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Alignment-dependent ionization probability of molecules in a double-pulse laser field

Z. X. Zhao, X. M. Tong,* and C. D. Lin
Physics Department, Kansas State University, Manhattan, Kansas 66506-2601

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We demonstrate the possibility of determining the dependence of ionization probabilities on the alignment of molecules in a double-pulse laser experiment. A short pump pulse is used to generate a rotational wave packet which produces aligned molecules during the periods of rotational wave packet revival. The ionization probabilities by a subsequent probe laser vs the time delay are calculated for O_2 and N_2 molecules at different temperatures. Distinct time dependence is predicted, and the results are interpreted in terms of the geometry of the charge distributions of the valence electrons of the two molecules.

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In recent decades there has been great interest in exploring the nonperturbative interaction between molecules and intense lasers. Problems of basic scientific and practical importance include the orientation, steering, and focusing of molecular beams [1–3]. In particular, the ionization of molecules by short pulse lasers may be used as a soft ionizer [4] for large molecules and for efficient high-order harmonic generation into the soft x-ray region [5]. Further development of these and other applications of intense lasers to manipulate molecules requires a solid theoretical foundation for understanding the detailed dynamics of molecules in strong laser fields. While several simple theoretical models [6–9] have been successfully employed to interpret the ionization of atoms in intense laser fields, these models have limited validity for molecules.

Unlike atoms, molecules are not isotropic systems, and it is clear that the ionization rate can be strongly influenced by the alignment angle θ between the molecular axis and the laser electric field vector. Since the rotation period of a typical molecule (a few picoseconds) is much longer than the pulse duration (100 fs or less) of Ti:sapphire lasers, each ionization can be considered to occur for a molecule fixed in space. The ionization rate of such an aligned molecule in a laser field can be calculated in principle, but few calculations have been done [10,11] and no general understanding has emerged. In a recent paper [12], we developed a molecular tunneling ionization model for calculating the ionization rate of molecules in an intense laser field. This model is an extension of the ADK (Ammosov-Delone-Krainov) model [9] for atoms which has been successfully used for describing the ionization rate of an atom in the tunneling ionization regime. The molecular (MO) ADK model has been used to calculate the ionization rates for molecules and the results have been shown to be in good agreement with experimental data [13–17]. The MO ADK model has also successfully interpreted the origin of the so-called ionization suppression for some molecules [12]. In order to compare with experiments, the ionization rates predicted by the MO ADK model have to be averaged over an ensemble of randomly distributed molecules; thus the alignment dependence of the ionization rate has not been tested directly. In the present paper we suggest a double-pulse experiment to test such alignment dependence.

In the MO ADK theory, the ionization rate of a diatomic molecule in a parallel static electric field is given by (atomic units $m=\hbar=e=1$ are used unless otherwise indicated)

$$w_{stat}(F)=\frac{B^2(m)}{2^{|m|}|m|!}\frac{1}{\kappa^{2Z_c/\kappa-1}}\times\left(\frac{2\kappa^3}{F}\right)^{2Z_c/\kappa-|m|-1}e^{-2\kappa^3/3F}, \tag{1}$$

with

$$B(m)=\sum_l C_{lm}(-1)^m\sqrt{\frac{(2l+1)(l+|m|)!}{2(l-|m|)!}}, \tag{2}$$

where κ is related to the ionization energy I_p by $\kappa=\sqrt{2I_p}$, m is the projection of the electronic orbital angular momentum along the internuclear axis, and F is the field strength. In Eq. (1), the parameters C_{lm} are determined from the valence electron wave function of the molecule in the asymptotic region. To obtain the ionization rate by a laser, we need to average over the field strength of one-half cycle,

$$w(F)=\frac{1}{\pi}\int_0^\pi w_{stat}(F\cos\tau)d\tau=\left(\frac{3F}{\pi\kappa^3}\right)^{1/2}w_{stat}(F), \tag{3}$$

where F now stands for the peak field strength within the half cycle. If the molecule is aligned at an angle θ with respect to the laser polarization direction, the ionization rate is given by

$$w(F,\theta)=\sum_{m'} w(F), \tag{4}$$

with

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*Email address: xmtong@phys.ksu.edu

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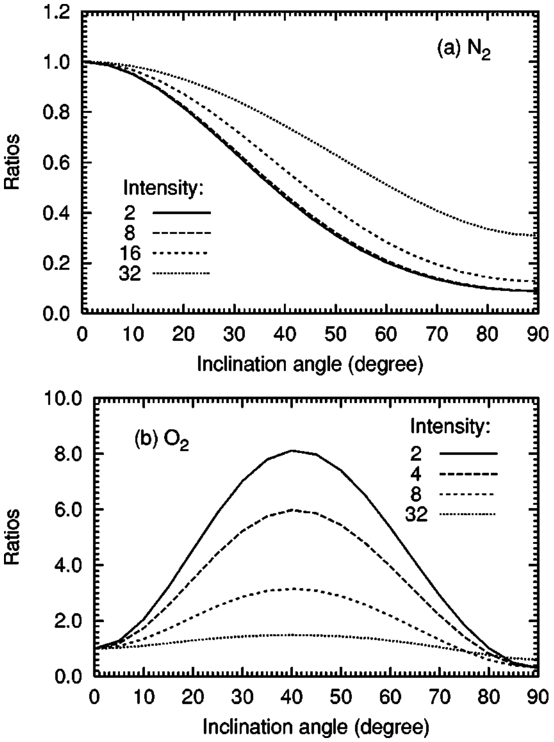

FIG. 1. The ionization rates as a function of the angle θ between the laser field direction and the molecular axis for (a) N_2 and (b) O_2 molecules. The laser peak intensity is in units of 10^{13} W/cm^2. The rates are normalized at 0°.

$$B(m') = \sum_{l} C_{lm} D^{l}_{m',m}(0,\theta,0) \times (-1)^{m'} \sqrt{\frac{(2l+1)(l+|m'|)!}{2(l-|m'|)!}}, \tag{5}$$

where the D function reflects the rotation of the electronic wave function from the direction of the molecular axis to the laser polarization direction. In the MO ADK model, Eq. (2) reduces to the traditional ADK model for atoms if l is taken to be the orbital angular momentum quantum number of the valence electron. For diatomic molecules, the summation over l is a consequence of expanding the two-center electronic wave function of a valence orbital in terms of single-center atomic orbitals. We note that the valence electron for N_2 is a σ_g orbital such that $m=0$ in Eq. (1), while for O_2 it is a π_g orbital such that $m=1$ in Eq. (1). The molecular parameters needed for performing these calculations for N_2 and O_2 molecules have been listed [12].

In Fig. 1 we show the alignment-dependent ionization rates for N_2 and O_2 molecules at peak field intensities from 2×10^{13} W/cm^2 to 32×10^{13} W/cm^2, normalized with respect to $\theta=0$. For N_2 the ionization rate decreases monotonically with increasing θ. This is not the case for O_2 molecules where the ionization rate peaks at θ near 40°. With higher field intensities the dependence of ionization rate on θ becomes weaker.

These calculated alignment-dependent ionization rates from the MO ADK model can be qualitatively understood in terms of the geometry of the charge distribution of valence electrons for each molecule. For N_2, the valence electron is a σ_g orbital, and its electron cloud is preferentially lying along the internuclear axis. Thus when the molecule is aligned along the field direction, the electronic density along the field direction is maximum and the electron is most easily ionized. When the molecule is aligned at an angle θ with respect to the field, the effective electronic density in the field direction is reduced, and the ionization rate becomes smaller. The situation for O_2 is different. Its valence electron is a π_g orbital. When the molecular axis coincides with the laser polarization direction, there is little valence electron density. On the other hand, when the field direction is at 45° with respect to the molecular axis, the electron cloud will have maximum density along the field direction and thus the ionization rate is maximum. The results in Fig. 1 are consistent with this simple geometric interpretation.

In the last decade, many experiments have been carried out with the aim of investigating the alignment dependence of the ionization rates of molecules using the Coulomb explosion technique [18–23]. By detecting two dissociated ions in coincidence, the alignment of the molecule before ionization may be deduced. However, the Coulomb explosion technique works better if the molecular ions are doubly or multiply ionized by the laser. At present even the single ionization of molecules is not well understood, not to mention multiple ionization [24]. Dissociative ionization may occur at different internuclear separations, and the ion products could also be deflected by the laser fields before they reached the detectors. These unknown factors make it difficult to extract quantitative alignment dependence of ionization rates from these experiments directly.

In this paper we propose a double-pulse experiment where the alignment-dependent ionization rates for molecules predicted by the MO ADK model [12] can be directly and unequivocally tested. We started with a short pump laser and waited for the molecules to be aligned at a later time when they undergo "rotational revival." During this interval, which lasts for about a few hundred femtoseconds, the degree of alignment of the molecules changes rapidly. A second short probe laser is used to ionize these aligned molecules and the ionization yield can be measured against the delay time between the two pulses. The short pulses are used such that molecules are not aligned by the laser during the time when the pulses are on. The laser parameters are chosen to ensure that rotation-vibration coupling does not play a role, and the molecule does not stretch or ionize significantly. In this limit the effect of the laser field on the rotation of the molecule can be described by the rigid rotor model [25–29]. Within this model, the alignment of the molecules in the laser field can be calculated rigorously using quantum mechanics, but the effect can also be understood by treating the rotor motion classically. Through the anisotropic induced electric dipole moment, the molecule experiences a torque proportional to sin(2θ), where θ is the angle between the polarization axis and the molecular axis. Thus molecules at different angles tend to "converge" along the field direction

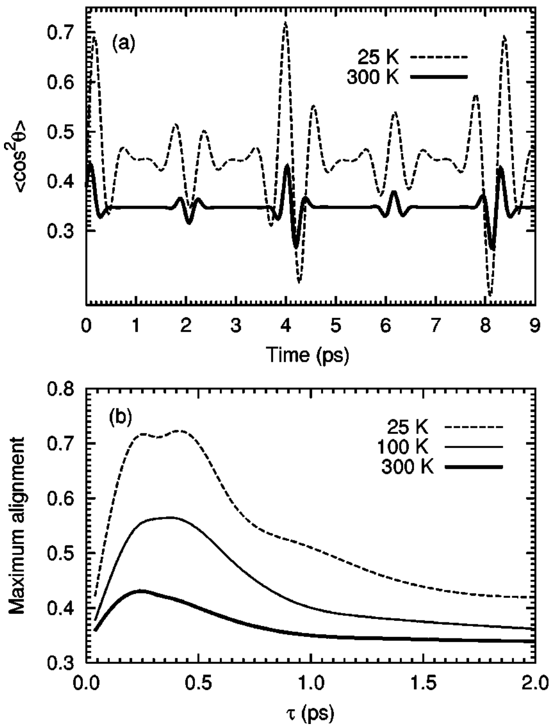

FIG. 2. (a) Calculated time-dependent alignment parameter $\langle\cos^2\theta\rangle$, and (b) maximum alignment parameter as a function of the pump pulse duration with peak laser intensity of 2×10^{13} W/cm^2 for N_2, at three temperatures.

at a later time, at the time of rotational revival. The degree of alignment can be conveniently measured by $\langle\cos^2\theta\rangle$. When the molecules are randomly distributed, this average is 1/3. If the molecules are all lined up in the field direction, this average is 1.0. In Fig. 2(a), we show the alignment of N_2 molecules after they have been exposed to a 250 fs laser with peak intensity of 2×10^{13} W/cm^2 (the laser referred to in this paper is always the Ti:sapphire laser at 800 nm, assuming a Gaussian pulse shape).

The calculations of the angular distribution and the degree of alignment, as shown in Fig. 2(a), were carried out quantum mechanically. For each well-defined field-free rotational eigenstate, we calculated the rotational wave function by solving the time-dependent Schrödinger equation of a rigid rotor exposed to the laser pulse. The laser-rotor interaction potential is $V=-[\epsilon^2(t)/2](\alpha_\parallel\cos^2\theta+\alpha_\perp\sin^2\theta)$. Here $\epsilon(t)$ is the electric field of the pump laser, θ is the angle between the electric field and the internuclear axis, and $\alpha_\parallel,\alpha_\perp$ are the components of the anisotropic polarizability for fields respectively parallel and perpendicular to the axis. The time-dependent Schrödinger equation was solved by the spilt operator method in the energy representation [30,31]. To account for the temperature dependence, the initial pure rotational states are thermally averaged with weights according to the Boltzmann distribution. For the homonuclear molecules considered here, the nuclear spin statistics has to be properly accounted for as well.

In Fig. 2(a) the time dependence of the alignment is shown at two temperatures. At 300 K, the molecules are not aligned except at several intervals during which the alignment changes rapidly. These rapid changes occur when the molecules experience rotational wave packet revival; see the structures near 4 ps and 8 ps in Fig. 2(a). The rotational revival repeats at intervals separated by T, where T is determined by the rotational constant of the molecule. For N_2, the revival time is 8 ps. For O_2 it is 12 ps. There are also partial revivals expected at $T/4$, $T/2$, and $3T/4$ [28,32] in general, but the alignment is less significant at partial revivals. At each rotational revival, for a period of a few hundred femtoseconds, the alignment of molecules changes rapidly. The anisotropic distribution of molecules in this short time interval offers the opportunity to investigate the alignment dependence of ionization rates without the need of determining the alignment of each molecule. Clearly, the degree of alignment for a given laser pulse increases if the molecules are at lower temperature. At 25 K, the alignment is more prominent [see Fig. 2(a)]. The partial revivals are also more clearly seen at lower temperatures.

The maximum alignment achievable by a laser field during the period of rotational wave packet revival depends on the laser pulse duration if the peak intensity is fixed. In Fig. 2(b) we show how the maximum alignment depends on the pulse length. The 250 fs pulse used in Fig. 2(a) was determined based on such a calculation. The peak laser intensity has been chosen so that few molecules are ionized by the pump laser. When the molecule is ionized, the rotational motion can no longer be described by the present rotor model. For the peak intensity of 2×10^{13} W/cm^2, from the MO ADK theory, we calculated that the ionization probability for such a pulse is less than 10^{-10} for N_2 and less than 10^{-8} for O_2.

The rapid change of the alignment of molecules during the rotational revival period clearly offers an opportunity to probe the alignment-dependent ionization rates of molecules. By employing another "probe" laser at different time delays with respect to the weak "pump" laser, the ionization rates or signals from such aligned molecules can be measured. Consider a probe laser that has the same polarization direction as the pump laser. In Fig. 3 we show the predicted ionization signals at three temperatures when a second 25 fs "probe" pulse of peak intensity 8×10^{13} W/cm^2 is used to ionize the aligned molecules. Note that the ionization signals vary rapidly with the time delay. The ionization signal peaks when the alignment peaks. In fact, the time dependence of the ionization signal almost mimics the time dependence of the alignment of the molecules. This is a fortunate coincidence since the alignment-dependent ionization rate for N_2, as shown in Fig. 1(a), is approximately given by $\cos^2\theta$. Since the degree of alignment is defined to be the average of $\cos^2\theta$, the two averages are essentially identical mathematical expressions. In terms of relative magnitudes, at 25 K, the ratio of the maximum to minimum peak signals is more than a factor of 3. At 300 K, the ratio is still about 1.42.

The ionization signal vs time delay for O_2 molecules is markedly different, especially at lower temperature, as shown in Fig. 4. Clearly, the ionization signal does not peak at the time when the alignment is at the maximum. The reason was already given earlier. When O_2 molecules are aligned in the direction of the laser field, the density of the

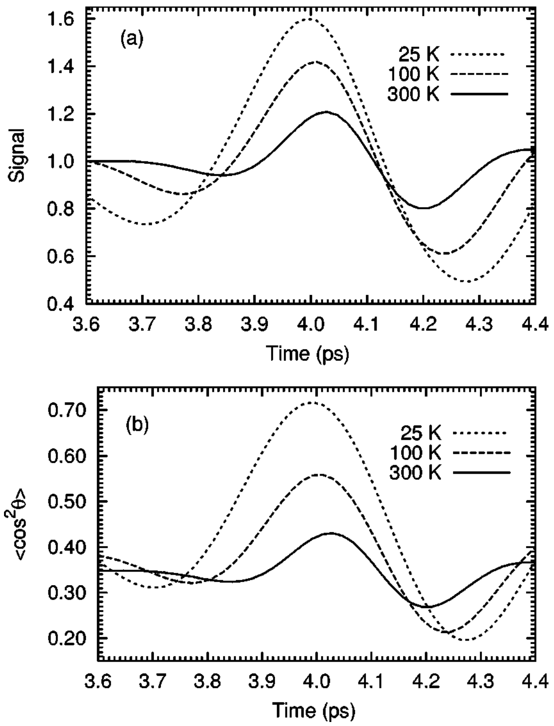

FIG. 3. (a) Ionization signal as a function of the delay time between the pump and probe laser pulses, and (b) time-dependent alignment parameters after the pump pulse for N_2 at 25, 100, and 300 K. The pump and probe laser intensities are 2×10^{13} W/cm^2 and 8×10^{13} W/cm^2, respectively.

valence electron in the field direction is small. At each time delay, the molecules are distributed over a broad range of angles even if the molecules are aligned. At lower temperature the distribution becomes sharper, i.e., the molecules are distributed more sharply along the field direction. Thus, for example, at 25 K, the ionization signal is at a local minimum when the alignment is maximum. At higher temperature, the ionization signal does not change with time delay as strongly as in N_2. The ionization signal is the average of two functions. One is the distribution of the molecular alignment, which peaks at $\theta=0°$. The other is the alignment-dependent ionization rate, which peaks at θ near 45°. As a result, the ionization signal does not depend on the alignment as strongly for O_2. At 25 K, the ratio of maximum to minimum ionization rates is 1.6, as compared to 3.0 for N_2.

So far we have chosen the polarization of the probe pulse to be parallel to the polarization of the "pump" pulse. An alternative method to test the prediction of the MO ADK theory is to study the ionization signal vs the relative polarization direction. In Fig. 5 we show the calculated dependence of the ionization signals at three different relative polarizations between the two laser pulses for O_2 at 25 K. At this low temperature and at the time of maximum alignment, the ionization signal is near maximum when the two polarizations are at 45° with respect to each other. At the maximum alignment, the molecules are preferentially aligned in the direction of polarization of the "pump" laser. When the probe laser is set at 45° with respect to the pump laser, it is the direction where the charge density of the O_2 valence

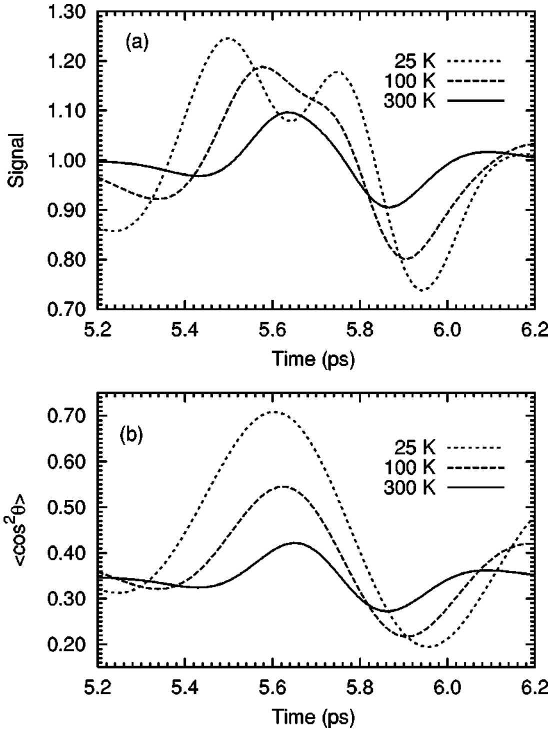

FIG. 4. (a) Ionization signal as a function of the delayed time between the pump and probe laser pulses, and (b) time-dependent alignment parameters after the pump pulse for O_2 at 25 K, 100 K, and 300 K. The pump and probe laser intensities are 2×10^{13} W/cm^2 and 4×10^{13} W/cm^2, respectively.

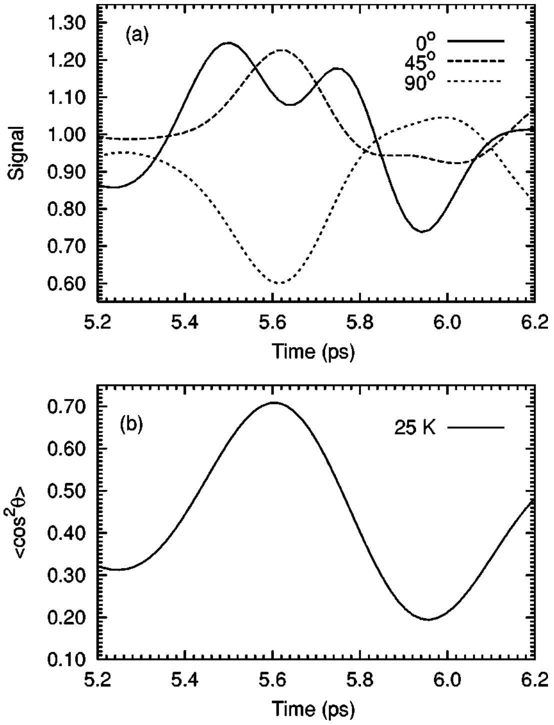

FIG. 5. (a) Ionization signal as a function of the delayed time between the pump and probe laser pulses with different probe laser polarizations, and (b) time-dependent alignment parameter after the pump pulse for O_2 at 25 K. The pump and probe laser intensities are 2×10^{13} W/cm^2 and 4×10^{13} W/cm^2, respectively.

electron is maximum, and thus the ionization rate will be maximum. In this way, the directional property of the valence electron can be probed directly in a two-pulse experiment, and such a method probably can be extended to study more complex molecules.

In summary we propose a double-short-pulse laser experiment to measure the alignment-dependent ionization probability of N_2 and O_2 molecules. A short weak pump pulse is used to align the molecules during the period where the molecules undergo rotational wave packet revival. During this revival period a second ''probe'' pulse is used to ionize the molecules at different time delays. It is predicted that the ionization signal depends sensitively on the time delay. For N_2 maximum ionization was predicted to occur when the molecules have maximum alignment. For O_2, because its valence electron is a π orbital, the ionization signal is smaller when the alignment is at the maximum. The behavior predicted for O_2 should be applicable to other molecules with π valence electrons. Similarly, the predictions for N_2 should be characteristic of molecules with σ valence electrons. As noted previously [12], molecules whose valence electron is a π orbital would exhibit ''ionization suppression.'' From the existing ionization measurements on diatomic molecules, the only molecule that has π valence electrons but whose ionization does not exhibit ionization suppression is the F_2 molecule. Following the predicted distinct difference between O_2 and N_2, it may be desirable to perform double-pulse experiment on F_2 to check if the ionization rate of F_2 vs time delay is closer to that for O_2 or N_2. The proposed double-pulse experiment would shed light on our understanding of the interaction of lasers with molecules.

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