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High-resolution electron-ion coincidence spectroscopy of ethanol in intense laser fields

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High-resolution electron-ion coincidence spectroscopy is used to (i) map correlations between electrons and ions from atomlike ionization of ethanol by intense 400 and 800 nm light pulses and (ii) disentangle the effects of dissociative multiphoton ionization (MPI) and tunneling ionization (TI) ionization. Electron spectra correlated with C\textsuperscript{6+} (n=1,2,3) exhibit a continuum structure with a high-energy tail due to inelastic collisions involving rescattered electrons while those correlated with C\textsubscript{2}H\textsubscript{4}O\textsuperscript{+} have structure characteristic of MPI and above-threshold ionization.

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Following Volkov’s solution, in 1935, of the Dirac equation in the presence of a plane wave [1], the theoretical underpinnings of electron behavior in intense electromagnetic fields [2] have constituted one of the foundations on which modern strong-field science has developed. Within the framework of the Keldysh-Faisal-Reiss (KFR) theory [3], electron ejection from an atom in a strong optical field is described in terms of multiphoton (MPI) or tunneling (TI) ionization (TI); the boundary between the two is quantified by the adiabaticity or Keldysh parameter $\gamma = (I_0/2U_p)^{1/2}$, the ratio of the tunneling time to the optical period. $I_0$ is the ionization energy and $U_p$ is the ponderomotive potential due to the optical field. Experimentally, $\gamma$ values can be readily selected by varying the laser intensity and/or the nature of the irradiated target. It is established that TI dominates the dynamics for $\gamma<1$. Here the ejected electron’s energy distribution is largely determined by its classical propagation in the optical field. For large values of $\gamma (>1)$, the MPI picture is more appropriate in describing the dynamics. Now, atomic resonances and above-threshold ionization (ATI) peaks manifest themselves in electron spectra.

Experimentally, electron spectroscopy is a potent weapon in the arsenal employed to probe light-matter interactions in the strong-field regime. It is now possible to probe ionization dynamics in a kinematically complete fashion in certain cases. Electron and ion momenta that are correlated with atomic double ionization have been measured in the TI regime (see, e.g., [4]) and a reasonably robust framework exists within which to understand atomic TI and the subsequent electron rescattering dynamics [5]. Only a few coincidence measurements have been reported on atoms in the MPI regime [6] and in the MPI to TI transition region [7]: electron spectra from MPI of Xe show well-resolved resonances while in TI of Ar only featureless spectra are obtained.

On the molecular front, the first kinematically complete dissociative ionization experiment [8] detected coincidences between all ionic fragments from the triatomic molecule CS\textsubscript{2}. Thereafter, very few kinematically complete fragmentation experiments have been reported [9]. Most strong-field studies continue to rely on measurement of ion yields alone; little is reported on either electron spectroscopy [10] or kinematically complete experiments that include electron detection [11].

The results that we report in the following emerge from experiments in which we apply the electron-ion coincidence method that has been successfully implemented in studies of photofragmentation by synchrotron radiation [12] to probe strong-field dynamics of a polyatomic molecule, ethanol. Electron spectra that we detected in coincidence with selected ions open new vistas. We focus here on the ability of our coincidence experiments to enable unambiguous delineation of the molecular dynamics into MPI and TI regimes. We regard ethanol as an archetypal linear polyatomic of modest dimensions whose strong-field ionization dynamics has attracted much contemporary attention [13,14]. To our knowledge, no one has previously attempted to probe strong-field polyatomic ionization dynamics using electron-ion coincidence spectroscopy.

In our coincidence apparatus, we detected electrons using a 264-mm-long linear time-of-flight (TOF) spectrometer with a limited detection angle ($\sim 0.0014 \times 4 \pi$ sr) so as to achieve sufficient energy-resolving power. An ion TOF spectrometer was mounted opposite the electron spectrometer. Either the fundamental (800 nm) or the second harmonic (400 nm) from a Ti:sapphire laser system (pulse width 150 fs, repetition rate 1 kHz) was used as ionizing radiation that was focused by an f=60 mm concave mirror to a location between pusher and extractor electrodes (graphite-coated Al with 80% transmission Cu mesh). Linear polarization was along the TOF axes. Ethanol vapor was effusively introduced such that, at 80 TW cm\textsuperscript{-2} intensity, a working pressure of $5\times10^{-10}$ mbar (base pressure $5\times10^{-11}$ mbar) ensured less than one ionized molecule per laser shot. No extraction field was present in the interaction zone when the laser illuminated the C\textsubscript{2}H\textsubscript{4}OH molecules: only electrons ejected in the direction of the electron TOF spectrometer passed the pusher electrode into the TOF tube, to be detected by tandem microchannel plates (MCP). A few 100 ns after each laser pulse, high-voltage pulses ($\pm 300$ V) were applied to the pusher and extractor electrodes to extract ions into our 457-mm-long field-free ion TOF tube held at $-2000$ V; detection was by an 80-mm-diameter MCP detector.

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based on the precisely measured energy shift of the Xe ATI peaks.

It is pertinent to briefly note differences between our method and kinematically complete experiments. Electron energy information in the latter is from three-dimensional (3D) momentum imaging while we make angle-restricted TOF measurements. Electron 3D momentum imaging has high collection efficiency but low resolving power due to poor resolution for the momentum component \( p_z \) along the TOF axis; typically \( E/\Delta E \sim 5 \) and at best 15, due to both electrons and ions being extracted by the same dc field. In 3D momentum imaging, low dc fields determine the \( p_z \) resolution, while we use a high pulsed field for ion TOF analysis. This difference enables us to also attain a significantly higher mass resolution (typically, \( m/\Delta m \sim 200 \)) for nonenergetic ions than in 3D momentum imaging \( (m/\Delta m \sim 10, \text{ at best } 20) \). As a result, 3D momentum imaging is a complementary technique that is most appropriate for kinematically complete experiments on small molecules (two-body breakup in general, three-body breakup at most) while our approach enables studies of even large polyatomics where higher mass resolution is indispensable. Note that neutral fragments may also be emitted; thus, ion measurements are kinematically incomplete.

Figure 1(b) shows the ion yield obtained in coincidence with all electrons using 400 nm light. Almost all possible fragment ions are seen, in line with thermochemical expectation of equal propensity for ethanol’s C—O and C—H bonds to break. The dominant ion is \( C^+ \), with significant amounts of \( \text{OH}^+ \) \((n=0–2) \) and \( \text{H}^+ \). \( \text{H}_2\text{O} \) impurity may be a possible precursor for \( \text{H}^+, \text{H}_2^+, \text{OH}^+ \), and \( \text{O}^+ \) fragments and, therefore, we exclude these ions from our discussion. The energy spectra measured for \( C^+ \) and \( C_2^+ \) fragments at two intensities indicate that the high-energy tail is essentially determined by the Coulomb explosion process. Increase of laser intensity makes the Coulomb tail more prominent in comparison to the lower-energy molecular dissociation part of the energy spectrum.

Figure 2 shows electron spectra measured with 400 and 800 nm light at different intensities. At lower intensities structure due to ATI is clearly resolved and extends to an energy corresponding to \( 10U_p \). Such structure is commensurate with the corresponding \( \gamma \) values (in the atomic KFR model, \( \gamma \sim 1 \) corresponds to the MPI regime). At higher intensities, as \( \gamma \sim 1 \), ATI peaks become less prominent as a consequence of the transition to the TI regime. Strong-field ionization of ethanol appears to be atomlike in that the electron spectra are adequately rationalized within the atomic KFR framework [13]. To probe this facet of atomlike molecular dynamics more deeply, we turn now to electron-ion coincidences.

Figure 3 shows spectra of electrons correlated to different ions. We noticed similarity between spectra correlated with each ion in the group \( \text{C}_2\text{H}_5^+ \) and, thus, we present the sum of the spectra correlated with these fragments in Fig. 3(b). Similarly, spectra correlated with each ion in the group \( \text{C}_2\text{H}_5^+, \text{CHO}^+, \) and \( \text{CO}^+ \) were also summed. In the latter spectrum, besides a continuum component that constitutes a sharply dropping baseline, some additional humplike features are recognizable. The solid line in Fig. 3(a) denotes the
distinct morphology: the intensity of electron emission first drops sharply at low energies and then exhibits a broad hump at higher energies. Note that the drop-off is very similar to that predicted by the ADK theory [Fig. 3(a)].

As already noted [13], the broad featureless spectra seen in Fig. 3 are indicative of the onset of the TI regime. Our spectra bring to the fore a special facet of TI dynamics that involves rescattering in the molecular context: electrons that are emitted by tunnel ionization from ethanol continue to “feel” the effect of the optical field even after the initial ionization event is over. The electron wave packet initially moves away from the vicinity of C2H5OH+ but, half an optical cycle later, is pulled back toward the parent core. At high enough intensities, inelastic collisions of the rescattered electron with the molecular ion may contribute to washing out the effect of ATI peaks. If the rescattering leads to ejection of a second electron, the excess energy is distributed among the two electrons in continuous fashion, ruling out any structure in the resulting spectrum.

Focusing specifically on spectra in Fig. 3(d), we attribute the sharply dropping part on the low-energy side to TI, whereas the broad hump at the high-energy side is due to rescattered electrons. The field-ionized electron at zero kinetic energy can gain energy 3.17Up upon its return to the ethanol core. When the electron is then backscattered, it can gain energy up to 10Up [18]. The electrons correlated with C3+ are seen to possess higher energy than electrons correlated with C2+, which, in turn, appear to be pushed out to higher energy with respect to electrons correlated with C+. This rescattering type of behavior agrees well with what has been reported for TI of He and Ar [7,19] and lends credence to the notion of ethanol strong field ionization being atomlike [13]. Along the same lines, it is possible to attribute the sharply dropping baseline and the structure on top of it [seen in the electron spectra correlated to relatively large fragments in Fig. 3(b)] to TI and MPI, respectively.

Formation of multiply charged atomic fragments is indicative of multiply charged ethanol precursors, while fragments like C2H5+, CHO+, and CO+ mostly have excited states, C2H4O2+, as precursors. It is known that focal volume effects govern fragmentation patterns seen in TOF spectrometry. In intensity-selective TOF spectrometry [20], in which only a small part of the laser-molecule interaction volume is monitored such that detected events are predominantly from regions of maximum intensity, the resulting fragmentation patterns are significantly different from those obtained when measurements are made in the spatially averaged (intensity averaged) mode that is conventionally used. In the latter case the fragmentation mostly reflects low-intensity processes, as a consequence of relatively low-intensity regions dominating the geometrical volume of the interaction zone [20]. As a result, single MPI of ethanol occurs predominantly in the wings of the focus. Conversely, a preponderance of highly charged atomic fragments is from high-intensity parts of the focal region, where TI dominates the dynamics. In the intensity regime in which we have conducted experiments, the spatial regions map onto zones in which dissociative ionization dynamics are predominantly MPI or predominantly TI dominated. In the electron channel, the morphology of spectra that we measure proves to be a sensitive probe of the two dynamical regimes.

FIG. 3. (Color online) Electron spectra from C2H5OH using 400 nm light at 80 TW cm−2 in coincidence with (a) any ion; (b) C2H3O+ and sum of C2H5+, CHO+, and CO+; (c) sum of CH3+ and CH2+, CH+, and C+; (d) C2+ and C3+.
most always one slow electron is produced. Comparing the
dences that probe double and triple ionization, in which al-
the C\(^{+}\)-C\(^{+}\) combination, we see the same behavior as for
coincidences with C\(^{3+}\) and C\(^{2+}\): the higher the charge state,
ion pairs, as indicated.

Figure 4 shows spectra from electron-ion-ion coinci-
dences with 

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\text{Electron kinetic energy (eV)}
\]

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