Effects of orbital symmetries in dissociative ionization of molecules by few-cycle laser pulses

A. S. Alnaser, C. M. Maharjan, X. M. Tong, B. Ulrich, P. Ranitovic, B. Shan, Z. Chang, C. D. Lin,
C. L. Cocke, and I. V. Litvinyuk

J. R. Macdonald Laboratory, Physics Department, Kansas State University, Manhattan, Kansas 66506-2601, USA

We have measured angular distributions of ion fragments produced in dissociative double ionization of CO, CO_2, and C_2H_2 by intense ultrashort laser pulses. This report extends similar recent studies of O_2 and N_2 to a wider set of molecules. We found that for sub-10-fs pulses of sufficiently low intensity the fragments' angular distributions for all studied molecules are determined by angular dependence of the first ionization step. Those experimental angular distributions were in good agreement with angular dependent ionization probabilities calculated with the molecular tunneling ionization theory. The measured angular distributions directly reflect the symmetry of the corresponding molecular orbitals. For higher laser intensities and longer pulse durations, dynamic alignment and postionization alignment start to affect the angular distributions and ion fragments are preferentially ejected along the laser-polarization direction.

Molecules subjected to nonresonant infrared laser pulses of sufficiently high intensity undergo single or multiple ionization often followed by immediate dissociation. Though this process is of great fundamental and practical interest and has been studied extensively for many molecules, its detailed mechanism remains poorly understood. In particular, the nature of strongly anisotropic angular distributions of resulting ion fragments has been a matter of some debate. Specifically, the argument has centered around the relative importance of two possible mechanisms: angular dependence of molecular ionization rates (the so-called "geometric" alignment, when molecules of certain orientation are selectively ionized); and dynamic alignment by the pulse (when molecules actually reorient before dissociating). For heavy molecules (such as I_2) geometric alignment is clearly a dominant mechanism [1,2]. For light molecules both mechanisms may play a role and deconvolving their relative contributions is not straightforward.

Until very recently most studies of dissociative ionization in diatomic molecules reported strongly asymmetric angular distributions with ion fragments ejected in a narrow angle around the laser polarization direction [3–5]. At the same time, the recently developed theory of molecular tunneling ionization (MO-ADK) predicts that for some molecules, due to the symmetry of their molecular orbitals, the ionization probability is the highest when the molecular axis is not parallel to the laser electric field [6]. In general, there not need to be a direct correlation between the fragment angular distributions and the angular dependence of the ionization probability, because, in addition to dynamic alignment by the pulse, several ionization steps with different angular dependences may be involved in the process [7]. Nevertheless, a recent report on dissociative ionization of O_2 and N_2 [8] presents experimental angular distributions that are in almost perfect correlation with the corresponding angle-dependent single ionization probabilities calculated with molecular ADK theory. In that study, the dynamic alignment effects were minimized by using very short (8 fs) laser pulses of low intensities, where excitation into the dissociative state

and further ionization were achieved by electron-ion recollision, the process whose cross section was lately found to be only weakly dependent on molecular orientation [9,10]. Thus, the measured angular distributions directly reflected the corresponding angle-dependent ionization probabilities, which depend on the symmetry of corresponding molecular orbitals [7,8]. Here we present the results of extending those studies to heteronuclear diatomic (CO), triatomic (CO_2), and polyatomic (C_2H_2) molecules. In each of the above cases we measured the angular dependence of dissociative ionization using intense 8-fs laser pulses. Though several different dissociation channels were observed for each of the molecules, we focused our attention on the dissociation of doubly charged molecular ions into a pair of singly charged fragments, namely, on the following channels: $CO^{2+} \rightarrow C^+ + O^+$; $CO_2^{2+} \rightarrow CO^+ + O^+$; $C_2H_2^{2+} \rightarrow CH^+ + CH^+$. That allowed us to detect two fragments in coincidence and to use momentum conservation for establishing that they both originate from the same molecule. Then for those linear molecules the relative momentum of the two fragments directly measures the alignment and/or orientation of the molecular axis immediately before dissociation with respect to the laser polarization. We measured the dependence of the relative yield for each channel on the angle between the molecular axis and polarization direction of the laser pulses. The detailed description of the experimental apparatus was given previously [7,8]. Briefly, 35-fs 790-nm laser pulses were generated by a multipass Ti:sapphire amplifier and then compressed to an 8-fs duration using self-phase modulation in an Argon-filled hollow fiber followed by a chirped-mirror compressor. The laser beam was focused by a spherical mirror (f=75 mm) on the supersonic jet of target molecules inside the experimental high vacuum chamber (10^{-10} torr background pressure). Ion fragments were accelerated by a uniform electric field onto a position and time-sensitive multihit delay-line anode detector. A complete three-dimensional momentum vector of each detected ion fragment was measured. The intensity was estimated by measuring momentum distributions for hydrogen molecules with circular polarization as described previously
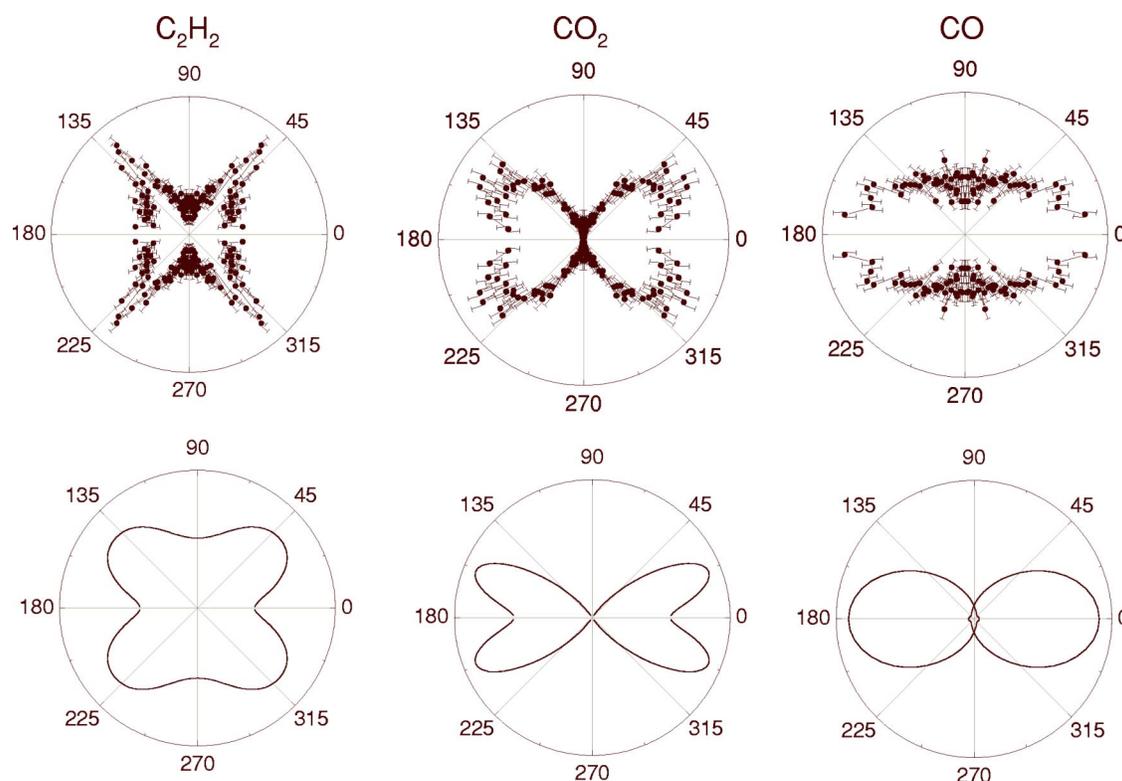
FIG. 1. (Color online). Experimental angular distributions for pairs of singly charged fragments detected in coincidence. Distributions were measured for $C_2H_2^{2+} \rightarrow CH^+ + CH^+$, $CO^{2+} \rightarrow C^+ + O^+$; $CO_2^{2+} \rightarrow CO^+ + O^+$; channels. Estimated pulse peak intensity is 6×10^{13} W/cm^2, pulse duration is 8 fs, central wavelength is 800 nm, polarization is horizontal. Presented below are the angular-dependent single-ionization rates for neutral molecules calculated using Molecular ADK theory for electric field of the same strength. For CO, the MO-ADK rate depends on orientation of the molecule and the symmetrized distribution is shown.

[11]. The main result of this study is presented in Fig. 1. It shows the polar plots of angle-dependent yields of the chosen dissociation channels for the three molecules. In these plots, the measurements were obtained between 0°–90° and reflected in the other quadrants to give a complete picture. Only for CO the yield is highest along the laser-polarization direction, similar to N$_2$ [7,8]. For CO$_2$ and C$_2$H$_2$ the fragmentation is most probable at some angle between 0° and 90° in respect to laser polarization, similar to O$_2$ [5]. To interpret these observations, we compare the experimental angular distributions with theoretical single-ionization probabilities for neutral molecules calculated using the molecular ADK theory [6], also shown in Fig. 1. The molecular structure and orbital wave functions were calculated using the *ab initio* quantum chemistry code GAMESS [12]. The MO-ADK coefficients were obtained by fitting the wave function in the asymptotic region. The angular-dependent ionization rates are obtained from the MO-ADK theory [6]. As for N$_2$ and O$_2$ earlier [7,8], for all targets we observe a remarkable correlation between the angle-dependent single-ionization probabilities predicted by molecular ADK for neutral molecules and experimental angular distributions of ion fragments. The experiments were performed in the intensity regime well below saturation for single ionization. At such intensities double ionization is dominated by a nonsequential rescattering mechanism. In this case, the overall angular dependence of dissociative double ionization is determined by the more orientation-sensitive first-ionization step. The results pre-

sented here confirm this interpretation. The angular dependence of single-ionization probability, reflected in the experimental angular distribution of the fragments, is qualitatively determined by the structure and symmetry of the molecular orbital from which the electron is removed. As the tunneling ionization rate exponentially depends on ionization potential, the electron almost always will be ionized from the highest occupied molecular orbital (HOMO). Thus, it is the HOMO symmetry that determines the overall shape of the experimental angular distributions. For example, if the HOMO has nodal planes containing (perpendicular to) the molecular axis, the molecule will have a low probability to tunnel ionize when aligned parallel (perpendicular) to the laser electric field vector due to the low orbital electron density in the tunneling region. That is the case for CO$_2$, with a π_g HOMO, which exhibits pronounced minima in fragment angular distributions both at 0° and 90° with respect to the laser polarization, because molecules with such orientation are less likely to ionize. Both O$_2$ and CO$_2$ angular distributions are of the butterfly pattern, a characteristic of the π_g orbital. The peak of the CO$_2$ angular distribution is closer to the molecular axis due to the larger nuclear distance between the two Os in the CO$_2$. Somewhat similarly, π_u symmetry of the C$_2$H$_2$ HOMO results in angular distribution with an ionization yield being the highest for molecules having their axes somewhere between 0° and 90° to the ionizing field. For CO (σ_g) the molecules aligned parallel to the field are the easiest to ionize according to molecular ADK theory, result-
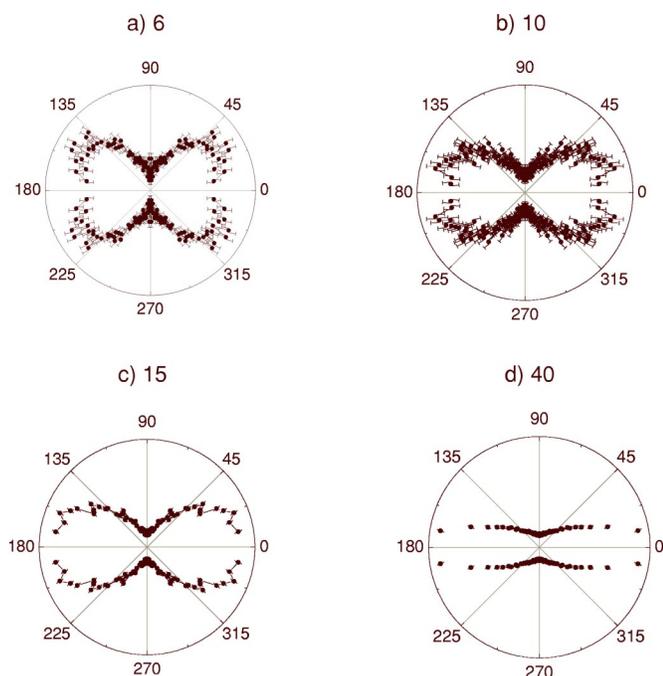
FIG. 2. (Color online). Experimental angular distributions for correlated (CO^+, O^+) ion pairs produced by dissociation of CO_2 by 8-fs (800-nm central wavelength) laser pulses. Laser polarization is horizontal. Estimated peak intensities are $(10^{13}$ W/cm^2): (a) 6; (b) 10; (c) 15; (d) 40.

ing in the dumbbell-shaped experimental angular distributions. Of course, the angular distributions of the fragments are also affected by other factors, such as laser-pulse peak intensity and duration. For ultrashort pulses of relatively low intensity, used in experiments described above, effects of those factors are minimized. As the intensity and/or duration of the pulses increases, the experimental angular distributions begin to deviate from the predictions of the molecular ADK theory. Figure 2 presents experimental fragment angular distributions for CO_2 measured for various pulse peak intensities. For increasing intensities more and more fragments are emitted into a small angle around the laser polarization direction, finally acquiring the characteristic strongly anisotropic shape.

Several possible mechanisms can cause the dependence of experimental angular distribution on laser intensity. First, for sufficiently high intensities the first ionization step becomes saturated for all molecular orientations and ionization probability loses its angular dependence. Second, as the first ionization saturates, the second ionization can switch from nonsequential to sequential regime with much different angular dependence. If that sequential double ionization were to involve charge-resonance states of the ion, similarly to the enhanced ionization in H_2 [13], it will be strongly favored for molecules aligned parallel to the electric field. Third, sufficiently strong pulses can themselves reorient the molecules prior to or during dissociation (dynamic alignment) [14], thus affecting the measured angular distributions of the fragments. All these mechanisms can act simultaneously, and their relative contributions may be difficult to disentangle. While we know of no definitive reports of charge-resonance enhanced ionization (CREI) in molecules other than hydrogen, theoretical modeling confirms that dynamic alignment does play a role in dissociative ionization even for short pulses. Finally, the postionization alignment effect may also attribute to the alignment along the laser-polarization direction as the laser intensity or duration increases [15].

In summary, we studied strong-field dissociative double ionization of three different molecules by sub-10-fs laser pulses. We found that in all cases for intensities below saturation, the experimental angular distributions of singly charged fragments are well described by angle-dependent single-ionization probabilities calculated using the molecular ADK theory. These distributions reflect the structure of molecular orbital from which the electron is removed. We also found that (except for CO) it takes a much higher pulse-peak intensity to produce a characteristic uniaxial anisotropic distributions of fragments typically observed in strong-field experiments. At lower intensities, when dynamic alignment effects are negligible, the fragment angular distributions are almost entirely determined by angular dependence of the first-ionization step. The detailed physics of dissociative double ionization in sequential regime (high intensity) requires further studies.

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