

Intense laser ionization of transiently aligned CO

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We have measured the ionization rate for CO molecules exposed to intense 30 fsec 780 nm laser pulses as a function of the angle between the molecular and laser polarization axes. Nonionizing, 70 fsec laser pulses are used to coherently prepare the molecules, preferentially aligning them for the strong-field ionization experiments. We find a 2:1 ionization-rate ratio for molecules aligned parallel or perpendicular to the ionizing field.

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I. INTRODUCTION

The availability of aligned rather than randomly oriented molecular samples is enabling a new class of strong-field molecular physics experiments. The unprecedented clarity and precision of these measurements [1–3] can offer further insight into a variety of complex phenomena. For example, processes such as high-harmonic generation and nonsequential multiple ionization in atoms and molecules are mediated by electrons that are first tunnel-ionized and then driven back into their parent ions by an intense laser field [4,5]. However, in molecules, accurate rates for the critical ionization step are extremely difficult to calculate, and significant discrepancies between theory and experiment persist [6–9]. Direct comparisons between theory and experiment are complicated by the random alignment of molecules in experiments, uncertainties in the degree to which molecules align during the ionizing pulse, and the lack of experimental data on ionization-rate anisotropies for molecules aligned at different angles relative to the ionizing field. These issues can be eliminated or significantly reduced by using transiently aligned molecular targets. Indeed, such coherently prepared molecules have recently been used to measure ionization-rate anisotropies [1] in N_2 in an attempt to illuminate the origin of the suppression of intense laser ionization in some molecules but not in others [6,10–12]. The use of aligned targets was also the key to recent experiments exploring tomographic reconstruction of molecular orbitals from high-harmonic emission [3]. Here we report the use of transient laser alignment [13] to measure the angular dependence of intense laser ionization rates for CO. The highest occupied molecular orbital for CO is $1\sigma^+$ yet it exhibits moderate ionization suppression relative to its companion atom Kr [7] with nearly identical ionization potential [$(V_{\text{ion}})_{\text{CO}} = 14.01$ eV, $(V_{\text{ion}})_{\text{Kr}} = 14.00$ eV]. We find a 2:1 ionization-rate ratio for molecules aligned parallel vs perpendicular to the ionizing laser field.

Although it has only recently been observed in the laboratory [1,14–17], laser-induced, field-free alignment of molecules is a topic of significant current interest with potential applications to laser-pulse shaping, enhancing high-harmonic generation, and controlling molecular fragmentation branching ratios [13]. The basic mechanism responsible for transient alignment is well understood and has been described in detail elsewhere [2,18–20]. An intense, short, linearly polar-

ized, nonresonant laser pulse drives a series of Raman transitions, coherently populating a superposition of rotational states (i.e., a rotational wave packet) within each molecule in an experimental ensemble. Insight into the temporal behavior of the wave packet can be obtained from a semiclassical picture. The aligning laser pulse $\vec{F}(t)$ induces an electric dipole moment whose magnitude $d(t) \propto F(t)$ within each molecule. For molecules with an anisotropic polarizability, $\vec{d}(t)$ need not be parallel to $\vec{F}(t)$. Thus, the molecules experience a torque, $\vec{d}(t) \times \vec{F}(t) \propto F^2(t)$. A laser pulse, whose duration τ is much less than the molecules' fundamental rotational period T_{rot} , gives each molecule an angular impulse or “kick” that tends to align its axis with the laser field. Due to this angular impulse, the probability that a given molecule will be found with its axis aligned with the laser field begins to increase with time. The alignment probability reaches a maximum during or soon after the laser pulse, but then decreases as the molecules continue to rotate in the absence of the field.

In an ensemble of classical rotors, a continuous distribution of rotational kinetic energies is produced by the angular impulse from such a laser field. These rotors have different periods. Therefore, in spite of the fact that each individual rotor periodically realigns along the original laser polarization axis, there is no revival in the macroscopic alignment of the classical ensemble. However, for quantum rigid-rotor molecules, the energy differences between rotational states are discrete integer multiples of the rotational constant B_0 . Hence, the initial macroscopic alignment parallel to the laser polarization axis is periodically regained at times equal to integer multiples of the fundamental rotational period $T_{\text{rot}} = \pi/B_0$. In addition, immediately prior to the parallel alignment revival, there is an enhanced probability for finding the rotating molecules aligned in a plane perpendicular to the initial laser polarization. The integer revivals, as well as partial revivals at rational integer fractions of T_{rot} , are a consequence of the discretization of the quantum rotor energies and, therefore, are nonclassical in origin. Experiments with preferentially aligned field-free targets exploit this quantum behavior by exposing the molecules to additional short laser pulses at or near alignment revival times [1,3,14,15].

The precise time dependence of the macroscopic alignment of an experimental ensemble depends on a number of factors including the anisotropy in the molecule's polariz-

ability, the time-dependent laser intensity, and the initial rotational temperature of the molecular ensemble. In general, larger polarizability anisotropies, higher laser intensities, and lower rotational temperatures lead to better alignment. For nonzero rotational temperatures, the rotational probability distribution for the ensemble is given by an incoherent superposition of wave packets created from a set of initial rotational states $|J_0 M_0\rangle$, weighted according to their thermal population just prior to the alignment pulse. The degree of alignment and maximum parallel and perpendicular alignment times depend on the initial rotational state. Therefore, the broad incoherent state distributions associated with high rotational temperatures can lead to a significant smearing of the temporal variations in the time-dependent probability distribution. This effect can be reduced by cooling the molecular target, e.g., in a supersonic expansion, or by maximizing the rotational kinetic energy impulsively delivered to the molecules. Unfortunately, the use of very intense alignment pulses can result in vibrational excitation, dissociation, and/or ionization of the molecules. However, these deleterious effects can be minimized without compromising large rotational energy transfer through the use of multiple, time-delayed alignment pulses. Following previous theoretical and experimental work [16,20,21] we use two laser kicks temporally separated by the wave-packet revival time T_{rot} to enhance the degree of alignment while reducing the level of unwanted ionization as compared to a single, more intense alignment pulse.

We have explored transient alignment of several different diatomic species including N_2 , O_2 , and CO using laser intensities near the ionization threshold for each molecule. In each case, the time-dependent angular distributions of the coherently prepared molecular samples have been experimentally analyzed via Coulomb explosion of the molecules using an intense, circularly polarized probe. The results of these measurements are in good agreement with numerical simulations that model the generation of molecular alignment under our experimental conditions. We then utilize a less intense linearly polarized time-delayed ionization pulse and exploit the well-characterized temporal behavior of these rotational wave packets to measure the ionization yields of preferentially aligned CO molecules relative to Kr atoms. From these measurements, we extract an experimental determination of strong-field ionization rates in CO as a function of the relative alignment between the ionizing field and the molecular axis. Our results, including the coarse intensity dependence of the ionization anisotropy, are in qualitative agreement with the predictions of molecular orbital Ammosov-Delone-Krainov (MOADK) theory [8,22].

II. EXPERIMENTAL PROCEDURE

The experiments utilize a Ti:sapphire oscillator and a multipass chirped-pulse amplifier to produce 30 fsec, 780 nm pulses with energies up to 1.6 mJ at a 1 kHz repetition rate. The amplified laser pulses are characterized using frequency-resolved optical gating in a single-shot second-harmonic-generation configuration [23]. Each amplified pulse is split into an “ionization” pulse and two “alignment” pulses. An

iris diaphragm is used to reduce the diameter of the alignment beams to approximately one-third that of the ionization beam. The relative delay between the alignment and ionization pulses is controlled using standard translation stages, and the polarization of the pulses is independently controlled using zero-order wave plates. A 30 cm lens focuses the parallel, but noncollinear, laser beams into the interaction region of a single-stage time-of-flight (TOF) mass spectrometer which is housed inside an ultrahigh-vacuum chamber with a base pressure of 6×10^{-10} Torr. The alignment and ionization beams cross at an angle of approximately 2° in the interaction region. A leak valve introduces room-temperature target gas into the chamber while a liquid-nitrogen cold trap reduces the pressure of contaminant atoms and molecules, particularly H_2O , to negligible levels. The compressor for the chirped-pulse laser amplifier is set to precompensate for the group velocity dispersion (GVD) that the probe pulse accumulates during its propagation through the beam splitter, focusing lens, and vacuum chamber window. The alignment pulses are linearly polarized, and their intensity is adjusted to produce little or no ionization (10^{13} W/cm² for CO). To accomplish this without compromising the net angular impulse transferred to the molecules, the aligning pulses pass through a ~ 1.3 -cm-thick crown glass window and a 0.6-cm-thick crown glass beam-splitter substrate. Uncompensated GVD in this glass stretches the pulses to 70 fsec but maintains their energy. Immediately prior to the experiments, the spatial overlap of the laser beams and precise temporal delay between the three pulses is characterized by diverting the focusing laser beams through a 100- μ m-thick β -barium borate (BBO) crystal. Sum-frequency generation in the crystal is used to measure the cross correlations of the three laser pulses at their mutual focus. By translating the BBO crystal along the beam propagation direction we find that the longitudinal overlap region of the three beams is approximately one-third of the confocal parameter of the ionizing beam. However, due to the highly nonlinear intensity dependence of ionization and/or dissociation rates for the molecules of interest, below the saturation intensity for a given ionization channel, ions are only produced at the highest intensities very near the center of the focus. Thus, the factor of 1/3 represents a lower limit on the fraction of aligned molecules that contribute to the ionization yield. As discussed in more detail below, for our ionization measurements in CO, comparisons between experiment and numerical simulations indicate that aligned molecules are responsible for approximately 50% of the measured signals.

To characterize the time-dependent alignment in various diatomic species, we use a circularly polarized ionization pulse as an unbiased probe [24]. At some time after the molecules are kicked by the alignment pulse(s), the ionizing pulse rapidly dissociates the molecule via Coulomb explosion [25]. The resulting ion fragments fly apart in a direction defined by the intramolecular axis at the instant of the explosion. They are then pushed by a 110 V/cm extraction field through the 9 cm acceleration region in the TOF spectrometer. Ions fly down an 18 cm field-free drift region before striking the front plate of a 100×100 mm² microchannel plate detector stack that is backed by a helical delay-line anode (DLA) detector. We adjust the explosion beam inten-

sity and gas pressure for roughly 1 ion hit per laser shot ($\sim 10^{15}$ W/cm² at 10^{-7} Torr for CO). The TOF and two-dimensional position information for each detected ion are used to infer its vector momentum immediately following the Coulomb explosion. We selectively examine the triply charged ions (N^{3+} for N_2 , O^{3+} for O_2 , C^{3+} for CO), because the time scale for dissociation into these species is significantly less than the time scale for reorientation of the parent molecule [2]. The angular distribution of neutral molecules in the ionizing laser's focal volume is recovered from several hundred to several thousand fragment momentum measurements at a given delay between the alignment and ionization pulses. Specifically, we determine the probability that molecules in our ensemble were aligned in the polarization plane of the Coulomb explosion pulse, with their axes at an angle θ , relative to the aligning lasers' polarization. Because the actual three-dimensional angular distributions must have cylindrical symmetry about the alignment laser polarization, the measured planar distributions are rotated through an angle of 2π about this axis to quantify the delay-dependent alignment for the ionization experiments. Following the standard approach, we use the expectation value $\langle \cos^2 \theta \rangle$ computed from our angular distributions as a measure of the alignment quality [1,2,14,15].

For the CO experiments, we implement the double-alignment-pulse scheme described above, with the second alignment pulse arriving 8.664 psec (approx. one full rotational period) after the first pulse. In spite of the fact that the molecules enter the chamber at room temperature, and the focused alignment beams do not fully overlap the ionization volume we observe a variation $0.31 \leq \langle \cos^2 \theta \rangle \leq 0.36$ between times of maximum parallel and maximum perpendicular alignment.

Alternatively, at a given probe delay, a qualitative measure of alignment can be obtained in a single laser shot by examining the TOF distribution of the ion fragments. Explosion partners from molecules aligned perpendicular to the spectrometer axis have no initial velocity along the extraction field. These ion fragments arrive at the detector at the same instant and, therefore, produce a single peak in the TOF spectrum. Conversely, molecules that are preferentially aligned along the axis of the mass spectrometer, dissociate into ion pairs with initial velocities that are parallel and antiparallel, respectively, to the extraction field. This forward-backward velocity distribution produces a bimodal TOF feature that straddles the perpendicular alignment peak for each fragment species. By recording, as a function of the Coulomb explosion delay, the ratio of ion signal in the wings of the TOF peak relative to that at the peak center, we measure the variation in the ratio of molecules aligned parallel or perpendicular to the laser electric field. These delay scans do not require single-event-mode analysis and, therefore, can be taken rapidly with good signal to noise using higher gas pressures and current-mode detection. Figure 1(a) shows representative alignment data observed using the single-shot TOF detection method for room-temperature CO. The temporal dispersion in the high-order revivals at large delays is the result of centrifugal distortion of the molecule. The Fourier transform of the time-dependent signal reveals the energy differences responsible for the temporal evolution of the

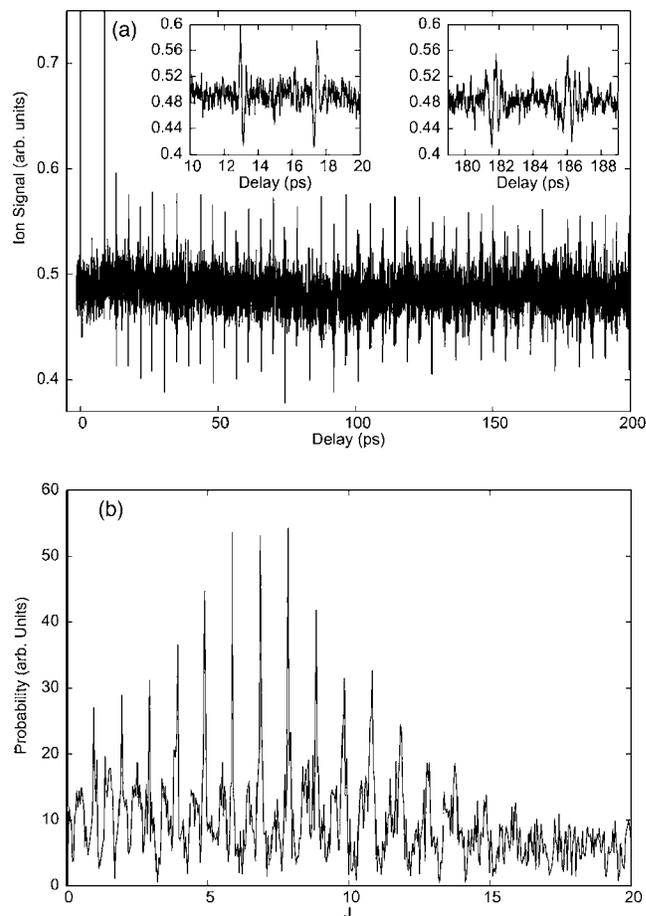


FIG. 1. (a) Ratio of C^{3+} fragments traveling parallel vs perpendicular to the TOF spectrometer axis following Coulomb explosion of laser-aligned CO molecules. The ratio provides a qualitative single-shot measure of molecular alignment as a function of time delay after the aligning laser pulses. Larger (smaller) ratios indicate preferential alignment parallel (perpendicular) to the alignment-laser polarization direction. The molecules are exposed to two 70 fsec, 10^{13} W/cm² alignment pulses that are linearly polarized along the spectrometer axis at $t=0$ and 8.664 psec, respectively. The insets show magnified views of the alignment-dependent ion ratio near the first and 20th half and full revivals following the second alignment pulse. The higher-order revivals are imperfect replicas of the first due to centrifugal distortion of the molecule. Note that temporal overlap between the circularly polarized Coulomb explosion pulse and either of the alignment pulses results in enhanced ionization and a significant increase in the ion ratio. Comparison of the signal variations during the first half revivals immediately following each of the two alignment pulses clearly shows the significant improvement in alignment that is achieved by the addition of the second alignment pulse. (b) The squared Fourier transform of the revival structure in (a) identifies the J -states contributing to the rotational wave packet. The horizontal axis has been scaled from energy to J -value using the rigid-rotor energy differences.

wave packet, and therefore, identifies the eigenstates that contribute to the rotational wave packet [see Fig. 1(b)].

The degree of alignment we observe is consistent with a quantum simulation that models our CO sample as a thermal ensemble of nearly rigid rotors with a polarizability

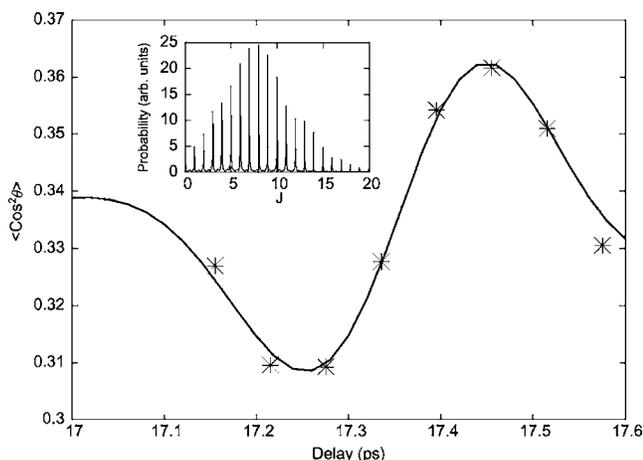


FIG. 2. Variation in $\langle \cos^2 \theta \rangle$ over a range of delays near the second full wave packet revival, for an ensemble of coherently prepared CO molecules. The delay scale is relative to the first of two alignment pulses and the laser pulse parameters are identical to those described in the caption for Fig. 1. Data points (*) are extracted from the measured angular distributions of C^{3+} fragments produced during Coulomb explosion of the CO molecules. The solid curve is the result of a numerical simulation of the alignment as described in more detail in the text. The inset shows the Fourier transform of the simulated temporal variation in $\langle \cos^2 \theta \rangle$ over a 200 psec delay range. The horizontal axis has been scaled from energy to J value using the rigid-rotor energy differences. The simulated spectrum should be compared with the experimental distribution shown in Fig. 1(b).

anisotropy $\alpha_0 = \alpha_{\parallel} - \alpha_{\perp} = 6.5$ (a.u.), where α_{\parallel} and α_{\perp} are the molecular polarizabilities parallel and perpendicular to the molecular axis, respectively [26]. Rotor eigenenergies are corrected for lowest-order centrifugal distortion, $E_J = B_0 J(J+1) - D_e J^2(J+1)^2$ ($B_0 = 8.79 \times 10^{-6}$ a.u., $D_e = 2.79 \times 10^{-10}$ a.u.) and our numerical approach is nearly identical to one previously reported [2]. We utilize a second-order Runge-Kutta algorithm to integrate the time-dependent Schrödinger equation in the presence of an induced dipole interaction potential, $V(\theta, t) = \frac{1}{4} F^2(t) \alpha_0 \cos^2 \theta$ a.u., where $F(t)$ is the combined electric field envelope for the two alignment pulses and θ is the angle between the molecular axis and the alignment lasers' polarization direction. The alignment pulses are assumed to be Gaussian with peak intensities, durations, and relative delays that match, within our experimental uncertainties, those used in the experiments. We compute, individually, the time-dependent angular probability distribution created from initial rotational levels $|J_0 M_0\rangle$ that have thermal populations greater than 10^{-5} . These probability distributions are added to simulate the angular distribution of the ensemble. The Fourier transform of the time-dependent expectation value, $\langle \cos^2 \theta \rangle$ identifies the J -states in the coherent wave packet. The best agreement between the measured [Fig. 1(b)] and simulated (Fig. 2 inset) spectra is obtained by assuming an initial rotational temperature of 200 K. This temperature is not unreasonable given the presence of the large liquid-nitrogen trap at the gas inlet to the chamber and the fact that the gas is being continuously pumped by a large-volume turbo. However, we note that this

choice is not critical and similar results are obtained over a range of temperatures. In general, higher (lower) temperatures result in spectra peaked at higher (lower) J values than observed in the experiments. For example, at 300 K, the simulation predicts that the feature associated with $J=9$ will be most important, whereas the experimental spectrum peaks at $J=7$.

Assuming a rotational temperature of 200 K, very good agreement between the measured and simulated delay-dependent variations in $\langle \cos^2 \theta \rangle$ is obtained after the imperfect experimental overlap between the alignment and ionization beams is taken into account (see Fig. 2). The solid curve in Fig. 2 is computed under the assumption that half of the ionized molecules have been coherently prepared by exposure to the full intensity of the alignment beams while the other half of the ions originate from outside of the aligned volume. As mentioned previously, the 50% aligned fraction estimate is reasonable given results of the cross-correlation measurements and the nonlinear intensity dependence of the multiple-ionization process that is responsible for Coulomb explosion.

III. EXPERIMENTAL RESULTS

The well-characterized, coherently prepared molecular targets are then used to measure the angle-dependent ionization probability for CO. For these single-ionization experiments, the quarter-wave plate is removed from the circularly polarized Coulomb explosion beam. In addition, the explosion pulse intensity (10^{15} W/cm²) is reduced, resulting in a less intense (10^{14} W/cm²) ionization pulse that is linearly polarized in the same direction as the alignment pulses. The DLA detector is configured as an ion counter capable of detecting up to 15 ion hits per laser shot and a 50-50 mixture of CO and Kr gas is leaked into the vacuum chamber. CO and Kr have similar ionization rates [7] and the alignment pulses have a negligible impact on the Kr ionization yield. By measuring the $[CO^+]:[Kr^+]$ yield ratios, we normalize out the influence of laser intensity fluctuations on the ionization signal at each delay. Partial pressures of the two gases are measured with a residual gas analyzer and are corrected for 70 eV electron impact ionization cross sections [27,28]. We record the ionization yield over a range of delays spanning the maximum parallel (along the laser polarization) and perpendicular (in a plane normal to the laser polarization) alignment times during the first full revival after the second alignment pulse. The delay-dependent changes in the $[CO]:[Kr]$ ionization ratio indicate an alignment sensitivity in the CO ionization rate (see Fig. 3). The results shown in Fig. 3 are the averages of 13 different measurement sets collected on six different days under essentially identical conditions. We find that the average value $\langle R \rangle$ of the CO:Kr ionization-rate ratios obtained at maximum parallel and perpendicular alignment times is equal to the rate ratio for an unaligned sample, $R_0 = 0.55$. Accordingly, systematic errors caused by small changes in the relative partial pressures of Kr and CO for different data sets are eliminated by individually normalizing each data set such that $\langle R \rangle = 0.55$.

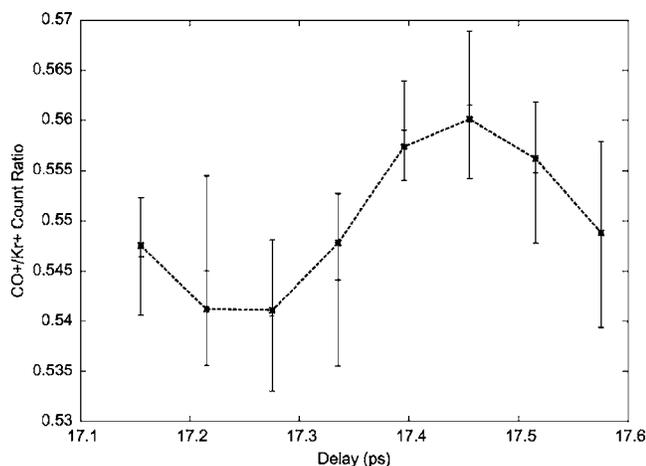


FIG. 3. Variation in the $[\text{CO}^+]/[\text{Kr}^+]$ ionization yield ratio as a function of delay between the alignment and ionization pulses. The data points are the mean values of 13 different measurement sets and the error bars reflect the standard deviations of those measurements. As described in the text, the dashed curve is a fit to the data in terms of measured delay-dependent moments $\langle \cos^{2N} \theta \rangle$. Specifically, we find that the angle-dependent ionization ratio has the form $P(\theta) = 0.43 + 0.36 \langle \cos^2 \theta \rangle$.

Analogous measurements were also made for ionizing laser intensities a factor of $1.14\times$ lower and $1.25\times$ higher than those used to obtain the data shown in Fig. 3. Within the experimental error bars, the rate ratios at lower intensity are identical to those in Fig. 3. However, significantly reduced ($3\times$ smaller) variations are observed at higher intensities.

IV. ANALYSIS AND DISCUSSION

The relatively small delay-dependent variation in the measured ionization yield ratios can be attributed to the limited macroscopic alignment achieved in the experiments. This is due, primarily, to the high initial rotational temperature of the sample and the imperfect spatial overlap between the alignment and ionization beams. Nevertheless, our detailed Coulomb explosion measurements enable us to extract the functional form of the angle-dependent ionization rate $P(\theta)$ for CO. Specifically, $P(\theta)$, or any positive definite θ -dependent observable with symmetry about $\theta = \pi/2$, can be expanded in moments $\langle \cos^{2N} \theta \rangle$ of the molecular angular distribution for $N=0, 1, 2, \dots$. Accordingly, the dashed curve in Fig. 3 is a least-squares fit of the measured ionization yield ratios to the delay-dependent moments obtained from the experimental CO distributions. The χ^2 value for the fit is not improved by including terms beyond $N=1$ in the expansion. Thus, the best-fit function has the form $P(\theta) = A + B \langle \cos^2 \theta \rangle$, with $A=0.43$ and $B=0.36$. From this expression, we obtain the ionization anisotropy for molecules aligned parallel or perpendicular to the ionizing field, $P_{\parallel}/P_{\perp} = 1.9 \pm 0.6$, by setting $\langle \cos^2 \theta \rangle = 1$ and 0 for P_{\parallel} and P_{\perp} , respectively.

Our ionization measurements are in qualitative agreement with recent theoretical results based on a molecular-orbital

ADK tunneling (MOADK) model [22,29]. For ionization with low-intensity 8 fsec, 800 nm laser pulses, the MOADK calculations predict an ionization anisotropy $P_{\parallel}/P_{\perp} \approx 4.7$. This value is nearly constant for intensities up to $8 \times 10^{13} \text{ W/cm}^2$ but then decreases rapidly with increasing intensity such that $P_{\parallel}/P_{\perp} \approx 3.4$ and 1.5 at 1.6×10^{14} and $3.2 \times 10^{14} \text{ W/cm}^2$, respectively [22]. More generally, $P(\theta)$ has a functional dependence which is indistinguishable from $A + B \cos^2 \theta$ for intensities above 10^{14} W/cm^2 , with only a slight variation from this form at lower intensities. The prediction of a constant ionization anisotropy at low intensity and nearly isotropic ionization rate at higher intensities is consistent with our results. While our measured value $P_{\parallel}/P_{\perp} \approx 1.9$ is approximately a factor of 2 lower than predicted for an intensity of 10^{14} W/cm^2 , quantitative agreement is obtained if we increase our experimental intensity estimate by a factor of 2. Another possible source of the discrepancy is the MOADK approximation itself. We note that for 100 fsec, 800 nm pulses, MOADK calculations underestimate the $[\text{CO}^+]:[\text{Kr}^+]$ yield ratio by a factor of 2.5 [8]. In addition, while the change in molecular alignment during an 8 fsec ionization pulse should be negligible, our Coulomb explosion measurements indicate that partial alignment does occur during our 30 fsec ionization pulses. Thus we expect that the theoretical predictions for 8 fsec pulses will overestimate the ionization anisotropy for the 30 fsec case.

In conclusion, we have used intense short laser pulses to transiently align diatomic molecules from an effusive room-temperature source. The delay-dependent angular distributions of the coherently prepared molecules have been recovered from Coulomb explosion measurements using both qualitative and quantitative methods. The preferentially aligned targets have been used to determine, for the first time, the angular dependence of the ionization rate for CO molecules exposed to 30 fsec, 780 nm laser pulses. We find that below the saturation intensity, the ionization probability is two times larger for molecules aligned parallel rather than perpendicular to the laser polarization direction. These results are in qualitative agreement with MOADK predictions. In the future we intend to extend this measurement technique to other molecular species, enabling more direct comparisons between experiment and theory which, in turn, may lead to a more complete understanding of the complex dynamics associated with intense laser ionization of molecules.

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