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Off-resonant vibrational excitation: Orientational dependence and spatial control of photofragments

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Off-resonant and resonant vibrational excitation with short intense infrared (IR) laser pulses creates localized oscillating wave packets, but differs by the efficiency of the excitation and surprisingly by the orientational dependence. Orientational selectivity of the vibrational excitation of randomly oriented heteronuclear diatomic molecules can be obtained under simultaneous irradiation by a resonant and an off-resonant intense IR laser pulse: Molecules with one initial orientation will be vibrationally excited, while those with the opposite orientation will be at rest. The orientation-dependent response to the IR fields is due to the anharmonicity of the potential. A subsequent ultraviolet laser pulse in resonance at the outer turning point of the vibrational motion can then dissociate the oscillating molecules, all with the same orientation, leading to spatial control of the photofragment distribution. © *2000 American Institute of Physics.* [S0021-9606(00)01642-1]

I. INTRODUCTION

The goal of laser control[1,2] is to obtain high selectivity in photochemical processes, e.g., selective bond breaking of polyatomic molecules. Laser induced wave packet (WP) dynamics in the electronic ground-state potential well has been proposed as an initial step in a two-step ''pump–pump'' control scheme for selective bond breaking in small polyatomic molecules.[3–5] It was shown that an intense IR pulse can induce oscillations of a WP. In a nearly harmonic potential well, the WP will stay localized preserving the initial width, while the amplitude of the oscillations will increase in the presence of the IR pulse. The amplitude of the oscillations can easily be several times the width of the WP. With two molecular bonds oscillating out of phase, e.g., an asymmetric stretch, one of the bonds can be broken selectively if a short ultraviolet (UV) laser pulse is applied at an appropriate time. In a model keeping the orientation of the molecule fixed with respect to the laser polarization axis, high selectivity for breaking a specific bond in, for example, $^{16}O^{16}O^{18}O$ was demonstrated.

Many apparently promising control schemes give less satisfactory results, when we take into account the effect of initial random orientation of molecules in a typical gas phase experiment. However, in some cases the molecules can be aligned or even oriented prior to the control step.[6] To that end, a scheme for the orientation of polar molecules was presented recently, based on the simultaneous irradiation with two infrared (IR) laser frequencies.[7]

Alternatively, we can selectively make use of molecules with a fixed initial orientation and leave molecules with other orientations untouched by the photochemical process. We demonstrate in this paper that simultaneous irradiation with two intense IR laser pulses may force the WP dynamics on the electronic ground-state potential surface such that molecules with one initial orientation will oscillate when the field is turned off, while molecules initially with the opposite orientation will be at rest. If only excited (oscillating) molecules are accessed in the second step of the control scheme, only molecules with one initial orientation will participate in the photochemical process and high selectivity can be obtained.

We investigated recently a heteronuclear diatomic molecule in an intense IR field, in particular, the effect of the initial orientation of the molecules with respect to the polarization vector in three dimensions. We found that the phase of the WP oscillations depends on the initial orientation of the molecule or more precisely depends on the orientation of the permanent dipole moment in the electronic ground state: Two molecules initially with opposite orientation will oscillate out of phase.[8]

One way to overcome the problem caused by initial isotropic orientation of molecules in an experiment will be to orient the sample of molecules prior to the application of the IR pulse. We propose in this paper an alternative scheme: Two IR laser pulses, one having a one-photon resonance with the $v=0 \rightarrow v=1$ transition, the other having a two-photon resonance with the same transition, are applied on a sample of randomly oriented molecules. All molecules aligned along the laser polarization will oscillate while the laser fields are present, but we will demonstrate that as the field intensity decreases, molecules with one initial orientation will continue to oscillate while the oscillations of initially oppositely oriented molecules will be damped and eventually completely die out. Thus, if the second bond breaking step in the above ''pump–pump'' control scheme is applied after the IR pulses have disappeared, it may only interact with the oscillating molecules, which are all oscillating in phase with the same orientation, see Fig. 1.
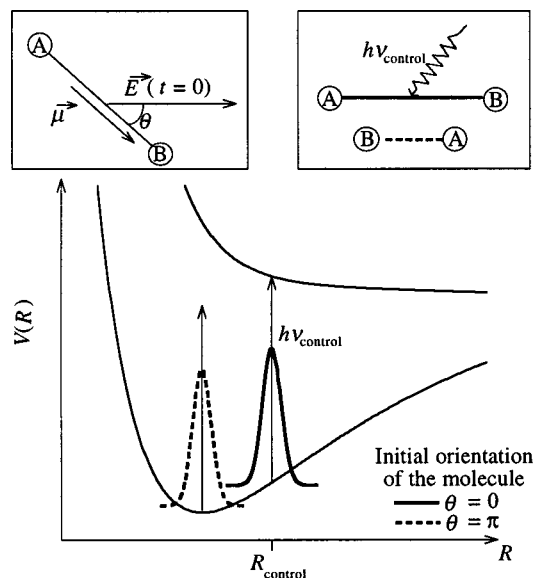
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FIG. 1. Control scheme for selective dissociation of a heteronuclear diatomic molecule AB. θ is the angle between the permanent dipole moment $\hat{\mu}$ and the electric field vector $\hat{E}$ of the linearly polarized laser field. Molecules with an orientation corresponding to $\theta=0$ are vibrationally excited whereas molecules with the opposite orientation are left in the vibrational ground state. The vibrationally excited molecules are in resonance with respect to the electronic transition at the outer turning point.

The phenomenon presented is indeed a kind of coherent control. The two IR pulses have to be phase locked, and the relative phase of the IR pulses determines which molecules will end up oscillating. For simplicity the effect is demonstrated on heteronuclear diatomic molecules. The computational models, which were presented in Ref. 8, are extended to include two IR laser pulses in Sec. II. The control scheme is applied to the heavy NaI and the light LiH molecule. The orientational dependence for off-resonant vibrational excitation is discussed in Sec. III, and we show that the phenomenon is due to the anharmonicity of the nearly harmonic electronic ground-state potential. The response to the combined resonant and off-resonant field is presented in Sec. IV, and used for the proposed control scheme in Sec. V. The implications for polyatomic molecules will be considered in the concluding Sec. VI.

II. TIME-DEPENDENT CALCULATION

The theoretical model used is the same as in Ref. 8 except that the IR laser field now consists of two components,

$$E_{IR}(t)=E_{IR,1}(t)\cos(\omega_{off}t)+E_{IR,2}(t)\cos(\omega_{res}t+\phi), \quad (1)$$

where $E_{IR,i}(t)$ is Fourier transform limited Gaussian pulse shape functions. The off-resonant field has been chosen with $2\omega_{off}=\omega_{res}$, where the resonance is to the first vibrational excitation ($v=0\rightarrow v=1$) in the electronic ground state. We solve the time-dependent Schrödinger equation by wave packet propagation with a splitting of the short-time propagator. The kinetic term is evaluated in the momentum space using fast Fourier transformation (FFT) between coordinate (R) and momentum (k) representation, and the potential energy term and the interaction term are split further to avoid

numerical diagonalization at each time step and R-grid point, as in Ref. 9. Calculations are performed both in a one- and a three-dimensional model. In the one-dimensional (1D) model the molecular axis is aligned with the polarization axis of the laser field, and the permanent dipole moment has two possible orientations depending on the initial orientation of the molecule. In the three-dimensional (3D) model the wave function is expanded in spherical harmonics. With the linearly polarized laser field we get the selection rule $\Delta m=0$, which limits the number of states involved in each 3D calculation.

We follow the WP dynamics by calculating the expectation value of R, $\langle R \rangle$, and the standard deviation: $\Delta R = \sqrt{\langle R^2 \rangle - \langle R \rangle^2}$ as a function of time. In the 1D model, $\langle R \rangle$ and ΔR are calculated only for $\theta=0$ and π, where θ is the angle between the internuclear axis and the polarization vector of the field.

Orientation-dependent WP oscillations induced by the IR pulses allow us to control the spatial photofragment distribution in a subsequent dissociation via an excited state. A delayed UV laser pulse excites the molecules having a bond length around $R_{control}$ (see Fig. 1) to a dissociative electronic state. In the calculations where the control step is included the WP is propagated on the coupled ground and excited states. We calculate probabilities for excitation to the excited state and investigate the dependence on the initial orientation.

The initial state is in all cases the vibrational ground state $v=0$ and the corresponding wave function is the numerically exact wave function in the grid representation. The 3D calculations are carried out for an initial $l=0$, $m=0$ state unless otherwise stated. The effect of a thermal averaged sample is discussed in Secs. III and IV.

The model is applied to NaI and LiH. The potentials and dipole moments are taken from Refs. 10 and 11, respectively, and calculated according to semiempirical valence-bond theory. A good representation of the NaI potential (around the equilibrium position) is given by the Morse potential $V(R)=D\{1.0-\exp[-\beta(R-R_e)]\}^2$, where $D=3.48$ eV, $\beta=0.90$ Å^{-1}, $R_e=2.68$ Å, and -0.3 Å$<R-R_e<0.3$ Å.

III. ORIENTATION DEPENDENCE IN OFF-RESONANT FORCED WP MOTION

The efficiency of forcing vibrational motion in the ground-state potential well depends strongly on the frequency of the forcing field. If the IR field is in resonance with the first vibrational transition, a moderately intense field ($I>10^8$ W/cm^2) will make the WP oscillate. Off-resonant forcing is much less efficient than resonant forcing of the WP motion of a bound molecule. Therefore we need higher field intensities, approximately 250 times larger than in the resonant case to obtain the same amplitude of WP oscillations at the peak of the pulse. This can be seen by comparison of Figs. 2(a) and 2(b). In both cases the WP will oscillate with the frequency of the field, and the WP will stay localized. For the resonant case, energy is efficiently deposited in the vibrational mode, and the WP is oscillating with the eigenfrequency. In the special case of $2\omega_{off}=\omega_{res}$, we see
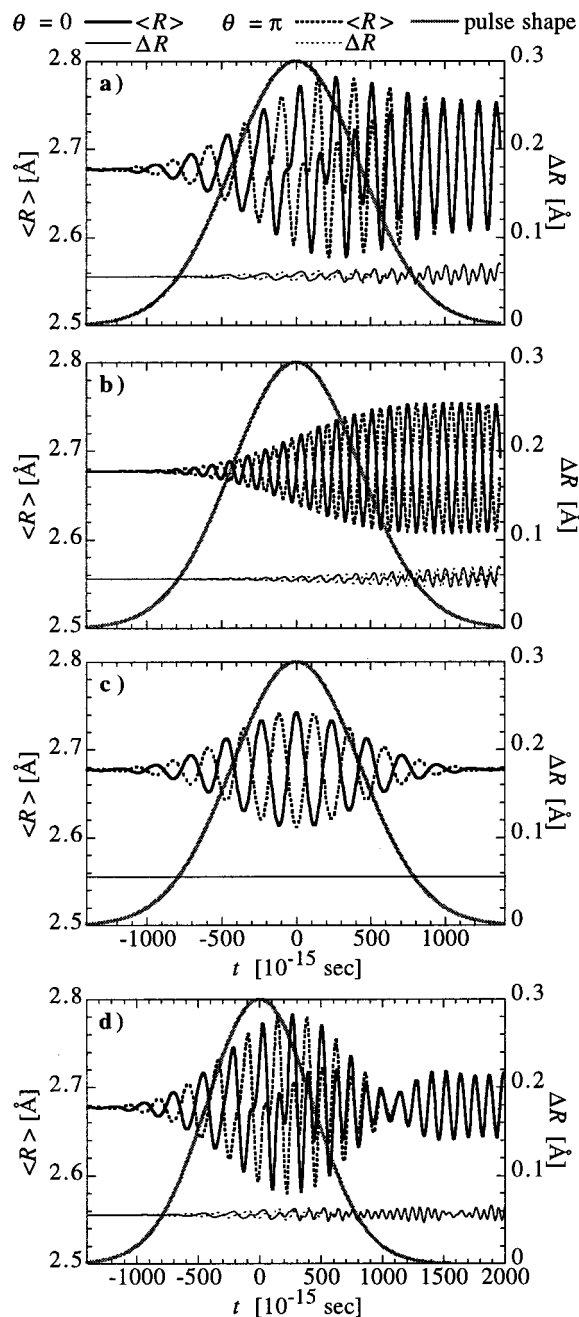
FIG. 2. The expectation value of the bond length $\langle R \rangle$ as a function of time depending on the initial orientation of the NaI molecule. (a) 1D model, off-resonant, (b) 1D model, resonant, (c) 1D model, off-resonant in harmonic potential, and (d) 3D model, off-resonant. $\hbar\omega_{\text{off}} = 140\,\text{cm}^{-1} = 0.5 \times \hbar\omega_{\text{res}}$, $I_{\text{off}} = 10^{12}\,\text{W/cm}^2$, and $I_{\text{res}} = 3 \times 10^9\,\text{W/cm}^2$ [in (b)]. Pulse length for intensity $T_{\text{FWHM}} = 714\,\text{fs}$, equivalent to a pulse length $T_{\text{FWHM},E} = 1010\,\text{fs}$ for the E-field, as shown in the figures.

WP oscillations with the frequency of the field during the pulse and toward the end of the pulse transfer of energy to the vibrational mode. If the two-photon resonance criterion is not fulfilled, the WP will still oscillate with the field frequency, but the energy transfer is negligible, thus the amplitude of the WP oscillations follows the field strength of the pulse, and the molecule returns to rest when the field vanishes.

Now, the dependence on the initial orientation of the molecule is very different in the resonant and the off-

resonant cases. The resonant case was discussed in detail in Ref. 8, and we found that molecules with opposite orientations will oscillate out of phase, as seen in Fig. 2(b). In the off-resonant case the slow oscillations with the frequency of the field show the same out-of-phase WP oscillations as in the resonant case. However, when the vibrational energy is transferred to the vibrational mode, all molecules will oscillate in phase. Figure 2(a) shows this orientational effect: During the transition to the fast oscillations the WP gets an additional outward acceleration at the inner turning point, and the fast oscillations build up with two periods placed within one of the slow oscillations. Therefore all molecules are oscillating in phase at the end of the off-resonant IR pulse.

The energy transfer from the off-resonant field to the molecular vibration, and the orientational effect, is due to the anharmonicity of the molecular potential well. In the Appendix of Ref. 8, we derived an analytic expression (A15) for the WP motion in a harmonic potential. According to that expression, molecules which initially have opposite orientation will always oscillate out of phase. Furthermore, for an off-resonant Gaussian pulse, the amplitude of the WP motion is approximately proportional to $n \exp[-n^2\pi^2/(2\ln 2)]$, after the pulse has vanished, n being the number of optical cycles within the pulse. Thus, the amplitude will be negligible in the present case where $n \sim 5$. The numerical simulation in Fig. 2(c) confirms this result. In this calculation the NaI ground-state potential has been replaced by a corresponding harmonic potential. At short times, as long as the amplitude is small, the oscillations in the anharmonic and the harmonic potential are very similar. In the harmonic potential, the WP oscillates with the frequency of the driving field, while the field amplitude is large. At the peak of the pulse the amplitude of the WP motion is 60% of what we find in the anharmonic potential. The oscillations vanish as the field strength goes to zero. Thus, the energy transfer from the off-resonant field to the molecular vibration and, in particular, the orientational effect, is due to the anharmonicity of the molecular potential.

The amplitude of the WP oscillations as a function of the field strength also reveals the importance of the anharmonicity of the potential. The amplitude of the slow oscillations during the pulse is proportional to the field strength E ($\propto \sqrt{I}$). This is the same intensity dependence as found in the case of a resonant field. Yet, the amplitude of the fast oscillations after the IR pulse increases faster than $E^2 (\propto I)$. The ratio of the fast to slow amplitudes increases from 1.6% to 71% when I changes from 10^8 to $10^{12}\,\text{W/cm}^2$. Thus, the coupling to the vibrational mode of the molecule only becomes large when the WP is moved far from the equilibrium position to regions where the anharmonicity is important.

To further test the dependence on the anharmonicity we have performed some simulations with a potential of the form $V(R-R_e) = \alpha(R-R_e)^2 + \beta(R-R_e)^3$, where α is fixed by the vibrational resonance frequency of the NaI molecule, and β is varied between 0 and a value corresponding to a good representation of the anharmonicity found in the full NaI potential. For $\beta \neq 0$, post-pulse oscillations are seen, and in all cases they are in phase for oppositely oriented mol-
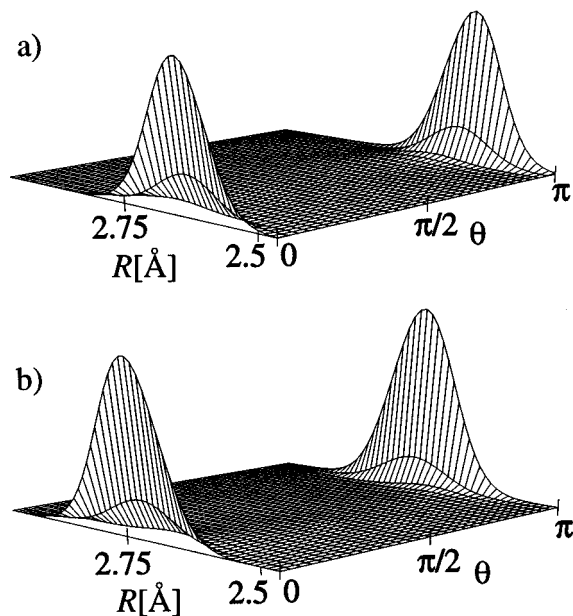
a)

b)

FIG. 3. The nuclear wave packet of NaI in the off-resonant IR field, corresponding to Fig. 2(d). The molecules are strongly aligned along the polarization axis of the IR field. (a) The molecular bond compressed, $t = 682$ fs. (b) The molecular bond stretched, $t = 742$ fs.

ecules. The amplitude of the fast post-pulse oscillations varies approximately linearly with β.

The orientational effect described above seems to be quite robust with respect to the form of the pulse shape function, as long as it is reasonably smooth. Thus, the result is unchanged when the pulse length of the Gaussian pulse is reduced or when a sine-square pulse is employed. The in-phase oscillations for oppositely oriented molecules disappears, however, for a rectangular pulse shape function.

The full 3D calculation qualitatively agrees with the 1D results [Figs. 2(a) and 2(d)]. The oppositely oriented molecules oscillate in phase. Yet, some differences occur. In the resonant case discussed in Ref. 8, we showed perfect agreement between the 1D and 3D model, and interpreted this as the absence of coupling between the rotational and vibrational motion, allowing us to represent the full 3D simulations as a sum over θ of independent 1D simulations. The resonant field only makes very small changes to the angular distribution, even if the intensity is increased to the same value as the off-resonant field, $I = 10^{12}$ W/cm^2.

The off-resonant field changes the angular distribution: The molecules become strongly aligned along the polarization axis of the field even after the field has vanished, see Fig. 3. The degree of alignment is not constant, and at times with extreme degree of alignment, the vibrational motion is reduced, as around $t = 1000$ fs in Fig. 2(d). A rotational wave packet is created by the off-resonant field, thus the complete dynamics of the system cannot be represented by independent 1D simulations in the off-resonant case.

Many l states are populated in the off-resonant case due to the high intensity of the laser field. For $I = 10^{11}$ W/cm^2 about 20 l states get a population above 10^{-6}, for $I = 10^{12}$ W/cm^2 about 30 l states are involved. We use a basis of $l_{max} = 50$–80, depending on the field strength. The reso-

nant case in Ref. 8 had fewer l states involved due to lower intensity, but for a simulation with a resonant field of the same intensity as the present off-resonant fields, a similar number of l states is involved at the peak of the pulse. The final l-state distribution only contains even or odd l states, depending on $l_{initial}$ being even or odd. For $I = 10^{12}$ W/cm^2 and $l_{initial} = 0$, the final distribution has a maximum at $l = 16$. In the resonant case the final population was mainly in $l = l_{initial} \pm 1$.

Now, we consider the effect of the initial rotational state. In Ref. 8, we showed that the results for resonant forcing of the WP are robust to thermal averaging under typical conditions in gas phase experiments using supersonic expansion ($T < 10$ K). The above results are obtained with the rotational ground state as the initial state. In an experiment, a molecular beam produced by supersonic expansion will be rotationally cold, but with a finite rotational temperature, typically $T < 10$ K. At 5 K the $l = 3$, and at 10 K the $l = 5$ state, is the most populated level for NaI, and more than 90% of the population is in $l \leq 7$ and $l \leq 10$, respectively. We have performed independent simulations for different initial (l, m) states determining the wave function $\Psi_{lm}(R, \theta, t)$, which is represented in a basis of (l', m) states. By integration over R and sum over l', we calculate the $l_{initial}$-dependent weighted sum of all the m states,

$$\langle R - R_e \rangle_l (\theta, t) = \frac{\sum_m \langle R - R_e \rangle_{lm}(\theta, t) \text{norm}_{lm}(\theta, t)}{\sum_m \text{norm}_{lm}(\theta, t)}, \quad (2)$$

where

$$\text{norm}_{lm}(\theta, t) = \int_{R_{min}}^{R_{max}} \Psi_{lm}^*(R, \theta, t) \Psi_{lm}(R, \theta, t) dR \quad (3)$$

and

$$\langle R - R_e \rangle_{lm}(\theta, t) = \int_{R_{min}}^{R_{max}} \Psi_{lm}^*(R, \theta, t) R \Psi_{lm}(R, \theta, t) dR - R_e. \quad (4)$$

The WP's with different $l_{initial}$ oscillate in phase and with approximately the same amplitude. At times with very high degree of alignment some differences are seen. In conclusion, the off-resonant results are more sensitive to thermal averaging than the resonant case in Ref. 8, which was effectively independent of $l_{initial}$. But for low temperatures ($T < 5$ K) a thermal average over $l_{initial}$ will not destroy the qualitative result. In case the complications from the thermal average are to be eliminated, a single $l_{initial}$ can be selected prior to the application of the IR field.[12]

IV. WP MOTION FORCED BY TWO IR FIELDS

In this section we demonstrate that a superposition of the in- and out-of-phase WP oscillations obtained above in the off-resonant and the resonant cases is very useful in creating an orientation-dependent response to IR fields. To that end, we note that for a one-dimensional harmonic oscillator, it can be shown analytically that a superposition of fields as in Eq. (1) gives an expectation value of the position corresponding to a classical superposition of the effect of each field without interference terms.[8]
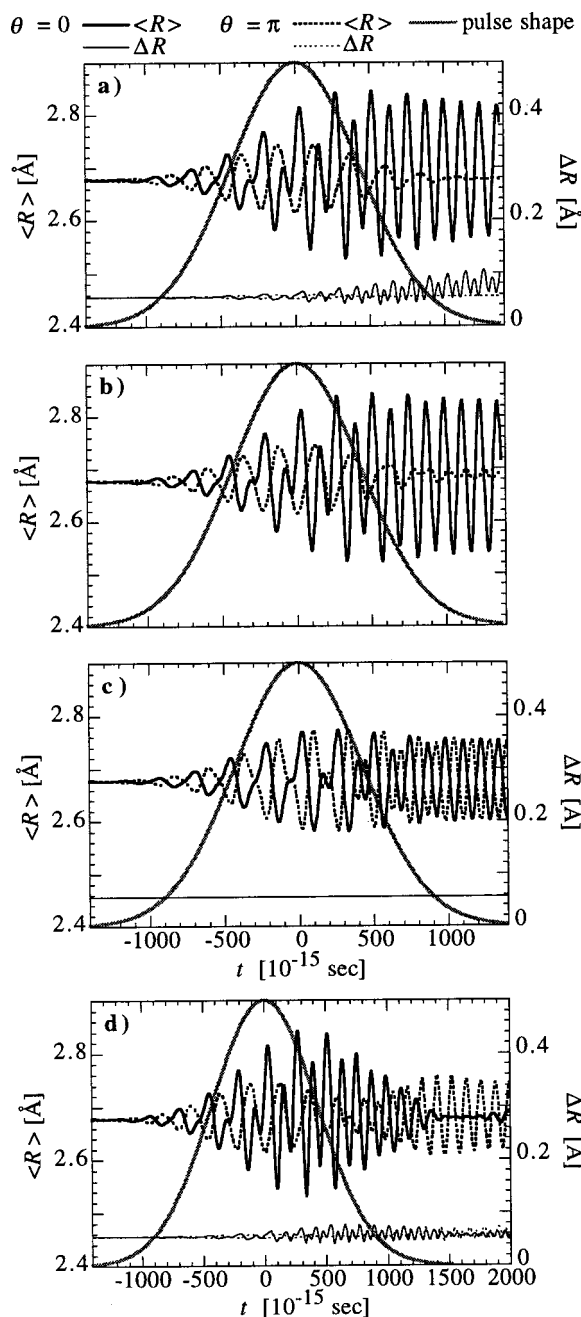
FIG. 4. Forcing WP dynamics with two IR fields. $T_{FWHM}=714$ fs, $\hbar\omega_{off}=140$ cm$^{-1}=0.5\times\hbar\omega_{res}$, $I_{off}=10^{12}$ W/cm^2, $I_{res}=3\times10^9$ W/cm^2, (a)–(c) 1D model, (b) addition of off-resonant and resonant result in Figs. 2(a) and 2(b),(c) harmonic potential with parameter of the NaI molecule, (d) 3D model.
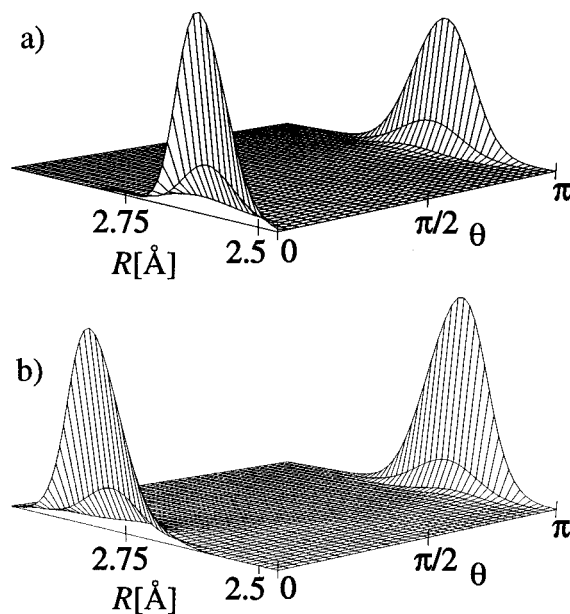

FIG. 5. The nuclear wave packet of NaI corresponding to Fig. 4(d). (a) $t=682$ fs: WP ($\theta=0$) at the inner turning point, (b) $t=742$ fs: WP ($\theta=0$) at the outer turning point. Notice that the molecules at $\theta=\pi$ are at rest around R_e.

Figure 4(a) shows the WP motion resulting from forcing with a combined resonant and off-resonant IR field. After the pulse vanishes, molecules with an initial orientation corresponding to $\theta=0$ oscillate, while those with $\theta=\pi$ are at rest. The relative phase of the two IR fields [the phase ϕ in Eq. (1)] controls which molecules are oscillating. In Fig. 4(a) $\phi=0$, if $\phi=\pi$ the molecules at $\theta=\pi$ will be oscillating and those at $\theta=0$ will be at rest.

The amplitude of the WP oscillations is slightly less than that of the sum of the amplitudes for the resonant and off-resonant fields alone, 0.25 Å compared to 2×0.14 Å [com-

pare Fig. 4(a) with Figs. 2(a) and 2(b), at $t=1400$ fs]. Thus, the two-field orientation-dependent WP motion is, essentially, a classical superposition corresponding to the addition of the contributions from each of the fields. In Fig. 4(b) the amplitude of the WP motion obtained as the sum of the independent off-resonant and resonant WP motion $[(\langle R\rangle_{off}-R_e)+(\langle R\rangle_{res}-R_e)+R_e]$ is shown. Compared to the simultaneous application of the two IR fields [Fig. 4(a)] only very small differences can be seen, especially in the $\theta=\pi$ orientation, where the two fields cancel the WP motion better than the added results from the two independent calculations.

Again we see that the orientational effect depends on the anharmonicity of the potential. Figure 4(c) shows the two-field forced WP motion in a purely harmonic potential. When the pulse vanishes the WP is left oscillating as in the case of only resonant forcing.

The 3D result qualitatively agrees with the 1D results: The molecules in one hemisphere are at rest, while the molecules in the other hemisphere are oscillating, see Fig. 4(d). In Fig. 5, two snapshots of the corresponding WP show the angular dependent WP oscillations. For $\theta=0$, the WP is at the inner or outer turning point in Figs. 5(a) and 5(b), respectively. For $\theta=\pi$, the WP is at rest. Note the WP is well localized in R. The WP is strongly aligned along the polarization axis of the field. This is due to the off-resonant component of the IR field, as discussed in Sec. III.

The strong alignment and mixing of l states are the main limitations to the robustness of the results. The result is qualitatively independent of $l_{initial}$ when the WP is not too strongly aligned. The WP aligns when the pulse is vanishing. The time the WP is most focused depends on the intensity of the IR field; the stronger the field the earlier the WP focuses in θ. This limits the off-resonant field strength to $I_{off}\lesssim10^{12}$ W/cm^2. With $I_{off}<10^{11}$ W/cm^2 the amplitude of

the WP oscillations becomes too small to be useful for the below described control scheme.

The maximum l state involved is the same for the combined IR fields as for the off-resonant IR field alone. Again the even or odd l states dominate the final distribution depending on l_{initial} being even or odd. For the combined IR fields the difference between even and odd states is about one order of magnitude, for the off-resonant field alone the difference is three orders of magnitude.

We have also applied the 1D and 3D models on LiH to test the effect of molecular mass (the reduced mass of LiH is 22 times smaller than that of NaI). The 1D model works equally well for LiH and NaI. But the alignment seen in the LiH 3D case becomes even more pronounced than for NaI, and therefore the upper intensity limit becomes $I_{\text{off}} \lesssim 10^{11}$ W/cm^2, and the amplitude of WP oscillations is too small to be useful.

V. CONTROLLING THE SPATIAL DISTRIBUTION OF PHOTOFRAGMENTS

Previously, we have demonstrated that the orientation-dependent out-of-phase WP oscillations can be utilized in a control scheme for the dissociation of molecules with a selected initial orientation, resulting in spatially separated photofragments. For NaI, e.g., Na fragments into one hemisphere and I fragments into the other.[8] The controlling UV laser pulse dissociating the molecules was fulfilling the following criteria: (i) providing resonant excitation to a dissociative electronic state around the outer turning point of the WP oscillations (in Fig. 1, at R_{control}), (ii) pulse length shorter than the vibrational period of the molecule and centered at a time where molecules with the selected initial orientation are stretched to the maximum. Many molecules oscillate fast (≈ 10 fs), thus the second criterion demands very short UV laser pulses. These pulses may be difficult to generate experimentally, but more crucially to the control scheme: They are very broad banded, thus the first criterion becomes difficult to fulfill, because eventually the excitation to the dissociative state will be resonant in the full range of the WP oscillations. The two criteria limit the pulse length with both an upper and lower boundary.

In the present case only molecules with a selected initial orientation are left oscillating after the intense IR pulses vanish. Molecules with the opposite orientation never reach R_{control}. Thus, criterion (ii) is not needed. In fact, a long pulse length only means that molecules will dissociate every time the WP passes the R_{control} region.

In Fig. 6(a), a control UV pulse of 90 fs has been applied and we analyze the orientation-dependent probability for excitation to the dissociative state. The selectivity of the photofragment orientation is quantified by

$$D = \frac{P(\theta=0)-P(\theta=\pi)}{P(\theta=0)+P(\theta=\pi)}, \quad (5)$$

which is in the range from -1 [when $P(\theta=0)=0$] to 1 [when $P(\theta=\pi)=0$]. We also consider the total excitation probability, in the 1D case given by $P(\theta=0)+P(\theta=\pi)$. The frequency of the UV pulse, and thereby the position of
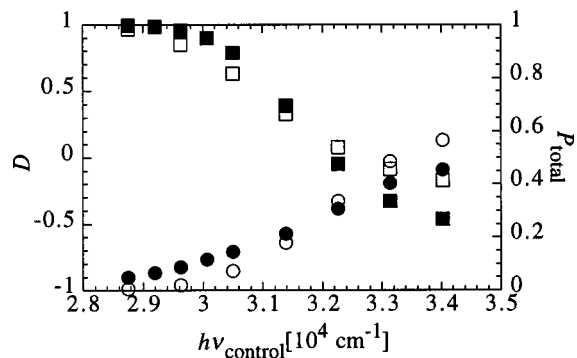

FIG. 6. Frequency dependence of the selectivity parameter $D=[P(\theta=0)-P(\theta=\pi)]/[P(\theta=0)+P(\theta=\pi)]$ and the total probability for transition to the excited state $P_{\text{total}}=P(\theta=0)+P(\theta=\pi)$. 1D calculation. $T_{\text{peak,UV}}=2015$ fs and $I_{\text{UV}}=10^{12}$ W/cm^2 and $T_{\text{FWHM,UV}}=95$ fs. Circles: P_{total}, squares: D. Filled symbols: $I_{\text{res}}=3\times10^9$ W/cm^2, $I_{\text{off}}=10^{12}$ W/cm^2, open symbols: $I_{\text{res}}=8\times10^8$ W/cm^2, $I_{\text{off}}=5\times10^{11}$ W/cm^2.

R_{control}, is varied. To obtain high selectivity, R_{control} has to be displaced far from R_e, further than in the control scheme discussed in Ref. 8. In that case the oppositely oriented molecules oscillated out of phase, that is the $\theta=\pi$ molecules were compressed below R_e when the $\theta=0$ molecules were moved to R_{control}. Yet, we obtain $D>0.995$ in the best case shown in Fig. 6.

Figure 7 shows an example of the orientational dependence of the probability for excitation to the excited electronic state as resulting from a 3D simulation. A clear orientational selectivity is demonstrated with preferred excitation for molecules oriented with $\theta=0$. Compared to the selectivity obtained with only a resonant IR field and a very short UV pulse in Ref. 8, the forward/back selectivity is slightly reduced. However, due to the alignment caused by the off-resonant IR field, the photofragments will be ejected with a very narrow angular distribution around $\theta=0$.
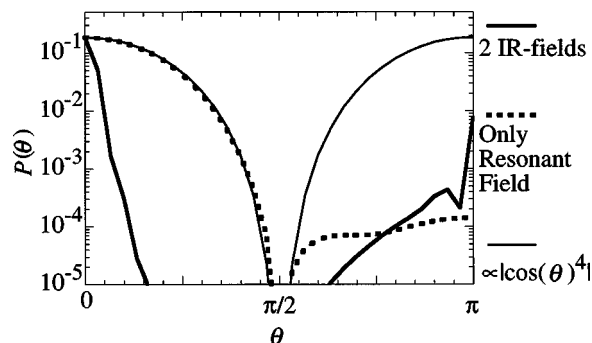

FIG. 7. 3D calculation showing the angular dependence of the probability for transition to the excited state. Bold full line: $P(\theta)$ for $\omega_{\text{UV}}=28\,092$ cm^{-1}, $T_{\text{peak,UV}}=742$ fs, $I_{\text{res}}=3\times10^9$ W/cm^2, $I_{\text{off}}=10^{12}$ W/cm^2, $I_{\text{UV}}=10^{12}$ W/cm^2, and $T_{\text{FWHM,UV}}=130$ fs. Integration of this result over the two hemispheres yields $D=0.922$. The dotted line shows the angular dependence obtained in Ref. 8 with only a resonant field $I_{\text{res}}=5\times10^9$ W/cm^2 and a very short UV pulse. The resonant result is normalized to the peak height of the result with two IR fields by multiplication of a factor of 4.14. Note the angular distribution is very narrowly peaked around $\theta=0$. For comparison the thin full line shows $|\cos(\theta)|^4$.

VI. CONCLUSION

We have considered spatial control of molecular wave packet dynamics. We studied vibrational dynamics induced by intense IR laser pulses. Resonant excitation (with respect to the vibrational $0 \rightarrow 1$ transition) implies that oppositely oriented molecules will oscillate out of phase. Off-resonant excitation (a two-photon transition with respect to the $0 \rightarrow 1$ transition) surprisingly implies that all molecules oscillate in phase when the pulse has decayed, irrespective of the initial orientation. When the molecule is subject to simultaneous irradiation by both pulses, we demonstrated that for properly chosen intensities of the two pulses, it is possible to obtain constructive and destructive superpositions such that vibrational excitation will occur, only for molecules pointing into one of the two hemispheres of randomly oriented molecules.

The high intensities which were employed gave, in addition, strong alignment along the polarization axis of the laser field.

The orientational effect demonstrated in this work is due to the anharmonicity of the electronic ground-state potential. The vibrational amplitude created by the simultaneous irradiation of two intense IR laser fields is; essentially, equivalent to a classical superposition corresponding to the addition of the amplitudes created by each of the fields.

We have studied a heteronuclear diatomic molecule, but the orientational effects in resonant and off-resonant forcing of the molecular WP motion are expected to apply also to linear polyatomic molecules. Consider, e.g., the linear OCS molecule. One of the normal modes of this molecule corresponds essentially to a pure C–O oscillation. Starting with randomly oriented OCS molecules, we should be able to excite the C–O vibration such that all C–O oscillations are in phase. This will make it possible to apply the above-mentioned ''pump-pump'' control scheme for selective bond breaking without a previous orientation step. Application of the orientational effect, suggested in the present paper, to nonlinear molecules like HOD,[4] needs further investigation, also in order to establish the limits of application due to the high field intensities needed in off-resonant forcing.

[1] M. Shapiro, J. W. Hepburn, and P. Brumer, Chem. Phys. Lett. **149**, 451 (1988).
[2] D. J. Tannor and S. A. Rice, J. Chem. Phys. **83**, 5013 (1985).
[3] M. Grønager and N. E. Henriksen, Chem. Phys. Lett. **278**, 166 (1997).
[4] B. Amstrup and N. E. Henriksen, J. Chem. Phys. **97**, 8285 (1992).
[5] B. Amstrup and N. E. Henriksen, J. Chem. Phys. **105**, 9115 (1996).
[6] J. Phys. Chem. A **101**, 7463 (1997), special issue on Stereodynamics of Chemical Reactions; V. A. Cho and R. B. Bernstein, J. Phys. Chem. **95**, 8129 (1991); B. Friedrich and D. R. Herschbach, Nature (London) **353**, 412 (1991); H. J. Loesch and A. Remscheid, J. Phys. Chem. **95**, 8194 (1991); B. Friedrich and D. R. Herschbach, Phys. Rev. Lett. **74**, 4623 (1995).
[7] C. M. Dion, A. D. Bandrauk, O. Atabek, A. Keller, H. Umeda, and Y. Fujimura, Chem. Phys. Lett. **302**, 215 (1999).
[8] M. Machholm and N. E. Henriksen, J. Chem. Phys. **111**, 3051 (1999).
[9] E. Charron, A. Giusti-Suzor, and F. Mies, J. Chem. Phys. **103**, 7359 (1995).
[10] G. H. Peslherbe, R. Bianco, R. Hynes, and B. M. Ladanyi, J. Chem. Soc., Faraday Trans. **93**, 977 (1997).
[11] Y. Zeiri and G. G. Balint-Kurti, J. Mol. Spectrosc. **99**, 1 (1983).
[12] R. B. Bernstein, *Chemical Dynamics via Molecular Beam and Laser Techniques* (Oxford University Press, New York, 1982).