

Resonant Inelastic Scattering Spectra of Free Molecules with Vibrational Resolution

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Inelastic x-ray scattering spectra excited at the $1s^{-1}\pi^*$ resonance of gas phase O_2 have been recorded with an overall energy resolution that allows for well-resolved vibrational progressions. The nuclear wave packet dynamics in the intermediate state is reflected in vibrational excitations of the electronic ground state, and by fine-tuning the excitation energy the dissociation dynamics in the predissociative $B'^3\Pi_g$ final state is controlled.

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Resonant inelastic soft x-ray scattering (RIXS) probes ultrafast molecular dynamics [1]. The local nature of the intermediate state core vacancy together with the short duration of the scattering process imply atomic precision on the femtosecond time scale. Furthermore, the time scale for the interaction can be controlled by fine-tuning the energy of the exciting radiation [2,3]. The potential of gas-phase RIXS has long been recognized [4–7], and it is now being pursued by several groups (see, e.g., [8–10]). Here we demonstrate that inherent potentials of the method are realized when RIXS spectra are recorded with an energy resolution which is sufficient to resolve vibrational substates.

Via measurements of the complementary autoionization process, the dynamics following the $1s^{-1}\pi^*$ excitation in O_2 has been the showcase for demonstrating the connection between lifetime-vibrational interference and ultrafast wave packet dynamics [11–13]. Because of the formal similarity with a RIXS process, autoionization following resonant excitation has often been termed “nonradiative Raman scattering.” There are, however, several pertinent differences between the two decay channels. In particular, the validity of the dipole approximation makes the RIXS process highly selective. Since nonresonant inelastic scattering is dipole forbidden, any interference with the direct channel, which is often strong in the electronic channel, can be safely neglected. In symmetric systems a subset of dipole allowed neutral final states is selected, and the process becomes very sensitive to any dynamic symmetry breaking [2,6,7].

We present RIXS spectra excited at the $1s^{-1}\pi^*$ resonance in gas phase O_2 with an overall energy resolution of 50 meV. We observe two electronic final states, both with

well-resolved vibrational fine structure: the ground state and the predissociative $B'^3\Pi_g$ state. The vibrational progression in the ground state monitors the development of the vibrational wave packet in the intermediate state, and allows for an accurate determination of its potential surface and lifetime. By detuning the excitation energy, the wave packet development is controlled to selectively populate various sets of vibrational wave functions in the $B'^3\Pi_g$ state. Quasibound states in the shallow potential minimum are resonantly populated, as are continuum states at and above the avoided curve crossing.

We have exploited the unprecedented capabilities in terms of high intensity and energy resolution which are now available with the SAXES spectrometer [14] at the ADDRESS beam line [15] at the Swiss Light Source of the Paul Scherrer Institute. Measurements were performed using a flow cell with a 100 nm thick diamondlike window, separating the ultrahigh vacuum from the sample gas. Incoming and outgoing radiation passed through the same window, both at an angle of 45° . The sample was air at atmospheric pressure.

Scattering at $1s^{-1}\pi^*$ resonance (Fig. 1) in gas phase O_2 is dominated by a vibrational progression in the 0–2 eV energy-loss range and a structure around 6.5–8 eV, both features showing a pronounced excitation-energy dependence. At room temperature the oxygen molecules are almost exclusively in the vibronic ground state of the electronic ground state, $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2 \Sigma_g^-$. Approximately, the RIXS process can be described by a two-step model with one-electron transitions between single-configuration wave functions: in the first step of the process an intermediate state is excited as a core electron is promoted to a previously unoccupied orbital,

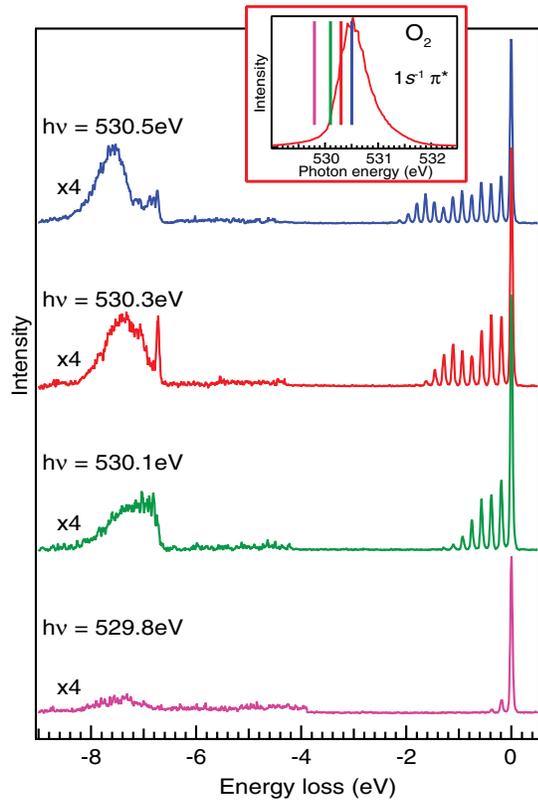


FIG. 1 (color online). RIXS spectra excited as indicated in the inset at the $1s^{-1}\pi^*$ resonance in gas phase O_2 are dominated by a vibrational progression in the 0–2 eV and a structure in the 6.5–8 eV energy-loss range, assigned to transitions to electronic ground state, ${}^3\Sigma_g^-$, and to the $B'{}^3\Pi_g$ state, respectively.

and in the second step an electron from an outer orbital fills the core vacancy. From the intermediate $1\sigma_u^{-1}1\pi_g^{+13}\Pi_u$ state only two single-configuration final states are dipole allowed in this energy range: the ${}^3\Sigma_g^-$ ground state and the $3\sigma_g^{-1}1\pi_g^{+13}\Pi_g$ state [6]. Beyond the single-configuration picture, it is recognized that the electronically excited final state, $B'{}^3\Pi_g$, is composed out of two interacting states, forming a predissociative state with a shallow energy minimum and an avoided curve crossing [16,17]. The two main features in the RIXS spectra are accordingly assigned to the $X^3\Sigma_g^-$ (0–2 eV) and the $B'{}^3\Pi_g$ (6.5–8 eV) states. In earlier RIXS studies on O_2 [6], the issue was raised whether core-hole localization in the intermediate state would lead to violation of the selection rules imposed by inversion symmetry, and it was concluded that no violation of the dipole selection rules could be observed. Additionally, the present data comply with the dipole selection rules, supporting the conclusions of the earlier investigation. Thus, the RIXS process selects final states out of a multitude of states in this energy-loss range, and allows for a detailed study of the situation described by the potential curves in Fig. 2. We first turn our attention to

scattering to the vibronic substates of the electronic ground state.

At resonant excitation (530.5 eV) we observe 13 distinct vibrational excitations, spanning an energy range of more than 2 eV. The vibrational peaks are symmetric and almost pure Gaussians, and we compare to theoretical predictions convoluted with a Gaussian with a full width at half maximum of 50 meV, to account for the overall instrumental broadening. The energies of the ground state vibrational levels have been determined with high accuracy in low-energy experiments [18], giving us the opportunity to calibrate the energy dispersion of the spectrometer with an accuracy which is superior to what has so far been possible in this energy range. The Gaussian fit which determines the center of each peak limits the accuracy to around 1 meV. Using the diffuse reflection of the incident light into the spectrometer this precise energy definition can be transferred to the monochromator. We therefore propose to use well-defined vibrational levels in the ground state of simple molecules as a general calibration method and expect wide applications at synchrotron radiation beam lines.

The intensity modulation of the vibrational progression reflects the development of the nuclear wave packet in the intermediate state. Maxima in the progression envelope can be related to the turning points of the oscillator, and it has earlier been demonstrated that the lifetime of the intermediate state is insufficient for one full classical oscillation [11–13]. As the excitation energy is lowered by 700 meV, the number of observed vibrational excitations decreases from 13 to 2, in line with the notion that the effective scattering time is reduced upon detuning [3]; in this case the vibrational wave packet is given less time to develop during the scattering process and in the limit of a prompt process a complete “collapse” of the vibrational progression is expected [2,3].

To simulate the cross section the Kramers-Heisenberg scattering amplitude was computed using a discrete variable representation discretization, combined with smooth exterior scaling [19] to enforce scattering boundary conditions. The $X^3\Sigma_g^-$ potential was taken from Cheung *et al.* [18] and parameters for the ${}^3\Pi_u$ core excited state from Coreno *et al.* [20].

The theoretical description (Fig. 2) critically depends on the equilibrium distance and the lifetime of intermediate state. To get the excellent agreement shown in Fig. 2, we use $r_e = 1.34$ Å and $\Gamma = 150$ meV for the equilibrium distance and the lifetime width, respectively, in concordance with earlier published values [20]. The agreement between the predictions and the experimental data does not require any dependence of the total decay rate or specific yield channels on the nuclear distance. Such a dependence has been demonstrated for the electronic decay [13], and may have been anticipated also in this case.

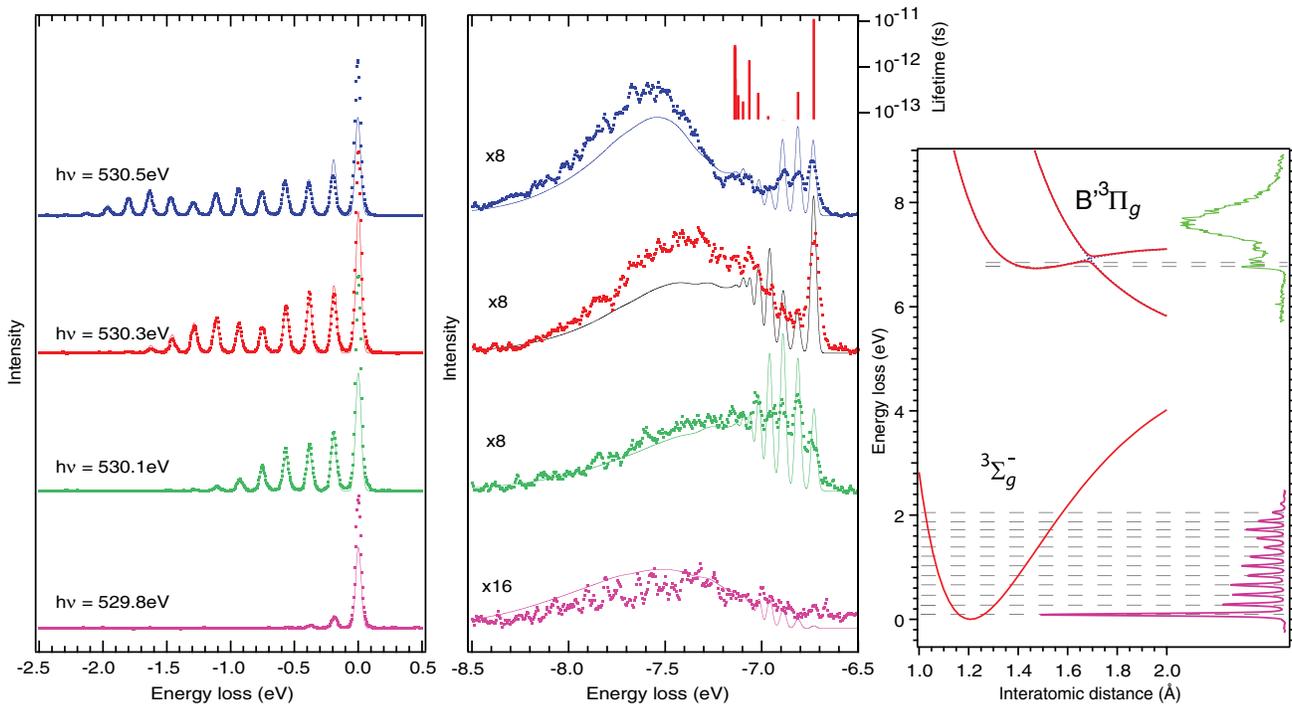


FIG. 2 (color online). Comparison of the experimental results and theoretical predictions for scattering to the ${}^3\Sigma_g^-$ ground state (left) and to the $B'{}^3\Pi_g$ state (middle), where the theoretical lifetimes of the vibrational substates are indicated in the upper right-hand corner. The right-hand panel shows the potential surfaces of the final states and the vibrational energy levels.

Whereas the excitation-autoionization channel may interfere with direct photoionization to the ionic ground state, direct nonresonant Raman scattering in the radiative case is dipole forbidden except for strictly elastic Thomson scattering. This may influence the intensity of the $\nu = 0$ peak, and any additional intensity enhancement of this peak in our data may also be due to diffuse reflection in the carbon window. The remaining differences between the data and the model we attribute to self-absorption effects, slightly attenuating the lower energy region of the spectra.

The agreement between the model and the measured population of the ground state vibrations ensures that the wave packet development in the intermediate state is well described by theory. We now turn our attention to the electronically excited final state.

We observe a broad (FWHM >0.5 eV) structure with an intensity maximum around 6.5–8.0 eV energy loss (Fig. 2). The structure has pronounced excitation-energy dependence. At 530.3 eV excitation energy a sharp peak at 6.73 eV appears, and on resonance there is resolved vibrational fine structure following the low-energy peak with peak distance of around 80 meV.

Although several *gerade* states of triplet multiplicity have been observed [16,21] in electron energy-loss spectroscopy and resonantly enhanced multiphoton ionization, and have also been identified as magnetic dipole transitions [17] in optical spectroscopy, only the B' state is expected to be excessively populated in the RIXS process, and we assign the 6.5–8.0 eV energy-loss feature accordingly.

The prediction uses the diabatically coupled $\Pi^3\Pi_g-I^3\Pi_g$ potential curves of Lewis and co-workers [17,22] with a coupling of 500 cm^{-1} for the B' final state.

The agreement between experimental results and theoretical description is very good, and all the salient features are reproduced, fully confirming the assignment. Since the B' state is predissociative, the fine structure does not represent bound states but rather resonances in the continuum, the width of which can be deduced from the potential curves. The theoretical width of the sharpest lowest-energy-loss peak is rather small (0.01 meV), representing a quasibound state in the shallow energy minimum; in a time-dependent picture the width of the state corresponds to a lifetime which can be compared to the typical time for a classical vibration on the order of 50 fs. Thus, for the lowest-energy-loss peak the lifetime allows for several molecular oscillations before dissociation. The natural widths of the next three higher resonances, in the vicinity of the avoided curve crossing, are predicted to be 0.5, 4.3, and 6 meV, and their theoretical widths imply lifetimes on the order of magnitude of classical vibrational periods (1.3 ps, 150 fs, and 110 fs, respectively). The broader peak at higher energy losses corresponds to several close-lying resonances with the width of a few meV.

Variation of the excitation energy changes the development of the nuclear wave packet in the intermediate state, thereby influencing the population of the final states. At the largest detuning, the nuclear wave packet development is minute, and the transition from initial to final state is

ultrafast. Here, the sharp lowest-energy-loss resonance does not get any measurable intensity. This result demonstrates that a direct transition from ground to final state would be completely dominated by higher losses, corresponding to fast dissociation. To get appreciable intensity on the lowest-energy-loss resonance, some intermediate state time evolution is required. Thus, a slower RIXS process effectively slows down the dissociation process.

We note that the Born-Oppenheimer approximation breaks down at the avoided curve crossing. As the two interacting states have different RIXS amplitude in regions where they do not interact, one may have expected different spectral weight in regions of large mixing. However, no such weighting is needed to get a good description of the spectra.

In the 7–9 eV energy range optical (UV) spectra are dominated by the Schumann-Runge (SR) absorption band due to the transition from the ground state to the B state, $1\pi_u^{-1}1\pi_g^{+13}\Sigma_u^-$. This process largely determines the opacity of the atmosphere to solar radiation in this energy region. The $B'^3\Pi_g$ state observed in this work gives the main contribution to the intensity underlying the SR band, and it can be especially important in the window just below 7 eV, where it may contribute appreciably to the total absorption cross section [17,22]. These results may therefore be of importance in atmospheric photochemistry [23,24], concerning greenhouse gases and atmospheric thermal balance considerations. In particular, there are uncertainties in atmospheric modeling concerning the sources and sinks of NO and NO₂ [25,26], which play an important role, e.g., as catalysts in destruction of ozone.

In conclusion, we have demonstrated that a wealth of new opportunities for gas-phase RIXS is currently arising. The vibrational intensities associated with the electronic ground state allow for an accurate determination of the development of the vibrational wave packet in the intermediate state and its crucial parameters. Selection rules in the RIXS process facilitate detailed studies of specific final states, and by controlling the development of the nuclear wave function various parts of the final state potential surfaces are highlighted. The rich phenomenology of a predissociative state with a shallow energy minimum has been explored.

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