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Vibrational scattering anisotropy in O₂—dynamics beyond the Born–Oppenheimer approximation

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Abstract. Born–Oppenheimer and Franck–Condon approximations are two major concepts in the interpretation of electronic excitations and modeling of spectroscopic data in the gas and condensed phases. We report large variations of the anisotropy parameter (β) for the fully resolved vibrational sub-states of the $X^2\Pi_g$ electronic ground state of O₂⁺ populated by participator resonant Auger decay following excitations of K-shell electrons into the σ^* resonance by monochromatic x-rays. Decay spectra for light polarization directions parallel and perpendicular to the electron detection axis recorded at four different excitation energies in the vicinity of the O 1s $\rightarrow \sigma^*$ transition are presented. Breakdown of the Born–Oppenheimer approximation is for the first time selectively observed for the lower vibrational sub-states, where two quantum

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paths—resonant and direct—leading to the same final cationic state exist. The higher vibrational sub-states can only be populated by resonant photoemission; hence no interference between these channels can occur.

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1. Introduction

In the Born–Oppenheimer (BO) approximation the electronic wave functions $\Psi_e(\mathbf{r}, \mathbf{R})$ are functions of the electronic coordinates $\mathbf{r}$ but are only parametrically depending on the nuclear coordinates $\mathbf{R}$, thus making possible the independent determination of electronic and nuclear motions [1, 2]. When the interaction between light and matter is described within this picture, only the electronic equation involves the dipole operator—leading to an expected dependence of the electronic wave functions on the polarization of the light. Consequently, there is no particular reason to expect electron emission anisotropy to be different for different vibrational sub-states of the same final electronic state when the transition dipole moment is independent of the molecular geometry. This can be understood from the Franck–Condon (FC) principle [3, 4]. From the *Condon approximation* one infers that an electronic transition between two states occurs on a short enough time scale that the transition probability can be computed in a fixed geometry. This is a consequence of the BO approximation. The FC principle thus states that the transition dipole moment is independent of the nuclear coordinates for the considered vibronic transition. If this principle holds, the matrix element describing a transition between two molecular electronic states is a product of two parts: a vibrational wave function overlap integral over nuclear coordinates (the FC factor) and an integral over electronic coordinates that defines the (dipole) transition probability between these two states (see, for instance, [5]).

Even though the BO approximation allows for a geometry dependence of the transition dipole moments describing the electronic transitions, when potential curve crossings occur in the final state one has to take into account the non-adiabatic coupling between these states beyond the BO approximation [2, 6, 7]. While such phenomena are well known in vacuum ultraviolet spectroscopy of isolated molecules [8–12], they are also present in condensed phases such as liquids [13], at surfaces [14] or even in quantum particles [15].

In soft x-ray photoemission, valence-ionized states can be produced through either direct or resonant processes, and in general, their description has to take into account *lifetime vibrational interference* as well as the interference between continuum (direct) and bound (resonant)

states [16]. Owing to a lack of systematic high-resolution measurements until now, only a few studies have reported unusual angular dependences of the vibrational envelopes in the soft x-ray region, and interpreted them as being related to these interference processes [17, 18], without supporting these interpretations by full scale simulations of the nuclear dynamics that are crucial in the analysis of the vibrational spectra. Only very recently, ultrahigh resolution soft x-ray electron spectroscopy measurements in acetylene combined with *ab initio* simulations allowed clear identification and modeling of the so-called *vibrational scattering anisotropy* (VSA) phenomena [19]. The cause of the VSA effect is twofold. The first reason is that the direct and the resonant scattering channels have different angular distributions of the ejected electrons. The second one is the nuclear dynamics taking place in the intermediate core-excited state, strongly affecting the resonant channel but not the direct photoionization channel, which has a qualitatively different vibrational profile. Acetylene presents a complex case: besides typical non-BO phenomena (such as the Renner–Teller effect), several decay channels interfere with each other and lead to the breakdown of the BO approximation. In this context, it may be inquired whether the VSA is characteristic of polyatomic species where multichannel interference occurs [20, 21] or whether it is a more general phenomenon that can also be observed in the simpler case of diatomic molecules, where only direct and resonant channels may interfere.

This work addresses the question above by making a clear demonstration that even in the case of single-mode systems such as diatomic molecules, one has to take into account the non-adiabatic couplings and the interference between the direct and resonant channels simultaneously to properly model the experiments. Our finding will be widely applicable to detect non-adiabatic couplings between two or more electronic states and phase transition-like phenomena in both isolated and condensed species through the observation of VSA in ultrahigh resolution resonant photoemission spectroscopy.

To avoid any confusion, let us clarify at this point the distinction between the BO and the FC approximations. Whereas the FC approximation is widely used in the interpretation of electronic transitions, it is not applicable to the cases when the final state changes its character within the vibrational region of the initial state and the transition dipole is heavily dependent on geometry. We would like to stress here that the BO approximation might still be valid in these cases. However, when the BO approximation is broken, the FC approximation is necessarily broken as well. Furthermore, the BO approximation is not able to account for phenomena such as the VSA, where the effective final state wave function cannot be factorized as the product of electronic and nuclear wave functions due to the coupling of the vibrational dynamics in the intermediate and final states through inter-channel interference.

The consequences of interference phenomena between direct and resonant photoemission channels have been studied previously in the soft x-ray range using resonant Auger (or resonant photoemission) spectroscopy for a series of diatomic molecules, e.g. in oxygen [22], nitrogen [6], nitric oxide [23], hydrogen chloride [24] or carbon monoxide [25, 26]. In [27], for instance, it was shown that the isotropic resonant Auger scattering cross section in the oxygen molecule is affected by such interference. The number of examples of recorded anisotropy for individual vibrational sub-states after resonant Auger decay is scarce. In diatomics, observations have been reported for CO [25, 26] and NO [23], whereas the larger systems studied were water [28] and acetylene [19].

In this paper, we present a study of the electron emission *anisotropy* in the resonant Auger scattering occurring upon soft x-ray photo-excitation of the oxygen molecule with the

polarization vector of the photons parallel or perpendicular to the electron detection axis. The experimental data have sufficient resolution to fully resolve the vibrational components of the resonant Auger spectrum of the oxygen molecule. The integral anisotropies for various final electronic states have been reported in the literature [22]—the new data allow for the identification of anisotropies as a function of the vibrational excitation.

The analysis of the spectra shows that the anisotropy parameter varies significantly with the amount of vibrational excitation in the final state. Furthermore, the magnitude of the anisotropy change also varies with the excitation energy (i.e. with the energy detuning from the resonance maximum). The former variation can be modeled by the interference between the direct and resonant ionization channels, while the latter type of variation is heavily influenced by the non-adiabatic coupling between Rydberg and valence states, which was shown to play a crucial role in the formation of the x-ray absorption profile [29, 30]. The angularly independent resonant Auger scattering cross section changes as a function of the excitation energy will be the subject of a separate publication [31].

The oxygen molecule has been extensively investigated by resonant x-ray scattering involving core levels and the unoccupied molecular states. Besides the resonant photoemission spectrum involving the prominent π^* resonance [32], particular attention has been paid to non-radiative (Auger) decay processes associated with the excitation to the σ^* resonance (which is non-adiabatically coupled with Rydberg progressions, as discussed below): a neutral dissociation process in the core-excited state was shown to lead to the Auger–Doppler effect [33–35], whereas more recently second step auto-ionization of excited atomic fragments has also been discussed [36]. The radiative decay channels of the core-excited state have also been investigated via resonant inelastic x-ray scattering [37, 38], where the effect of spatial quantum beats was observed [39], whereas in [40, 41], the O $1s^{-1}$ photoelectron spectra recorded at threshold ($E_{\text{kin}} = 0$ eV) without post-collision interaction broadening were presented and discussed.

Various aspects of the decay dynamics and their imprint on the resonant Auger decay following resonant x-ray excitations of free molecules have recently been reviewed from the viewpoint of either coincidence measurements [42], of high-resolution electron spectroscopy [43], or of both [44]. More precisely, for the oxygen molecule the x-ray absorption and associated resonant Auger scattering spectra have been investigated by Feifel *et al* in a series of publications [27, 45, 46].

Since the oxygen molecule has already been studied intensively, it provides an excellent playground to investigate various phenomena—in particular non-adiabatic coupling and interference between direct and resonant ionization channels. Hence, in contrast to the cases of complex molecules, it provides a textbook example: only one of the interference phenomena contributing to VSA is isolated and pinpointed. We will show that even in the case of a single-vibrational-mode system, a non-adiabatic coupling between states arises and abolishes the BO approximation and thus also the FC principle.

The paper is organized as follows: firstly, the experiment is described, as the performance of the x-ray source and spectrometer used is crucial for such investigations; the experimental results are presented and analyzed—the extracted parameters are used in the discussion section, which follows the description of the theoretical framework used to model the phenomenon.

2. Experimental details

The experiments were performed at the soft x-ray spectroscopy PLEIADES beamline [47] at the 2.75 GeV SOLEIL synchrotron, France.

The photon source used was an 80 mm period Apple II undulator—allowing the polarization vector of the x-rays to be rotated arbitrarily in the plane perpendicular to the photon beam propagation axis. The beamline allows photon energies within the range 7–1000 eV, and consists of a pair of prefocusing mirrors and an in-house modified Petersen monochromator using varied line spacing and varied groove depth plane gratings. The x-ray beam is then focused to one of the three optical branches where several permanent end-stations are available (photoelectron spectroscopy [48–51], Auger electron–ion momentum coincidence setup [42, 52, 53] and photoionization of ions setup [54, 55]) together with free ports for user setups (see [47]). For the experiments considered here, a 2400 lines mm^{−1} grating was utilized; the transverse position of the grating was adjusted so as to provide optimum flux at the selected energies—a criterion which was checked by an AXUV100 photodiode from IRD Inc., and a total ion yield detector, both situated after the photoelectron spectroscopy station.

The spectrometer used at the beamline is a VG Scienta R4000 hemispherical electron energy analyzer with its wide-angle lens mounted vertically, perpendicular to the light propagation direction. Oxygen gas (purity 99.9995%, Air Liquide Alphagaz 2 quality) was introduced into a differentially pumped gas cell. The gas cell allows for a higher local pressure of the sample gas (without adversely influencing the working conditions for the spectrometer) in the interaction region, where the x-ray beam hits the sample; at modest gas cell pressures no pressure effects influence the recorded spectra. Inside the gas cell, correction electrodes allow for the compensation of the local plasma potential created by the varying density of ionized gas created along the photon beam [56].

The combined experimental resolution, obtained from a least-squares curve fit to the typical measured electron spectra, was 96 ± 0.1 meV. The contributions to the combined broadening can be decomposed as a series of Gaussian broadenings from: the monochromator bandwidth about 30 meV at the photon energy $\hbar\omega = 539$ eV; about 40 meV from the electron energy analyzer, and about 51 meV accounting for the well-established translational [56], and recently discussed rotational Doppler broadenings [50, 57], as well as from other causes including unresolved rotational excitation or recoil-induced rotational broadening [58].

The resonant Auger decay spectra were recorded under resonant Auger–Raman conditions, i.e. monochromator bandwidth (30 meV) significantly lower than the core hole lifetime (about 155 meV for the O 1s^{−1} state [59]). All data have been normalized, wherever appropriate, with respect to sample pressure, photon flux and acquisition time.

3. Experimental results

3.1. Total ion yield spectrum

The total ion yield spectrum of oxygen, which mimics the x-ray absorption spectrum in the region between 537 eV and the O 1s^{−1} ionization thresholds (543.39 and 544.43 eV for ⁴Σ[−] and ²Σ[−], respectively [60]) has been studied extensively due to its intricacy, i.e. consisting of overlapping dissociative $\sigma^* \equiv 3\sigma_u$ states (associated with the doublet and quartet core-ionized

states, respectively) and Rydberg progressions [29, 30, 35, 46, 61]. Velkov *et al* [30] provide a detailed interpretation of the components of this spectrum. Pioneering angle-resolved ion yield spectra were recorded by Kosugi and co-workers in 1992 and 1994 [29, 61], and show the partition of the resonance's components into the σ^* and the Rydberg orbitals belonging to excitations involving quartet and doublet states, as also reviewed by Adachi *et al* [62]. The role of the non-adiabatic coupling between the Rydberg and valence states in this energy region [30] is also very important in the build-up of the angularly independent resonant Auger decay, as discussed in [31]. A recent measurement of this spectrum can also be found in [46].

The total ion yield spectrum shown in figure 1 was calibrated by the $4p\sigma_u(^4\Sigma_g^-) v=0$ state (541.80 eV [63]). In the figure the black triangles mark the photon energies at which the resonant Auger decay spectra were recorded—in the following they will be referred to as A, B, C (mainly valence excitation) and R (Rydberg and valence excitation), corresponding to excitation energy detunings (Ω) 0.0, -0.26 , -0.79 and $+0.4$ eV relative to the first sharp maximum in the spectrum at 538.95 eV, respectively.

3.2. Resonant Auger decay spectra

Figure 2 presents the resonant Auger decay spectra, fingerprinting the resonant Auger scattering process, recorded for the four excitation energies marked by triangles in figure 1. The binding energy scale $E_b = \hbar\omega - E_k$, where E_k is the Auger electron kinetic energy, was calibrated using the known binding energy of the $X^2\Pi_g(v=0)$ ground state of O_2^+ : 12.074 eV [64]. For each energy detuning, spectra were recorded with the x-ray polarization vector parallel (pluses) and perpendicular (crosses) to the electron detection axis. Solid lines represent the results of the calculations described below.

For linearly polarized light the differential photoionization cross section can be written as [65] ($\sigma = \frac{d\sigma}{d\Omega}$):

$$\sigma = \frac{\sigma^{(0)}}{4\pi} [1 + \beta P_2(\cos \vartheta)]. \quad (1)$$

Therefore an electron spectrum measured with linearly polarized light can be described in terms of the total isotropic cross section $\sigma^{(0)}$, the angle ϑ between the electron momentum (detection axis) and polarization vector of the light and the anisotropy parameter β . P_2 is the second-order Legendre polynomial. The anisotropy parameter β can take values between -1 and 2 .

The degree of linear polarization of the light in the present experiments is assumed to be close to unity, as indicated by independent measurements of Ar 2p and 3p as well as Ne 2s and 2p atomic samples for a discrete set of photon energies. The anisotropy parameter β of the electron emission process can then be expressed from the spectra recorded with the polarization vector of the light perpendicular or parallel to the detection axis⁸. For each excitation energy,

⁸ The angularly independent cross sections can be extracted by constructing a linear combination of the parallel $\sigma_{\parallel}$ and perpendicular $\sigma_{\perp}$ photoionization cross sections. From equation (1), it follows that

$$\frac{\sigma^{(0)}}{4\pi} = (\sigma_{\parallel} + 2\sigma_{\perp})/3. \quad (2)$$

This corresponds to a cross section observed at the angle 54.7° between the light polarization vector and the electron detection axis, commonly referred to as the *magic angle*. This angle is the root of P_2 , i.e. the second term of equation (1) becomes zero.

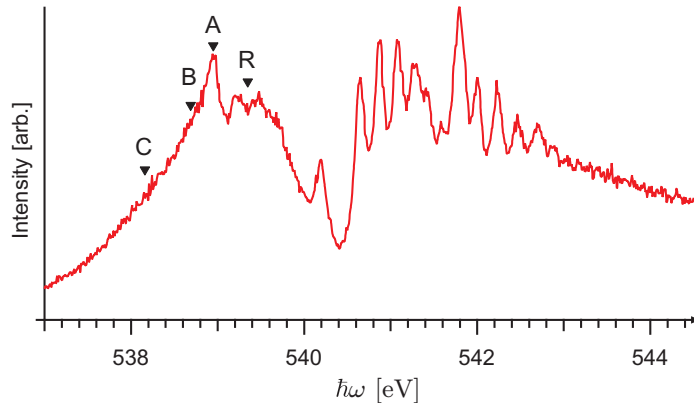


Figure 1. Total ion yield spectrum of oxygen in the vicinity of the σ^* and Rydberg manifolds below the $^4\Sigma^-$ and $^2\Sigma^-$ O $1s^{-1}$ ionization thresholds. The triangles mark the excitation energies at which the resonant Auger decay spectra were measured.

the anisotropy parameter $\beta = \beta(E_b, \omega)$, as obtained from

$$\beta(E_b, \omega) = \frac{2 [\sigma_{\parallel}(E_b, \omega) - \sigma_{\perp}(E_b, \omega)]}{2 \cdot \sigma_{\perp}(E_b, \omega) + \sigma_{\parallel}(E_b, \omega)}, \quad (3)$$

is plotted in the upper panels (dotted line) of figure 2. Additionally, the areas (proportional to $\sigma_{\parallel}$ and $\sigma_{\perp}$) for each vibrational peak in the progressions were extracted from the spectra by least-squares fits using a sequence of Gaussian peak shapes, using the SPANCF macro package for the Igor Pro software package [66]. The anisotropy parameter obtained per peak is shown with solid circles, where the error bars were obtained by error propagation for the standard deviation. The larger error bars for higher binding energies reflect the lower count rate in those experiments.

The lower panel of figure 3 presents an angularly independent experimental direct photoemission (off-resonance) spectrum (dashed, plus-markers) recorded for a photon energy set in between the π^* and σ^* resonances. The spectrum was constructed from the perpendicular and parallel component spectra using equation (2). The data here were recorded using the same overall experimental settings as for the resonant spectra. A photoelectron spectrum of the same state recorded with He II radiation [64] contains the same vibrational components with comparable branching ratios to the ones in our spectrum.

The experimental anisotropy extracted from the off-resonance spectra in figure 3 is 0.40(1), the same as the anisotropy per vibrational component. This number also coincides with the integral anisotropy for the whole progression. The theoretically modeled spectrum (discussed below), accounting exclusively for the direct ionization channel, is shown as a solid line underneath that spectrum. The good agreement between experimental and theoretical spectra demonstrates that for this excitation energy the contribution of the resonant channel is negligible. This is also corroborated by the fact that the extracted anisotropy parameter does not change with the vibrational excitation.

The long vibrational progression of the $X^2\Pi_g$ final state, observed for both polarizations and for all excitation energies, reflects the nuclear dynamics in the core-excited state. This can be understood from the contribution of the strongly repulsive σ^* components to the resonance. The excited wave packet will rapidly propagate and promote the molecular system towards

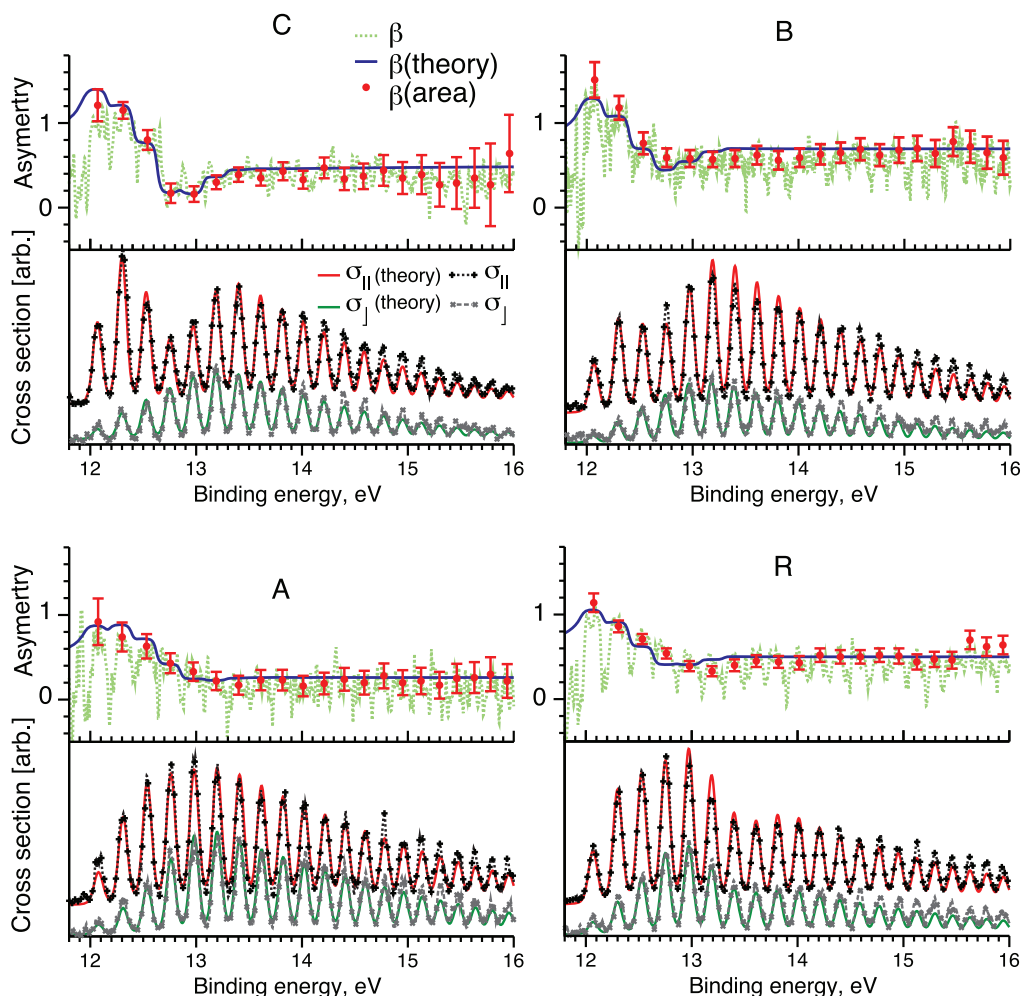


Figure 2. Experimental resonant Auger spectra (bottom panels, dashed with markers) obtained for two different light polarization directions of 0° and 90° with respect to the electron detection axis, with $+0.4$, 0.0 , -0.26 and -0.79 eV energy detunings (labeled R, A, B and C, respectively) from the first maximum observed in the ion yield spectrum. Solid lines in the bottom panels are the results of the theoretical description of the process, as discussed in the text. Top panels show values for the anisotropy parameter extracted from the experimental spectra directly (green dotted line), for each vibrational peak in the spectra (red dots) and the calculated ones (blue solid line) from equation (3). Colors refer to the online version of this paper.

longer bond distances. Therefore, the subsequent Auger decay into the cationic $X^2\Pi_g$ state will lead to a significant excitation of higher vibrational levels, in contrast to the photoionization occurring in the direct channel, which is governed by the FC factors involving the vibrational wave functions of the ground and final states only.

According to Sorensen *et al* [67], excitation to high Rydberg states does not seem to lead to a strong vibrational excitation of the $X^2\Pi_g$ final state. A more detailed survey, as done in [45], reveals that certain features in the x-ray absorption spectrum can indeed give rise to

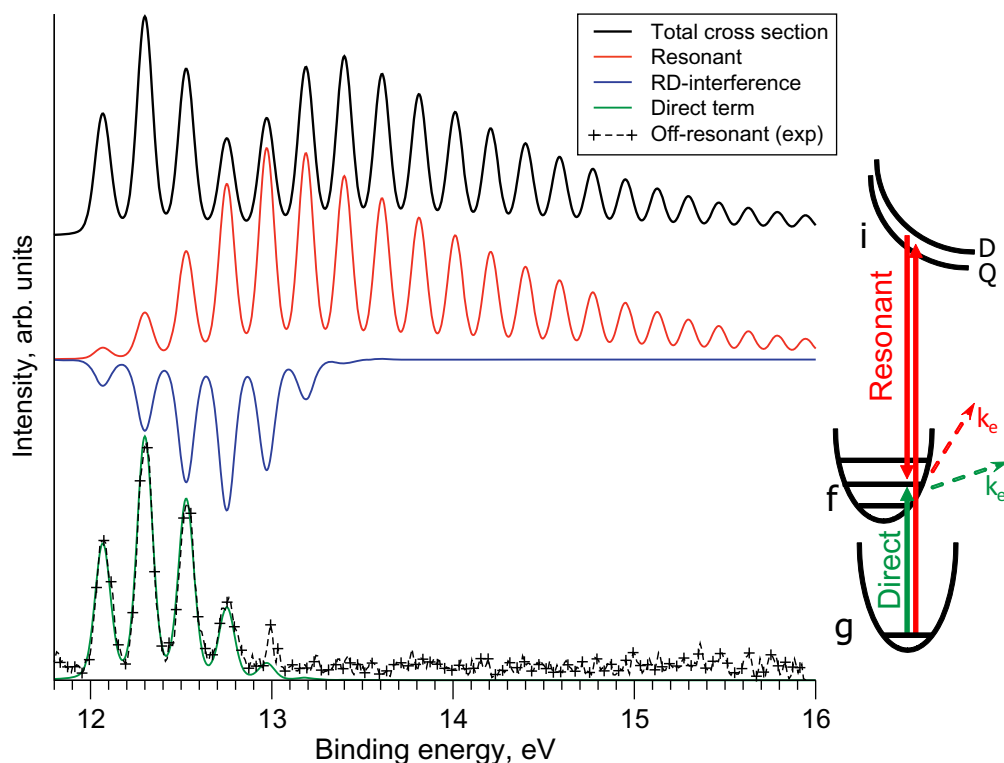


Figure 3. Theoretical total cross section $1\sigma^{(0)}$ (computed using equation (2)) for the spectra recorded for a -0.79 eV energy detuning. Also shown are the calculated spectra corresponding to the direct, the resonant and the interference term. The dashed line decorated with pluses indicates the off-resonance experimental spectrum. The calculated direct photoemission spectrum is shown in the bottom panel with a continuous green line. The right panel shows a schematic of the processes discussed in the text.

a resonant Auger decay spectrum very similar to the off-resonance spectrum (see figure 3), whereas excitation to other resonant features can result in a significant population of higher vibrational sub-levels of the $X^2\Pi_g$ state—therefore suggesting some repulsive character for the core-excited state potential. This highlights that the resonant Auger scattering process is very sensitive to the non-adiabatic coupling between the Rydberg and valence states and this question will be specifically addressed, as mentioned, in a forthcoming publication [31].

Figure 2 of [45] contains the extended resonant Auger decay spectrum (as well as an off-resonance spectrum) measured at the first sharp feature of the x-ray absorption spectrum. This can be directly compared to our spectrum measured on resonance (detuning 0.0 eV, point A). These data are represented for the *magic angle*, thus being related to our spectra via equation (2). Spectra taken at similar excitation energies as those presented here can also be found in [27].

To investigate the impact of the improved energy resolution on the spectral features, we reconstructed a *magic angle* spectrum at the 0.0 eV detuning point, which can therefore be directly compared to the corresponding spectrum in [27] (see figure 4). The peak to valley intensity ratio can be used as a measure of how well overlapping spectral features are discerned [68]. If taking the valley on the high binding energy side, this value varies between

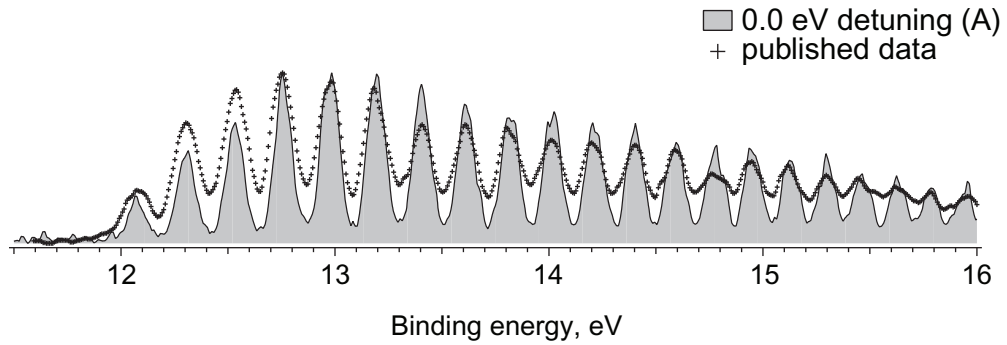


Figure 4. Comparison between the data presented in this paper (solid) and a previously published spectrum [27] (plus markers) taken on top of the first sharp feature found in the x-ray absorption spectrum (point A).

0.15 and 0.13 for peak $\nu = 1, \dots, 4$ (the ratio is 0.24 for the first peak $\nu = 0$); in the previously published data [27] the corresponding variation is 0.41–0.3 (with the ratio 0.5 for the first peak). The separation in the data presented here is thus sufficient to extract for the first time anisotropy parameters per peak. The present and earlier published data differ not only in resolution; the differences might be due to the normalization of either data set with respect to photon flux, measurement duration and gas pressure.

In table 1, the integral anisotropy parameter (using the integrals of the spectra for $\sigma_{\perp}$ and $\sigma_{\parallel}$ in equation (3)) for each excitation energy, as well as the values for the first seven vibrational components, are listed. The integral anisotropy parameter $\tilde{\beta}$ measured by Kivimäki *et al* on top of the first peak (A) in the absorption spectrum, 0.3(2) [22], is in agreement with our measurement. The integral anisotropy parameter oscillates as a function of the excitation energy, going through a minimum for point A in our measurements.

The spectrum for case C exhibits the largest oscillation in the anisotropy parameters of the individual vibrational levels. The difference between the highest and the lowest measured β values is about 1.05. For the neighboring points B, A and R the corresponding values are: 0.94, 0.85 and 0.75.

At the level of theory employed here, the anisotropy parameters do not change when there is not enough transition amplitude for both direct and resonant channels, since no interference is possible then. This holds true for each excitation energy. However, the mean values of the experimental anisotropy parameters for peak $\nu = 6$ and upwards attain values 0.45, 0.1, 0.58 and 0.39 for points R, A, B and C, respectively. This oscillation of the anisotropy parameter's value as a function of the excitation energy is a consequence of the strongly changing non-adiabatic coupling between the Rydberg and valence states used in the description of the states involved in the resonant Auger scattering process—as discussed in the theory section.

4. Theoretical framework

The neutral ground state's electronic configuration of the oxygen molecule is $^3\Sigma_g^-$:

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2.$$

Table 1. The first row of data is the integral anisotropy parameter. For off-resonance the integral anisotropy parameter is 0.40(1). The errors for the individual anisotropy parameters are about 10%.

	R	A	B	C
$\tilde{\beta}$	0.48	0.28	0.58	0.57
$\beta_{v=0}$	1.14	0.95	1.51	1.21
β_1	0.86	0.78	1.18	1.15
β_2	0.71	0.64	0.76	0.80
β_3	0.54	0.41	0.59	0.17
β_4	0.39	0.29	0.58	0.16
β_5	0.40	0.19	0.57	0.30
β_6	0.45	0.10	0.58	0.39

The first cationic state, having the lowest binding energy in the molecular ion, is the $X^2\Pi_g$, which has the electronic configuration:

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^1.$$

The x-ray Raman scattering process studied here transfers the ground state $|0\rangle X^3\Sigma_g^-$ neutral O_2 molecule to the ground state of the singly ionized molecule $X^2\Pi_g$ with the emission of an electron from the outermost molecular orbital. This process is induced when the excitation energy is tuned near the $O\ 1s \rightarrow \sigma^*$ resonance referred to as the intermediate state $|i\rangle = |1\sigma_g^{-1}3\sigma_u^1\rangle$. There are two channels which can bring the system to the final state:

$$|0\rangle + \hbar\omega \rightarrow |i\rangle \rightarrow |1\pi_g^{-1}\psi_k\rangle \quad (R),$$

$$|0\rangle + \hbar\omega \longrightarrow |1\pi_g^{-1}\psi_k\rangle \quad (D).$$

Since the ground $|0\rangle$ and final $|f\rangle$ states are the same for both channels above, these two channels—resonant (R) and direct (D)—will interfere with each other giving rise to an interference term. Indeed, in the time-dependent formulation of the Kramers–Heisenberg formalism using the auto-correlation function [69], the cross section $\sigma_0(\tau)$ can be expressed in terms of the time τ elapsed from the starting point by

$$\sigma_0(\tau) = \langle \Psi(0) | \Psi(\tau) \rangle + |A|^2 \langle 0 | \varphi(\tau) \rangle + i [A \langle \Psi(0) | \varphi(\tau) \rangle - A^* \langle 0 | \Psi(\tau) \rangle]. \quad (4)$$

Here the first term describes the resonant channel, while the second and third terms are responsible for the direct and interference contributions, respectively. The amplitude of the direct contribution, relative to the resonant one

$$|A|^2 = |a e^{i\phi}|^2, \quad (5)$$

is usually rather small, while the interference term can be quite strong and should be taken into account for a proper description of the total scattering process.

The wave packets required for the calculation of the time-dependent cross section using equation (4) are [27, 69]

$$\begin{aligned} |\Psi(0)\rangle &= \Gamma_{A_i} \int_0^\infty e^{-i(\mathcal{H}_i - E_0 - \omega)t} d_i |0\rangle e^{-\Gamma_i t} dt, \\ |\Psi(\tau)\rangle &= e^{-i(\mathcal{H}_f - E_0)t} |\Psi(0)\rangle, \end{aligned} \quad (6)$$

$$|\varphi(\tau)\rangle = e^{-i(\mathcal{H}_f - E_0)\tau} |0\rangle, \quad (7)$$

where E_0 is the ground-state energy, Γ_i is the lifetime broadening of the core-excited state, d_i and Γ_{A_i} are the transition dipole moment ($g \rightarrow i$) and the Auger decay rate ($i \rightarrow f$), respectively, and $\mathcal{H}_i$ and $\mathcal{H}_f$ are the nuclear Hamiltonians of the intermediate and final states, respectively.

The resonant Auger scattering cross section can be computed as

$$\sigma(E_b, \omega) = \Re \int_0^\infty \sigma_0(\tau) e^{i(E_b + i\Gamma_f)\tau} d\tau, \quad (8)$$

where Γ_f is the final state lifetime broadening.

In the case of the resonant Auger scattering through the oxygen $1s \rightarrow \sigma^*$ resonance studied here, the picture becomes more complicated due to the non-adiabatic coupling between Rydberg and valence orbitals in the core-excited state [29, 30, 38]. In the presence of two ionization thresholds $^4\Sigma^-(Q)$ and $^2\Sigma^-(D)$, there are six electronic configurations contributing to the formation of the main resonant spectral features: two valence $2p\sigma^*$ (the $\sigma(D)$ and $\sigma(Q)$) and four Rydberg states: the $3s(D)$, $3s(Q)$, $3p(D)$ and $3p(Q)$. Near the crossing points of the potential energy curves the BO approximation is no longer valid, and the non-adiabatic coupling between the various diabatic electronic configurations has to be taken into account [70]. In this case, the wave packet evolution in the intermediate state is defined by the nuclear Hamiltonian $\mathcal{H}$ [30], which reads

$$\mathcal{H}_{mn} = \delta_{mn} \left(-\frac{1}{2\mu} \frac{d^2}{dR^2} + E_m(R) \right) + (1 - \delta_{mn}) V_{mn}, \quad (9)$$

where $E_m(R)$ is the diabatic potential energy curve of the m th electronic state, V_{mn} is the interaction matrix element between the states m and n and $m, n = \sigma(D), \sigma(Q), 3s(D), 3s(Q), 3p(D)$ and $3p(Q)$. Then, equation (6) becomes

$$|\Psi(0)\rangle = \mathbf{\Gamma}_A^\dagger \int_0^\infty e^{i(E_0 + \omega)t} e^{-\Gamma_i t} |\phi(t)\rangle dt, \\ |\phi(t)\rangle = e^{-i\mathcal{H}t} \mathbf{d} |0\rangle,$$

where $\mathbf{d}$ and $\mathbf{\Gamma}_A$ are the column vectors consisting of the transition dipole moments and Auger decay rates for each core-excited diabatic state, respectively. In the present calculations, both non-adiabatic coupling in the core-excited state and the interference between the direct and several resonant channels are implicitly taken into account.

Ab initio calculations of the potential energy curves, transition dipole moments and interaction matrix elements for the O $1s \rightarrow \sigma^*$ core-excited state used in the simulations were performed in previous studies [29, 30] using the configuration interaction approach implemented in the GSCF3 program package [71, 72]. The values of the Auger decay rates Γ_{A_i} were chosen such that $|\Gamma_{A_{\sigma(Q)}}|/|\Gamma_{A_{\sigma(D)}}| = 2\sqrt{2}$ following [27], with $|\Gamma_{A_{\sigma(Q,D)}}|/|\Gamma_{A_{3s(Q,D)}}| \approx |\Gamma_{A_{\sigma(Q,D)}}|/|\Gamma_{A_{3p(Q,D)}}| \sim 10$, in accordance with [73].

The results of the theoretical simulations are compared against the experimental data in figures 2 and 3. In the latter figure, a decomposition of the total calculated cross section into resonant, interference and direct contributions is shown, to allow for a qualitative interpretation of the interference term contribution. The calculated direct channel contribution is superimposed with the experimental spectrum recorded below the resonance.

Table 2. The resulting parameters for the description of the interference between direct and resonant channels.

	$a_{\parallel}$	$a_{\perp}$	$\phi_{\parallel}$	$\phi_{\perp}$
C:	0.27	0.11	-115°	-100°
B:	0.22	0.11	-100°	-100°
A:	0.11	0.11	-50°	-100°
R:	0.16	0.11	-70°	-90°

The numerical simulations in figure 3 suggest that both resonant and interference terms are rather weak around the first vibrational peak (12.074 eV), where the resonant Auger scattering profile is mainly formed by direct photoionization. The anisotropy parameter around this peak $\beta_0 = 1.21$ (see table 1) is similar to that discussed previously for direct photoionization at much lower electron kinetic energies [74]. On the other hand, the direct and interference terms are almost zero around the seventh vibrational peak ($\nu = 6$), where the anisotropy is solely related to the resonant process. The anisotropy parameter $\beta_6 = 0.39$ differs sufficiently from that for the direct ionization process. This observation immediately suggests that the relative amplitudes of the direct photoionization contribution with respect to the resonant ones A (see equation (5)) for the parallel $A_{\parallel}$ and the orthogonal $A_{\perp}$ cross sections are different, which is the first reason for the anomalously strong VSA effect observed in the present study.

Moreover, the amplitude a and the phase ϕ (see equation (5)) of the direct and interference terms change with excitation energy across the $1s \rightarrow 3\sigma_u^*$ resonance (see table 1), reflecting the complex character of the molecular orbitals in that spectral region owing to the strong non-adiabatic coupling between Rydberg and valence states [30]. For example, a significant contribution from Rydberg states when the excitation energy is tuned to the point R considerably suppresses the VSA effect (see figure 2 and table 1). More information on the specific role of the non-adiabatic Rydberg–valence coupling in the formation of vibrational profiles in resonant x-ray scattering (radiative and non-radiative) will be published elsewhere [31].

Numerical simulations at point C (see figures 2 and 3), where mainly one valence state $\sigma(Q)$ is contributing to the resonant scattering process and where the effect of non-adiabatic coupling with Rydberg states is absent [30], allow for an accurate estimation of the parameters a and ϕ using the angularly resolved experimental resonant Auger scattering profiles. However, for larger excitation energies, covering the region of non-adiabatic Rydberg–valence coupling, the complexity of the core-excited state and the high quality of the experimental data motivated us to use the comparison with the experiment to extract the angularly dependent scattering amplitudes of the resonant channel relative to the direct photoionization channel, which can be measured independently (far below resonance). When one knows the relative contribution of the direct and of the various resonant channels (with possibly different anisotropies), a detailed analysis of the angularly resolved vibrational progressions of the resonant photoemission spectra is possible and such is the characterization of the nuclear dynamics in the intermediate core-excited state. The relative amplitudes and phases of the direct and resonant channels used in the numerical analysis are summarized in table 2.

5. Discussion

The isotropic resonant Auger scattering cross section (e.g. measured at the magic angle $\vartheta = 54.7^{\circ}$ or reconstructed from cross sections obtained with the electron detection axis parallel

and perpendicular to the polarization vector according to equation (2)) involving the states considered here shows strong dependence on excitation energy, in accordance with [27]. This can be understood as being a consequence of the interference between direct and resonant channels and the non-adiabaticity in the coupling between Rydberg and valence states in the vicinity of the resonance maximum. The interference itself depends on the excitation energy through the changing ratios between the amplitudes of the direct and resonant channels.

In this study, we also have to consider the dependence on light polarization. The spectra with the light polarization vector perpendicular to the detection axis are dominated by the resonant channel's contribution. In the parallel polarization case, depending on the excitation energy detuning with respect to the resonance maximum, a more or less strong excitation of the σ^* resonance occurs [46]. The two points below resonance (C and B) are dominated by the excitation into valence orbitals, whereas the points on and above the first resonance (A and R) must be seen as constituted by a mixture of Rydberg and valence orbitals. In figure 2, this can be observed, as the perpendicular polarization scattering cross sections appear to consist of a single progression of vibrational lines, whereas the parallel polarization ones seem to consist of two contributions that vary with excitation energy (as highlighted in figure 3).

The direct photoionization and the resonant Auger scattering channels have different electronic anisotropies. Moreover, the interference term mixes the vibrational wave functions of the final and core-excited states. Considering the upper panels in figure 2 (curves constructed according to equation (3)) it is obvious that not only does the integrated electronic anisotropy change with excitation energy (as inferred from table 1 and [22]), but also it changes with increasing vibrational excitation within the same electronic state. Above a certain amount of vibrational excitation ($\nu > 6$) the anisotropy remains the same. The data hint at oscillatory behavior even above 13.5 eV, but with a much smaller amplitude. However, this oscillation is well within the error bars of our experiment.

When both direct and resonant channels are open, the scattering experiment is akin to a double slit experiment with both slits open. Direct photoionization cannot populate vibrational states above $\nu = 6$ —this slit is then closed. In contrast to the case of polyatomic molecules, where multichannel interference processes may occur in different energy regions [19], in the case of diatomic oxygen a single interference process occurs only when both channels can be accessed in the scattering process, i.e. below 13.5 eV. This aspect is well reflected in the theory, as well as in the experimental anisotropy curve, which is flat for the higher vibrational states.

The BO approximation decouples the nuclear and electronic wave functions. When this approximation is valid, the anisotropy is governed only by the electronic wave function. Let us consider the ideal situation when this approximation holds for both direct and resonant scattering channels when they are taken separately. However, when they are considered together, this approximation is not valid anymore for the whole process—due to the mixing of the vibrational wave functions of the core-excited and final states. Indeed, for the direct channel we may write the final state's wave function as a product of the electronic ψ and nuclear $|\nu\rangle$ wave functions:

$$\Psi_f^{\text{dir}} = \psi_f |\nu_f\rangle,$$

whereas for the resonant channel this reads

$$\Psi_f^{\text{res}} = \psi_i \langle \psi_i | \hat{\Gamma}_A | \psi_f \rangle \sum_{\nu_i} \frac{\langle \nu_i | \nu_f \rangle}{Z_{\nu_i}} |\nu_i\rangle.$$

When expressed as the sum of these two channels, the final state wave function does not fulfil the BO approximation any longer:

$$\Psi_f = \Psi_f^{\text{dir}} + \Psi_f^{\text{res}} \neq \psi_f |v_f\rangle.$$

Here $Z_{v_i} = \omega - \omega_{v_i,0} + i\Gamma_i$, ω is the photon frequency, ω_{v_i} is the transition frequency from the ground to the v_i th vibrational sublevel of the intermediate electronic state, $\hat{\Gamma}_A$ is the Coulomb operator—defining the decay rate between the intermediate and final states—and $\psi_f |v_f\rangle$ is the total final state wave function within the BO picture.

In the vicinity of the maximum of the absorption resonance, the resonant Auger (or resonant photoemission) process takes long enough for the vibrational wave functions of the intermediate state to establish (the duration of the scattering process is long for a small energy detuning [16]). Therefore the nuclear dynamics in the intermediate state is of crucial importance. This results in a strong mixing of the final (cationic) vibrational states with the vibrational states of the intermediate core-excited state. Hence, we experience a breakdown of the BO approximation, because the total wave function cannot be factorized into a product of electronic and nuclear wave functions.

When the excitation energy is tuned far away from the resonant intermediate state, the scattering duration becomes small. As a consequence, from the viewpoint of *nuclear dynamics*, this situation corresponds to a direct transition from the ground state potential to the final state potential (this is the case for direct photoionization). In this case, the relevant matrix element describing the process is the overlap between the ground and final state vibrational wave functions $\langle 0 | \mathbf{d}(\mathbf{R}) | v_f \rangle$. This matrix element is valid within the BO approximation, but the FC approximation can be broken when the $\mathbf{R}$ -dependence of $\mathbf{d}(\mathbf{R})$ is significant. We can identify at least two possible mechanisms for this $\mathbf{R}$ -dependence generating a breakdown of the FC approximation: the $\mathbf{R}$ -dependence of the unperturbed electronic wave functions of the ground ψ_0 and final ψ_f states, or the admixture of other electronic states in the scattering processes, for instance. The excitation in the vicinity of shape resonances is a well-known example leading to the breakdown of the FC approximation [9–12]. Interestingly, the photon energy detuning from the maximum of the photoabsorption resonance drives the transition from the non-BO regime studied here to the non-FC behavior met in photoionization where an $\mathbf{R}$ -dependence of the electronic transition dipole moment occurs.

For points A and R the theory employed here does not take into account, for instance, energy-dependent decay rates, considered to be beyond the scope of this paper. A more advanced description (energy- and Rydberg-dependent) of the potential energy curves, as well as of the wave functions, may improve the noticeable discrepancy between the theory and the experiment for the higher vibrational excitations (starting from 14 eV binding energy and above).

The oxygen case described here represents a textbook example of vibrational scattering anisotropy, where a single interference process occurs, pointing out that this is a general phenomenon. In contrast to this simple situation, in a polyatomic molecule such as acetylene [19], interferences also arise from a Renner–Teller split double-well potential of a bending mode in the core-excited state and via a doubly degenerate vacant molecular orbital, making the description of the single contributions to the vibrational scattering anisotropy much more complex to analyze.

6. Conclusion

Detailed data on anisotropies of model systems, such as the one considered here, are necessary in the quest for ‘complete’ characterizations of the decay processes following photoexcitation. A recent example is that of the fluorescence decay spectra of resonantly excited NO, where the characteristics of the non-radiative resonant Auger decay channel needed to be part of the analysis [75].

We have made measurements of the vibrational scattering anisotropy in the $X^2\Pi_g$ cationic final state populated by resonant Auger scattering with x-ray excitations in the vicinity of oxygen’s core-shell to σ^* manifold. The excitation energies were -0.79 , -0.26 , 0.0 and 0.4 eV (C, B, A and R) relative to 538.95 eV, i.e. the energy of the first sharp feature in the x-ray absorption spectrum recorded between 537 and 544 eV on the excitation energy scale. One additional point measured off resonance is included in the analysis; its accurate theoretical description needed only the inclusion of the direct photoionization channel.

The integral anisotropy, understood as the β parameter computed using the area of the whole $X^2\Pi_g$ state for each polarization direction, changes with excitation energy as $0.4(1)$ (off-resonance) to $0.45(9)$, $0.17(6)$, $0.25(5)$ and $0.36(8)$ (C, B, A and R). It goes through a minimum when approaching the 0.0 eV energy detuning point. A recent investigation [27] has concentrated on the excitation energy dependence of the *isotropic* resonant Auger scattering cross section that could be understood through: (i) the interference between the direct and the resonant ionization channels and (ii) the mixing between the valence and Rydberg orbitals involved.

Presented here are the *angularly resolved* experimental resonant Auger scattering cross sections with full vibrational resolution such that a detailed investigation of the anisotropy of the scattering process became possible: the anisotropy parameter depends on the final vibrational state as long as both the direct and resonant ionization channels can interfere (in the present case this condition is fulfilled below $v = 6$). It is shown that even if the BO approximation held for both direct and resonant ionization channels individually (not the case here for the resonant channel due to the non-adiabatic Rydberg–valence mixing in the core-excited state), it would still not be applicable to the scattering process as a whole. In other words, the breakdown of the BO approximation occurs due to the mixing of different nuclear dynamics between the autoionizing state and the continuum states in which the former is embedded. The measurements and interpretation are supported by time-dependent wave packet propagation calculations providing very good agreement with the data.

The observed anisotropy of the resonant Auger scattering in oxygen, in the region of the σ^* resonances, thus showcases a single process (interference between resonant and direct ionization channels) that can give rise to vibrational scattering anisotropy (VSA) [19]. The VSA phenomenon thus appears to be a general phenomenon, that may be observed as soon as the experimental conditions allow for a fully vibrationally resolved measurement. The results presented here highlight a methodology which, given sufficient experimental resolution, can be widely applicable in the x-ray regime to detect non-adiabatic couplings between two or more electronic states—not only in molecules but also for phase-transition phenomena in solid state or in nanomaterials—through vibrational scattering anisotropy. Finally, we would also like to point out the importance of extracting the anisotropy data of the resonant channels based on the experiment–theory comparison to reveal non-BO effects in the spectra previously interpreted within the BO or FC approximation.

We hope that such investigations will encourage further studies of this process—not the least using the rich information it provides to better understand non-adiabatic processes in complex systems such as biopolymers or quantum dots, to cite only a few.

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