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Experimental evidence for molecular ultrafast dissociation in O_2 clusters

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Abstract. Resonant Auger spectra of O_2 clusters excited at the O1s edge are reported. After excitation to the repulsive $1s^{-1}3\sigma^*$ state, the resulting resonant Auger spectrum displays features that remain constant in kinetic energy as the photon energy is detuned. The shift between known atomic fragment features and these features is consistent with that observed for atoms and clusters in singly charged states in direct photoemission. These findings are strong evidence for the existence of molecular ultrafast dissociation processes within the clusters or on their surface.

PACS. 36.40.-c Atomic and molecular clusters – 36.40.Mr Spectroscopy and geometrical structure of clusters – 33.80.Eh Autoionization, photoionization, and photodetachment

1 Introduction

One way of inducing intra-molecular bond breaking is to excite an electron from a core level to an anti-bonding orbital. The core-excited system then typically undergoes electronic Auger decay, in which one valence electron fills the core vacancy and another is ejected from the sample. This experimental method of probing a system is often referred to as resonant Auger spectroscopy (RAS). If the core-excited state is purely repulsive, the molecule can dissociate on an extremely short timescale, often in the low femtosecond range. The femtosecond time duration of the decay creates an internal time scale for the system, relative to which the speed of other processes competing with this decay can be measured [1–3]. As mentioned above, the timescale of the intra-molecular bond breaking can be in the fs range, which may be comparable to the lifetime of the core-excited state. When this is the case, a mixture of excited molecules as well as non-excited and excited fragments of the molecule is produced. This phenomenon is known as ultra-fast dissociation (UFD) [4].

O_2 is an example of a system dissociating on a femtosecond time scale, when the core 1s electron of one of the atoms is excited to the $3\sigma^*$ level [5]. From this excited state, the molecule decays by either ejecting an electron, or by dissociating into two atomic fragments. In the latter case the electron is subsequently ejected from the excited fragment. The Auger electrons coming from the molecule and from the atomic fragment differ in kinetic energy, allowing accurate monitoring of the process [6]. For many molecules, oxygen among them, the positions of the features stemming from fragments due to ultra-fast dissociation is well-known. In the case of clusters the situation is more complex. The existence of neighbouring molecules could, for example, suppress the UFD channel by caging the fragments inside the lattice or inter-molecular hybridization could reduce the anti-bonding character of the $1s^{-1}3\sigma^*$ state. Because of these factors, it is not evident that UFD should be present. By using the core-hole clock concept [1,2], one can calculate the path length of the fragments before the decay. If one compares this with the inter-molecular spacing in the lattice of the cluster, it gives an idea of whether a caging effect should affect the UFD process. The core-hole lifetime of O_2 is of the order of 3 fs. A characteristic dissociation time for the molecule can be calculated by using the following definition;

$$t_D = -\tau \ln(1 - n_{decays(\mathrm{O_2})}) \qquad (1)$$

where t_D is the dissociation time, τ is the core-hole lifetime and $n_{decays(\mathrm{O_2})}$ is the fraction of core-hole decay events occurring in the O_2 species relative to the total number of core-hole decay events. Deducing exactly how large a fraction of the electronic decays takes place in the fragments in the cluster case is hard, due to limited resolution and low signal to noise ratio. Therefore we use an estimate of about 10% of fragment decays [5,7], which is what has been found for free O_2 molecules. Such a calculation yields a value for t_D of about 7 fs for O_2. Using the velocity measured for the atomic fragments from a free molecule [8], 0.14 Å/fs, an upper limit to the pathlength can be found. The characteristic pathlength is thus in the order of 1 Å, which is much less than the intermolecular

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spacing of 3.2–3.3 Å found for a van der Waals bound O_2 dimer [9]. This means that caging need not significantly suppress the UFD process even inside a cluster. Relatively recently, investigation of UFD in condensed and adsorbed H_2O [10–12] has been performed. The different approaches of these studies has led to ambiguous results as discussed in [10]. Some of the groups mentioned measured a depletion of the H-ion yield while other measure an increase in the same yield after core-excitation. In all of these studies, this was interpreted as a sign of UFD. In addition, some ten years ago, Kuiper and Dunlap reported on the existence of UFD in adsorbed, bulk O_2 [13]. To shed light on the situation, it is possible to probe the effect in van der Waals clusters, where problems like surface contamination and charging are not present. We have chosen clusters of O_2 as test systems since they are fairly simple to produce and handle.

2 Experimental

The measurements presented in this work were carried out using the synchrotron light at beam-line I411, MAX-Lab, Lund [14,15]. The Auger- and photoelectrons were detected by a Scienta R4000 electron spectrometer. The spectrometer was mounted perpendicular to the cluster beam, and the whole arrangement was rotated to the so called magic angle between the spectrometer lens axis and the electric vector of the plane polarized synchrotron light. This eliminated angle dependent effects in the spectra. A supersonic jet cluster source [16] was attached to the spectrometer chamber, providing a beam consisting of a mixture of clustered and free O_2 molecules. The clusterization process occurs when O_2 gas passes through a conical nozzle from a stagnation volume into an expansion chamber, where the pressure was maintained at 10^{-4} mbar when the gas flow was turned on. The cluster beam was then further defined by a skimmer before letting it into the experimental chamber, allowing the pressure in the spectrometer chamber to be in the 10^{-6}–10^{-5} mbar range during the measurements. The degree of cluster formation was controlled by altering two parameters: the stagnation pressure and nozzle temperature. The temperature was varied by using a liquid nitrogen cooling system together with an electrical heater, and the pressure was controlled by using calibrated pressure gauges and regulators. For rare gases, the size distribution of the clusters in the beam can be determined via the variable of state Γ^* [17,18], that describes the degree of clusterization in the beam. For molecular expansions, the Γ^*-formalism is still applicable [19], but the accuracy is likely worse than in the case of monoatomic expansions. For O_2, our expansion conditions give an average size of $\langle N \rangle = 10000$ molecules per cluster.

The spectrometer was operated in a spatially resolved mode [20]. The supersonic cluster jet was much smaller than the total focus volume of the spectrometer, while residual O_2 gas filled the rest of this volume. These conditions allowed us to choose whether we suppressed the cluster signal, the molecular signal, or none of these, by using different active parts of the detector. In the case of UPS and XPS, no suppression was used, while in the RAS spectra, full molecular suppression was utilized to maximize the cluster contribution to the spectra. In the present case, the resolution of the spectrometer in both the RAS and O1*s* XPS was 350 meV, giving a total experimental resolution of 500 meV including the photon bandwidth.

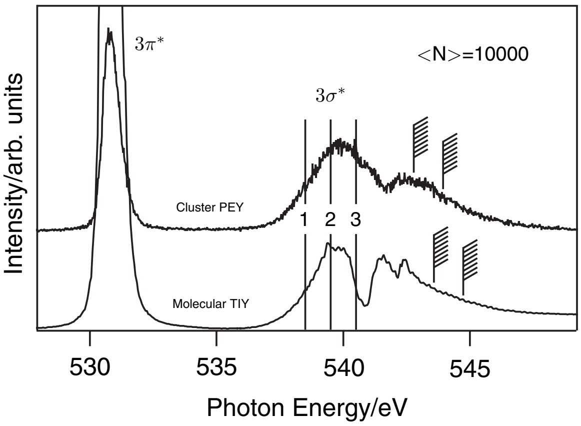

Fig. 1. PEY spectrum of oxygen clusters (top) and TIY of O_2 molecules (bottom) for comparison. The numbered excitation energies for RAS are marked by vertical lines, and are 538.5, 539.5 and 540.5 eV. The cluster spectrum is not normalized for the photon flux. Hatched bars indicate ionization potentials.

3 Results

The spectra in Figure 1 show the cluster partial electron yield (PEY), where the selected kinetic energy range was 465 eV to 505 eV. This approximates the X-ray absorption spectrum. Also shown is the molecular total ion yield (TIY) spectrum measured at the O1*s* edge.

The spectra were calibrated using a value of 530.75 eV for the excitation energy at the maximum of the $1s^{-1}3\pi^*$ absorption [21]. This gives an excitation energy value of 540 eV for the absorption maximum of the cluster $1s^{-1}3\sigma^*$ feature. From the spectra it is clear that the latter feature is blue-shifted by approximately 0.5 eV compared to the gas phase. One can also note that it is broadened so that it extends over the highest excitation energy used here (540.5 eV). This is common in the case of clusters of homonuclear molecules, and has been attributed to the fact that properties such as the dynamics of the intra-molecular relaxation in the core-excited molecule, inter-molecular orbital hybridization, orbital confinement and the core-hole hopping influence this spectral regime strongly [22]. For shape resonances, one should also consider the electron trapping time, which corresponds to the interaction between the photoelectron and the short range molecular potential. The presence of Rydberg states in the vicinity of the $3\sigma^*$ resonance is well-known for the molecule [6,23]. These states will not be treated to any large extent in this work, partly since Rydberg states have been found to be damped in molecular clusters [22] and partly because it was established that these states are not responsible for the ultra-fast dissociation in the molecular system. The dynamics that occur in the bulk- or cluster phase might change the latter fact, but since the electron structure of the individual molecule is almost unaffected by van der Waals clustering, the $1s^{-1}3\sigma^*$ state will still give the largest contribution to the spectrum.

In oxygen, an excitation from the molecular core orbital to the σ^* shape resonance is related to the atomic $1s \rightarrow 2p$ transition. Such core-to-valence transitions are highly localized within a separate molecule. Although, in a van der Waals bound cluster the situation will essentially remain the same [22], the $3\sigma^*$ state is affected by clustering, so the UFD decay channel may be influenced as well. In a cluster, both the atom in the core-excited state and the ion in the final state are initially surrounded by at least a few neighbours. In the ionized final state of a van der Waals cluster, the originally neutral environment becomes polarized in the field of the ion. This gives rise to polarization screening of the various final states, and manifests itself as a shift in binding energy, and thus in the kinetic energy of the spectral cluster features relative to the free atomic and molecular spectral features [24,25]. By taking the localization of an excited electron to the molecular system and the polarization screening in the cluster into account, we know where to expect features from fragmentation in the clusters in the resonant Auger spectra. This is schematically shown in Figure 2.

One can deduce whether UFD is taking place or not in clusters by first determining the kinetic energy positions of the fragment peaks in the free molecule resonant Auger spectra, and then comparing them to the cluster resonant Auger spectra. The fragment peaks in the latter can be expected to be shifted towards higher kinetic energy in the cluster case, and if observed would be a clear indication that UFD takes place in clusters. As mentioned above, the UFD case for the O_2 molecule is well known [5–8,23], thus providing ample reference material acquired by a range of different experimental techniques. Whether UFD is occurring on the surface or in the bulk could in principle be possible to determine, but is not clear in the present situation, due to the lack of surface/bulk resolution in the resonant Auger spectra (see below).

Resonant Auger spectra were measured (see Fig. 3) at the cluster $3\sigma^*$ absorption maximum, and also at points detuned towards both higher and lower excitation energy. The kinetic energy of the Auger electrons from the excited fragments remains constant with changing photon energy during such a detuning, while the kinetic energy of electrons coming from molecules shifts in energy [23]. In the molecular spectra, we located the peaks from atomic fragments, [23,24]. These features are a fingerprint of the UFD process and should be present in cluster RAS if the process is not suppressed. When analyzing the cluster spectra, it is clear that a similar group of features is present. The cluster features have the same separation as the molecular features, their kinetic energy is blue-shifted relative to the latter, and they are broadened to a certain extent.

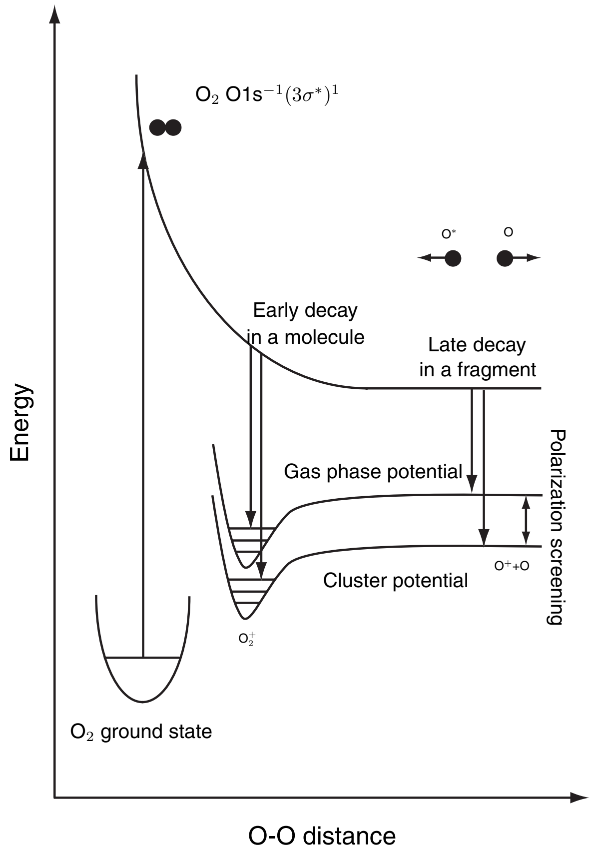

Fig. 2. Schematic picture of the molecular and atomic gas-phase and cluster potentials.

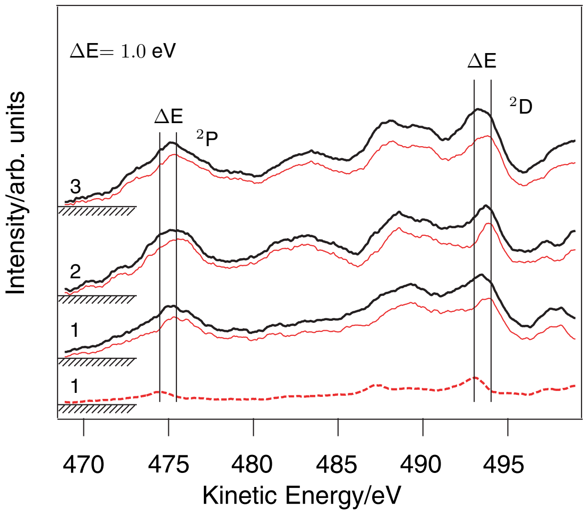

Fig. 3. (Color online) Resonant Auger spectra of O_2. The lowerermost is the spectrum for the excited monomer, while the three above are cluster spectra. The monomer spectrum (dashed line) has been subtracted from the total spectra (black lines) to show the cluster contribution (red lines) more clearly. The excitation energies of the cluster spectra correspond to those marked in Figure 1. Horizontal hatched bars represent the zero levels. The data has been smoothed for presentation.

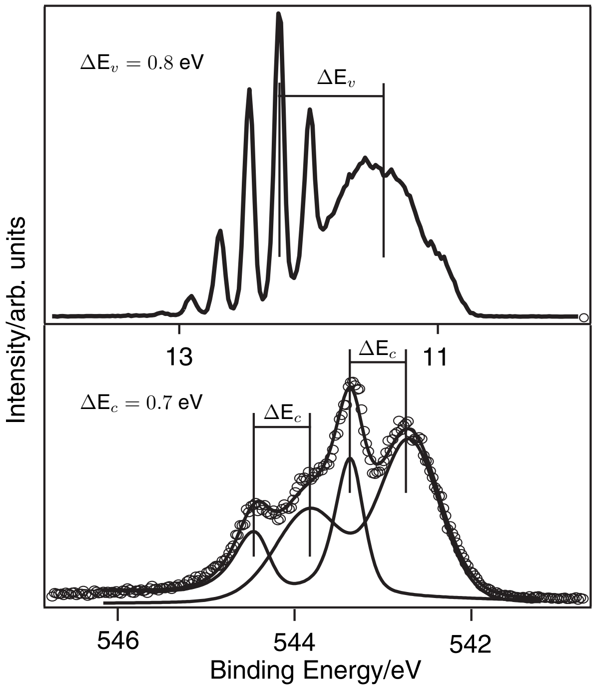

Fig. 4. Photoelectron spectra of the O_2 cluster valence X-state (top) and the O1s core level (bottom). Fits of the XPS (solid lines) are included in the lower panel. For the XPS fit, the molecular spectrum of [26] was used.

This shift is consistent for all detuning energies and is 1.0 ± 0.2 eV (denoted as ΔE in Fig. 3), indicating that the features have a constant kinetic energy. This allows us to identify atomic fragment peaks in the cluster spectra at 475.4 and 494.0 eV kinetic energy. The features that lie between the two atomic fragment peaks stem partly from two weaker atomic transitions (^{2}P and ^{2}S), and partly from Auger transitions. The situation in clusters is such that the Rydberg state transitions are shifted in energy, and broadened. This leads to different Auger-channels in the cluster than in the isolated molecule. Additional support for the present interpretation is given by the shift values of singly charged valence- and core-ionized states determined by UPS and XPS respectively, since the charge is what primarily determines the amount of polarization screening regardless of which final state is involved [25].

In Figure 4, photoelectron spectra of the outer valence X-state and the core-level O1s^{-1} states are presented. The X-state of clusters in Figure 4 has its weight shifted 0.8 ± 0.1 eV with respect to the molecular feature. The binding energy scale was calibrated with the vertical energy of the molecular X-state at 12.26 eV [27], and the total experimental resolution is 50 meV in the UPS spectrum. The shift between the molecular O1s^{-1} $^2\Sigma$ and $^4\Sigma$ states and the corresponding states in cluster XPS was determined to be 0.7 ± 0.2 eV. The accuracy of these values is influenced by the fact that there exists a bulk/surface splitting with a relative intensity ratio that is kinetic energy dependent [28]. The XPS spectrum in Figure 4 was calibrated with the O_2 molecular $^2\Sigma$ peak at 544.48 eV and the $^4\Sigma$ peak at 543.37 eV [29]. A secondary factor contributing to the shift in the RAS spectra is the geometric arrangement of the atomic surroundings when a core- or valence-hole is created, in a way such that the screening increases when the distance to the nearest neighbour decreases. In the present case, this means that the screening for a fragment that has been displaced in the cluster matrix will be larger than for the undisplaced molecule. By electrostatic calculations, we estimate the contribution to the shift due to changes in the geometry to be about 0.2 eV. The 1.0 ± 0.2 eV shift of the fragment peaks in the cluster RAS spectra is consistent with what we see in the cluster XPS (0.7 ± 0.2) eV and UPS (0.8 ± 0.2) eV if we take the additional shift due to the geometric displacement of the fragments (0.2 eV) into account. We conclude that there are charged final state fragments that are screened during the Auger decay, and thus that UFD is taking place within or on the surface of O_2 clusters.

To gain more quantitative information is hard at the present time, because of experimental limitations. One could, in principle, measure UFD in different surface/bulk components, or make an angle dependent study to probe the Doppler splitting of the atomic fragment Auger features [8], but due to the very dilute nature of a cluster beam, this becomes extremely time-consuming with current synchrotron sources. Future development may allow for these measurements and also for size selection.

4 Conclusions

In this paper, we have found that clustering only weakly influences the ultra-fast decay process. It is clear that the dissociative character of the $1s^{-1}3\sigma^*$ resonance in O_2 molecules remains in a van der Waals cluster, although the resonance feature is blueshifted and broadened, and also that UFD is not quenched to any observable degree by neighbouring molecules. On the contrary, at the highest excitation energy, there is a significant atomic contribution to the cluster resonant Auger spectrum in contrast to the molecular case where the σ^* cross-section at the same energy is close to zero [6].

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