$) asymptote, in excellent agreement with the difference of the Na atom ionization potential (5.138 eV) and the I atom electron affinity (3.0591 eV). This indicates that the relative positions of the ionic and covalent 0^+ states at large internuclear separations are reproduced correctly in the present calculations.

There are three Ω states which are accessible from the $X0^+$ ground state via dipole-allowed transitions at excitation energies of $30\,000-33\,500$ cm⁻¹. These are the $A0^+$ state, with a vertical excitation energy of $32\,380$ cm⁻¹, and two $\Omega = 1$ states: 1(I) (30 220 cm⁻¹) and 1(II) (31 696 cm⁻¹). The $A0^+ \leftarrow X0^+$ transition is the strongest ($D_{12} = 0.862$ a.u. at $R_e = 5.2$ a.u.), but transitions to the 1(I, II) states are also fairly strong, with the perpendicular transition dipole moments of 0.265 and 0.225 a.u., respectively, at $R_e = 5.2$ a.u. Therefore, perpendicular optical transitions via the 1(I,II) molecular states lead to the background production of $I({}^{2}P_{3/2})$ at lower excitation energies. While the $A0^{+} \leftarrow X0^{+}$ transition is characterized by the strong $2 {}^{1}\Sigma^{+} \leftarrow X {}^{1}\Sigma^{+}$ contribution, the $1(I,II) \leftarrow X0^+$ transitions borrow their intensity from the $1 \, {}^{1}\Pi \leftarrow X \, {}^{1}\Sigma^{+}(\sigma^{*} \leftarrow \pi)$ transition. In the present study, we shall concentrate, however, on the dissociation processes on the 0^+ potential-energy curves which have been the focus of a number of femtosecond laser spectroscopy studies in recent years.

III. POTENTIAL CURVES

The adiabatic potential curves and the eigenvectors of the dipole matrix between the $X^{1}\Sigma^{+}$ and the $2^{1}\Sigma^{+}$ potentials are used to construct the corresponding diabatic potential curves and dipole moments. The diabatic representation is more convenient for solving the time-dependent Schrödinger equation with the coupled electronic states because the nuclear kinetic-energy operator is diagonal and the couplings are restricted to the off-diagonal part of the potentialenergy matrix. The dipole moments in the diabatic representation are obtained by diagonalizing the corresponding adiabatic dipole matrix **D**,

$$\mathbf{d} = \mathbf{U}^{\dagger} \mathbf{D} \mathbf{U},\tag{1}$$

where **U** is the eigenvector matrix and \mathbf{U}^{\dagger} is its conjugate transpose. It may be mentioned that **U** is also the transformation matrix between the diabatic and adiabatic representation of the $X^{1}\Sigma^{+}$ and $2^{1}\Sigma^{+}$ potential curves. In Fig. 3, we show the dipole moments of the ground and the excited-state potentials and the transition dipole moment connecting them. The change in the sign of the adiabatic dipole moments at the crossing is due to change in the character of the ionic or covalent wave functions. The computed dipole moment at the experimental equilibrium distance of the NaI ground state is 9.44 Debye, in good agreement with the value of 9.41 Debye by Sakai *et al.*¹⁰ and the experimental value of 9.21 Debye by Hebert *et al.*²⁴

The electronic Hamiltonian matrix relevant to the 0^+ adiabatic potential curves shown in Fig. 2 may be written

$$\mathbf{H}_{\rm so} = \begin{cases} X^{1} \Sigma^{+} & 0 & a & -a \\ 0 & 2^{1} \Sigma^{+} & b & -b \\ a & b & {}^{3} \Pi_{x} & c \\ -a & -b & c & {}^{3} \Pi_{y} \end{cases},$$
(2)



FIG. 4. Spin–orbit coupling elements as functions of the internuclear separation: The matrix element *a* is shown by the solid curve, the matrix element *b* is shown by the dotted curve and the matrix element *c* is shown by the dashed curve. The labels refer to the \mathbf{H}_{so} interaction matrix in Eq. (2).

where the matrix elements *a*, *b*, and *c* are, respectively, the $X^{1}\Sigma^{+}-{}^{3}\Pi_{x}$, $2^{1}\Sigma^{+}-{}^{3}\Pi_{x}$, and ${}^{3}\Pi_{x}-{}^{3}\Pi_{y}$ spin-orbit couplings, shown in Fig. 4. The diagonal elements in Eq. (2) are the adiabatic potential energies.

Of the four adiabatic potentials resulting from the diagonalization of the spin-orbit Hamiltonian, three have $\Omega = 0^+$ molecular symmetry and one has $\Omega = 2$ molecular symmetry. The $\Omega = 2$ potential curve is purely repulsive and correlates with the ground-state covalent fragments. It does not exhibit a radial avoided crossing with the 0^+ potential curves and is omitted in the dynamics calculation.

The Hamiltonian matrix in Eq. (2) refers to the interaction in the adiabatic representation. We define a diabatic set through a transformation

$$\mathbf{V}^d = \mathbf{S}^\dagger \mathbf{H}_{so} \mathbf{S},\tag{3}$$

where the transformation matrix **S** with conjugate transpose \mathbf{S}^{\dagger} is constructed from the eigenvector matrix **U** and the coefficients of the linear combination of the ${}^{3}\Pi_{x}$ and the ${}^{3}\Pi_{y}$ states that give rises to the $B0^{+}$ potential

$$\mathbf{S} = \begin{cases} U_{11} & U_{12} & 0\\ U_{21} & U_{22} & 0\\ 0 & 0 & \frac{1}{\sqrt{2}}\\ 0 & 0 & -\frac{1}{\sqrt{2}} \end{cases},$$
(4)

where U_{ij} are elements of U. The nonsquare matrix S excludes the contribution from the $\Omega = 2$ electronic state which does not play a role in the predissociation dynamics.

This transformation gives the correct ionic curve but the two covalent potential curves are shifted from the corresponding adiabatic $A0^+$ and the $B0^+$ potential curves in the limit $R \rightarrow \infty$ with a constant coupling matrix element V_{23}^d . A coupling matrix element that is finite in the asymptotic limit is problematic and is due here to the strong spin–orbit mixing of the $X^1\Sigma^+$ and ${}^3\Pi$ symmetries at large distances, see Fig. 4. To remedy this problem, we diagonalize the 2×2



FIG. 5. Adiabatic and diabatic potentials obtained by including spin–orbit coupling. The adiabatic potential curves are denoted by the symbols: $X0^+$ (open circles); $A0^+$ (open squares); $B0^+$ (open triangles). The corresponding diabatic potential curves are denoted by the broken lines: Ionic (dotted curve); lowest excited covalent state (dashed curve); second excited covalent state (dashed–dotted curve).

block of the diabatic potential matrix \mathbf{V}^d , consisting of the two covalent diabatic potentials at a very large value of $R \sim 10^8$ a.u., to match the diabatic potentials with the adiabatic $A0^+$ and $B0^+$ potentials at infinity. Applying the (*R*independent) transformation that diagonalizes the 2×2 block at infinity to the diabatic potential-energy matrix at all values of *R* yields an improved set of diabatic potential curves that have smooth characteristics and tend asymptotically to the correct dissociation thresholds. In Fig. 5, we show the adiabatic and diabatic potential curves as functions of *R*. The energy splitting between the $I({}^2P_{3/2})$ and the $I({}^2P_{1/2})$ spin–orbit states obtained from our calculation is 7322 cm⁻¹, in satisfactory agreement with the experimental value of 7603 cm⁻¹.

The first crossing between the ionic potential and the covalent potential correlating with the Na+I(${}^{2}P_{3/2}$) products occurs at R_1 =13.5 a.u. The energy splitting between the $X0^+$ and the $A0^+$ potentials at this separation is 0.098 eV which is in close agreement with the semiempirical value of 0.1 eV by Grice and Herschbach.²⁵ Sakai *et al.*¹⁰ obtained a value of 0.13 eV at R_1 =13.5 a.u. The second crossing, between the ionic potential and the excited covalent potential correlating with the Na+I(${}^{2}P_{1/2}$) products, occurs at R_2 =23.7 a.u. It is worth noting that the value of the first crossing, R_1 =13.5 a.u., is smaller than the crossing value of 15.5 a.u., obtained excluding the spin–orbit interaction.

Figure 6 shows the diabatic coupling matrix elements as a function of the internuclear distance. The off-diagonal coupling matrix elements exhibit exponential and inverse powerlaw dependence with R at large internuclear distances; an attractive feature for performing multichannel quantummechanical calculations. Rose *et al.*² modeled the diabatic coupling element V_{12}^d as a Gaussian centered at the crossing with a value of 0.055 eV at $R_1 = 13.1$ a.u. As seen in Fig. 6, V_{12}^d obtained from our calculation is not a Gaussian and falls off exponentially at large internuclear separations. The magnitude of the coupling strength at the first crossing is 0.05 eV, in accord with that adopted by Rose *et al.*,² Schaefer



FIG. 6. Diabatic coupling elements as functions of the internuclear distance: Solid curve (V_{12}) ; dashed curve (V_{23}) ; dotted curve (V_{13}) .

et al.,²⁶ and in close agreement with the semiempirical valence bond calculation of Peslherbe *et al.*¹⁵ who obtained a value of 0.06 eV.

IV. PHOTODISSOCIATION DYNAMICS

We use a time-dependent wave packet propagation scheme²⁷ to describe the photopredissociation dynamics of NaI on the three 0^+ potential curves. The time-dependent Schrödinger equation in the diabatic representation is written as

$$i\hbar \frac{\partial \Psi(R,t)}{\partial t} = \mathbf{H}\Psi(R,t),$$
 (5)

where Ψ is a column vector of the wave functions, ψ_i , i = 1,3 which are, respectively, the components on the $X0^+$, $A0^+$, and $B0^+$ electronic states. The Hamiltonian is

$$\mathbf{H} = \mathbf{T} + \mathbf{V} = -\frac{\hbar^2}{2m} \mathbf{I} \frac{d^2}{dR^2} + \mathbf{V},$$
 (6)

where *m* is the reduced mass of the molecule, **I** is the 3×3 identity matrix and **V** is the diabatic potential-energy matrix (the superscript *d* is omitted for brevity). The diagonal elements $V_{i,i}$, i=1,3 are the diabatic potential curves and the off-diagonal elements $V_{i,j}=V_{j,i}$ are the diabatic couplings. The wave functions, potentials, and coupling elements are represented on a set of equally spaced grid points. The Schrödinger equation is solved using the split-operator method²⁸ which employs a symmetric splitting of the kinetic and potential energy operators to approximate the evolution operator

$$\Psi(R,t+\Delta t) = e^{-i\Delta t \mathbf{H}/\hbar} \Psi(R,t)$$

= $e^{-i\Delta t \mathbf{V}/2\hbar} e^{-i\Delta t \mathbf{T}/\hbar} e^{-i\Delta t \mathbf{V}/2\hbar} \Psi(R,t) + \mathcal{O}(\Delta t^3),$
(7)

where Δt is the increment in time. The action of the potential-energy operator is carried out in the coordinate space and that of the kinetic-energy operator in the momentum space, where it is diagonal. A fast-Fourier-transform algorithm is used to switch efficiently between the coordinate and momentum spaces following the application of each ex-

ponential operator. The exponential potential-energy part in Eq. (7) is evaluated by diagonalizing the 3×3 potentialenergy matrix at each grid point in the radial coordinate *R*.

In the time-dependent quantum-mechanical formalism, the total photoabsorption spectrum as a function of the photon energy $\hbar\omega$ is given by the Fourier transform of the auto-correlation function²⁹

$$\sigma(\omega) = \frac{2\pi\omega}{3\hbar c} \int_{-\infty}^{\infty} dt w(t) C(t) e^{iEt/\hbar},$$
(8)

where $E = E_{v''J''} + \hbar \omega$ is the total energy with $E_{v''J''}$ being the energy of the initial rovibrational eigenstate and C(t) is the autocorrelation function. A Hann window function w(t) = 1 $+\cos(\pi t/T)$ is included in Eq. (8), because we truncate the temporal integration limits to a finite range [-T,T], where T is the total propagation time. This prevents undesirable sidebands in the absorption spectrum. The autocorrelation function is defined as the projection of the propagated wave function onto the initial state wave function at each time step

$$C(t) = \langle \Psi(t=0) | \Psi(t) \rangle.$$
(9)

For Eq. (8) to represent the photoabsorption spectrum, the initial state in Eq. (9) must be a product of the rovibrational wave function of the ground-state potential and the transition dipole moment between the ground and excited electronic states. In the diabatic representation used here, the dipole moment matrix is diagonal and the initial condition is given by

$$\psi_1(R,t=0) = d_1(R) \phi_{v''J''}(R),$$

$$\psi_2(R,t=0) = 0,$$
(10)

$$\psi_3(R,t=0) = 0,$$

where $\phi_{v''J''}(R)$ is a rovibrational eigenfunction of the ionic potential with vibrational and rotational quantum numbers, v'' and J'' and d_1 is the dipole moment matrix element given by Eq. (1)

The dissociation probability in each channel can be calculated from the probability flux of the wave function at the nuclear separation R_f . The value of R_f is chosen such that the wave function has reached its asymptotic form but has not yet been attenuated by the absorbing potential. The probability flux in channel *i* is

$$J_i(t) = \frac{\hbar}{m} \operatorname{Im} \left[\psi_i(R,t) \frac{\partial \psi_i(R,t)}{\partial R} \right]_{R=R_f},$$
(11)

and the time-integrated flux yields the dissociation probability. In the femtosecond laser pump-probe studies of NaI, the dissociation leading to Na+I product channel is monitored by tuning a probe laser pulse in resonant with the D-line of the Na atom but delayed with respect to the pump laser pulse. When the probe laser pulse is detuned (off-resonance) from the Na-D line, it detects the bound NaI* complex. The time-evolution of the bound NaI* complex is usually followed by monitoring the probability of the wave packet in the covalent channel ($A0^+$) for $R \leq R_1$:



FIG. 7. Survival probability of the wave packet on the $A0^+$ adiabatic potential curve as a function of time. This probability is related to the motion of the wave packet on the $A0^+$ surface from origin to the $R=R_1$ avoided crossing. Note the rapid rate of decay of the peak amplitudes with time. Such rapid decay has been observed in experiment.

$$p_2(t) = \int_0^{R_1} |\psi_2(R,t)|^2 dR.$$
(12)

Due to the large values of the diabatic coupling matrix elements in the range $0 \le R \le R_1, p_2(t)$ is highly oscillatory, see Fig. 7. Accordingly, we determine the bound survival probability from the wave packet in the adiabatic representation

$$p_2^a(t) = \int_0^{R_1} |\psi_2^a(R,t)|^2 dR,$$
(13)

where the superscript *a* refers to the adiabatic representation. The diabatic to adiabatic transformation matrix is obtained by diagonalizing the diabatic potential energy matrix.

To obtain the partial photodissociation cross section, the wave packet at R_f is Fourier transformed from the time to the energy domain

$$\psi_i(E) = \frac{1}{2\pi} \int_0^\infty \psi_i(R_f, t) \exp(-iEt/\hbar) dt, \qquad (14)$$

and the partial cross section in channel i is extracted according to³⁰

$$\sigma_i(\omega) = \frac{4\pi^3}{3c\epsilon_0 m} k_i \omega |\psi_i(E)|^2, \qquad (15)$$

where $k_i = (1/\hbar) \sqrt{(2m(E - V_i(R_f)))}$ is the wave vector in channel *i*, $V_i(R_f)$ is the value of the potential energy in channel *i* at $R = R_f$, and ϵ_0 is the permittivity of free space. It can be shown that the total cross section in Eq. (8) is the sum of the partial cross sections in Eq. (15),³⁰ i.e.

$$\sigma_{\text{tot}}(\omega) = \sum_{i} \sigma_{i}(\omega).$$
(16)

V. RESULTS AND DISCUSSION

We consider photoexcitation from the ground rovibrational (v''=0 and J''=0) level in the ground (ionic) electronic state. The bound state wave function $\phi_{00}(R)$ is computed using the Fourier-grid Hamiltonian method.³¹

The computed *ab initio* potential-energy values and coupling elements are restricted to $3.75 \le R \le 25$ a.u. For R > 17 a.u., the ionic potential curve is well approximated by the Coulomb potential. The two covalent diabatic potential curves and the coupling elements are extended to large internuclear distances by fitting to exponentially decaying functions of the form $A_L \exp(-B_L R)$ where A_L and B_L are fitting parameters. The ab initio data are interpolated using a cubic spline technique in the range $3.75 \le R \le 17$ a.u. For R \geq 17 a.u., the Coulomb potential is used to represent the ionic curve and the exponential form is used for the covalent potentials and the coupling elements. The wave functions, potentials, and coupling elements are represented on an equally spaced grid of 2048 points with $3.0 \le R \le 50.0$ a.u. Absorbing potentials are added in the diagonal channels for $R \ge 45$ a.u. to attenuate the dissociative wave packets and prevent reflection into the inner region.

The time-resolved dynamics of NaI predissociation has been the subject of extensive experimental studies by Zewail and co-workers^{1–3} as well as a number of theoretical explorations.^{1,2,7–9,12,14,16,32} The main features of the dynamics are understood and good correspondence between theory and experiment has been achieved. However, the discussion of the dissociation process and the interpretation of the experimental data have mostly centered around a two-state model of the potential curves without explicitly addressing the role of the spin–orbit interaction. Here, we provide a description of the temporal evolution of the wave packet on the three coupled electronic states and examine the specific changes in dynamics that result from the inclusion of the spin–orbit coupling.

In Fig. 7, we show the "bound" survival probabilities $p_2(t)$ and $p_2^a(t)$ evaluated in the diabatic and adiabatic representations, respectively, as functions of the time during the first ten picoseconds of the evolution. This is an approximation to the probe signal in the femtosecond pump-probe experiments when the probe laser frequency is tuned offresonance to the Na-D line, where it detects the fluorescence from the bound NaI^{*} complex. It is seen that the probability as a function of time exhibits a series of damped oscillations with a period of ~ 1.3 ps. The damping is due primarily to predissociation leading to neutral Na+I(${}^{2}P_{3/2}$) products whereas the oscillations occur due to the periodic motion of the wave packet on the $A0^+$ potential curve. The time scale of the oscillations coincides with that found in the femtosecond experiments of Zewail and co-workers.⁵ The rate of decay of the peak amplitudes in Fig. 7 is also reminiscent of the observed decay.² Previous theoretical calculations⁷ which attempted to model the observed decay of the survival probability^{8,9} reproduced the spacing between the oscillations but not the rapid damping of the peak intensities. This may be a consequence of using unrealistic diabatic coupling, a Gaussian localized at the crossing, and the neglect of the spin-orbit interaction.

The long-time evolution of the bound survival probability $p_2^a(t)$ is shown in Fig. 8, for $t \le 240$ ps. Two different time scales are clearly visible in the time-dependence of the survival probability: The narrow oscillations with the time scale of about 1.3 ps discussed above and the broad oscilla-



FIG. 8. Survival probability of the wave packet on the excited $A0^+$ curve. Note the revival of the wave packet with a characteristic period of about 40 ps.

tions (or the dephasing and rephasing of the wave packet) that recur with a period of about 35–40 ps. The latter oscillations were first seen in the experimental studies of Zewail and co-workers³ and subsequently investigated using wave packet methods by Tang and Rice¹⁴ and using semiclassical methods by Chapman and Child³² (see the discussion on the photodissociation cross sections below). The broad oscillations arise due to the interference between quasi-bound states with long predissociation lifetimes.

The dissociative wave packet carries signatures of the dynamics on the excited-state potentials. This can directly be followed from the probability flux, $J_i(t)$ given by Eq. (11). The probability flux in the two covalent channels is shown in Figs. 9(a) and 9(b) as a function of the time. The probability flux in the I(${}^2P_{1/2}$) channel is shown in Fig. 9(a). It is seen that the excited-state product is formed in the first passage of the wave packet through the second crossing, R_2 , with the



FIG. 9. Probability flux of the wave packet in the Na+I(${}^{2}P_{1/2}$) (upper panel) and Na+I(${}^{2}P_{3/2}$) dissociative channels (lower panel). Note the signatures of the interference in the wave packet at later times in the lower panel.



FIG. 10. Cumulative probability of dissociation to Na+I(${}^{2}P_{1/2}$) and Na+I(${}^{2}P_{3/2}$) products. Note the step-wise buildup of the probability in the Na+I(${}^{2}P_{3/2}$) channel separated by ~ 1.3 ps, the time of oscillation of the wave packet in the potential well of the $A0^+$ electronic state. The probability for dissociation to Na+I(${}^{2}P_{1/2}$) channel settles into a constant value in ~ 0.8 ps.

Gaussian shape of the initial wave packet retained during the initial motion. The subsequent motion of the wave packet does not lead to any noticeable production of the $I({}^{2}P_{1/2})$ product. However, as shown in Fig. 9(b), in the $I({}^{2}P_{3/2})$ channel the flux appears as bursts separated by about 1.3 ps, but quickly becomes a train of waves modulated by interference patterns formed at the avoided crossing, R_1 . The separation between the bursts is the same as that of the oscillations in Fig. 7 for the bound part of the wave packet. Accordingly, a part of the wave packet is leaked to the dissociative channel during each passage through the avoided crossing. The first burst in Figs. 9(a) and 9(b) that appears at about 0.8 ps arises from the first passage of the wave packet through the avoided crossing and hence before the buildup of any interference. The time at which the initial burst appears is arbitrary because it depends on the location R_f where the flux is evaluated. However, the spacing between the adjacent bursts is independent of the value of R_f provided $R_f > R_1$. The spread and additional structures in the subsequent bursts arise due to dispersion and the multiple interferences between the different frequency components of the wave packet on the excited-state potentials.

The dissociation probability in each asymptotic channel is obtained by integrating the corresponding probability flux. The cumulative dissociation probabilities for the $I({}^{2}P_{3/2})$ and $I({}^{2}P_{1/2})$ products are shown in Fig. 10. The steplike structure of the probability for the ground-state products separated by about 1.3 ps can easily be traced to the bursts in the timedependent flux shown in Fig. 9(b). Similar stepwise build up of the laser induced fluorescence from the free Na atoms has been observed in the femtosecond experimental studies^{1,2,4} when the probe laser is tuned to the sodium D-line. No such step-wise buildup of the probability is seen for the excitedstate products because the dissociation occurs primarily in the first transit of the wave packet through the second avoided crossing as shown in Fig. 9(a). Hence the probability in the excited spin–orbit channel settles to a constant value



FIG. 11. Partial photoabsorption cross section of NaI (in cm²) as a function of the photon wavelength in nm. The upper panel shows the partial dissociation cross section for forming iodine atoms in excited $({}^{2}P_{1/2})$ level and the lower panel shows the dissociation cross section for producing iodine atoms in the ground $({}^{2}P_{3/2})$ state. The predissociating resonances in the upper panel are multiplied by a factor of 10. They belong to the same series as in the lower panel. The broad envelopes in both panels form very early during the dissociation process and have comparable magnitudes.

in about 0.8 ps, the time necessary for the first passage of the wave packet through the second avoided crossing.

Though the time-resolved dynamics of NaI predissociation has been extensively explored in the past, much less attention has been devoted to the absorption spectrum. In particular, the influence of the spin-orbit coupling on the absorption spectrum has not been investigated. Since the excited-state covalent potential curves are significantly modified in the Franck-Condon region by the addition of spin-orbit interaction, the absorption spectrum can be quite different. In Figs. 11(a) and 11(b), we show the partial photoabsorption spectra computed using Eq. (15) as a function of the photon energy. The upper panel (a) shows the cross section for the $I({}^{2}P_{1/2})$ product and the lower panel (b) that for the $I({}^{2}P_{3/2})$ product. We have verified that Eqs. (8) and (16) give identical results for the total cross section. The total propagation time needed to resolve the features to the extent shown in Fig. 11(b) is 240 ps. The $I({}^{2}P_{1/2})$ spectrum shows a discrete part in the wavelength range 310-325 nm and a smooth Gaussian envelope centered at 263 nm. The discrete part is magnified by a factor of 10 for clarity and it arises from predissociation of the quasibound levels of the $B0^+$ adiabatic potential. These are the low-frequency components of the wave packet that lie close to the minimum of the potential well. The smooth Gaussian part of the spectrum arises from the direct dissociation of the wave packet in its first transit through the second crossing point, R_2 . The peak value of the cross section occurs at a wavelength of 262.8 nm, in close agreement with the experimental value of 260 nm.³³ That we do not observe any discrete lines in this region is due to the fact that the motion of the wave packet along the second crossing, R_2 is more diabatic in nature, i.e., the bound part of the wave packet follows the ionic curve for $R \ge R_2$. Alternatively, in the adiabatic representation, the



FIG. 12. Expanded view of the absorption spectrum in a typical energy range which show the broad and narrow resonances.

wave packet motion on the $B0^+$ potential is mostly restricted to $R \ge R_2$. However, this could change if the initial wave packet is prepared differently.

The spectrum of the $I({}^{2}P_{3/2})$ channel has also a Gaussian envelope but superimposed with a series of extremely narrow resonances separated by broad window resonances that recur periodically. The peak of the distribution which occurs at a wavelength of 322 nm, compares well with the experimental value of 325 nm. We have carried out a separate calculation in which the $B0^+$ potential curve and the associated couplings are omitted. The absorption spectrum in this case is found to peak at 315 nm, significantly shifted from the experimental value.

The absorption spectrum in Fig. 11(b) resembles that of LiF³⁴ which also exhibits a series of broad (window) and narrow resonances. As shown in the expanded view in Fig. 12, the window resonances in NaI are narrower than those in LiF, owing to the longer time associated with the motion of the wave packet, and subsequent dispersion and interference.

We have verified that a Fourier transform of the shorttime autocorrelation function yields comparable values for the $I({}^{2}P_{3/2})$ and $I({}^{2}P_{1/2})$ photoabsorption peaks, a fact that becomes obscured by the presence of long-lived resonances in the $I({}^{2}P_{3/2})$ partial cross section. This can be reconciled by recognizing that the two diabatic covalent potentials couple to the ionic curve with nearly equal strength at $R = R_{e}$.

The details of the absorption spectrum are related to specific features of the time-domain dynamics. This can be best understood by examining the decay of the autocorrelation function with time. The initial decay determines the broad features of the absorption spectrum: The shape and width, as shown in Fig. 13. The initial decay occurs in a time span of about 20 fs which corresponds to an energy uncertainty of about 1670 cm⁻¹. This is roughly equal to the full width at half maximum of the Gaussian envelope of the absorption spectrum. The narrow oscillations in Fig. 13 occur on a time scale of about 1.05 fs which translates into an energy uncertainty of about 31 500 cm⁻¹, equal to the vertical separation between the ground and excited states in the Franck–Condon region. The oscillations are driven by the diabatic coupling



FIG. 13. Modulus of the autocorrelation function vs time showing the initial decay of the wave packet. The recurrence period of 4 to 5 fs is also evident.

element V_{12} , which is nonzero in the Franck–Condon region. The spacing between the oscillations is constant because the energy spread of the wave packet created by the instantaneous excitation on the upper state is small compared to the vertical excitation energy. The revival of the oscillations has an approximate period of about 4 to 5 fs, corresponding to an energy of about 7000–8000 cm⁻¹. For short propagation times, these revivals correspond to the beating between the two covalent potentials which are strongly coupled to the ionic potential curve in the small-*R* region.

The finer details of the absorption spectrum are related to the longtime evolution of the wave packet and the associated dispersion, revivals, and interference. This is shown in Figs. 14(a) and 14(b). The former depicts the autocorrelation function for the first 10 ps and shows two distinct time scales. The small background oscillations with constant amplitude and period of about 130 fs arise from the bound part of the wave packet on the $X0^+$ state which has a small component in the first excited vibrational level, v''=1. The



FIG. 14. Modulus of the autocorrelation function vs time showing the longtime evolution of the wave packet. The upper panel shows the recurrences during the early stages of the evolution and the lower panel shows the complete loss of coherence of the wave packet after about 6 ps due to multiple recurrences and the reappearance of the coherence after about 35–40 ps.

energy separation between v''=0 and v''=1 vibrational levels is consistent with the period of the oscillation. This occurs because only part of the wave packet is transferred to the excited state by the action of the transition dipole moment. We mention that such features have not been explored previously because the role of the transition dipole moment is usually ignored and the diabatic coupling matrix elements are assumed to be localized near the crossing points.

The second type of oscillation in Fig. 14(a) with a time scale of about 1.3 ps originate from the recurrent motion of the wave packet on the $A0^+$ and the $B0^+$ potential curves. The envelope shows that the Gaussian shape is almost maintained during the first return of the wave packet to the Franck-Condon region. The additional structures seen atop the broad envelope in the subsequent revivals of the wave packet are due to the interference of different frequency components of the wave packet during its undulatory motion on the excited adiabatic potentials. Due to multiple interferences, the autocorrelation function develops more structure for t > 6 ps, and hence the recurrence period of 1.3 ps no longer holds. The longtime behavior of the autocorrelation function in Fig. 14(b) shows continued dephasing of the wave packet till about 35-40 ps and a gradual rephasing afterwards and is analogous to that of the bound survival probability shown in Fig. 8. The dephasing and rephasing of the wave packet has been observed in experiments and in two-state wave packet dynamics calculations.^{3,7,8,14,35} The rephasing occurs because the frequency components in the wave packet corresponding to the short-lived window resonances have already decayed and those corresponding to the narrow resonances continue to interfere.

VI. SUMMARY AND CONCLUSIONS

The dynamics of NaI predissociation is explored using newly constructed ab initio potential energy curves, transition dipole moments and spin-orbit coupling matrix elements. The three lowest 0^+ potential curves in a diabatic representation are used to elucidate the quantum dynamics using a coupled-channel wave packet approach. The timedependence of the survival probability of the wave packet is found to be in accord with femtosecond pump-probe experimental data. In particular, the observed rapid decay of the survival probability with time is near quantitatively reproduced in our calculations. The dephasing and rephasing of the wave packet observed on a timescale of about 30-40 ps in the pump-probe experiments is also reproduced by our calculation and we predict similar recurrences to continue for at least 200 ps or longer. The details of the dynamics that give rise to specific features in the frequency resolved absorption spectrum are studied and analyzed through the timedependence of the autocorrelation function. Partial cross sections for producing the ground $I({}^{2}P_{3/2})$ and excited $I({}^{2}P_{1/2})$ states of the iodine atom are calculated and found to peak at excitation wavelengths of 322 and 263 nm, respectively, in accord with experimental data, further demonstrating that the new potential curves provide a reliable description of the predissociation dynamics.

ACKNOWLEDGMENTS

This work was partially supported by a grant by the National Science Foundation to the Institute for Theoretical Atomic and Molecular Physics at the Harvard-Smithsonian Center for Astrophysics and by the Deutsche Forschungsgemeinschaft within the Schwerpunktprogramm *Theorie relativistischer Effekte in der Chemie und Physik schwerer Elemente.*

- ¹T. S. Rose, M. J. Rosker, and A. H. Zewail, J. Chem. Phys. **88**, 6672 (1988).
- ²T. S. Rose, M. J. Rosker, and A. H. Zewail, J. Chem. Phys. **91**, 7415 (1989).
- ³P. Cong, A. Mokhtari, and A. H. Zewail, Chem. Phys. Lett. **172**, 109 (1990).
- ⁴A. H. Zewail, J. Phys. Chem. **100**, 12701 (1994).
- ⁵J. L. Herek, A. Materny, and A. H. Zewail, Chem. Phys. Lett. **228**, 15 (1994).
- ⁶M. Baba, T. Kokita, S. Kasahara, and H. Katô, J. Chem. Phys. **111**, 9574 (1999).
- ⁷V. Engel, H. Metiu, R. Almeida, R. A. Marcus, and A. H. Zewail, Chem. Phys. Lett. **152**, 1 (1988).
- ⁸V. Engel and H. Metiu, J. Chem. Phys. **90**, 6116 (1989); **91**, 1596 (1989).
- ⁹S. E. Choi and J. C. Light, J. Chem. Phys. **90**, 2593 (1989).
- ¹⁰Y. Sakai, E. Miyoshi, and T. Anno, Can. J. Chem. **70**, 309 (1992).
- ¹¹J. R. Waldeck, M. Shapiro, and R. Bersohn, J. Chem. Phys. **99**, 5924 (1993).
- ¹²T. J. Martinez and R. D. Levine, Chem. Phys. Lett. 259, 252 (1996).
- ¹³C. J. Bardeen, J. Che, K. R. Wilson, V. V. Yakovlev, P. Cong, B. Kohler, J. L. Krause, and M. Messina, J. Phys. Chem. A **101**, 3815 (1997).
- ¹⁴H. Tang and S. A. Rice, J. Phys. Chem. A **101**, 9587 (1997).

- ¹⁵G. H. Peslherbe, R. Bianco, J. T. Hynes, and B. M. Ladanyi, J. Chem. Soc., Faraday Trans. **93**, 977 (1997).
- ¹⁶M. Grønager and N. E. Henriksen, J. Chem. Phys. 109, 4335 (1998).
- ¹⁷L. F. Pacios and P. A. Christiansen, J. Chem. Phys. 82, 2664 (1985).
- ¹⁸L. A. LaJohn, P. A. Christiansen, R. B. Ross, T. Atashroo, and W. C. Ermler, J. Chem. Phys. **87**, 2812 (1987).
- ¹⁹A. B. Alekseyev, H.-P. Liebermann, R. Lingott, R. J. Buenker, and J. S. Wright, Mol. Phys. **91**, 777 (1997).
- ²⁰ R. J. Buenker and S. D. Peyerimhoff, Theor. Chim. Acta **35**, 33 (1974);
 39, 217 (1975); R. J. Buenker, S. D. Peyerimhoff, and W. Butscher, Mol. Phys. **35**, 771 (1978).
- ²¹ R. J. Buenker and R. A. Phillips, J. Mol. Struct.: THEOCHEM **123**, 291 (1985).
- ²² K. Yamashita and K. Morokuma, Faraday Discuss. Chem. Soc. **91**, 47 (1991).
- ²³ K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. 4. Constants of Diatomic Molecules* (Van Nostrand Reinhold, Princeton, NJ, 1979).
- ²⁴ A. J. Hebert, F. J. Lovas, C. A. Melenders, C. D. Hollowell, T. L. Story, Jr., and K. Street, Jr., J. Chem. Phys. 48, 2824 (1968).
- ²⁵R. Grice and D. R. Herschbach, Mol. Phys. 27, 159 (1974).
- ²⁶S. H. Schaefer, D. Bender, and E. Tiemann, Chem. Phys. 89, 65 (1984).
- ²⁷ N. Balakrishnan, C. Kalyanaraman, and N. Sathyamurthy, Phys. Rep. 280, 79 (1997).
- ²⁸M. D. Feit, J. Fleck, Jr., and A. Steiger, J. Comput. Phys. 47, 412 (1982).
- ²⁹ E. J. Heller, Acc. Chem. Res. 14, 368 (1981).
 ³⁰ G. G. Balint-Kurti, R. N. Dixon, and C. C. Marston, J. Chem. Soc., Faraday Trans. 86, 1741 (1990).
- ³¹C. C. Marston and G. G. Balint-Kurti, J. Chem. Phys. **91**, 3571 (1989).
- ³²S. Chapman and M. S. Child, J. Phys. Chem. **95**, 578 (1991).
- ³³P. Davidovits and D. C. Brodhead, J. Chem. Phys. 46, 2968 (1967).
- ³⁴N. Balakrishnan, B. D. Esry, H. R. Sadeghpour, S. T. Cornett, and M. J. Cavagnero, Phys. Rev. A 60, 1407 (1999).
- ³⁵H. Kono and Y. Fujimura, Chem. Phys. Lett. **184**, 497 (1991).