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# Time-resolved photodissociation of oxygen at 162 nm

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Oxygen was excited by 10-fs pulses in the Schumann-Runge continuum at 162 nm, which is by 0.57 eV above the dissociation limit. It was probed by high-intensity ionization at 810 nm with $10^{14}$ W cm$^{-2}$, measuring the ion yields. The $O_2^+$ signal decays in 4.3 fs, which is much shorter than the expected time for dissociation. It is ascribed to a rapid decay of the ionization probability. In a similar time, the ion in the second excited state (with excess energy taken over from the neutral) reaches the dissociation limit, whereas this time would be much longer from the two lower ion states. In fact, the $O^+$ signal rises to a (first) maximum at 6 fs. The preference for the higher ion state is rationalized by an intermediate resonance in the neutral molecule, for which the polarization dependence also provides evidence. But the shape of the $O^+$ signal is very odd: it exhibits three maxima (at 6, 29 and 53 fs) of increasing intensity, before decaying rapidly (≤3.5 fs) to a pedestal. In contrast to the first maximum, the others appear at times when there is practically no interatomic force left in the excited state. We postulate a highly repulsive doubly excited state as a resonance for interpreting the second maximum, and for the third an ion-pair state lying further outside. Comparison is made with enhanced ionization, which has often been found at large interatomic distances on *multiple* ionization in strong laser fields. Consistent with this mechanism is the absence of similar observations at negative delay times, where five fundamental photons act as a pump and the fifth harmonic as a probe.

## 1. Introduction

Oxygen is a molecule with a non-closed valence shell (ground-state configuration $\pi^4\pi^{*2}$, where "$\pi$" is short for the bonding $\pi_u$ and "$\pi^*$" for the antibonding $\pi_g$ orbitals.) It has therefore many excited states [1,2]. The lowest one connected with the ground state (X $^3\Sigma_g^-$) by a fully allowed transition is the B $^3\Sigma_u^-$ state ($\pi^3\pi^{*3}$). In absorption it gives rise to the Schumann-Runge bands (200 – 175 nm) and adjacent continuum (maximum near 142 nm) (see the review of spectra and experimental data on states of Krupenie [3] and the compilation of Huber and Herzberg [4]; a spectrum is shown, for example, in [5,6]). Photodissociation and predissociation in these regions are the origin of oxygen atoms and of ozone formation in the stratosphere. This state has

therefore been well investigated [3,4]. We report on time-resolved photodissociation in the continuum with much better resolution than before. In previous such investigations, Farmanara et al. used pulses at 155 nm (duration 350 – 450 fs) to excite the oxygen, probing it by ionization at 258 nm [7]; they reported a decay time of the $O_2^+$ signal of 40 fs, obtained by deconvolution. Peralta Conde et al. used 27-fs pulses at 160 nm both for pumping and probing [8]; also in this experiment the decay of the $O_2^+$ signal was clearly shorter than the time resolution. As pointed out in [8], differences in time constants are conceivable, however, because the ionization windows may differ in the two methods. We used 10-fs pulses at 162 nm for pumping and probed by ionization with high-intensity 810-nm pulses of 12 fs. We also briefly consider the situation at negative delay times, where oxygen can be pumped by five fundamental photons and probed by the vacuum UV radiation. It is worth mentioning that this work concerns the dissociation of neutral excited oxygen, whereas investigations with a single wavelength (≈800 nm) at high intensities investigated wave packet dynamics and dissociation of oxygen ions (see e.g. the recent works [9,10]).

## 2. Experiment

Using (nominal) pressures of $4\times10^{-6}$ and $4\times10^{-4}$ mbar for measuring the stronger ($O_2^+$) and weaker ($O^+$) signals, respectively, oxygen ($^{16}O_2$ and $^{18}O_2$) was excited in the ionization region of a time-of-flight mass spectrometer by the fifth harmonic (162 nm, 10 fs, $10^{10}$ W cm$^{-2}$) of a Ti-sapphire laser, whose fundamental (810 nm, 12 fs, ≈(3–10)$\times10^{13}$ W cm$^{-2}$) served for probing by (multiphoton or optical-field) ionization. The instrumental function (cross correlation between the pump pulse and a high power of the probe pulse) has a width of 11 fs, which is the time resolution. The instrumental function and UV pulse duration were determined in our previous work from the shape of the $H_2O^+$ signal [11]. The $Ar^+$ signal is slightly broader (13.4 fs, see below), which may be due to some degree of saturation (as with $Xe^+$ in [11]). The shortening of the fundamental by self-phase modulation in argon and compression by chirped mirrors is described in [12] and the generation of the fifth harmonic in a short argon cell in [13]; for a brief description see also [14]. The pump-probe delay was varied in steps of 3.3 fs. The time zero is derived from the maximum of the $Ar^+$ signal (from added Ar) measured in every pulse together with the $O_2^+$ or $O^+$ signal. The $O_2^+$ signal (time-dependent ion yield) was evaluated by fitting an exponential to its decay. Small pedestals (typically of the order of 1% of the maximum, also for the $Ar^+$ signal) at long positive and negative delay times were subtracted to show exponential decays in logarithmic plots more clearly. In previous works (e.g. in [11]), we also evaluated the earlier part, simulating it by the same exponential, convoluted with the instrumental function.

This was, however, prevented by the observation (see sec. 3.3) that at negative delay times the roles of pump and probe were reversed: $O_2$ was there pumped (probably with minor efficiency) by five fundamental photons and probed by the fifth harmonic. This effect should also have an influence during the pump-probe overlapping time.

Details of the technique – time-resolved intense field dissociative ionization – including evaluation are given, for example, in ref. [15]. The use of rate equations (i.e. exponential fitting) is normally not expected to be suitable for wave packet dynamics in small molecules; however, it is justified in [14,16-18] by the fact that the observation windows are broad; see also the end of sec. 3.1. Both lasers were linearly polarized, in most of the measurements parallel to each other and to the axis of the time-of-flight mass spectrometer. In principle, one could use the magic angle (55°) between the two polarizations to avoid effects due to rotation of the molecule. However, rotational anisotropy would show time-dependent effects on a much longer time scale (100 fs, calculated at 295 K as in [19] from the moment of inertia) than the time evolution found here, so that there was no necessity to choose such an angle.

## 3. Results and discussion

### *3.1. Parent ion signal: Rate of dissociation versus decay of ionization probability*

Fig. 1 shows the time dependent $O_2^+$ signal, together with that of argon ions from added Ar. The exponential tail of $Ar^+$ ($\tau_{Ar}$ = 3 fs) either means that the laser pulses deviate from a Gaussian below a level of about $3\times10^{-2}$ of the maximum, or that a real intermediate state of argon can contribute (see the discussion in [11]). The time constant for the decay of $O_2^+$ ($\tau_{O2}$ = 4.3 fs) is sufficiently larger that it can be considered real.

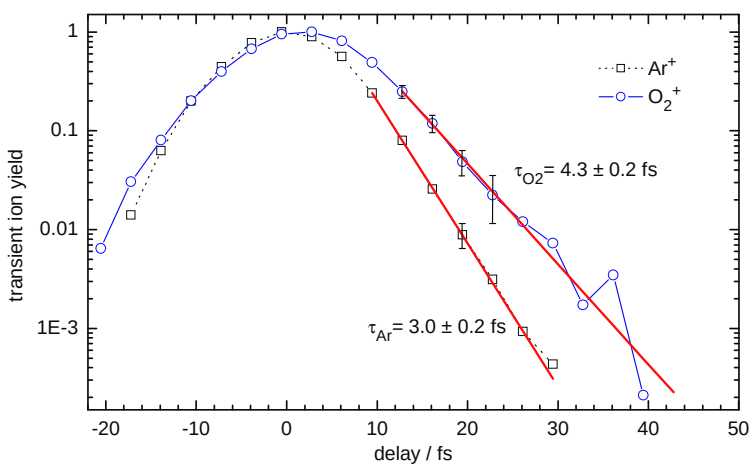

*Fig. 1.* Transient ion yields of $O_2^+$ and $Ar^+$. The wings are simulated by exponentials with the indicated time constants. The error bars indicate standard deviations in averaging 5 runs; they are smaller than the size of the data points at higher signal intensities but increase at smaller yields, because a pedestal (around 1%) was subtracted. (Fitting was done before subtraction.)

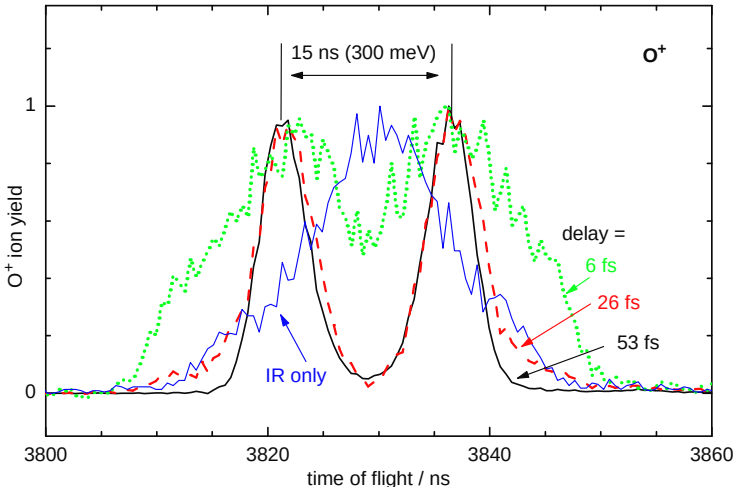


*Fig. 2.* Time-of-flight spectrum of $O^+$, produced by the fundamental alone (810 nm, 12 fs, "IR only") or by the pump (162 nm, 10 fs) plus the probe at various delay times; all polarizations are parallel to the mass-spectrometer axis. The splitting is caused by the time-of-flight difference between forward and backward ejected ions; it can be converted to the recoil energy of $O^+$; the neutral oxygen atom must have the same recoil.

The pump laser at 162 nm (7.65 eV, half-width 0.25 eV [14]) excites the molecule to an energy, which is by 0.57 (±0.125) eV above the dissociation limit [3]. This is in fact confirmed by the recoil energy, found from the difference of arrival times of the forward and backward ejected $O^+$ (Fig. 2). (The temporal splitting $\Delta t$ is converted to the recoil energy $E_{rec}$ as in [20,21], with $E_{rec} \propto \Delta t^2$. The narrower widths in Fig. 2 are broader than expected from the energetic width of the pump laser; they probably reflect the time resolution of the spectrometer.) This recoil energy also shows that, besides the B state, the slightly higher $^3\Pi_u$ state (the only state nearby, see e.g. [22]) is not noticeably populated: It would dissociate to two ground-state oxygen atoms with a total recoil energy of 2.55 eV. This energy corresponds to a final rate of bond extension of 3.8 pm/fs, corresponding to bond lengthening of a fraction of an Ångström in 4 – 5 fs. Obviously, dissociation of $O_2$ is far from complete in this time. (For example, extending the OO distance to 2.4 Å, twice its original value, would require 23 fs according to the calculations below.) The parent-ion signal can, however, decay for different reasons, as argued in [11]:

(1) On vertical ionization by the probe, such as by nonresonant ionization, the most probable transition conserves not only the location but also the momentum and hence the kinetic

energy. In Fig. 3 we therefore added the distance-dependent kinetic energy of $O_2$ in the B state to the ionic potentials. There is a definite distance (where the broken lines in Fig. 3 reach the dissociation energy), after which the parent ion (depending on its electronic state) is not stable anymore. It can also sometimes happen that further probe photons excite the ion to another electronic state [11].

(2) The ionization probability in general depends on the reaction coordinate. In the case of nonresonant ionization, it is expected to decrease steadily due to the increasing ionization energy (distance between B state potential and ion potentials). If there is an intermediate resonance of the probe, the response can also be nonmonotonic.

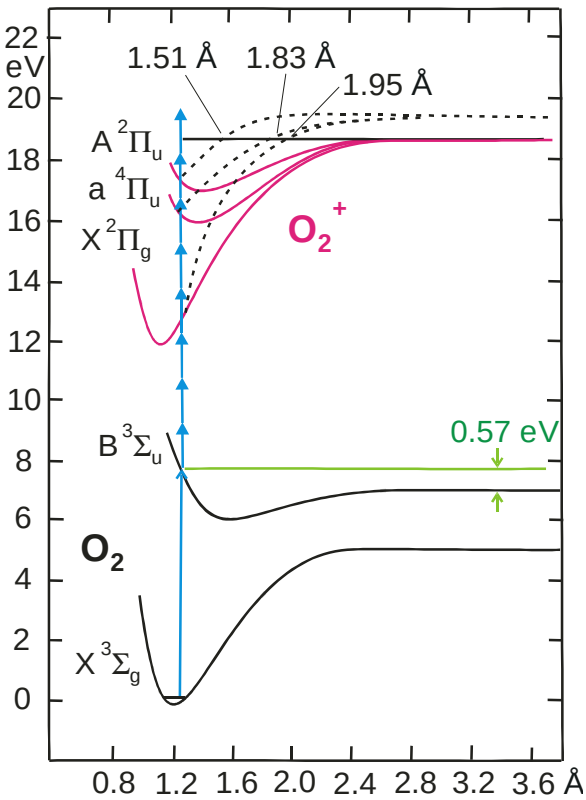


*Fig. 3.* Potentials (according to [3]) involved in the pump and probe processes. With delayed probing, ion states are populated with excess kinetic energies taken over from the B state; potential plus kinetic energies are shown by the broken lines for the three lowest ion states. The fast rise of the $O^+$ signal is only consistent with the early crossing of the ionic dissociation limit by the uppermost line, i.e., with population of the second excited ion state (A) by the probe.

Whereas mechanism (2) should produce a decay of both, the $O_2^+$ and the $O^+$ signals, the first mechanism should lead to opposite changes of the two signals. We find that $O^+$ rises in about the same time (4 – 6 fs, see below) as $O_2^+$ disappears. Hence at first sight mechanism (1) seems

to be the main reason for the decay of the parent ion signal. But below we will argue that different electronic states of the ion are responsible for the two signals: the A state for the early part of $O^+$ and the X state for $O_2^+$.

Fig. 3 shows that the bond length, beyond which the parent ion is not stable anymore, is smallest, if the probe populates the second excited state (A $^2\Pi_u$) of the ion. To calculate the time, when the neutral molecule reaches such a distance, we solved the equation for the kinetic energy

$$\frac{1}{2}m_1v_1^2+\frac{1}{2}m_2v_2^2=\frac{1}{2}m_1\left(\frac{\mathrm{d}r_1}{\mathrm{d}t}\right)^2+\frac{1}{2}m_2\left(\frac{\mathrm{d}r_2}{\mathrm{d}t}\right)^2=E_{ini}-\mathrm{U}(R) \qquad (1)$$

$$m_1=m_2=16\ \mathrm{g/mol},\ r_1=-r_2,\ v_1=-v_2\ ,\ R=r_1-r_2$$

for the bond length change d$R$/d$t$ and integrated its inverse over $R$. The B potential U($R$) was modeled beyond its minimum ($R_0$ = 1.604 Å) by a Morse function

$$\mathrm{U}(R) = E_{\mathrm{diss}}\,(1-\exp(-(R-R_0)/R_{00}))^2 \qquad (R > R_0) \qquad (2)$$

($E_{\mathrm{diss}}$= 1.007 eV, $R_{00}$ = 0.3689 Å, calculated from $E_{\mathrm{diss}}$ and the vibrational frequency [23]). For the initial energy $E_{\mathrm{ini}}$ we took the pump photon energy minus the minimum of U (6.173 eV, normalized to 0 in (2)) plus the zero-point energy in the ground state (0.1 eV). For short $R$, U is perturbed by mixing with a Rydberg state [24-26]. Therefore we took there the experimental (RKR) data for the bound part of the potential, tabulated in [3], and for $R$ = 1.2075 Å (ground-state bond length) the value 2.66 eV calculated from the absorption maximum at 142 nm. These points were fitted by a Boltzmann function

$$\mathrm{U}(R) = E_0 + (E_1 - E_0)/(1+\exp((R-R_0)/\Delta R)) \qquad (R < R_0) \qquad (3)$$

Note that the pump photon reaches this curve at $R_{\mathrm{ini}}$ = 1.27 Å (not at 1.2075 Å, the center of the zero-point vibration, because the excitation is in the wing of the absorption spectrum), corresponding to $E_{\mathrm{ini}}$. The result of the integration, starting at $R_{\mathrm{ini}}$, is shown in Fig. 4. The three distances, beyond which the ion would dissociate from its three lowest electronic states (Fig. 3), are reached after 13, 11 and 6 fs, respectively. Obviously only the third is compatible with the observed rise of the $O^+$ signal. Even shorter times are calculated for reaching distances, after which 4 – 5 probe photons do not suffice anymore for reaching the ion ground state (1.34 and 1.4 Å, respectively, corresponding to 3.2 and 4 fs).

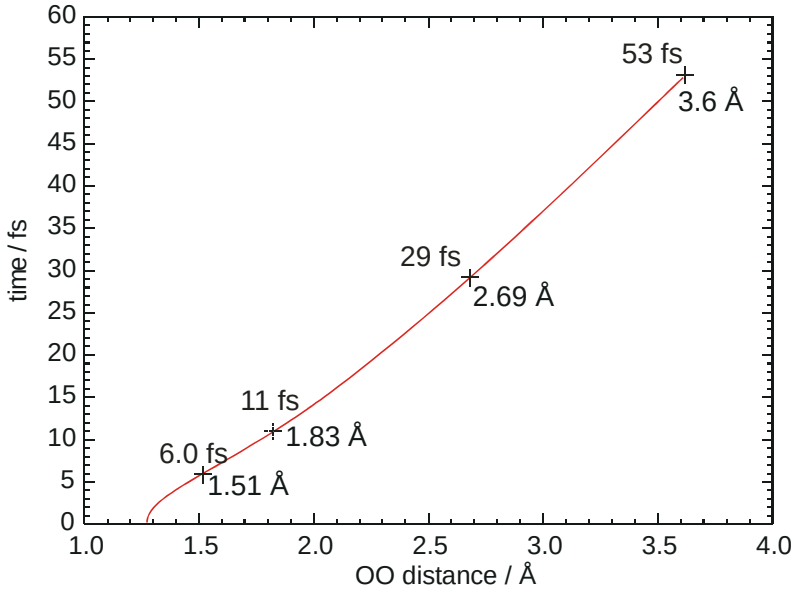


*Fig. 4*. Calculated times *t* after which a bond length *R* is reached on starting from 1.27 Å.

In fact there is evidence that the parent ion is practically only due to the ionic ground state, although the atomic ion with its fast rise must come from the A state: The former signal is stronger than the latter by a factor >100 (sec. 2). This is readily rationalized by the different number of probe photons (8 versus 4 – 5, Fig. 3) required to form $O^+$ and the ground state of $O_2^+$, respectively. If most of the parent ion would be in the A state, this difference of signal strengths could hardly be explained. Hence we interpret the decay time of $O_2^+$ (4.3 fs) as the time, after which the number of photons required for ionization would rapidly rise to beyond 4 – 5.

According to Fig. 3, ground-state ions produced beyond 1.95 Å would not be stable anymore. According to Fig. 4, this corresponds to a time of 13 fs. So, how can it be that the exponential decay in Fig. 1 reaches much beyond this time, to 30 fs (= 7 × 4.3 fs), for example. The answer is that Fig. 4 represents only the molecules with the most probable velocity, whereas the pump laser produces also much slower molecules: With a Gaussian half width of 0.25 eV [14], one calculates a probability of $2\times10^{-3}$ (relative to the maximum) for an excess energy of 0.57 eV/√7 (i.e., for a velocity of 1/7 of the most probably one). This is well consistent with the signal strength at this time. Hence also the signal beyond 13 fs (or even at >30 fs) is formed from molecules with bond lengths <1.95 Å. Certainly, the width of the velocity distribution is also responsible for the fact that an exponential decay is observed instead of anything reminding of the laser pulse shapes (expected in the case of wave packet dynamics).

We also mention the half-width (15 fs) of the $O_2^+$ signal. It is caused by convolution of the instrumental function (slightly narrower than the $Ar^+$ signal) with the exponential decay. Such as the latter, the half-width is caused by the steep increase of ionization energy (decrease of ionization probability) near 1.5 Å on the one side and the velocity spread of bond extension on the other.

*3.2. Atomic ion signal: Intermediate resonances and enhanced ionization*

With this mechanism, one expects for the $O^+$ signal an initial fast rise (≈6 fs, due to population in the ionic A state), followed by another or a continued rise, reaching an asymptote beyond 13 fs (when the population in the X state – and possibly the a state – reaches the dissociation threshold). Note that early and late formation of $O^+$ have the same order of ionization (8 probe photons, Fig. 3), so that similar contributions can be expected from the early and later channels. However, the $O^+$ signal is very different, even unusual (Fig. 5): It exhibits three maxima of growing intensity, two of them at much longer time than expected, with no indication of another rise near (11 or) 13 fs (there is even a minimum at 15 fs); thereafter there is an irreversible very rapid decay down to a pedestal. To check whether perhaps part of the signal comes from some background gas, we repeated the experiment with isotopically labeled oxygen ($^{18}O_2$) and found practically the same signal.

The final pedestal can readily be interpreted as the signal arising from one of the dissociation products, O ($^1$D). As already mentioned, nonmonotonic signals can be expected, if there are intermediate resonances. They can temporarily raise the signal above the asymptotic value. Hence one should look for three suitable intermediate states. All three should have $^3\Sigma^-$ symmetry, so that they can be reached from the B $^3\Sigma_u^-$ state with the same polarization as the pump transition; this would explain the observation that the $O^+$ signals in the maxima was several times stronger with parallel than with perpendicular polarization of pump and probe laser. The observation in turn also supports the existence of a resonance, because nonresonant ionization is expected to be not (or not much) dependent on polarization.

For the first rise and maximum (6 fs) we should look for a resonance at OO distances around 1.5 Å (Fig. 4). According to quantum-chemical calculations [1], at such distances there are many steeply repulsive states, some of them of $^3\Sigma^-$ type which could provide a resonance with a number of probe photons; one of them (2 $^3\Sigma_g^-$) would be in resonance with one photon around 1.66 Å, another (2 $^3\Sigma_u^-$) with two photons at 1.55 Å. (The exact locations should not be taken too seriously, because the strong probe laser field will perturb the states. The calculation [1] also did not take perturbation by Rydberg states into account.) An intermediate resonant state within

the triplet manifold has an interesting implication: From there, the first excited state (a quartet: a $^4\Pi_u$) of the ion would not be reached but only the second (a doublet: A $^2\Pi_u$ ), as explained by Fig. 6. In one-photon ionization these ion states would be chosen according to their statistical weight (2:1 for $^4\Pi_u/^2\Pi_u$). In fact the contributions to the $O^+$ signal from the a state (near 11 fs) and from the X state (near 13 fs) can at best be very weak, as the signal instead of increasing has dropped there to 70% of the 6 fs maximum. Hence we attribute the first $O^+$ maximum and the preference of the ionic A state to a steeply repulsive intermediate $^3\Sigma^-$ state, providing a narrow resonance that does not extend to distances (such as 1.83 or 1.95 Å), where the two lower states would reach the dissociation threshold. Electronic selection rules (Fig. 6; for another selection rule, connected with perturbation by a Rydberg state, see Conclusion) may play a role in addition. Also the half-width (18 fs) of the first peak, which is similar to that of the $O_2^+$ signal (15 fs), is consistent with a sharp resonance (steep repulsive potential and perhaps a rapid variation of transition probability); it is hence dominated by the velocity distribution of OO bond extension (sec. 3.1).

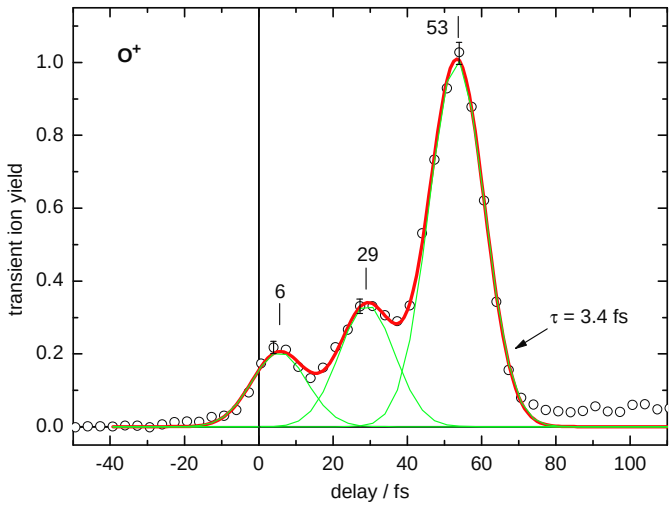


*Fig. 5.* Transient $O^+$ yield. To localize the maxima, three Gauss curves (thin solid lines) were fitted to the data (symbols); their sum is also shown. Error bars indicate standard deviations in averaging 8 runs. Compared to $O_2^+$, the signal strength is weaker by a factor of >100; for compensation, it was measured at 100 times higher pressure.

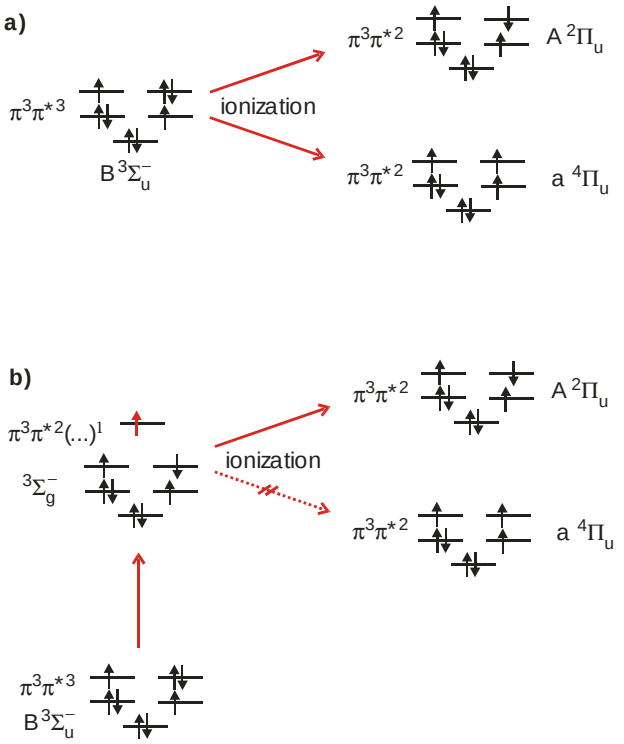


*Fig. 6*. Electron configurations before and after ionization. (The nondegenerate lowest orbital displayed is $\sigma_u$.) (a) On detaching an electron directly from the B state of the neutral, a quartet and a doublet state of the ion can both be reached. The two paths would differ only in the spin orientation of the electron being detached. (b) If the probe first excites an electron to an unspecified higher orbital in a triplet $\Sigma$ state and this electron is subsequently detached, only the doublet state of the ion is obtained. In this one-electron description, also the electronic ground state would not be reached in both a and b.

But what are the other maxima? The polarization dependence at these delays is the same as at earlier times. Also the recoil of $O^+$ is the same (Fig. 2); that is, the $O^+$ at these late times result from ionization of the dissociating neutral molecule, not from any secondary ionic process such as Coulomb explosion of multiply charged $O_2$ (in which the recoil is typically several electron volts).

At the times of the second and third maximum (29 and 53 fs) the wave packet has reached OO distances of 2.7 and 3.6 Å (Fig. 4). At such bond lengths all valence states of $O_2$ and $O_2^+$ have practically converged to the dissociation asymptote [1] (see also Fig. 3), so that one has nearly free atoms. Therefore we should also not take any molecular vibration into consideration. (Their frequencies [3,4] would anyway not fit, also not any coherent superposition of atomic states.) On the other hand the time dependence must reflect a distance dependence. That is, one has to look for states, whose potentials reach further out than valence states. Indeed those correlating with an ion pair ($O^+ + O^-$, which is by 1.465 eV below $O^+ + O$) converge only slowly (as $1/R$) to this limit. The inner (repulsive) part of their potentials has valence-state character. A $^3\Sigma_u^-$ state of this

type has been calculated near its minimum (≈2 Å, Fig. 7), besides one of $^5\Sigma_g^-$ and one of $^3\Pi_u$ symmetry [27,28]. Spectroscopic evidence for two of them was found in [29] and fs-time-resolved dissociation via the $^3\Sigma_u^-$ ion-pair state was studied in [30]. (Note that the dissociation limit of this or another ion pair state is not reached, if it is populated from the B state, because the kinetic excess energy is by far not sufficient. $O^+$ is produced in our experiment only by dissociative ionization.) There must also be another ion-pair state of $^3\Sigma^-$ type but with g symmetry [27,28], converging to the same asymptote. The inner – repulsive – part of the corresponding potential will again have valence character (because pure ion-pair states are only attractive). If it should provide a resonance with the probe laser at very long OO distances, it must come down from very high energy and be strongly repulsive. Because according to [1] all singly excited valence states correlate with lower dissociation limits, we suggest a doubly excited state with $\pi^2\pi^{*4}$ configuration and the same symmetry ($^3\Sigma_g^-$) as in the outer (ion-pair-like) branch. In Fig. 7 it is drawn in such a way that it would provide a five-photon resonance with the probe at 2.7 Å, the distance reached at the time (29 fs) of the second $O^+$ maximum.

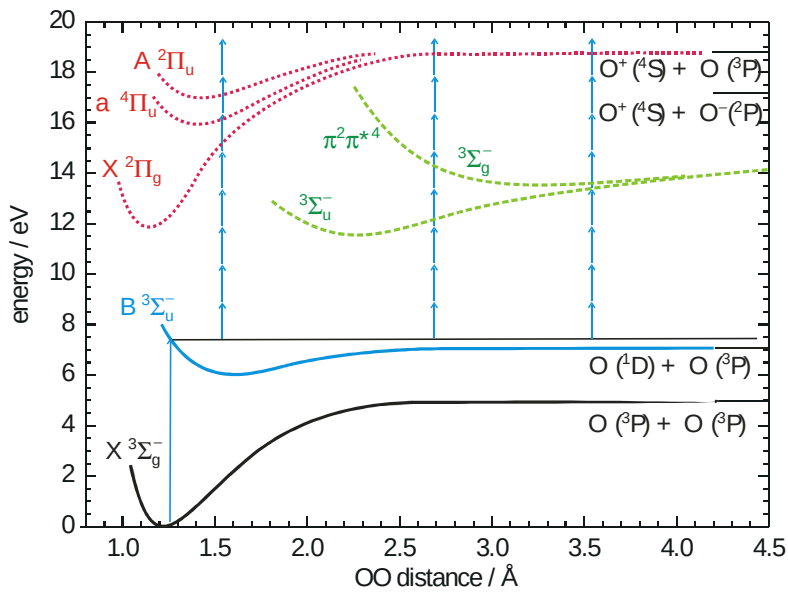


*Fig. 7.* Potentials (according to [3]) of states involved in pumping (solid lines; the pump process starts in the outer wing of the zero-point vibrational wave function) and probing (dotted: ion states; broken lines: ion pair states, converging to the energy of $O^+ + O^-$). Whereas the lower ion pair state was calculated [27,28], the upper one is postulated here, as well as its inner repulsive wing with doubly excited valence character. The multiple vertical arrows indicate three positions for probing, corresponding to the times of the three maxima of the $O^+$ signal. Note that for this signal everywhere (≥) 8 probe photons are required and that dissociation via the ion-pair channel cannot contribute, because there would be not sufficient kinetic excess energy.

Further out, the potentials in Fig. 7 have been drawn with Coulombic energy ($E = -1/R$ in atomic units (au)). One can see that the $^3\Sigma_u^-$ and $^3\Sigma_g^-$ states would be near a four-photon resonance near 3.5 Å (the latter symmetry allowed from the B state). However, these energies are drastically changed in the strong laser field due to the large dipole moment ($\approx R$ in au) of the ion-pair states. Furthermore, the field will – by the help of the large transition moment ($R/2$) [31] – mix $^3\Sigma_u^-$ and $^3\Sigma_g^-$ states, repel them in energy from each other and cause transitions between them. Similar phenomena in $H_2^+$ have been described quantitatively by Zuo and Bandrauk [32] and by Posthumus [33]. In both works a connection was made to the so called enhanced ionization (leading to multiple ionization with enhanced efficiency at long bond lengths, see e.g. the review [33]) and its description by a less quantum mechanical model, using barrier-suppression or tunnel ionization. This connection may also be helpful in the given case:

(1) The pure resonance model does not tell, how efficient a five-photon transition would be near 2.7 Å. However, the description of a large oscillating dipole moment as a large-amplitude motion of an electron moving in a potential that is not harmonic (sum of Coulomb terms) suggests that also high-order susceptibilities (e.g., $\chi^{(5)}$) will be large.

(2) In view of the flat Coulomb potentials, it seems hard to understand, how the $O^+$ signal can decay after the last maximum in such an exceedingly short time (≤3.5 fs (Fig. 5)), corresponding to movement over 0.13 Å only). However, the distance between $^3\Sigma_u^-$ and $^3\Sigma_g^-$ decreases exponentially with $R$ (because the valence character of the upper one is diminishing with $R$); thus any transition between them (when the energies are perturbed by the laser, as suggested above) goes rapidly out of resonance. The classical model says that an electron in the upper state, localized on one side of the molecule, has to tunnel through a barrier between the atoms to leave the molecule; as this barrier increases with growing $R$, the probability of tunneling (hence: of ionization) decreases exponentially [32-34]. (The rising barrier also decreases the splitting between the states, which indicates the connection of this model to the concept of the approaching $^3\Sigma_u^-$ and $^3\Sigma_g^-$ states .)

We suggest that the enhanced-ionization mechanism not only applies for the last $O^+$ maximum but also to the second. In this case, we can suppose that also the lower ion-pair state ($^3\Sigma_u^-$) might provide a resonance (with two probe photons, Fig. 7), after being lowered in the strong laser field.

It is worth noting that the times for the $O^+$ maxima did not change with probe intensity, that was varied by 25% (which changes the yields drastically, due to the high order of ionization). Also in

enhanced ionization, the times of signal maxima were practically intensity independent; this was interpreted by the potentials and their barriers, which depend primarily on *R* [33,34].

### *3.3: Negative delay times: Probing the B state by one 162 nm photons*

The resonances and high-field effects discussed here are not expected, if instead of the high-intensity fundamental as a probe one takes a weak fifth harmonic. In fact, on pumping and probing by 160 nm such as in [8], the $O^+$ signal showed a simple decay (below the time resolution) [35]. A. Peralta Conde drew our attention to the possibility that our high intensity at the fundamental wavelength could also excite $O_2$ to the B state, for example at negative delay times, where the fifth harmonic would act as a probe. In fact, we find signals there, which show simple exponential decays ($Ar^+$ 3.0 fs, $O_2^+$ 4.2 fs and $O^+$ 5.4 fs)[1]. That is, $O^+$ shows no maxima at negative times, which indeed the model would predict only for long-wavelength high-intensity probing. The fact that the molecular and atomic ion signals both *decay*, even with similar time constants, must obviously be attributed to departure from the window, in which the ground state (see below in Conclusion) X $^2\Pi_g$ of the parent ion is energetically accessible by one-photon ionization (see Fig. 3, replacing five fundamental photons by one of the fifth harmonic); with a limited probability a second such photon can then reach the repulsive branch of the $^2\Sigma_u^+$ potential (calculated in [2]) of $O_2^+$. Hence the 4 – 5 fs again do not represent the dissociation time of $O_2$. Obviously it is more difficult to monitor the full dissociation process by probing with vacuum UV radiation than with high-intensity 800 nm. The time constants observed here at negative times are consistent with those observed by Peralta Conde et al. [8] by 160-nm probing (which were below their time resolution).

### *3.4. Further remarks on the atomic ion signal and its interpretation*

In view of some ad-hoc postulates to interpret the $O^+$ signal, it would be desirable to check them quantum chemically or by another theoretical approach. Compared to previous such approaches,

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[1] Whereas the $Ar^+$ signal probably reflects properties of the pulse shapes, we again consider the time constants for oxygen and argon as sufficiently different to assign the former to a time-dependent process. It is hard to tell from the signals alone, whether those for oxygen are weaker at negative than at positive times. But probably they are weaker: If they were equal, the signal maximum should be at time 0. Due to this complication, one cannot extract the time constants from the position of the maximum (or from deconvolution). In principle, a similar complication should be considered in water photodissociation, in which we derived a time constant of 1.8 fs from the shift of the maximum [11]. However, from the exponential tail of $D_2O$ we also deduced an upper bound of the $H_2O$ time constant of 2.1 fs, and the shift showed the expected isotope effect [11].

our observations agree in some respects with enhanced (multiple) ionization at long interatomic distances and the polarization dependence. But a number of aspects are new:

(1) We observe enhanced ionization on detachment of a single electron. All previous cases involved multielectron ionization with Coulomb explosion. The small recoil energy in our case shows that it is only due to the repulsive part in the neutral molecule (Schumann-Runge continuum); no additional recoil is acquired by the ion e.g. on any ionic potential. By contrast, in most cases of enhanced ionization observed so far, the extension of the bond and eventual dissociation was driven by ionic potentials, which were perturbed by the laser field.

(2) The quantum-mechanical description predicted two maxima of enhanced ionization from $H_2^+$; only one was observed experimentally in this and other molecules [32,33]. We find for excited $O_2$ more than one: whereas the first of three can be interpreted by a resonance with a valence-excited state, the other two occur at longer bond lengths such as in enhanced ionization, and both probably require participation of ion-pair states.

(3) It was predicted for $H_2^+$ that on starting from a $\pi$ electron (instead of $\sigma$ as usually) enhanced ionization will not exhibit a maximum but will monotonically rise to an asymptote on extending the bond [36]. Ionization of oxygen from its B state detaches an electron of $\pi$ symmetry; nevertheless the signal decays again. The difference can be rationalized by the *R* dependence of the ionization energy: Detaching the last electron from a $\pi$ state of $H_2^+$ requires around 30 eV (although less, if the process is not vertical) but after dissociation only 3.4 eV (from the 2p state of H); for $\sigma$ electrons the variation is from ≤30 eV to 13.6 eV. It seems plausible that the very small ionization energy for the former case prevents that the probability of the process decays at large distance. (In [36] the effect was interpreted in terms of nodes of the orbitals, and a monotonic increase of ionization probability was also expected for $O_2$.) For the oxygen B state there is only a minor *R* dependence of the energy to reach a dissociative level of the ion (Fig. 3).

We mentioned above (sec. 3.1) that in some molecules further probe photons can excite the ion to higher states. We have previously presented examples such as $H_2O$ [11] or cyclohexadiene [15], where such higher states affect the signals. Calculated potentials for many $O_2^+$ states are presented in [37]. All converge to their individual dissociation limits already at distances of 2.5 Å or even before, so that they cannot explain the late maxima of $O^+$. Detailed inspection of the higher potentials also suggests that they could hardly provide an explanation of the early nonmonotonic $O^+$ signal (the initial rise and passage through a maximum, that was interpreted above by a resonance in the neutral molecule). It was, however, demonstrated [9,10] that with

intensities as that of our probe laser, such higher states of the ion are indeed populated and cause dissociation to O + $O^+$. Hence in our experiment repulsive parts of these potentials probably contribute a weak and unnoticed monotonic decay or background of $O^+$, and bound upper potentials add a weak constant background to the $O_2^+$ signal. Note that for explaining the $O^+$ signal on probing by 162 nm (such as in this work at negative delay times) one must invoke a (repulsive) higher ion state ($^2\Sigma_u^+$, sec. 3.3).

## 4. **Conclusion**

The 4.3 fs decay time of $O_2^+$ is attributed to the rapid decrease of ionization probability, when after short extension of the OO bond (from 1.27 to ≈1.4 Å) the need of probe photons to reach the ion ground state drastically increases beyond the initial value of 4 – 5. Dissociation itself takes clearly longer. For example, from the excess energy of 0.57 eV resulting from pumping and confirmed by the observed recoil of $O^+$ (also confirmed by the $O_2^+$ time constant), one calculates 23 fs for extension of the OO bond to 2.4 Å, i.e., to twice its ground state length, where all valence potentials have practically converged to their dissociation limits. The exponential shape of the signal is ascribed to the width of the pump laser and the distribution of excess energies, which implies also much slower bond extension than on the average.

The initial rise of the $O^+$ signal is assigned to the time (≈6 fs), in which vertical ionization reaches a dissociative energy level of the second excited state (A) of $O_2^+$. An (early) intermediate resonance to a steeply repulsive state of the neutral is invoked, which enhances ionization with maximum probability near 6 fs. It not only rationalizes, why the $O^+$ yield decreases again after the first maximum but also why the A state of the parent ion is so effectively reached. Dissociative ionization via the lower ion states (a and X) at these early times (perhaps till 20 fs) seems much less effective. The evidence is that via a and X, the dissociation energy would be overcome only at longer bond lengths and hence at longer times (11 and 13 fs), where the observed $O^+$ signal has decreased instead of increased. Also the fact that the $O^+$ signals were much stronger with the probe polarization parallel to that of the pump (parallel to the molecular axis) is interpreted by the resonance, assuming a Σ intermediate state; only at much longer OO distances, another reason for the same polarization dependence begins to play a role: enhanced ionization, which profits from the large polarizability along the molecular axis (or alternatively: from intermediate ion pair states of Σ symmetry).

Nevertheless, at early times (e.g. before the first $O^+$ maximum) the ion ground state is most effectively populated, as demonstrated by the intensity ratio of >100 of the $O_2^+$ versus $O^+$

maxima. This can be rationalized by the large difference in the order of ionization, where the energetic distance between the two potentials is still large. Where the two curves converge, both ionization paths are dissociative, so that there the relative efficiency cannot be distinguished anymore.

It is not self-evident that the ion ground state (configuration $\pi^4\pi^*$) can be directly populated: One-electron ionization from the neutral B state ($\pi^3\pi^{*3}$) leads to an excited ion ($\pi^3\pi^{*2}$, that is a or A). However, the B state contains near the Franck-Condon region a small admixture of a Rydberg state ($\pi^4\pi^*3p$) [22,25,26,38], which should provide a minor probability (corresponding to this admixture) to reach the ionic ground state. In particular, this ion state was also involved in the experiments with UV probing (ref. [7,8] or this work with negative delay times). The possibility to reach the ion ground state from the neutral B state implies that one could measure a time constant below 1 fs with suitable laser pulses: On pumping with the fifth harmonic of the Ti-sapphire laser and probing by the third harmonic (similarly as in [7] but with shorter pulses) one just reaches the bottom of the lowest ion potential, but not anymore on extension of the OO bond in the 1-pm range. The same principle allowed us to detect the dynamics of $H_2O$ photodissociation in times below 2 fs [11].

The two next maxima of the $O^+$ signal could not be interpreted in a similar way, because at the corresponding long OO distances all (singly excited) valence states have practically converged to their dissociation asymptotes. We postulated a doubly excited state ($\pi^2\pi^{*4}$), whose potential should come steeply down only at long bond lengths, and the contribution of ion-pair states, whose Coulombic wing reaches far out. Due to the partial charges, this wing is, however, distorted by the strong field of the probe laser. Such phenomena have previously been investigated in the theory of enhanced (multiple) ionization, which also made clear the connection to tunnel or barrier-suppression ionization. We invoked such a connection also to rationalize the exceedingly fast decay of the $O^+$ signal (≤3.5 fs, i.e., near or below time resolution, faster than in any previous case). A closer theoretical investigation seems to us worthwhile, not only to check whether such a fast decay can be expected but also because (a) two maxima are observed, as predicted but previously not observed, (b) it is the first observation of enhanced single-electron ionization, starting from a neutral molecule, (c) the dissociation is driven by the well known neutral potential (not by interaction with the laser field), and the time-dependent position of the wave packet (the time-dependent bond length) before ionization is well known, (d) the electron detached has $\pi$ symmetry, in contrast to all previous cases that ionized $\sigma$ electrons.

This work also demonstrates that it is possible – and makes sense – to distinguish different phases during dissociation, during which different processes and/or features of the potentials can be observed. To some extent this may be surprising for a molecule with only two atoms and just one potential involved in the excited neutral molecule. In all photochemical reactions of polyatomics that we previously investigated, there were also different phases, sometimes many. This seems less surprising, because these phases often involved a change of coordinate (direction of motion) or change of potential (electronic state). But it seems also interesting to follow the wave packet on just one (instantaneous) potential along one (instantaneous) coordinate with sub-Ångström or even picometer resolution; this not only requires pulses in the lower femtosecond or even sub-femtosecond range, but also a detection method which provides a sufficient number of distinguishable detection windows.

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