Autoionization dynamics and Feshbach resonances: Femtosecond EUV study of O₂ excitation and dissociation

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Abstract. In this work, we present a time-domain study of the complex, multi-step, evolution of highly excited states of oxygen (O₂) that result from EUV photoionization. By monitoring the dissociation of molecular oxygen ions, we show that autoionization cannot occur until the internuclear separation is 30 Å or greater. As the ion and excited neutral atom separate, we directly observe the transformation of electronically bound states of the molecular ion into Feshbach resonances of the neutral oxygen atom. We achieve this by using laser high-harmonics in a femtosecond EUV-IR pump-probe scheme, combined with a triple coincidence reaction microscope measurement. Finally, we show control of the dissociation pathway through IR pulse induced ionization.

1. Introduction

Auto-ionization following photoionization of an inner-valence electron from a molecule[1-4] is a topic of great interest. Autoionization represents an important electronic many-body problem in molecules, and the electron and ion fragments produced in the process also contribute to radiation damage in materials and biological systems. Autoionization of an inner-valence vacancy is typically energetically-forbidden in the case of isolated atoms, but may be energetically allowed in molecules due to the role of the molecular environment. In particular, inner valence photoionization in molecular oxygen (O₂) is followed by an interesting autoionization process[1,2]. Feifel et al.[1] performed a high-resolution electron coincidence study of inner-valence ionized O₂, and found that autoionization takes place at large interatomic distances. Unfortunately, due to the lack of time-resolution, they were unable to offer further information about the mechanism for autoionization.

In this work, we directly observe the evolution of a highly excited O₂⁺ state using a triple coincidence study between an electron and two fragment ions by combining momentum imaging reaction microscopy [5-7] with an ultrafast (few-femtosecond) EUV high-harmonic source[8-10]. We observe the birth of a state of negative binding energy (Feshbach resonance) during the dissociation of O₂ following inner valence photoionization. We thus deduce that the autoionization in molecular oxygen occurs only at large interatomic distances of 30 Å or greater.
2. Experimental
The experimental setup is shown in Fig. 1 along with the schematic of the molecular autoionization process. The output from an ultrafast Ti:Sapphire amplifier system (2mJ, 30fs, 2kHz), is split into pump and probe beams. Part of the beam (~1.2 mJ) is used to generate an ultrashort (<10 fs) EUV pump beam with photon energy 42.7 eV (FWHM ≈ 1.5 eV) through high-harmonic up-conversion. The net photon flux after selecting a single harmonic using a pair of multilayer mirrors is ~2 x 10^9 photons/sec. The remainder of the beam (~0.8 mJ) is time delayed and recombined with the EUV pump beam to dynamically probe the autoionization process. This infrared (IR) probe beam passes through an optical chopper with a 50% duty cycle, which allows us to acquire data for the EUV-only case and the EUV-plus-IR case simultaneously, allowing us to normalize our data. The IR probe beam intensity in the interaction region is 4.9x10^{12} W/cm^2. The cold target O_2 gas beam density in the interaction region is estimated to be ~10^{11} – 10^{12} cm^{-3}. A reaction microscope (COLTRIMS) collects the photo-fragments with near 4π collection efficiency for both electrons and ions generated in each laser shot. This experimental setup was run continuously with excellent stability for > 100 hours.

![Figure 1](image)

**Figure 1.** (a) An ultrashort EUV pulse is produced through high-harmonic generation in Ar filled waveguide. EUV photons are energy filtered and used as pump. A part of the IR pulse serves as probe. (B) Reaction microscope for analyzing reaction fragments. Time of flight and position information from delay line anodes is used to reconstruct 3-dimensional momentum of electrons and ions in coincidence. (c) Autoionization channel showing a highly-excited O_2 molecular ion that is dissociating. At large internuclear distances, the autoionization leads to electron ejection and formation of two O+ ions.

3. Results and Discussion
The double ionization potential of O_2 is 36.38 eV. While the photon energy of our EUV beam (~42.7 eV) is sufficient for direct double ionization, it has been observed[1,11] that the ionization by the EUV photons above double ionization threshold predominantly leads to formation of a highly excited (O_2^+*). The highly-excited molecular ion then dissociates, and at some stage autoionizes resulting in O+/O+.

In particular, O_2 the excitation and dissociation study performed by Feifel *et al.*[1] at photon energies 40.8 eV and 48.3 eV reported a distinct lines spectra for autoionizing electrons that corresponds to the autoionization happening near the dissociation limits where O_2^+* evolves into oxygen ion and excited oxygen atom. This mechanism is expressed in the following equation.
Here, $e_1^-$ is the direct photoelectron and $e_2^-$ is the autoionizing electron. In their experiment, Feifel et al. [1], observe two prominent lines (A1,A2) around 0.5 eV energy for the autoionizing electron. These lines correspond to the atomic excited states 3p'(3D) (A1) and 3p'(3F) and 3s''(3P) (A2), auto- ionizing to the O$^+$ ground state ($^4$S). The primes and double primes refer to, respectively, the 2p$^3$(2D) and 2p$^3$(2P) ion cores. However, the exact dynamics of this process and the autoionization time scale could not be identified in that experiment due to lack of time resolution in synchrotron experiments.

We perform the O$_2$ excitation and dissociation study with femtosecond EUV pulses to resolve the fast dynamics. Figure 2 shows electron and ion kinetic energy release spectra acquired following excitation by a pulse of ~5fs duration with photon energy 42.7±0.7 eV. Here an electron was detected in coincidence with two O$^+$ ions (triple-coincidence). The broad diagonal feature centred at ~2 eV in the electron energy in Fig. 2 corresponds predominantly to the photoelectron (one-photon single ionization). The width of this feature is partly determined by the distribution of binding energies of the various autoionizing states of O$_2^+$ that are populated in the Frank-Condon region. The sharp vertical feature centered at ~0.5 eV electron energy corresponds to electrons uncorrelated with ion energies. This feature matches the A1, A2, atomic lines as defined by Feifel et al. [1], and thus represents the electrons resulting from autoionization near the dissociation limit.

Next, we introduce an IR pulse that is time delayed with respect to the EUV pulse in order to study the evolution of the excited molecular ion. Figure 3 shows the time dependent spectra of electrons detected in coincidence with two O$^+$ ions at six different time delays: 0 fs, 50 fs, 100 fs, 300 fs, 1000 fs, and 14000 fs. The gray curves represent the electron spectra in the presence of the EUV beam only, while the black curves correspond to the case when both the EUV and IR pulses are present. The 'EUV only' electron spectrum (gray curve) consists of two contributions (just as in Fig. 2): 1) auto-ionization electrons, corresponding to a sharp feature centered at 0.5 eV electron energy; and 2) the photoelectrons corresponding to the broad feature centered around 2 eV electron energy.

We observe that at zero time delay (Fig. 3a), the presence of the IR pulse strongly suppresses the auto-ionization electron peak near 0.5eV. This is due to the fact that EUV-generated O$_2^{2+}$ states,
lying in the gray region shown in figure 4(a), are further photo-ionized by the IR pulse to form $O_2^{2+}$
dissociative states. The IR pulse thus serves to disrupt the naturally occurring autoionization channel.

Figure 3. Electron energy spectra are acquired at varying delay between the EUV and IR pulses. Data are filtered so that only electrons detected in coincidence with two correlated oxygen ions are selected. The gray curves are the EUV-only spectra. The black curves are the EUV-plus-IR spectra.

More importantly, two new features begin to appear at 300 fs and become more pronounced at 1000 fs and 14000 fs (Fig. 3d,e,f): a peak at electron energy of approximately 2 eV and a peak at near-zero electron energy. The peak at near-zero electron energy can be explained by considering the excited dissociation limit of the di-cation $[O^+(4S) + O^+(2D)]$ at 35.7 eV and the dissociation limit of the autoionization state (Fig. 4(b)). As shown in the Feifel et al.[1], the A1/A2 lines correspond to autoionizing $O_2^{2+}$ states with dissociation limit energies ~0.5eV above the $O_2^{2+}$ ground state, which places the autoionizing states around 32.8 eV. A two-photon (~3.1eV) IR induced ionization from the autoionizing states can lead to formation of $O^+(4S) + O^+(2D)$ accompanied by an electron of very low energy (~0.1-0.2 eV). This mechanism is labeled “1” in figure 4(b).

The second feature, a peak centered at an electron energy of approximately 2 eV, appears around 300fs (Fig. 3d) and moves toward higher energy as the time delay increases. This peak is a direct indication of the creation of a Feshbach resonance and opening of the autoionization channel. The mechanism leading to this peak involves a single photon (~1.55 eV) electronic transition from an autoionizing state to a continuum state, which then decays to a $O_2^{2+}$ ground state producing a ~ 2 eV electron as shown in figure 4b (process labeled “2”). Because the electron kinetic energy is greater than the photon energy responsible for its formation, this corresponds to a system with negative
binding energy with respect to the di-cation ground state i.e. $O^+ (^{4}S) + O^+ (^{4}S)$ limit. However, the same $O_2^{2+}$ state near the dissociation limit represents an electron bound to an excited di-cation [$O^+ (^{4}S) + O^+ (^{2}D)$] with a positive binding energy. Thus, the excited neutral oxygen atom in the autoionizing $O_2^{2+}$ system is a Feshbach resonance with the open channel being the dication ground state [$O^+ (^{4}S) + O^+ (^{4}S)$] and the closed channel the first excited state of dication [$O^+ (^{4}S) + O^+ (^{1}D)$]. This Feshbach resonance forms at the point where $O_2^{2+}$ and $O_2^{4+}$ states intersect. As shown in figure 4(b), this occurs near 30 Å internuclear separation, where the calculated[12] dication ground state and autoionizing states deduced from Feifel et al.[1] cross each other.

The curve crossing of $O_2^{2+}$ and $O_2^{4+}$ near 30 Å also defines the opening of the autoionization channel. Below this distance, the autoionization is energetically not feasible and above this distance the excited states autoionization lifetimes are determined by the selection rules. Using the kinetic energy release information we find that it should take approximately 220-280 fs for $O^+/O^*$ fragments to reach 30 Å internuclear distance. Accordingly, the 2eV feature in electron spectrum is also not observed below 300fs (Fig. 3d). Hence, our data shows the first real-time evidence of creation of a Feshbach resonance and sets an experimental lower limit for the autoionization timescale to about

![Figure 4](image-url)
Moreover, the fact that the center of the ~2 eV feature is moving toward higher energy at longer time delays is due to increasing energy separation between the autoionizing state and the $O_2^{2+}$ potential energy curve as a function of internuclear distance.

At 1000 fs (Fig. 3e), a small shoulder appears in the EUV+IR curve around 0.5 eV, where the EUV only curve (gray curve) is peaked. We believe this corresponds to a natural appearance of the A2 autoionization line originating from the transition from excited neutral oxygen in the $3p'(3F)$ electronic state to the $O^+$ ground state ($^3S$) releasing a ~ 0.5 eV electron. This $3p'(3F)$ electronic state transition is LS-allowed, with a lifetime on a picosecond time scale[13], compared to nanoseconds lifetime for the LS-forbidden transitions from other excited states.

4. Conclusion and Acknowledgements

In this work, we use a reaction microscope in conjunction with a tabletop ultrafast EUV light source to study the behavior of molecular oxygen when illuminated by 42.7 eV photons. We use this novel approach to perform a direct time-resolved observation of a highly excited molecular system. Using EUV pump-IR probe, we observe the birth of a Feshbach resonance in the neutral oxygen atom with a negative binding energy. We monitor, in real-time, the autoionization dynamics that occurs in highly excited O$_2$ and find that the lower limit for autoionization timescale is ~300fs.

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5. References

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