

Resonant excitation during strong-field dissociative ionization

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We studied dissociative ionization of oxygen by intense femtosecond laser pulses with central wavelengths between 550 and 1800 nm. We measured kinetic energy release spectra and angular distributions of fragments resulting from symmetric dissociation of doubly charged molecular ions ($O_2^{2+} \rightarrow O^+ + O^+$ channel). In the kinetic energy release spectra we identified a number of distinct excited states of the molecular ion. Angular distributions for all but one of those states were consistent with recollision excitation following single ionization of O_2 . For the remaining ($B^3\Pi_g$) excited state we observed a characteristic resonant dependence of its relative yield on the central optical frequency of the pulse, with the yield peaking at around 890 nm. This presents unambiguous evidence in support of importance of resonant excitation channels in strong field ionization of molecules.

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Interactions of molecules with intense femtosecond laser pulses have been studied extensively over the last decade. Though significant progress has been achieved towards understanding of these processes, many challenges and unanswered questions still remain. While simple intuitive models of ionization like Ammosov-Delone-Krainov theory [1] (ADK) and electron-ion recollision ("simpleman's model" [2]) successfully explain most of the strong-field phenomena studied in atomic targets, they have proven largely insufficient to account for more complex behavior experimentally observed in molecules.

The reasons for this extra complexity are both structural and dynamic. Dynamically, in molecules the strong laser field couples electronic motion (ionization and excitation) to additional nuclear degrees of freedom (vibrations and rotations) on a timescale comparable to a typical pulse duration (5–100 fs). Structurally, the multicenter nature of molecules breaks the spherical symmetry of the electronic wave functions, leading to interesting orientation-dependent interference effects in both ionization [3] and rescattering [4]. In addition, molecules are generally characterized by smaller separations between the adjacent electronic energy levels, giving increased significance to such excitation mechanisms as shake-up [5], multiphoton absorption [6], sequential nonadiabatic excitation [7], and nonadiabatic multielectron dynamics [8].

Recent experimental evidence [3,9] indicates that single ionization of small molecules in the tunneling regime can be successfully described by conventional single-active-electron models properly modified to account for molecular orbital structure [10]. However, it is becoming apparent that even for the simplest molecules multiple ionization involves a number of different mechanisms and pathways. For instance, in H_2/D_2 double ionization can proceed through recollision [11], enhanced ionization at the critical distance [12] and sequential [13] mechanisms, with all three pathways being observed simultaneously for some pulse parameters [14]. Recent reports on double ionization of N_2 and O_2 [3,15] are consistent with recollision being a dominant mechanism in nonsequential regime, though the behavior of the two mol-

ecules was dramatically different due to different symmetry of their electron wave functions.

It is also well established that strong-field multiple ionization of N_2 and O_2 produces electronically excited molecular ions and fragments [6,16]. The importance of excited states in multiple ionization pathways, as well as the mechanisms of these excitations has been a matter of debate. The direct fluorescence measurements using circular polarization ruled out recollision as a possible mechanism for production of most excited states observed in these experiments [6]. As a direct two-level multiphoton excitation is predicted to be inefficient due to small coupling strengths and large time-dependant ac Stark shifts, Gibson proposed a three-level model [17] which allows a strong multiphoton coupling, while minimizing the ac Stark shift and thus maintaining the resonance during the pulse. If such an excitation channel were to be operational, the corresponding yield should exhibit a resonant dependence on laser frequency.

In this paper we report the observation of resonant yield dependence during strong field dissociative ionization of O_2 . Specifically, we measured relative yield of the $B^3\Pi_g$ excited state of the oxygen dication as a function of laser frequency. This state was among several dissociative excited states of O_2^{2+} identified in previous work [15] by their distinct kinetic energy of resulting fragments (see Fig. 1). While all the other observed states exhibited fragment angular distributions consistent with the recollision excitation mechanism, the $B^3\Pi_g$ state did not fit that pattern and its origin remained unexplained.

Given that multiphoton excitation was a suspected mechanism of this state production, it was natural to investigate the dependence of its yield on laser wavelength. Since absolute yields of all strongly nonlinear multiphoton processes are extremely sensitive to small variations of pulse intensity, we resolved to measure the relative yield of the $B^3\Pi_g$ state with respect to the full production of excited oxygen dications. All the other known excitation channels were clearly attributed to recollision [15] and were not expected to exhibit a strong wavelength dependence. Nevertheless, we made our best effort to compare the results at different wavelengths but the

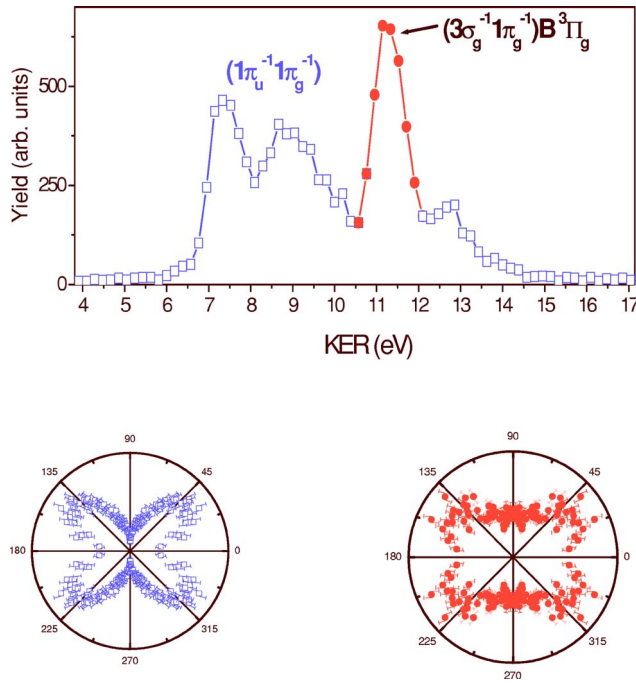


FIG. 1. (Color online) Upper panel: A typical KER spectrum of O^+ fragments at 800 nm and laser intensity $\sim 2 \times 10^{14} \text{ W/cm}^2$. Lower panel right: the angular distribution of the fragments resulting from the dissociation of the $B^3\Pi_g$ state in the dication. Lower panel left: the angular distribution of the fragments resulting from other states identified earlier in Ref. [15].

same intensity. In every case the experiment was performed in the nonsequential regime well below saturation for single ionization of O_2 .

A traveling-wave optical parametric amplifier of superfluorescence (TOPAS) (Quantronix) pumped by the output of Ti:sapphire multipass amplifier (790 nm, 35 fs, 1.5 mJ, 1 kHz) was used to generate pulses in the 1150–2300 nm range. The OPA output was frequency doubled in a nonlinear crystal to generate pulses in the 580–1150 nm range. To generate even shorter wavelengths the OPA output was nonlinearly mixed with 790 nm beam to produce the sum frequency. That produced broadly tunable (500–2300 nm) 50 fs pulses with energies of up to 100 μJ . The pulses were focused by a spherical mirror ($f=7.5 \text{ cm}$) on a supersonic jet of oxygen molecules inside a cold-target recoil-ion momentum spectroscopy (COLTRIMS) apparatus (described in detail elsewhere [15]). The pulse peak intensities were high enough to produce a sufficient yield of doubly ionized O_2 for all wavelengths within this range. The pulse energies were adjusted by using reflective neutral density filters when needed.

In the COLTRIMS apparatus the resulting ion fragments were projected by a uniform electric field (30 V/cm) onto a position-sensitive and time-sensitive delay-line-anode detector. The pairs of singly charged O^+ ions were detected in coincidence, their full three-dimensional (3D) momenta were measured, and ion pairs satisfying the zero-total-momentum condition were selected as originating from the $O_2^{2+} \rightarrow O^+ + O^+$ dissociation channel. The kinetic energy release (KER) spectra of such O^+ fragments were histogrammed. A typical

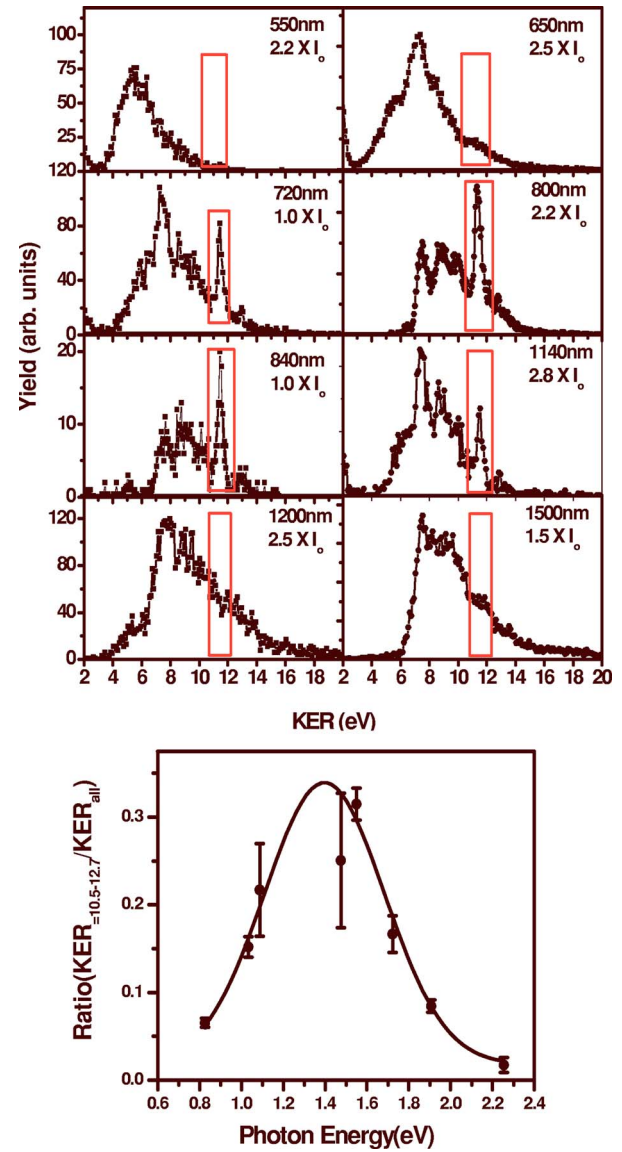


FIG. 2. (Color online) KER spectra of O^+ fragments at different laser intensities ranging from 550 to 1500 nm at the indicated laser intensities in units of I_0 ($I_0=10^{14} \text{ W/cm}^2$). The dependence of the $B^3\Pi_g$ state production on the laser wavelength is shown. In the lower panel, the yield's ratio of the $B^3\Pi_g$ state to all other states is plotted as a function of the laser photon energy. A resonancelike behavior is observed around 1.4 eV.

KER spectrum is shown in Fig. 1. It consists of a number of distinct bands, each corresponding to a certain dissociative excited state of oxygen dication. The assignment of these bands was made previously [15]. We focus our attention on the band corresponding to the $B^3\Pi_g$ state.

Previous studies have shown that the fragments corresponding to dissociation of the $B^3\Pi_g$ state exhibited very different angular distribution from the other observed channels [15]. All the other states yielded fragment angular distributions closely correlated with angular dependent single ionization probabilities predicted by molecular ADK theory [10], and their production was attributed to angle-anisotropic tunneling followed by almost isotropic electron recollision

[15]. The $B^3\Pi_g$ state did not conform to this pattern and its production mechanism remained a mystery. In this paper we present the results of the wavelength-dependent dissociative ionization study of O_2 , which allow us to claim that production of the $B^3\Pi_g$ state of O_2^{2+} involves a resonant excitation step.

The main result of this work is presented in Fig. 2. It shows a set of KER spectra for the $O_2^{2+} \rightarrow O^+ + O^+$ dissociation channel obtained at different laser wavelengths. One can see that the $B^3\Pi_g$ band is prominent for some frequencies and almost absent for others. The same Fig. 2 shows quantitative dependence of the $B^3\Pi_g$ state relative yield on the laser photon energy (at central wavelength). This dependence has a clearly resonant form, peaking at 1.4 eV.

In the absence of good knowledge of O_2^{2+} field-modified potential surfaces it is difficult to identify what exact pathway the production of the $B^3\Pi_g$ state takes. It is clear from our results that one of the steps involves efficient resonant excitation. We suggest a possible pathway. The configuration of the $B^3\Pi_g$ is largely $3s\sigma_g^{-1}1\pi_g^{-1}$ (relative to the neutral O_2 molecule [20,21]; as opposed to the dominant $1\pi_g^{-1}1\pi_u^{-1}$ configuration of the other states appearing in Fig. 1. It is possible that the resonance occurs in the excitation of an electron from the $3s\sigma_g$ to the $1\pi_g$ orbital, for which the required energy is around 8.6 eV [18,19]. The transition would be from the $^3\Sigma_g$ ground state to the lowest $^3\Pi_g$ excited state in

the neutral oxygen molecule. At laser wavelength of 890 nm, this will require that O_2 absorb six photons before removing the two electrons from the excited $1\pi_g$ state. One might also expect resonant behavior in the $1\pi_u$ to $1\pi_g$ transition, which feeds the other states appearing in Fig. 1, but we suspect that any resonant behavior of this transition is masked by the rescattering mechanism which would be expected to be stronger for this excitation than for the $3\sigma_g$ to $1\pi_g$ excitation.

In summary, we measured the dependence of relative yield of production for a selected dissociative excited state of oxygen dication on the wavelength of intense laser. This dependence is resonant in its form, providing direct proof that a resonant excitation mechanism is indeed operational in dissociative ionization of O_2 by intense laser pulses. The results presented here serve to underline the importance of resonant excitation during intense field-molecule interactions. These resonant excitation pathways must be taken into account, if we were to fully understand the behavior of molecules in strong laser fields.

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