Einstein–Bohr recoiling double-slit gedanken experiment performed at the molecular level

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Extended methods

EXPERIMENTAL METHODS

Experiments were performed using an electron-ion coincidence setup (see Fig. 1) and the vertically polarized monochromatic radiation from the ultrahigh resolution\textsuperscript{45} PLEIADES soft X-ray beamline\textsuperscript{46} at the SOLEIL Synchrotron (Saint-Aubin, France). The X-ray beam is focused in the interaction region down to a $150(V) \times 250(H)$ $\mu$m$^2$ spot using a pseudo–Wolter optical device with two horizontal-deviation mirrors. Molecular oxygen is introduced into the experimental chamber as an effusive beam by a 200 $\mu$m internal diameter gas needle mounted on a 3D (x,y,z) motorized stage. The background pressure in the experimental chamber is $2 \times 10^{-8}$ mbar, which increases to $2 \times 10^{-6}$ mbar when sample gas is introduced.

An electrostatic double toroidal electron energy analyzer (DTA) \cite{40} is used for the analysis of the resonant Auger electrons after they are retarded and focussed on the entrance slit of the DTA by a four-element, conical electrostatic lens \cite{41}. The electron energy resolution is better than 0.5 eV at a pass energy of 50 eV for electrons with kinetic energies in the range of interest 490.8–496 eV. The electron energy resolution and kinetic energy scale were calibrated by measuring the Xe 5p$_{3/2}$ valence photoelectron line at 12.1 eV binding energy\textsuperscript{47}. An electron kinetic energy step of 0.1 eV (1/5 of the kinetic energy resolution) was a natural choice, which ensured a good compromise between count rate per channel and the level of detail to be observed in the spectra. A commercial position sensitive detector based on microchannel plates (MCP) and a delay-line anode\textsuperscript{48} (DLD40 from RoentDek GmbH) is used for the detection of the electrons emitted within two cones with aperture angles of $54 \pm 3^\circ$ around the magic angle, and corresponding to $\approx 4.2\%$ of the full solid angle $4\pi$ \cite{42} (see Fig. 1). The azimuthal angular resolution is about $\pm 3^\circ$. When an electron is detected, a pulsed electric field (200 V across 15.5 mm) is applied (15 ns rise time) to extract ions towards the ion spectrometer operated in Velocity Map Imaging (VMI) mode. After a second (16 mm long) acceleration region, the ions enter a 280 mm long drift tube equipped
with two internal ring electrodes. With two acceleration regions and two ring electrodes, the 3D focusing condition of the ions can be achieved\textsuperscript{49}. The ion detector, using a delay-line hex-anode (HEX75 from RoentDek GmbH), is installed behind the drift tube. Based on the time-of-flight (TOF) and on the impact positions on the detector, the three components of ions’ momenta can be reconstructed. The momentum resolution for $P_z$ is about ±1.6 a.u., while for $P_x$ and $P_y$ the resolution is about ±1.2 a.u. These momentum resolutions correspond to an ion kinetic energy resolution of 0.28 eV at an ion kinetic energy of 3.5 eV. This value is also confirmed by the experimental width of the sharp AP profile. The step for the ion kinetic energy is also chosen to be 0.1 eV. Since the momentum of the O$^+$ ion in the present experiment is larger than 80 a.u., the ion angular resolution is estimated to be better than ±2°. The statistical error bar is better than 4% in the 2D-correlation maps obtained after multi-coincidence data filtering.

The whole experimental setup illustrated in Fig. 1 can be represented schematically as shown in Fig. 2. Since the 3D momenta of both electron and ions are measured, by assuming the axial recoil approximation valid, it is possible to obtain the electron angular distributions in the molecular frame [13]. In order to investigate the correlation between the resonant Auger electron and the fragment ion, revealing the relaxation dynamics of the system, we have chosen to represent our multi-particle, multi-coincidence data as 2D-correlation maps between the Auger electron kinetic energy and the ion kinetic energy (see Fig. 2ab of the main manuscript), between the ion kinetic energy and cos $\theta$, where $\theta$ is the angle between electron and ion momenta (see Fig. 2cd of the main manuscript), or between the electron kinetic energy and cos $\theta$ (see Fig. 4 of the main manuscript). It is possible to further simplify the representation of the multidimensional coincidence data by creating one dimensional cuts in the 2D-correlation maps. Such cuts are illustrated in panels c, f and i of Fig. 4 of the main manuscript. These 1D data have been obtained by the integration over a 1 eV wide Auger electron kinetic energy range of the experimental 2D-plots shown in the panels a, d, and g of the same figure in the regions of maximum fringe visibility for the MB shown in the panels a and d, and along the tilted atomic line in the case of the AP.
shown in panel g. The experimental data are plotted with filled circles with error bars, while the result of theoretical simulations is shown with blue solid lines. The agreement between experiment and theory is good and captures the main features of the experimental spectra: the YDS interference patterns observed for the MB in Fig. 4cf, as well as the quenching of YDS interference and a strong asymmetry (see dedicated paragraph in the Outline of the theoretical methods section below) for the AP in Fig. 4g.

Since only electrons emitted in the interval delimited by the collection cones (see above) can be collected and the electron detection efficiency is less than 1, the pulsed electric field can extract not only the ions produced in the current photoionization event, but possibly also those (slow ions) created by a previous X-ray photon pulse, and for which the electron was not detected. In other words, an electron can operate both as a true trigger for the event it is correlated to or as a random trigger for an event it is not correlated to. Since the true coincidence rate scales as $N_i$, where $N_i$ is ion production rate, while the false (or random) coincidence rate scales as $N_i^2$, the ion production rate has to be kept reasonably low. In our experiment, by reducing the X-ray intensity (closing the exit slit of the monochromator has the additional advantage of simultaneously increasing the monochromaticity of the X-rays) and gas pressure, the electron count rate was kept below 140 counts/s. In these conditions, the electron-ion coincidence count rates are reasonable, whereas the random coincidences contribution is generally less than 10%. Additionally, a signal generator is used to trigger the pulsed extraction field at a repetition rate of 140 Hz, which allows the random coincidence spectra to be recorded\textsuperscript{50,51}. By combining the random trigger and the true electron signal trigger, we make sure that all events are acquired under the same conditions. Therefore the contribution of the random electron–ion coincidences can reliably be subtracted from the data. All coincidence spectra described in the main manuscript and Supplementary Information were corrected for random coincidences as described above.
OUTLINE OF THE THEORETICAL METHODS

Let us theoretically analyze the situation of a dissociative core-excited state, such as the $\sigma^*$ discussed in the main manuscript. In the case of a homonuclear diatomic molecule the Auger scattering amplitude is the sum of the scattering amplitudes through the “left” (L) and “right” (R) oxygen atoms [11,28]

$$F = F_L + F_R,$$

$$F_{L,R} = \int dp \frac{\langle 0 | \psi_p | \psi_p | e^{\pm i k R \cos \theta / 2} | \psi_{pf} \rangle}{E_{el} - \hbar \omega_{\infty} - \left( \frac{p^2}{2\mu} - \frac{p_f^2}{2\mu} \right) + i\Gamma},$$

where $\mu = m/2$ is the reduced mass, the signs $+$/$-$ correspond to the L/R atoms, $\psi_p$ and $\psi_f$ being the nuclear wave functions with the nuclear momenta of relative motion $p$ and $p_f$ in the dissociative core-excited and final states, respectively. The phase factors $\exp(\pm ik R \cos \theta / 2)$ indicate an opposite phase shift of the wave functions of the Auger electrons ejected from the “left” and from the “right” oxygen atoms. This phase shift is crucial for the Young’s double-slit (YDS) interference. The Franck-Condon (FC) amplitudes $\langle 0 | \psi_p \rangle$ and $\langle \psi_p | e^{\pm i k R \cos \theta / 2} | \psi_{pf} \rangle$ correspond to the (X-ray driven) photoexcitation and Auger decay processes, respectively. To facilitate the analysis, it is useful to divide the dissociation process into two regions. The first region corresponds to the decay transitions taking place near the interatomic equilibrium distance $R_0 = 2.28$ a.u.: $R_0 < R < R_0 + \Delta R$. The early (with respect to the photoexcitation instant) Auger decay events taking place in this first region lead to the formation of the molecular band (MB), which has a rather broad spectral width because the potential energy curves of the core-excited and final states are not parallel to each other (see Fig. 3a of the main manuscript). Starting from the interatomic distance (bond length) $R_0 + \Delta R$, both potentials become flat and are parallel to each other. This is the onset of the second region $R > R_0 + \Delta R$, in which the Auger decay processes lead to the formation of a narrow atomic peak (AP) [11,28].

Spatial and temporal characteristics of the molecular and the atomic regions.

For the convenience of the reader let us give the characteristic length $\Delta R$ and the evolution time $\tau_{mol}$ for the molecular regions, and the wave packet propagation distance $R_{at}$ in the
atomic region. According to Ref. [24], the distance from equilibrium to the flat region of the potential is \( \Delta R \approx 0.4 \) a.u.. Due to the repulsive nature of the core-excited state potential, the nuclear wave packet moves with the acceleration \( a = v / \tau_{\text{mol}} \) and passes the distance \( \Delta R \approx a^2 / 2 = v \tau_{\text{mol}} / 2 \). Here \( v = 2u \) is the relative velocity of the oxygen atoms. Using the kinetic energy released upon dissociation \( \Delta E \approx 7.5 \) eV [24], we estimate the velocity \( v = \sqrt{2 \Delta E / \mu} \approx 0.006 \) a.u. Thus the wave packet moves in the molecular region during the time \( \tau_{\text{mol}} = 2 \Delta R / v \approx 3 \) fs. The total lifetime of the wave packet in the core-excited state is \( \tau = 1 / \Gamma \approx 9.4 \) fs since the natural lifetime broadening is \( \Gamma = 0.07 \) eV. Thus the wave packet explores the atomic region over a distance \( R \approx v \tau_{\text{at}} = v(\tau - \tau_{\text{mol}}) \approx 1.6 \) a.u..

Taking into account the above division into two regions, it is natural to also divide the nuclear wave function in the core-excited state, \( \psi_p \), into two contributions: one corresponding to the molecular region, \( \psi_{p, \text{mol}} \), and the plane wave \( \exp(ipR) \), which describes the atomic region

\[
\psi_p(R) = \psi_{p, \text{mol}}(R) + \frac{1}{\sqrt{2\pi}} e^{ipR}.
\]

(2)

The same applies to the nuclear wave function in the final state, \( \psi_{p,f} \), which is described by the same equation by simply replacing \( p \) by \( p_f \). Let us point out that \( \psi_{p, \text{mol}}(R) = 0 \) in the atomic region \( (R > R_0 + \Delta R) \) because \( \psi_{p, \text{mol}} \equiv \psi_p(R) - e^{ipR}/\sqrt{2\pi} \). Therefore, the FC amplitude of the Auger decay consists itself of two parts:

\[
\langle \psi_p | e^{\pm ikx \cos \theta/2} | \psi_{p,f} \rangle = e^{\pm ikR_0 \cos \theta/2} \int_0^\infty dx \psi_p^*(x) e^{\pm ikx \cos \theta/2} \psi_{p,f}(x) = \frac{1}{2} e^{\pm ikR_0 \cos \theta/2} \left[ \delta(p_f \pm k \cos \theta/2 - p) + \varphi_{L,R}^{\text{mol}}(p,p_f) \right].
\]

(3)

Here

\[
\varphi_{L,R}^{\text{mol}}(p,p_f) = 2 \int_0^{\Delta R} dx \psi_p^{\text{mol}*}(R) e^{\pm ikx \cos \theta/2} \psi_{p,f}^{\text{mol}}(R) \approx A_0 \pm i \vartheta A_1 \cos \theta,
\]

\[
A_n = 2 \int_0^{\Delta R} dx \psi_p^{\text{mol}*}(R) \psi_{p,f}^{\text{mol}}(R) \left( \frac{x}{\Delta R} \right)^n, \quad n = 0, 1,
\]

(4)

and \( x = R - R_0 \), \( \vartheta = k \Delta R/2 \). The Dirac \( \delta \) function describes the momentum conservation law, \( p_f = p \mp k \cos \theta \), which is only valid for the atomic region. In contrast, such a momentum
conservation law does not apply to the molecular region, where the potentials are not flat. Here the function $\varphi_{L,R}^{mol}(p, p_f)$ is qualitatively different from the sharp $\delta$ function, and this is at the origin of the large spectral width of the MB (see Fig. 3a of the main manuscript). The finite width of the momentum distribution in the molecular region makes the role of the internuclear distance variation $x = R - R_0$ in the FC amplitude (4) qualitatively different from the atomic region (see eq. (5) below). This variation results in a slight dephasing of the YDS pattern in the molecular region (see for example ref. 52).

**Quantum momentum exchange.** We would like to point out the fundamental difference between the YDS interference observed with classical macroscopic slits and with quantum atomic slits as studied here. Contrary to the case of classical slits, the momentum exchange (or momentum conservation law) for the quantum system studied here ($O_2$) is non-local. According to the Heisenberg uncertainty principle, the point $R$ where the momentum exchange takes place is unknown for a quantum system as soon as the momentum is well defined. Mathematically, the non-locality of the momentum exchange is described by the FC amplitude (5) but not by the cross section. Therefore, the integration over $R$ is performed in the FC amplitude (5), as it should be in quantum mechanics, and not in the cross section as one might think intuitively:

$$
\frac{1}{2\pi} \langle e^{ipR} | e^{\pm ik R_0 \cos \theta /2} | e^{ip_f R} \rangle = \frac{1}{2\pi} e^{\pm ik R_0 \cos \theta /2} \int_0^\infty dx e^{-ipx} e^{\pm ikx \cos \theta /2} e^{ip_f x} \\
= \frac{1}{2} e^{\pm ik R_0 /2} \delta (p_f \pm k \cos \theta /2 - p).
$$

This integration over $R = R_0 + x$ gives the Dirac $\delta$ - function and the YDS phase factor at the equilibrium distance $R_0$ [28] as seen in eq. (5). This results in a very important conclusion: in spite of the change in internuclear distance between $R_0$ and $\infty$ during the dissociation process this change does not wash out the YDS interference pattern, which only depends on $R_0$.

**Auger scattering amplitude.** Taking into account eq. (5) we obtain the following expression for the Auger scattering amplitude through the “left” and the “right” atoms of
Suppression of the YDS interference due the Doppler labeling of the counter-propagating atoms. According to eq. (1), the Auger scattering amplitude for the AP $F_{at} = F^a_{L} + F^a_{R}$ is described by the first term at the right-hand side of eq. (6). This leads to the following expression for the cross section for the AP

$$\sigma_{at} = \frac{1}{|\langle 0 | \psi_p \rangle|^2} \left( \frac{1}{(E_{el} - \hbar \omega_{cf} - k u \cos \theta)^2 + \Gamma^2} + \frac{1}{(E_{el} - \hbar \omega_{cf} + k u \cos \theta)^2 + \Gamma^2} + \sigma_{int} \right) \times \delta(E_{el} + E_{dis} + \hbar \omega_{f0} - \hbar \omega),$$

$$\sigma_{int} = 2 \text{Re} \left( e^{ik R_0 \cos \theta} \frac{1}{[E_{el} - \hbar \omega_{cf} - k u \cos \theta + i \Gamma][E_{el} - \hbar \omega_{cf} + k u \cos \theta - i \Gamma]} \right).$$

The examination of the orders of magnitude for the direct and interference terms above shows that the interference contribution is very strongly suppressed (by at least one order of magnitude), $\sigma_{int}/\sigma_{at} \sim \Gamma/ku < 10^{-1}$, except for a narrow region $|\cos \theta| < \Gamma/2ku$ near $\theta = 90^\circ$.

We would like to draw the reader’s attention to an additional possible mechanism for the suppression of the YDS interference term $\sigma_{int}$. The homonuclear diatomic molecules have two final states with opposite parities ($gerade$ and $unegrade$) but with the same dissociation limit. As it was shown earlier [28], the interference terms for these final states have opposite signs. The two contributions might cancel each other and result in an additional suppression mechanism of the YDS interference term in the atomic region. However, in the particular case of $O_2$ studied here the final states of opposite parities have rather different (non degenerated) potentials until $R = 4.5$ a.u. (see Fig. 3 from Ref. [24]). Since the wave packet reaches only $R_{max} < 5$ a.u. during the lifetime of core-excited state 1/Γ, the suppression of
the YDS interference term due to this mechanism does not exceed 50% (see left panel in Fig. 5 from Ref. [24]).

**Observation of YDS interference due to incomplete decoherence by momentum transfer: light versus heavy slits.** When the Auger electron is ejected the electron-nuclear wave functions $\Psi_{R,L} = \psi_{R,L} e^{i(p \pm k/2) \cdot x}$ of the right and left configurations have different nuclear parts $e^{i(p \pm k/2) \cdot x}$. Here $x = R - R_0$. Due to this recoil-induced symmetry breaking the *gerade* ($\Psi_g = (\Psi_L + \Psi_R)/\sqrt{2}$) and the *ungerade* ($\Psi_u = (\Psi_L - \Psi_R)/\sqrt{2}$) electron-nuclear wave functions cease to be eigenfunctions of the electron-nuclear Hamiltonian $H$ of the $O_2^+$ cation. Let us look for the solution of the Schrödinger equation $H \Psi = E \Psi$ as a linear superposition $\Psi = a_g \Psi_g + a_u \Psi_u$ of $\Psi_g$ and $\Psi_u$.

$$a_g \langle \Psi_g | H | \Psi_g \rangle + a_u \langle \Psi_u | H | \Psi_g \rangle = E \Psi_g,$$

$$a_g \langle \Psi_u | H | \Psi_g \rangle + a_u \langle \Psi_g | H | \Psi_u \rangle = 0,$$

(8)

Taking into account that

$$\langle \Psi_g | H | \Psi_g \rangle = \frac{1}{2} (E_L + E_R + \Delta), \quad \langle \Psi_u | H | \Psi_g \rangle = \frac{1}{2} (E_L + E_R - \Delta),$$

$$\langle \Psi_u | H | \Psi_u \rangle = \frac{1}{2} (E_L - E_R), \quad E_R - E_L = 2k \cdot u = 2ku \cos \theta,$$

(9)

$$E_L = \langle \Psi_L | H | \Psi_L \rangle, \quad E_R = \langle \Psi_R | H | \Psi_R \rangle, \quad \Delta = 2\langle \Psi_L | H | \Psi_R \rangle$$

we get the following solution of eq.(8)

$$\mathcal{E}_\pm = E_d \pm ku \sqrt{\cos^2 \theta + \rho^2}, \quad \rho = \frac{\Delta}{2ku},$$

(10)

$$a_g^\pm = \pm \frac{1}{2} \left[ 1 \pm \sqrt{\frac{\rho}{\cos^2 \theta + \rho^2}} \right], \quad a_u^\pm = \pm \frac{1}{2} \left[ 1 \mp \sqrt{\frac{\rho}{\cos^2 \theta + \rho^2}} \right],$$

$$\Psi_\pm = a_g^\pm \Psi_g + a_u^\pm \Psi_u = \frac{1}{\sqrt{2}} \left[ (a_g^+ + a_u^+ ) \Psi_L + (a_g^- - a_u^- ) \Psi_R \right].$$

The parameter $\Delta$ is the effective splitting between the *gerade* and the *ungerade* final states which is not equal to zero because in the core-excited state the wave packet reaches only an internuclear distance $R_{\text{max}} < 5 - 6$ a.u. during the lifetime $1/\Gamma$ of the core-excited state (see left panel in Fig. 5 from Ref. [24]). The solution (10) illustrates the “competition” of
the parameters $\Delta = 2 \langle \psi_L | H | \psi_R \rangle$ and $2k u$. The first one characterizes charge delocalization. Indeed, $\psi_{\pm} \rightarrow \psi_g$ or $\psi_u$ when $\rho = \Delta / 2k u \gg 1$. The Doppler splitting $2k u$ of the $\psi_L$ and $\psi_R$ states has the opposite effect – it breaks the symmetry due to the charge localization: $\psi_{\pm} \rightarrow \psi_L$ or $\psi_R$ when $\rho = \Delta / 2k u \ll 1$. Thus, one can expect an intermediate situation between these two limiting cases to occur when $\rho \sim 1$. More precisely, the solution $\psi_{\pm} (10)$ should be a mixture of the coherent state $\psi_{g,u}$ and of the localized solution ($\psi_L$ or $\psi_R$) where the coherence between $\psi_L$ and $\psi_R$ is lost. This expectation is readily confirmed by the expression for the cross section, written for $\rho < 1$

$$\sigma = \sigma_{\text{inc}} + \sigma_{\text{coh}},$$

$$\sigma_{\text{inc}} = \frac{\Gamma^2}{[\Delta E_{el} - k \cdot u]^2 + \Gamma^2},$$

$$\sigma_{\text{coh}} = \left[ \frac{\Gamma^2}{[\Delta E_{el} - k \cdot u]^2 + \Gamma^2} - \frac{\Gamma^2}{[\Delta E_{el} + k \cdot u]^2 + \Gamma^2} \right] \rho \sqrt{\cos^2 \theta + \rho ^2} \cos (k \cdot R_0).$$

We wrote this equation in terms of the energy of the Auger electron $\Delta E_{el}$ with respect to the nominal (unaltered by the Doppler shift) Auger energy. For simplicity the constant prefactor is omitted in the cross section. The first, “incoherent” term $\sigma_{\text{inc}}$ follows the dispersion law (see Supplementary Fig. 3a)

$$\Delta E_{el} = k \cdot u,$$

where $k \cdot u < 0$ and $k \cdot u > 0$ correspond to the left $\psi_L$ and right $\psi_R$ configurations, respectively. In the case of the $O_2$ molecule studied here, this “incoherent” contribution is the dominant one. The second contribution, $\sigma_{\text{coh}}$, is the coherent part of the process, which vanishes only when $\rho \approx 0$. Given the partial coherence between $\psi_L$ and $\psi_R$, the which path information about the ionization site is partially lost, giving rise to an additional weak band with an opposite dispersion law (see Supplementary Fig. 3a)

$$\Delta E_{el} = - k \cdot u.$$ 

To exemplify this case, let us consider the Auger process in the $Cl_2$ molecule, where a $2p$ electron of the chlorine atom is excited to the lowest unoccupied molecular orbital. According to the “$Z+1” approximation, this core-excited state will behave similarly to the ground state
of the unstable ArCl molecule, whose dissociation also makes the situation similar to our main case of study, the O$_2$ molecule. However, the main parameters responsible for the dynamics are rather different in the Cl$_2$ case: $m_{Cl} = 35.5$, $\Gamma = 0.045$ eV, $R_0 = 3.76$ a.u., $kR_0 = 12.4$, $ku = 0.19$ eV. The Doppler splitting $2ku$ is for Cl$_2$ significantly smaller than in the case of O$_2$ due to the heavier chlorine atom. As a consequence the parameter $\rho$ increases, being about $\rho \approx 0.2$. Despite the smaller velocity of Cl, the relative intensity of the atomic peak $\sigma_{at}/\sigma_{mol} \approx e^{-\Gamma t} \approx 0.3 - 0.4$ is large enough due to the longer lifetime of core-excited state $1/\Gamma = 14.6$ fs compared to the $O_2$ case. Here $t = \Delta R/2u$ is the propagation time of the nuclear wave packet in the dissociative region, $\Delta R \approx 2$ a.u..

Such a relatively simple estimation is extremely useful to illustrate the behavior of heavy recoiling slits versus that of light slits, since it allows to shed light on the partial coherence of the recoil induced localization of the charge when $\rho \neq 0$ (case of heavy slits). Supplementary Fig. 3a schematically shows that the partial coherence of the final state generates an additional spectral feature with an opposite dispersion law (13) compared to the dispersion law (12) for $\sigma_{inc}$ (see Fig. 4h of the main manuscript and Supplementary Fig. 3a). It is instructive to look at the behavior of $\sigma_{inc}$ and $\sigma_{coh}$ along the ridges of these cross sections, lying on the lines described by the dispersion laws (12) and (13) (see Supplementary Fig. 3b)

$$\sigma_{inc} = 1, \quad \sigma_{coh} = \frac{\rho}{\sqrt{\cos^2 \theta + \rho^2}} \cos(k \cdot R_0), \quad \Delta E_{el} = k \cdot u$$
$$\sigma_{inc} = 0, \quad \sigma_{coh} = -\frac{\rho}{\sqrt{\cos^2 \theta + \rho^2}} \cos(k \cdot R_0), \quad \Delta E_{el} = -k \cdot u$$

(14)

To conclude, in the case of light slits when $\rho \approx 0$ only the incoherent part of the cross section contributes to the cross section (11) and no YDS interference pattern is observed for the dispersion law $\Delta E_{el} = k \cdot u$ (the case of the AP studied here), but in the case of heavy slits when $\rho \neq 0$ a YDS interference pattern is observed due to the coherent part $\sigma_{coh}$ of the cross section with the dispersion law $\Delta E_{el} = -k \cdot u$.

The angular asymmetry caused by the forward/backward Auger electron scattering. A careful inspection of Fig. 4g–i of the main manuscript leads to the observation of a surprising angular asymmetry of the AP: its intensity is significantly stronger around
\( \theta = 180^\circ \) compared to \( \theta = 0^\circ \). Indeed, the knowledge of the ionization site makes the angular distribution of the Auger electron in the molecular frame asymmetric, and such an asymmetry is a direct evidence of symmetry breaking. The origin of the angular asymmetry is the qualitatively different scattering of the Auger electron ejected from the “left” or from the “right” core-excited oxygen atom by the neighbor \( O \) atom (Fig. 4). The effect of scattering is different for co- and counter-propagating core-excited atoms relative to the electron momentum \( k \). In the latter case the Auger electron ejected from the core-excited atom is forward scattered by the neutral oxygen atom (Fig. 4a) with a large scattering amplitude, \( |f(0^\circ)|/R > 1 \), while the role of scattering is small in the former case due to the significantly weaker backward scattering amplitude (Fig. 4b), \( |f(180^\circ)|/R \ll 1 \) [43]. This strong asymmetry is observed for the AP (Fig. 4g–i of the main manuscript), where the ionization site is known.

By neglecting the YDS interference term, and taking into account the large momentum of the Auger electron one can show (similar to Ref. [31]) that the cross section for the AP is described by the following equation

\[
\sigma_{at}(E_{el}) = \sigma_{at}(\theta) \Phi(E_{el} - \hbar \omega_{cf}^\infty - k u \cos \theta), \quad \Phi(E) = \exp \left( -\frac{E^2}{\Delta^2} \right), \quad (15)
\]

\[
\sigma_{at}(\theta) = \left[ 1 + \frac{2}{R_0} \text{Re} \left( e^{i k R_0 (1+\cos \theta)} f[\pi - \theta] \right) + \left| \frac{f[\pi - \theta]}{R_0^2} \right|^2 \right].
\]

In our simulations, we used the scattering amplitude of the Auger electron by the oxygen atom, \( f(\theta) \), from Ref. [43]. The gaussian function \( \Phi(E) \) with a total width \( \Delta \approx 0.5 \) eV takes into account the bandwidth of incident X-rays and the instrumental broadening. The situation is qualitatively different for the MB, where the ionization site is unknown. This explains why the angular distribution observed for core excitation (pre-selection) of the bound Rydberg state is almost symmetric (Fig. 4a–c of the main manuscript). The discrepancy between experiment and theory observed in Fig. 4c of the main manuscript for \( \cos \theta > 0.75 \) is, in our opinion, related to the fact that the selected core-excited Rydberg state is not 100% pure due to the high density of electronic states in this energy region, and some small residual contribution from neighbor core-excited Rydberg states contaminates the Auger
decay. As the theory supposes perfect pre-selection of the core-excited state, i.e. that the excitation takes place to a single core-excited Rydberg state, this feature is not reproduced.

The angular asymmetry caused by the asymmetry of the FC amplitude of the Auger decay. An intermediate situation occurs for the MB observed for the dissociative $\sigma^*$ core-excited state (Fig. 4d–f of the main manuscript), where a slight asymmetry is also observed, but for a different reason, as detailed below. Indeed, according to eq. (6) the partial Auger scattering cross sections for the MB corresponding to the ejection of the Auger electron from the “left” and the “right” oxygen atoms read

$$
\sigma_{mol}^{L,R}(E_{el}) = |\Phi_{mol}^{L,R}(E_{el})|^2 \approx \frac{\mu^2}{p^2} \left( |B_0|^2 \pm 2\rho \cos \theta \text{Im}(B_0 B_1^*) \right),
$$

$$
B_n = \int dp_1 \frac{\langle 0|\psi_{p_1}\rangle A_n}{p_1 - p - i\frac{\Gamma}{p}}, \quad n = 0, 1.
$$

The linear dependence of the partial cross sections on $\cos \theta$ gives rise to a second mechanism of angular asymmetry, as clearly seen in the MB observed for the dissociative $\sigma^*$ core-excited state (Fig. 4d–f of the main manuscript). Fig. 4f shows a good agreement between experiment and theory.

Complete simulation of the MB. On the basis of the previous discussions we are now in a position to outline the theoretical simulations of the MB by taking into account simultaneously the YDS interference and the angular asymmetry mechanisms. The reason for partial symmetry breaking for the MB is twofold. On the one hand, a strong mixing of the dissociative $1\sigma_g^{-1}3\sigma_u$ and bound Rydberg state $1\sigma_u^{-1}3s_g$ lying in the same excitation energy range results in a significant localization of the core hole near the equilibrium geometry. On the other hand, a second symmetry breaking mechanism occurs due to the fact that the defined separation into atomic and molecular region is not perfect and, as a consequence, symmetry breaking partially takes place for the molecular region as well. In these conditions the MB cross section $\sigma_{mol}(\theta)$ is the sum of the symmetric $\sigma_{coh}(\theta)$ and asymmetric $\sigma_{L}(\theta)$
contributions:

$$\sigma_{\text{mol}}(\epsilon, \theta) = \sigma_{\text{mol}}(\theta) \Phi(\epsilon),$$

$$\sigma_{\text{mol}}(\theta) = s \sigma_L(\theta)(1 + \eta \cos \theta) + (1 - s)s \sigma_{\text{coh}}(\theta),$$

$$\sigma_{\text{coh}}(\theta) = \sigma_L(\theta) + \sigma_R(\theta) + \sigma_{\text{int}}(\theta),$$

$$\sigma_L(\theta) = \left[1 + \frac{2}{R} \text{Re} \left(e^{ikR_0(1+\cos \theta)}f[\pi - \theta]\right) + \frac{|f[\pi - \theta]|^2}{R_0^2}\right],$$

$$\sigma_R(\theta) = \left[1 + \frac{2}{R} \text{Re} \left(e^{ikR_0(1-\cos \theta)}f[\theta]\right) + \frac{|f[\theta]|^2}{R_0^2}\right],$$

$$\sigma_{\text{int}}(\theta) = -2Pf \text{Re} \left(e^{ikR_0 \cos \theta} + \frac{e^{ikR_0}}{R_0} (f[\theta] + f[\pi - \theta]) + f[\theta]f^*[\pi - \theta] \frac{e^{-ikR_0 \cos \theta}}{R_0^2}\right).$$

where $P_f = \pm 1$ is the parity of the final state and $\epsilon = E_{\text{el}} - E_{\text{res}}$ is the kinetic energy of the electron relative to the nominal energy of the Auger transition. The parameter of decoherence $s$ is about 0.5. The parameter $\eta = 2 \varrho \text{Im}(B_0 B_1^*)/|B_0|^2$ is responsible for the angular asymmetry caused by the asymmetry of the FC amplitude of the Auger decay (16). This mechanism of asymmetry in important only in the case of the pre-selection of the repulsive core-excited $\sigma^*$ state, and it is thus the one responsible for the linear slope of the YDS interference pattern seen in Fig. 4f of the main manuscript.

SPECTRAL SHAPE OF THE ATOMIC PEAK

It might be instructive for the reader to additionally get a simple physical explanation of the spectral shape of the atomic peak (AP) neglecting the scattering effect. Here we will simply focus on the momentum exchange between the ejected Auger electron and the ion. The spectral shape of the cross section of the Auger process is given by the following equation [18, 28]:

$$\sigma_{\text{at}} \propto \frac{\delta(E_f - E_o)}{(E_f - E_o)^2 + \Gamma^2}$$

Here $E_i$ is the total energy of the whole system in the $i = 0, c, f$ state.Apparently $E_0 = \hbar \omega + E_0(R_0)$ and $E_c(R), E_f(R) = \text{const.}$ We are interested in the cross section in the region of formation of the AP, $R = \infty$, where $E_c = E_c(\infty) = 2q_c^2/2m + E_c(\infty)$ and $E_f = E_f(\infty) = \ldots$
$E_{el} + E_{dis} + E_f(\infty)$, and $\pm q_c$ are the momenta of the “right”/“left” dissociating atoms in the core-excited state. Let us consider the situation when the electron is ejected say from the “right” oxygen atom. The kinetic energy release, or the total dissociation energy, is the sum of the kinetic energies of the “left” neutral $O$ atom and of the “right” $O^+$ ion, in the final state and can be written as $E_{dis} = q_L^2/2m + q_R^2/2m$.

The Auger decay events which lead to the formation of the AP occur far from the equilibrium geometry, where the bond is weak (Fig. 3a of the main manuscript). Therefore, the emission of the electron from the “right” atom does not change anymore the momentum of the “left” atom

$$q_c = q_R + k = m\mathbf{u} + \mathbf{k}, \quad -q_c = q_L.$$

Thus only the “right” atom changes its momentum in the final state $q_R = m\mathbf{u} = q_c - k$. The momentum conservation law (19) results in

$$E_f - E_0 = E_{ion} + ku \cos \theta + \frac{k^2}{2m} - \frac{D}{2},$$

$$E_f - E_c = E_{el} - \hbar \omega_f \infty - ku \cos \theta - \frac{k^2}{2m},$$

$$E_{dis} = D - ku \cos \theta - \frac{k^2}{2m}.$$

This equation, together with equation (18), result in equation (1) of the main manuscript.

**ELECTRIC FILED INDUCED SYMMETRY BREAKING**

To give the reader a complete physical picture, let us notice that charge localization occurs even in the case of the MB due to the ion detection process itself, but happens much later after the Auger electron emission. The $O_2^+$ cation dissociates in the final state without symmetry breaking until the electric extraction field of our ion spectrometer, $\mathcal{E}$, is switched-on at $\tau \approx 200$ ns after the emission of the Auger electron. At this instant the internuclear distance $R$ has become macroscopic ($\sim 1$ mm). At this internuclear distance the splitting between the gerade and the ungerade final states\textsuperscript{53}, $|E_u - E_g| \approx 40 \exp(-R/a)R/a$ $eV$, becomes much smaller than the coupling between the $|u\rangle$ and $|g\rangle$ states $\langle u|V|g\rangle = e\mathbf{R} \cdot /2$ in
presence of the applied electric field $E \approx 10^4 \text{ V/m}$. Here $a \sim 0.5 \times 10^{-8} \text{ cm}$ is the size of the atomic valence orbital. This coupling localizes the charge on one of the atoms due to the mixing of these states of opposite parity. However, this field induced symmetry breaking (ns) does not affect the studied Auger process, which takes place much earlier (fs).

REPRODUCIBILITY OF THE EXPERIMENT AND EXPERIMENTAL ACCURACY

The experimental interference patterns (Fig. 4a,d and g of the main manuscript) are relatively noisy. To lift any ambiguity, we would like to underline the reproducibility of our data, and point out that the same type of YDS fringes are also nicely observed in other sets of data obtained for different experimental conditions, as for instance for a different frequency of the X-ray photons. As an example, we show in Fig. 5 the results of the measurements obtained for the MB 0.26 eV below the top of $\sigma^*$ resonance. They display the same YDS interference pattern as observed for the top of the $\sigma^*$ resonance (Fig. 4d of the main manuscript).

To make quantitative comparisons between the results of simulations with that of the experiment, we have collected in Table I the positions of the maxima of the YDS interference patterns. Within the accuracy of our measurements, both Rydberg and $\sigma^*$ excitations show good agreement between experiment and theory.

Finally, let us concentrate onto the observed angular asymmetry discussed in the main manuscript and in the previous sections of the Supplementary Information. In spite of the qualitative agreement between theory and experiment showing in both cases the same trend: a larger signal intensity is clearly observed at 180° compared to 0°, the quantitative agreement is not perfect (Fig. 4a–f of the main manuscript). The reason for this is twofold. On the one hand, there is the limited statistical quality of the experimental data, and on the other hand there is a possible minor contribution of other final ionic states. As a consequence, only a qualitative agreement between numerical calculations and experimental
data can be expected, and this is why our discussion stays rather qualitative in this respect.

REFERENCES


46 http://www.synchrotron-soleil.fr/portal/page/portal/Recherche/LignesLumiere/PLEIADES.


TABLE I. Positions of the maxima in the YDS interference patterns shown in Figure 4a,b,d,e of the main manuscript.

<table>
<thead>
<tr>
<th></th>
<th>$\cos \theta_{\text{max}}$: molecular band (4p)</th>
<th></th>
<th>$\cos \theta_{\text{max}}$: molecular band ($\sigma^*$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a(exp)</td>
<td>$-0.75 \pm 0.08$</td>
<td>$-0.48 \pm 0.05$</td>
<td>$-0.02 \pm 0.03$</td>
</tr>
<tr>
<td>b(theo)</td>
<td>$-0.81$</td>
<td>$-0.41$</td>
<td>$0$</td>
</tr>
<tr>
<td>c(exp)</td>
<td>$-0.55 \pm 0.03$</td>
<td>$-0.18 \pm 0.05$</td>
<td>$-0.14 \pm 0.05$</td>
</tr>
<tr>
<td>d(theo)</td>
<td>$-0.65$</td>
<td>$-0.21$</td>
<td>$0.21$</td>
</tr>
</tbody>
</table>
FIG. 1. The Auger electron–ion 3D momentum correlation coincidence setup. Synchrotron radiation (SR) crosses at right angle an effusive beam of molecular oxygen. Electrons are detected using an electrostatic double toroidal analyzer (DTA) collecting electrons close to the magic angle (54.7°) with respect to its symmetry axis, which coincides with the ion’s time-of-flight (TOF) spectrometer axis. The Auger electrons’ kinetic energy and emission angle are simultaneously determined using a delay-line based position sensitive detector. Ions are detected using a spectrometer allowing the reconstruction of the full 3D \((p_x, p_y, p_z)\) ion momentum based on the measurement of their TOF and \((x,y)\) position on a second time and position sensitive detector. Electron detection triggers a high voltage extraction field, and the arrival time and position of all particles are recorded using a time-to-digital converter (TDC).
FIG. 2. **Schematic view of the experimental arrangement.** The electrons emitted in the vicinity of a cone defined by the *magic angle* (54 ± 3°) and the ions emitted in the full 4π space are detected. The vector correlations between particles are determined from their measurement in coincidence.
FIG. 3. **Role of partial coherence in the case of heavy slits.** The partial coherence preserved when the ratio $\rho = \Delta / 2k u$ is nonzero leads to a partial loss of which path information about ionization site. **a,** This partial coherence results in an additional spectral feature with the opposite dispersion law $\Delta E_{el} = -k \cdot u$ shown by the red dashed line. The black solid line shows the main dispersion law $\Delta E_{el} = k \cdot u$ (see also Fig. 4h of the main manuscript). **b,** The YDS pattern appears due to the partial coherence. The blue solid line shows the angular dependence of the main “incoherent” resonance (neglecting the anisotropy caused by the scattering). The solid black and the dashed red curves show $\sigma_{coh}$ for the ridges shown by solid and dashed lines in the panel **a,** respectively. The cross section $\sigma_{coh}$ is the convolution of the cross section given by eq. (14) with the gaussian with the width $6^\circ$, accounting for the instrumental broadening.
FIG. 4. The angular asymmetry of the atomic peak. a, The counter-propagation of the Auger electron (black arrow) and of the ion (red) is accompanied by a strong forward scattering by the neutral oxygen atom (blue). b, The co-propagation of the Auger electron and of the ion is accompanied by a weak backward scattering. Owing to the large difference between the amplitudes of the forward scattering and of the backward scattering, an angular asymmetry appears in the energy/angle correlation maps (see text and Fig. 4g–i of the main manuscript).
FIG. 5. Correlation map between the Auger electron kinetic energy and $\cos \theta$. The correlation map is shown for the MB and has been recorded 0.26 eV below the top of $\sigma^*$ resonance. It shows an YDS interference pattern very similar to that observed in the case of strict resonance excitation shown in Fig. 4d of the main manuscript.