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Molecular orientation via a dynamically induced pulse-train: Wave packet dynamics of NaI in a static electric field

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We regard the rovibrational wave packet dynamics of NaI in a static electric field after femtosecond excitation to its first electronically excited state. The following quasibound nuclear wave packet motion is accompanied by a bonding situation changing from covalent to ionic. At times when the charge separation is present, i.e., when the bond-length is large, a strong dipole moment exists and rotational excitation takes place. Upon bond contraction, the then covalently bound molecule does not experience the external field. This scenario repeats itself periodically. Thus, the vibrational dynamics causes a situation which is comparable to the interaction of the molecule with a train of pulses where the pulse separation is determined by the vibrational period. © 2004 American Institute of Physics. [DOI: 10.1063/1.1695315]

It is well known that the outcome of a bimolecular reaction, due to the anisotropy of the interaction potential, depends critically on the relative orientation of the collision partners. In order to investigate these steric effects in detail, it is necessary to force isotropically distributed molecules to line up with an axis defined in the laboratory system. Several experimental methods have been devised to align or orient molecules. These techniques and also theoretical approaches have been reviewed most recently by Stapelfeldt and Seideman.¹

In order that an orientation process is effective, the molecule under consideration must possess a strong permanent dipole moment. One class of molecules which do have this property are the alkali halides which, in their electronic ground state, have an ionic bonding character.² In a theoretical study, Machholm and Henriksen investigated the dynamics of alkali halide molecules, namely NaI and LiH in their electronic ground states³ and showed how an orientation can be achieved by the interaction with a half-cycle electric pulse. Also, in a recent study, the influence of a train of short laser pulses on the rotational dynamics of a molecule was studied.⁴ Here, we consider the rovibrational dynamics of NaI in a static electric field and demonstrate that the vibrational motion, subsequent to excitation to the first electronically excited state, induces a field-molecule interaction which resembles a train of pulses. Therefore we regard the excitation scheme as displayed in Fig. 1. Excitation of NaI from the ground state with a femtosecond pulse at about 310

nm results in the preparation of rovibrational wave packets evolving in various electronic states, where one of them (denoted as $|e\rangle$ in what follows) exhibits an avoided crossing with the ionic ground state. The induced wave packet dynamics in the nonadiabatically coupled system of two electronic states was the subject of early experimental⁵ and quantum dynamical studies⁶ in gas-phase femtosecond spectroscopy. After excitation from the electronic ground state $|g\rangle$, the prepared wave packet moves outward, reaching the crossing-point region at $R_c \sim 7 \text{ \AA}$. Due to the weak nonadiabatic coupling, most of the wave packet remains in the excited state and only a small fraction crosses over to the lower state, leading to fragmentation. In passing the crossing point R_c , the bonding character in $|e\rangle$ changes from covalent to ionic⁷ and, on the way back inwards, the situation is reversed. This scenario repeats itself until the predissociation is completed on a nanosecond time scale.⁸

Suppose now, the femtosecond induced predissociation takes place in a static electric field. As long as the vibrational wave packet is in the covalent region of the excited state potential, only a negligible interaction with the relatively moderate external field is present which is due to the extremely small permanent dipole moment at small distances. However, after the crossing takes place, one basically finds a classical dipole $\text{Na}^+ - \text{I}^-$ which strongly interacts with the static field. As time goes along and the wave packet re-enters the covalent region, the interaction is eventually switched off again, etc. As a result, the vibrational dynamics modulates the interaction as long as the vibrational wave packet is fairly localized.

In order to theoretically describe this situation, we have

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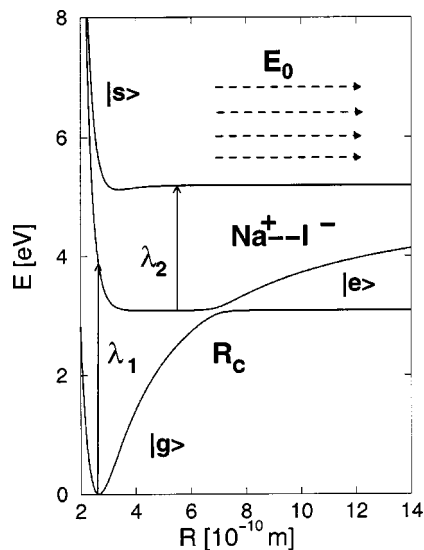


FIG. 1. Pump-probe ($\lambda_1 - \lambda_2$) excitation scheme for the NaI molecule. Within the electronic state $|e\rangle$, the bonding character changes from covalent ($R < R_c$) to ionic ($R > R_c$). If the vibrational wave packet is localized at distances $R > R_c$, the external electric field E_0 induces an orientation.

performed time-dependent quantum calculations for NaI molecules in a static field. Starting from the ground state of the molecule in the static field, a rovibrational wave packet $\Phi_e(R, \theta, t)$ is prepared. We calculate this function within first-order time-dependent perturbation theory, using a 50 fs Gaussian laser pulse with a carrier wavelength of 320 nm and a polarization vector pointing along the z -direction. After the pulse excitation, the wave packet's motion is determined by the Hamiltonian (atomic units are employed)

$$H_e^s = -\frac{1}{2m} \frac{\partial^2}{\partial R^2} + \frac{\mathbf{J}^2}{2mR^2} + V_e(R) - \mu_e(R)E_0 \cos \theta, \quad (1)$$

acting on the "reduced wave function" $\psi_e(R, \theta, t) = R\Phi_e(R, \theta, t)$, where Φ is the complete wave function. Here the superscript (s) indicates that the Hamiltonian contains the static field perturbation. The angular momentum operator is denoted as \mathbf{J} and V_e is the potential energy in state $|e\rangle$. Furthermore, m denotes the reduced mass of the molecule, $\mu_e(R)$ is the permanent dipole moment depending on the vibrational coordinate R , E_0 is the strength of the static electric field pointing in z -direction and θ is the polar angle.

The potential curves, as displayed in Fig. 1 are taken from the model described in Ref. 9 and the dipole moment is taken from Ref. 10. Here we treat only the wave packet motion in the adiabatic state $|e\rangle$, i.e., the predissociation channel is closed which, since the nonadiabatic coupling is weak, is a reasonable approximation for the times we regard.¹¹ The numerical time-propagation is performed employing a splitting approximation¹² to the short-time propagator as

$$U_e^s(t) = e^{\lambda V_e^s(R, \theta)/2} e^{\lambda T(R)/2} e^{\lambda \mathbf{J}^2/(2mR^2)} e^{\lambda T(R)/2} e^{\lambda V_e^s(R, \theta)/2}, \quad (2)$$

where $\lambda = -i\Delta t$ and Δt is a short time step. The sum of the interatomic potential V_e and the interaction term has been

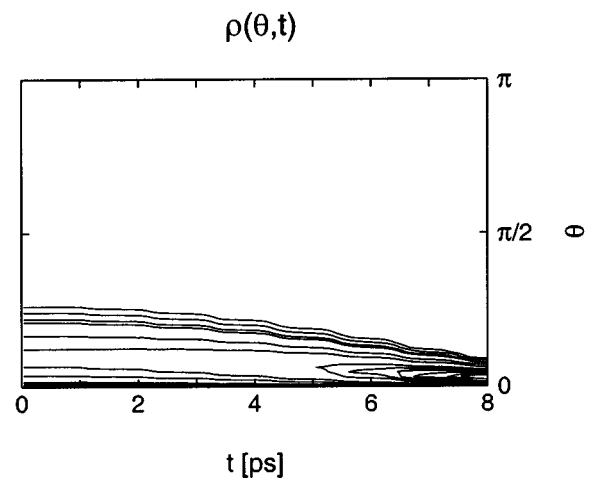
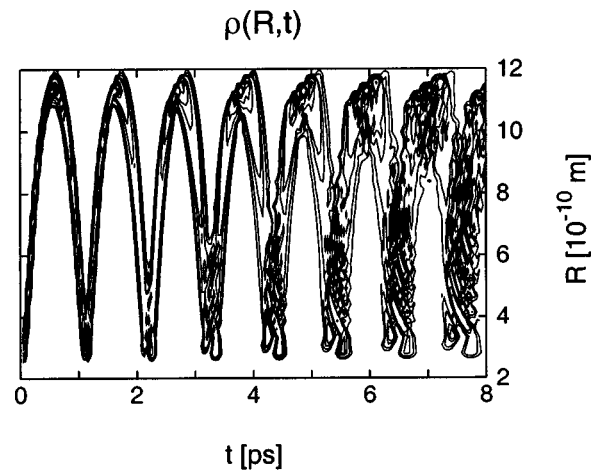


FIG. 2. Rotational and vibrational dynamics in a static field of 4×10^6 V/m. Contour plots of the radial (upper panel) and the angular (lower panel) densities are shown. The radial density shows a vibrational motion with a period of about 1 ps. At longer times, a rotational wave packet is prepared which is localized along the field direction at $\theta = 0$.

denoted as $V_e^s(R, \theta)$ in the latter equation. The action of the exponential containing the vibrational kinetic energy operator $T(R)$ is evaluated in momentum space. To treat the operator containing \mathbf{J}^2 , the wave function, which is represented on a two-dimensional grid of points (R_n, θ_m) , is expanded in terms of spherical harmonics $Y_{J0}(\theta)$. The expansion terms are then multiplied with the respective phase factors $e^{\lambda J(J+1)/(2mR^2)}$ and the resummation is performed.

The rovibrational dynamics of NaI in a static field of $E_0 = 4 \times 10^6$ V/m is displayed in Fig. 2 which contains the radial and angular densities

$$\rho(R, t) = 2\pi \int_0^\pi d\theta \sin \theta |\psi_e(R, \theta, t)|^2, \quad (3)$$

$$\rho(\theta, t) = 2\pi \int_0^\infty dR \sin \theta |\psi_e(R, \theta, t)|^2. \quad (4)$$

Note that, since we are working with the reduced wave function $\psi_e(R, \theta, t)$, the volume element is just dV

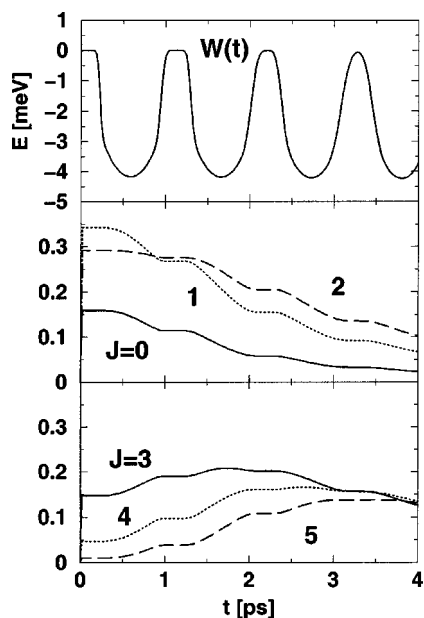


FIG. 3. Upper panel: Time-dependent expectation value of the interaction energy $W(t)$ between the molecule and the static field ($E_0 = 4 \times 10^6$ V/m). The lower panels show the population $P_J(t)$ corresponding to different rotational quantum numbers J , as indicated.

$= dR d\varphi d\theta \sin \theta$. The radial density clearly shows the vibrational motion of the wave packet. It remains rather localized, moving back and forth with a vibrational period of approximately 1 ps. As time goes along, the angular density exhibits an orientation around the direction of the applied field. This implies that, through the interaction with the static field, a more compact rotational wave packet is prepared. Note, that here we regard times shorter than typical rotational periods of freely rotating NaI molecules.³

In order to get more insight into the nature of the rotational excitation and the interplay between rotational and vibrational motion, we calculate the expectation value of the field-molecule interaction as

$$W(t) = -\langle \psi_e(R, \theta, t) | \mu_e(R) E_0 \cos \theta | \psi_e(R, \theta, t) \rangle. \quad (5)$$

This quantity is shown in Fig. 3, upper panel. As was argued above, the interaction is only effective at times, when the radial density is located in the ionic branch of the adiabatic potential. As a consequence, the molecular sample experiences a perturbation which is modulated with the vibrational period. In fact, the time-dependent interaction energy resembles a train of half-cycle pulses. This pulselike interaction is responsible for the rotational excitation which can be characterized by the populations $P_J(t) = |\langle Y_{J0} | \psi_e(t) \rangle|^2$ in different angular momentum eigenstates. The populations are displayed, for selected values of J , in the two lower panels in Fig. 3. Due to the static field, the initial state (at $t=0$) is composed out of several angular momentum eigenstates.¹³ We note that, at 8 ps, the rotational distribution $P_J(t)$ has its maximum at $J=6$ and a width (full width at half maximum) of $\Delta J=10$. A comparison of the population curves with the interaction function $W(t)$ shows that at times the latter function is nonzero, rotational excitation takes place. This, again, underlines the concept of a dynamically induced pulse-train.

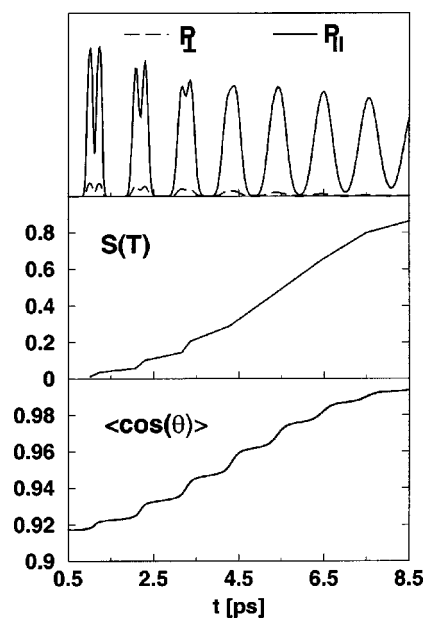


FIG. 4. Upper panel: Pump-probe signals for a probe pulse with a parallel (P_{\parallel}) and a perpendicular (P_{\perp}) polarization relative to the applied static field. Middle panel: Ratio of signals $S(T) = (P_{\parallel}(T) - 11P_{\perp}(T)) / (P_{\parallel}(T) + 11P_{\perp}(T))$. The lower panel shows the expectation value of $\cos(\theta)$.

We now consider the question of how to detect the orientational dynamics in the present system. Therefore, a pump-probe arrangement may be devised⁵ where in an additional probe-step (λ_2) an excitation to a higher electronic state $|s\rangle$ is induced at a delay time T , see Fig. 1. Then, the fluorescence yield from this state, detected as a function of the pump-probe delay is measured. Let us discuss the case of a parallel transition, where the transition-dipole moment points along the molecular axis (for a perpendicular transition the following argumentation has to be reversed). When a preferred orientation has been created, the pump-probe signal will be maximized if the probe-pulse polarization is chosen to be parallel (\parallel) to the static field. On the other hand, for a probe polarization perpendicular (\perp) to the static field direction, the signal will be minimal.

We calculated pump-probe signals for both probe-pulse polarizations employing a short pulse-length of 10 fs width and a carrier wavelength of 590 nm. In this case, the accessed state $|s\rangle$ corresponds to the asymptotic configuration $\text{Na}(^2P) + \text{I}(^2P_{1/2})$,⁵ and a parallel transition takes place. The populations in the upper state $|s\rangle$ which are assumed to be proportional to the fluorescence signal, are shown in Fig. 4, upper panel. They resemble the signals as detected in the case where no static field is present.⁵ For the employed wavelength, a transition is possible only in the covalent region of the potential, i.e., excitation is most probable around a bond-length of 5.7 Å. Thus, the maxima of the signal occur at times when the vibrational wave packet is located in this region and the forth and back motion induces the double peak structure¹⁴ at early times where the vibrational wave packet is well localized. The signal for the (\parallel) case is initially a factor of about 11 larger than the one for the (\perp) polarization.

In order to find the efficiency of the orientation, we calculate the ratio:

$$S(T) = \frac{P_{\parallel}(T) - 11P_{\perp}(T)}{P_{\parallel}(T) + 11P_{\perp}(T)}, \quad (6)$$

which, initially, is zero and for the case of perfect orientation approaches a value of 1. Figure 4, middle panel, contains the ratio $S(T)$ which was calculated at the maxima of the pump–probe signals (upper panel). We see that already after 5 ps, the ratio assumes a value of 0.5, suggesting an effective orientation. For comparison, we also show the expectation value of $\cos(\theta)$ (lower panel of Fig. 4) which is commonly chosen as a measure of orientation. Note, that the initial “field dressed” state yields a value larger than 0.9 for the expectation value. This number increases to become almost equal to one at 8 ps.

We have performed additional calculations for stronger static fields. The results are similar to the ones as presented here. As expected, with increasing field strength, the orientation occurs at earlier times. There is, however, the issue of the predissociation lifetimes and their dependence on the external perturbation. In order to investigate this question we plan to perform extensive calculations including the predissociation channel.

To conclude, we have shown how vibrational wave packet dynamics accompanied by an oscillating charge transfer between covalent and ionic states, can induce a time-dependent interaction with a static electric field. In the present case we find an interaction which resembles a train of

pulses. This then goes in hand with an orientation of the molecular sample. It has to be kept in mind that, at longer times, the vibrational wave packet disperses so that there are always molecules which are subject to the static field and others which are not. It is an interesting question of how the rovibrational dynamics will behave for longer times. We are currently building up a femtosecond pump–probe experiment to test the predictions as given in this paper.

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