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Enhancement of laser-induced molecular alignment by simultaneous photodissociation

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From a three-dimensional time-dependent Schrödinger equation simulation for alignment of Cl_2 by short laser pulses, we show that alignment of the ground state ($X\ ^1\Sigma_g^+$) can be increased by photodissociation via a repulsive dissociative state ($^1\Pi_u$). Initially, an intense nonresonant laser pulse (2×10^{13} W/cm^2, 1064 nm) with linear polarization aligns the molecule in the direction of the polarization as measured by $\langle\cos^2\theta\rangle$, which depends on the J, M_J initial conditions. Then, a second pulse with the same polarization is added in order to make perpendicular resonant transitions to the repulsive state (1×10^{13} W/cm^2, 375 nm). We show as an example for $J=4$ that the second pulse increases the alignment for each initial M_J condition as measured by $\langle\cos^2\theta\rangle_{J=4,M_J}$ and the average alignment $\langle\langle\cos^2\theta\rangle\rangle_{J=4}$ by reducing the proportion of the $M_J\neq0$ states. This improvement in the alignment of the molecule increases the amplitudes of the average rotational recurrences after the laser pulse and reduces the randomness in these recurrences by removing nonaligned $M_J\neq0$ states.

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Alignment of molecules by intense laser fields is a subject of current growing interest. There is now ample experimental observation that molecular fragments during ionization of diatomic molecules are almost parallel to the laser field [1] at high intensities. One explanation is that the rate of ionization is higher for molecules parallel to the laser field or alternatively, this is due to prealignment of the molecules before the ionization [2,3]. In order to quantify the relative importance of the two alignment mechanisms, Corkum *et al.* have proposed a method that compares the alignment signal when the laser field is linearly and circularly polarized [4]. This allows for discriminating prealignment as opposed to geometric effects.

The observation of prealignment of diatomic molecules during ionization when they are in a strong laser field has given rise to study the possibility of alignment below the ionization threshold [5]. Recent work by Friedrich *et al.* further indicates that alignment comes from the creation of pendular states in potentials created by the nonresonant interaction of the laser field with the induced dipole [6]. From this work, it is concluded that alignment depends on the initial rotational states J, M_J, the difference between the parallel ($\alpha_\parallel$) and the perpendicular polarizability ($\alpha_\perp$), the rotational constant of the molecule, and the average laser intensity. This has now been demonstrated experimentally [7,8] for various molecules. Nonadiabatic effects reduce the alignment when the rise of the laser field is faster than the rotational period [9]. This creates a rotational wave packet after the passage of the laser pulse and gives rise to rotational recurrences that offer the possibility of controllable realignment of the molecule [10,11]. For polyatomic molecules, Dion *et al.* studied numerically the possibility to align HCN in three-dimensional (3D) space [12]. Recently, Larsen *et al.* have demonstrated experimentally the alignment of planar molecules with elliptical polarization [13]. The possibility to align molecules in strong laser fields without ionization has many new applications, e.g., increase of the intensity of Raman spectra by orders of magnitude [14], control of fragment channels in photodissociation of diatomic or any linear molecule [15], simplification of photoelectron spectra [16], and dissociation of molecules as a molecular centrifuge [17,18].

Recently, we have reported the possibility to invert populations in high vibrational levels of symmetric diatomics by chirped adiabatic Raman passage. Using Cl_2 as an example, we obtained alignment of high vibrational v states in the direction of the polarization of the laser field [19]. We found that the maximum v one can obtain is limited by the wavelength of the pulse used due to photodissociation. We now show the advantage of photodissociation in order to eliminate high M_J sublevels that have low alignment. To study the efficiency of this scenario, we use our previous method of solving the time-dependent Schrödinger equation TDSE, in 3D by treating all *parallel* transitions with the field-polarizability interaction. This gives the following Hamiltonian for the ground state ($X\ ^1\Sigma_g^+$) of Cl_2 [19], which depends on the nonresonant parallel polarizability ($\alpha_\parallel$),

$$H_\Sigma^J = T^N(R) + V_\Sigma^J(R) - \tfrac{1}{2}\alpha_\parallel(R)\mathcal{E}(t)^2\cos^2\theta. \qquad (1)$$

For *perpendicular* transitions, in the presence of the low energy repulsive $^1\Pi_u$ state that converges to the ground state, we treat this coupling to the ground state exactly by the radiative dipole term $\mu(R)\sin\theta\mathcal{E}(t)$. In the numerical method, we expand the rotational wave functions in terms of spherical harmonics for the ground state. For the $^1\Pi_u$ state, we expand on $D^J_{M_J,\Omega}$ functions and evaluate the radiative couplings by calculation of the corresponding Clebsch-Gordan coefficients. The 3D TDSE is thus transformed to a multichannel one-dimensional (1D) problem:

$$i\hbar\frac{\partial\Phi_\Sigma^J}{\partial t} = \left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + V_\Sigma^J - \frac{1}{2}\mathcal{E}(t)^2\alpha_\parallel I_\Sigma^J\right]\Phi_\Sigma^J$$
$$-\frac{1}{2}\alpha_\parallel\mathcal{E}(t)^2[I_{J+2}\Phi_\Sigma^{J+2} + I_{J-2}\Phi_\Sigma^{J-2}]$$
$$+\sqrt{2}\mu(R)\mathcal{E}(t)[R_J\Phi_\Pi^{J+1} + Q_J\Phi_\Pi^J + P_J\Phi_\Pi^{J-1}], \qquad (2)$$

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$$i\hbar \frac{\partial \Phi_{\Pi}^{J'}}{\partial t} = \left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + V_{\Pi}^{J'} \right] \Phi_{\Pi}^{J'} + \sqrt{2}\mu(R)\mathcal{E}(t) \times [R_{J'}\Phi_{\Sigma}^{J'+1} + P_{J'}\Phi_{\Sigma}^{J'-1}], \tag{3}$$

$$i\hbar \frac{\partial \Phi_{\Pi}^{J''}}{\partial t} = \left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + V_{\Pi}^{J''} \right] \Phi_{\Pi}^{J''} + \sqrt{2}\mu(R)\mathcal{E}(t) Q_{J''}\Phi_{\Sigma}^{J''}. \tag{4}$$

The functions Φ^J are the nuclear functions that depend on R, the internuclear coordinate. The symbols R_J, Q_J, and P_J are the matrix elements for $\sin\theta$ for usual R, Q, and P branches ($\Delta J = 1,0,-1$). The I's are the $\cos^2\theta$ matrix elements for the $\Delta J = 2,0,-2$ transitions in Raman processes. The M_J subscript is omitted due to the selection rules $\Delta M_J = 0$. M_J does not change due to linear polarization of the total laser field. However, the coefficients R, Q, P, and I depend on M_J. We initialize the differential equations system [Eqs. (2)–(4)] from a pure ground state ($\psi_{\Sigma}^{v,J}$) and calculate with the Numerov method. The different constants in the last equations are give in our recent paper [19].

In the present paper, we demonstrate the possibility to use photodissociation via the repulsive $^1\Pi_u$ state in order to increase the alignment and the amplitude of the rotational recurrences after the laser pulse by dissociating preferentially $M_J \neq 0$ states. The total laser field is given by the following equation:

$$\mathcal{E}(t) = \mathcal{E}_{nr}^{o} f(t)_{nr} \sin(\omega_{nr} t) + \mathcal{E}_{r}^{o} f(t)_{r} \sin(\omega_r t). \tag{5}$$

In the last equation, the subscript *nr* refers to nonresonant and *r* resonant. The nonresonant laser pulse has a maximum amplitude $\mathcal{E}_{nr}^{o}$ which corresponds to the intensity $I = c\mathcal{E}^{o2}/8\pi = 2\times 10^{13}\,\mathrm{W/cm^2}$, an envelope $[f(t)_{nr}]$ with a time rise of 1 ps, a plateau of 3.98 ps and a short descent of 20 fs. The wavelength of this pulse (ω_{nr}) is 1064 nm. For the resonant laser pulse, $\mathcal{E}_r^o$, we use an intensity equal to $1\times 10^{13}\,\mathrm{W/cm^2}$, an envelope $[f(t)_r]$ with a time rise and descent of 0.1 ps with a plateau of 1.35 ps. The wavelength of this pulse (ω_r) is 375 nm in resonance with the repulsive $^1\Pi_u$ state. The resonant laser pulse has a delay of 2 ps with respect to the nonresonant laser pulse in order to align initially the molecule.

In order to demonstrate that photodissociation with states that have a perpendicular radiative coupling with the ground state increases the alignment, we have performed numerical simulations for the initial condition $v=0$: $J=4$ for each M_J state. In Fig. 1(a) we show the alignment calculated for $M_J = 0$, $|M_J| = 4$ and the average over the M_J states without the resonant laser pulse. The norm of the ground state after this nonresonant laser pulse is about the same for each M_J (only 2.5% of photodissociation). In Fig. 1(b), we show the enhancement of the alignment with the resonant laser pulse for the same conditions as in Fig. 1(a). From Figs. 1(a) and 1(b), we observe that alignment decreases when M_J increases. This is due to the smaller radiative coupling of these states via the parallel polarizability. In Fig. 1(b), we observe that the alignment of each pure M_J state increases when the resonant laser pulse is added.

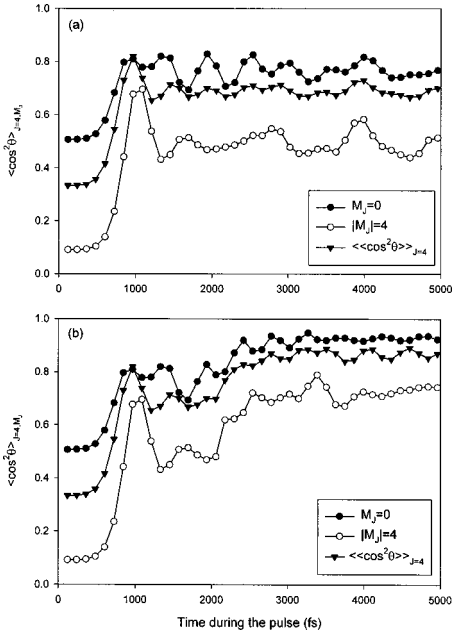

FIG. 1. Alignment of Cl_2 during the laser pulse [Eq. (5)] as measured by $\langle\cos^2\theta\rangle$ for $J=4$ and different M_J's: (a) Without the resonant laser pulse. (b) With the resonant pulse ($\lambda = 375$ nm).

To explain this enhancement effect we note that the rise time of the nonresonant laser pulse (1 ps) is faster then the fundamental rotational period ($\tau_R = \pi\hbar/B \simeq 71$ ps for Cl_2). As a consequence, many pendular states are excited. This pulse induced nonadiabatic effects creates a superposition of pendular states. The excited pendular states have a lower alignment compared to the ground state and this decreases the total alignment [9]. When the resonant laser pulse is added, one eliminates these excited pendular states by photodissociation due to stronger coupling with the $^1\Pi_u$ state (perpendicular coupling). Therefore, when the alignment reaches a plateau as measured by $\langle\cos^2\theta\rangle$, we obtain higher alignment than one can obtain with adiabatic conditions [6]. This is the first reason why the average alignment for $J=4$ in Fig. 1(b) increases after 2 ps. The second mechanism for increased alignment is via the higher rate of photodissociation of high M_J initial states. Because the most efficient radiative coupling to the $^1\Pi_u$ state is perpendicular, higher alignment results in lower photodissociation. In Fig. 2, we show the norm of the ground state after the laser field is off (at $t=5$ ps). We have chosen a total time of 1.55 ps for the resonant laser pulse in order to reduce to less then 10% the norm for $|M_J| = 4$. Therefore, because the average alignment for $J=4$ corresponds to all M_J states, the average alignment increases due to the decreased proportion of high M_J's in the incoherent superposition of these states. From Fig. 1(b) we can estimate that average alignment ($\langle\langle\cos^2\theta\rangle\rangle_{J=4}$) has increased from 0.69 to 0.87 due to the two mechanisms discussed above. We estimate an increase of 0.09 for both effects.

We show next that the enhancement of alignment by pho-

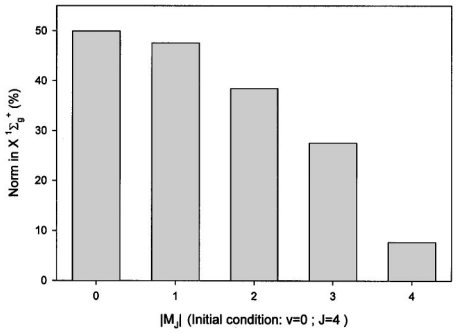

FIG. 2. Norm (%) of the electronic ground state ($X\ ^1\Sigma_g^+$) after the nonresonant laser pulse for different M_J's.

todissociation will increase the amplitude of rotational recurrences after the laser pulse. For a rigid rotor, the time dependence of the alignment after the laser pulse is give by the following equation:

$$\langle \cos^2\theta\rangle(t)=\sum_J P_J(t_c)\langle\cos^2\theta\rangle_J + 2\sum_J |a_J||a_{J+2}|\langle\cos^2\theta\rangle_{J+2}\cos(\Delta E t+\Delta\phi). \tag{6}$$

In the last equation, $P_J(t_c)=|a_J(t_C)|^2$ is the probability of population in each level J created at the time t_c when the laser field is switched off. $|a_J|$ and $|a_{J+2}|$ are the amplitudes of probability at t_c, $\Delta E=E_{J+2}-E_J=B_{\mathrm{Cl}_2}(4J+6)$ [where B is the rotational constant ($B_{\mathrm{Cl}_2}=0.23\,\mathrm{cm}^{-1}$)] and $\Delta\phi=\phi_{J+2}-\phi_J$ is the phase difference between the amplitudes $|a_{J+2}|$ and $|a_J|$ at t_c. From the last equation, we can predict recurrences of the alignment at each time $\hbar\pi/B_{\mathrm{Cl}_2}$, which corresponds to the fundamental rotational period of Cl_2. To assure complete realignment of the molecule after the laser pulse, one has to shut off rapidly the laser field in comparison with the rotational period (71 ps) in order to fix the amplitudes and the phase ($\Delta\phi$) in Eq. (6). Therefore $\Delta\phi$ can only give a positive cosine value [Eq. (6)] when it is in the first or last quadrant. To achieve this, we have chosen 20 femtoseconds as the laser field amplitude cutoff time. Longer cutoff time have the consequence to decrease the amplitude of the retrieval. At time $\hbar\pi/B$, the argument of the cosine phase factor is $n\pi+\Delta\phi$ (n even), which is equal to $\Delta\phi$. Because of this recurrence phase, we obtain the same alignment as occurs initially when the laser pulse is off. At time $\hbar\pi/2B$, there occurs a misalignment due to the cosine argument equal to $n\pi+\Delta\phi$ (n odd). Thus a change of π in the argument changes the sign of the cosine and decreases the alignment. At times $\hbar\pi/4B$ and $3\hbar\pi/4B$, there are minor recurrences that give simultaneously realignment and misalignment. At such times, the corresponding phase factors are $\pi J+3\pi/2$ and $3\pi J+\pi/2$, respectively. In our case, since J is even, these phase factors become $3\pi/2$ and $\pi/2$. Therefore, the cosine term in Eq. (6) at this time is transformed to $\sin(\Delta\phi)$ and $-\sin(\Delta\phi)$. Because $\Delta\phi$ is in the first or the last quadrants, the sign of this sine term can be positive or negative thus giving alignment and misalignment. If J is odd, we obtain the inverse ($\pi/2$ at $\hbar\pi/4B$ and $3\pi/2$ at $3\hbar\pi/4B$). Even if the phase is different, alignment and misalignment have to be observed for odd J condition.

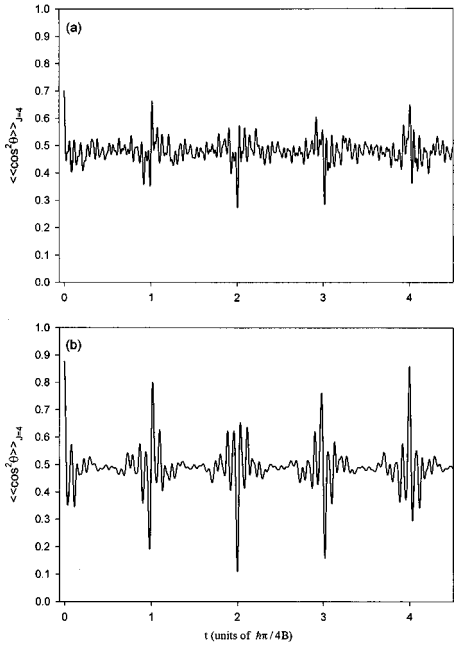

FIG. 3. Rotational recurrences in $\langle\langle\cos^2\theta\rangle\rangle$ after the laser pulse [Eq. (5)] for $J=4$: (a) Without the resonant laser pulse. (b) With the resonant pulse ($\lambda=375$ nm). Rotational period $\tau_R=\hbar\pi/B\simeq 71$ ps.

In Figs. 3(a) and 3(b), we show the average numerical alignment [obtained from the TDSE, Eqs. (2)–(4)] for $J=4$ after the laser pulse is off. We observe realignment at time $\hbar\pi/B$ and a misalignment at $\hbar\pi/2B$. At time $\hbar\pi/4B$ and $3\hbar\pi/4B$, there are minor recurrences that lead to alignment and misalignment. We observed that the slope (d/dt) of $\langle\cos^2\theta\rangle(t)$ is positive at $\hbar\pi/4B$ and negative at $3\hbar\pi/4B$. This results is confirmed by the derivitative of Eq. (6), which is written as follow:

$$\frac{d}{dt}\langle\cos^2\theta\rangle(t)=-2\sum_J |a_J||a_{J+2}|\langle\cos^2\theta\rangle_{J+2}\Delta E \times\sin(\Delta E t+\Delta\phi). \tag{7}$$

We have explained before that the phase factor at $\hbar\pi/4B$ is equal to $3\pi/2$ for even J and $\pi/2$ for odd J. At $3\hbar\pi/4B$, we obtain the inverse. This leads to alignment and misalignment. The insertion of these phase factors in the last equation leads to the following conclusion. At $\hbar\pi/4B$, the sign of the slope is positive for even J and negative for odd J. We obtain the inverse at $3\hbar\pi/4B$. These conclusions are in agreement with the numerical results that we present in Figs. 3(a) and 3(b). Therefore, the only single difference between odd and even J is the slope of $\langle\cos^2\theta\rangle(t)$ at $\hbar\pi/4B$ and $3\hbar\pi/4B$. At $\hbar\pi/2B$ and $\hbar\pi/B$, we obtain the same behavior for any initial J condition. Therefore, this will also apply for a thermal ensemble of J states. This alignment enhancement via photo-

dissociation can be really useful for molecules that have a broad distribution of J at room temperature. It can eliminate the high J, M_J states that have a small alignment in presence of the laser field [6] and therefore enhance the alignment of the ground state and the amplitude of the recurrence after the laser field. Because the recurrence depends on the value of the rotational constant, we can predict that vibrational states have different recurrence times. One can expect when v increases, the rotational constant decreases. For chlorine, this leads to a difference of $\sim$500 fs between the recurrence at $\hbar\pi/B$. However, this has no importance at room temperature because almost all vibrational population is in $v=0$ as in the present calculation.

We can see in Fig. 3(b) that the recurrence of alignment obtained after the photodissociation process is higher then in Fig. 3(a) due to the reasons explained above. In this simulation, we have performed a complete calculation of the rovibrational system. Therefore, we can observe in Figs. 3(a) and 3(b) that the alignment does not repeat exactly its value when the laser pulse is off. This is due to the rovibrational couplings that modify the energy of the rotational levels from the rigid rotor value $E_J=BJ(J+1)$. This deviation reduces the periodic alignment due to phase shifts between amplitudes and this effect increases for longer time after the pulse. As an example, we can observe that the minor recurrence at $\hbar\pi/4B$ gives a higher alignment than at time $\hbar\pi/B$ in Fig. 3(a). This is due to a phase shift more important at $\hbar\pi/B$ due to the accumulation of the deviation of energy with time, consequence of the rovibrational coupling. In Fig. 3(b), this random behavior is suppressed. This is due to lower J states in the average rotational population over M_J when the laser field is turned off. When only the nonresonant laser pulse is present, 95% of the rotational population is in J's less than 60 and when the resonant laser pulse is present, the population drops to $J=44$. Because the rovibrational coupling is less for lower J, the phase shift deviation from the rigid rotor is less in this case. Another interesting observation is that the ''noise'' of the alignment parameter $\langle\langle\cos^2\theta\rangle\rangle_{J=4}$ is reduced in Fig. 3(b) compared to Fig. 3(a). Two mechanisms explain this behavior. The first reason is that when the resonant laser pulse is present, the rotational population is in the lower J's than when it is not present ($J=44$ compared to $J=60$). Therefore, there are less high frequency components due to lower energy components in the mean value of alignment. This mean value is obtained by the summation over all M_J states. Because the amplitudes oscillate differently in the laser field for different M_J initial conditions [10], the amplitudes obtained at the turnoff of the laser pulse are not the same for different M_J's and the recurrences have therefore not the same frequency components. Then, by eliminating the high M_J states by photodissociation, the average alignment for $J=4$ has less noise due to the reduction of different frequency components. This is due to the fact that each M_J state is a coherent superposition of J states, but the M_J states themselves are incoherent (independent phase) with respect to each other [10].

In conclusion, we have demonstrated by numerical simulations of a 3D TDSE for Cl_2 with initial condition $v=0:J=4$ that alignment can be enhanced by photodissociation of the ground state ($X\ ^1\Sigma_g^+$) to the first $^1\Pi_u$ excited state. This is due to two reasons. First, one removes by this scenario excited pendular states from the wave packet superposition created by nonadiabatic effects of the laser pulse. Secondly, one photodissociates high M_J's that resist alignment due to their weak radiative coupling. This enhancement in the alignment by photodissociation of the ground state increases the amplitude of the recurrence of realignment after the laser field and thus reduces the noise by elimination of random amplitudes from different initial incoherent M_J states. Thus a combination of nonresonant alignment and resonant photodissociation should lead to controllable recurrences in alignment after the laser pulse is off. This technique should be applicable to any linear molecule.

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