Resonant X-Ray Emission Spectroscopy of Molecular Oxygen

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Resonant soft x-ray emission spectroscopy has been applied to study the issue of symmetry breaking upon core-hole excitation in molecular oxygen. The results provide direct evidence that the inversion symmetry is not broken in the core-excited states. Furthermore, the experiments themselves demonstrate a new experimental technique of broad applicability for studies of electronic structure and excitation dynamics in free atoms and molecules.

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Soft x-ray emission spectroscopy (SXES) using energy selective excitation has been used successfully for valence band studies of solids during the last decade. By choosing appropriate excitation energies it is possible to remove satellites present in broad-band or high-energy excited spectra [1], or to extract band information separately for the same element in inequivalent sites [2]. Strong excitation energy dependencies near the x-ray absorption thresholds have been observed for some broad-band materials [3,4] as well as for some condensed molecules [5]. It is also possible to use the polarization of the synchrotron radiation to gain symmetry information [5,6]. The observed phenomena were interpreted by means of a resonant inelastic x-ray scattering (RIXS) formalism [3,7]. This formalism entails simple rules [7] that select the possible symmetries for the final states of the resonant x-ray emission process.

We have performed resonant soft x-ray emission experiments where the symmetry selection rules are used to probe whether the intermediate core-excited state has broken symmetry or not, addressing a question which has been much debated over the years. These experiments themselves represent a new class of spectroscopic studies, namely, selectively excited soft x-ray emission of free molecules. It is important to study free molecules in many cases, since solid state effects can introduce ambiguities in the interpretation of the observations. Also, the possibility to explore soft x-ray emission from first principles makes gas phase studies highly valuable from a theoretical point of view. These experiments have become feasible owing to recent advancements in synchrotron radiation instrumentation and in experimental techniques.

The question of core-hole localization and symmetry breaking arises from the notion of the core orbitals as being strictly localized and nonoverlapping, and it is relevant to systems in which core orbitals are associated with atomic sites which are degenerate. Molecular orbitals delocalize according to the irreducible representations of the point group of the molecule. The question is if core excitation or ionization changes this condition for core orbitals. In nonresonant x-ray emission spectra of free molecules, excited by high-energy electrons, it has indeed been found that the so-called equivalent core model (or $Z + 1$ approximation) is valid, i.e., a core-ionized homonuclear diatomic molecule behaves like a heteronuclear diatomic molecule [8]. Thus, a core ionized O_2 molecule behaves much like an NO^+ molecule with respect to the valence electrons. However, the localized (symmetry broken) and delocalized pictures are equivalent for nonresonant x-ray emission spectroscopy. This spectroscopy cannot give an experimental solution to the core localization and symmetry breaking problem because the core-excited continuum states are infinitely degenerate representing all symmetries which makes no discrimination with respect to the dipole selection rules. Therefore all transitions are allowed independently of whether the core-hole state is symmetry broken or not. In fact, among the family of core-electron spectroscopic methods, neither nonresonant nor nonradiative members can provide the necessary symmetry information. Resonant x-ray absorption is also inconclusive in this context, because the symmetry adapted core level splittings are smaller than the lifetime width of the levels.

Resonant x-ray emission is a good candidate for investigating the symmetry problem. This is because the discrete nature of core-excited states prepares the symmetry for the emission step, and the dipole character of the absorption or emission then leads to simple selection rules for the full scattering process [7]. The parity selection rule connects initial and final excited states either as gerade-gerade or ungerade-ungerade. If the inversion symmetry is broken by core-hole localization, the parity selection rule evidently does not hold. For the O_2 molecule with a gerade ground state, this means that the appearance of ungerade final states would give conclusive proof that the inversion symmetry is broken, and the absence of ungerade states proves that the symmetry is kept.

For polyatomic molecules containing an element of symmetry, this symmetry can also be broken as an effect of vibronic coupling [9,10]. This possibility is not present for the homonuclear diatomics containing only one, totally symmetric vibrational mode. First row molecules, like N_2, O_2, or F_2, are ideal candidates, because the possible symmetry breaking depends only on electronic structure and electronic motion. Molecular oxygen is our first choice also because this species has previously been a popular showcase for the localization problem in core-electron spectroscopies, which we now address. Localization problems and symmetry instabilities of Hartree-Fock or other electronic structure methods have been addressed for more than 20 years [11,12]. Bagus and Schaefer [11] showed that the results from a self-consistent field calculation of the core-ionization potentials of molecular oxygen were about 15 eV in error when full molecular symmetry was imposed, whereas the error decreased to only 1 eV in the case of C_{2v} symmetry. The difference was related to a relaxation error in the high-symmetry case, implying unstable Hartree-Fock solutions. Localization is thus enforced in a one-particle Hartree-Fock description. Going beyond this picture with a multiconfiguration ansatz, symmetry is restored and the missing relaxation energy at the Hartree-Fock level appears as a correlation effect in the high point group symmetry [13]. Furthermore, as already indicated by Bagus and Schaefer [11], different broken-symmetry localized solutions can be superposed and the Hamiltonian diagonalized in this basis to regain solutions which adapt to the point group of the ground state molecule.

As shown in Refs. [7,14] there is a condition for observation of symmetry restriction in resonant x-ray emission, namely, that the experiment is conducted in the long wavelength limit. Channel interference plays an important role in this respect: it is nonzero only when the x-ray photon wavelength is comparable to or larger than the interatomic distance, in which case it will restore symmetry in the x-ray emission from two localized channels. By contrast, when the wavelength is much shorter than the interatomic distance, the interference of the localized channels is absent and the traditional theory of x-ray emission without (dipole) selection rules is valid. Therefore, there are two possibilities for the intermediate state to retain its symmetry: the core hole could be delocalized, or there could be an interference effect which gives the same result. What we investigate is whether the core-hole state is symmetry broken or not. First, we give a brief account of the experimental conditions and considerations.

The acceptance angle for grating spectrometers which are normally used for energies below 1 keV is much smaller than for the Bragg diffraction spectrometers that have been used successfully for higher energies [15]. This disadvantage together with a low fluorescence yield and target densities which are much smaller than those of solids are the major obstacles. To overcome the first of these problems, the emittance of the sample should be well matched to the spectrometer's limited acceptance. This can be done using the high brightness of a third generation synchrotron radiation source, since it can provide a well focused excitation source, while maintaining a high flux. Using a gas cell with window materials that have both a reasonable transmission and the ability to withstand a high pressure difference allows an optimization of the target gas density. These new solutions make these experiments possible. To our knowledge, these are the first spectra of their kind [16].

The experiments were performed at beam line 7.0 at the Advanced Light Source in Berkeley [17]. The incident photon beam entered a gas cell through a 1000 Å thick silicon nitride window. A gas pressure of 1 to 2 mbar was maintained in the gas cell. As an exit window for the emitted x rays a 5000 Å thick parylene-N window was used. The spectrometer [18] was mounted parallel to the polarization vector of the incident photon beam with its entrance slit oriented parallel to the direction of the incident beam. The length of the gas cell exit window allowed a large portion of the beam, at the gas pressures used, to be absorbed in the region observed by the spectrometer. We estimate the resolution of the monochromator and spectrometer in these measurements to be approximately 0.7 and 1.0 eV at full width half maximum, respectively.

The electronic configuration of ground state O_2 is $1\sigma_g^2$, $1\sigma_u^2$ $2\sigma_g^2$, $2\sigma_u^2$, $3\sigma_g^2$, $1\pi_u^4$, $1\pi_g^2\,{}^3\Sigma_g^-$. We will first consider the spectrum involving the partly occupied $1\pi_g$ shell and the transitions: ground state $\rightarrow 1\sigma_u^{-1}1\pi_g^3\,{}^3\Pi_u \rightarrow x_g^{-1}1\pi_g^3\,{}^3X_g$. [The corresponding SXES spectrum is shown in Fig. 1(a).] Apart from selection based on parity we must consider selection rules based on spin and spatial symmetries that also follow from the dipole character of the radiation. The two latter rules restrict the final states to be of triplet spin multiplicity (spin is conserved) and Σ, Π, or Δ symmetries. The one-particle approximation allows only those transitions which change occupation numbers of valence molecular orbitals by one unit and which keep the spin coupling of the passive open shells. This leads to only three possible bands in the SXES spectrum, the recombination band corresponding to $x = 1\pi_g$ and those corresponding to $x = 3\sigma_g$ and $x = 2\sigma_g$. The latter orbital is mainly of $2s$ character, and the transition is forbidden by the local dipole selection rule (it is very weakly

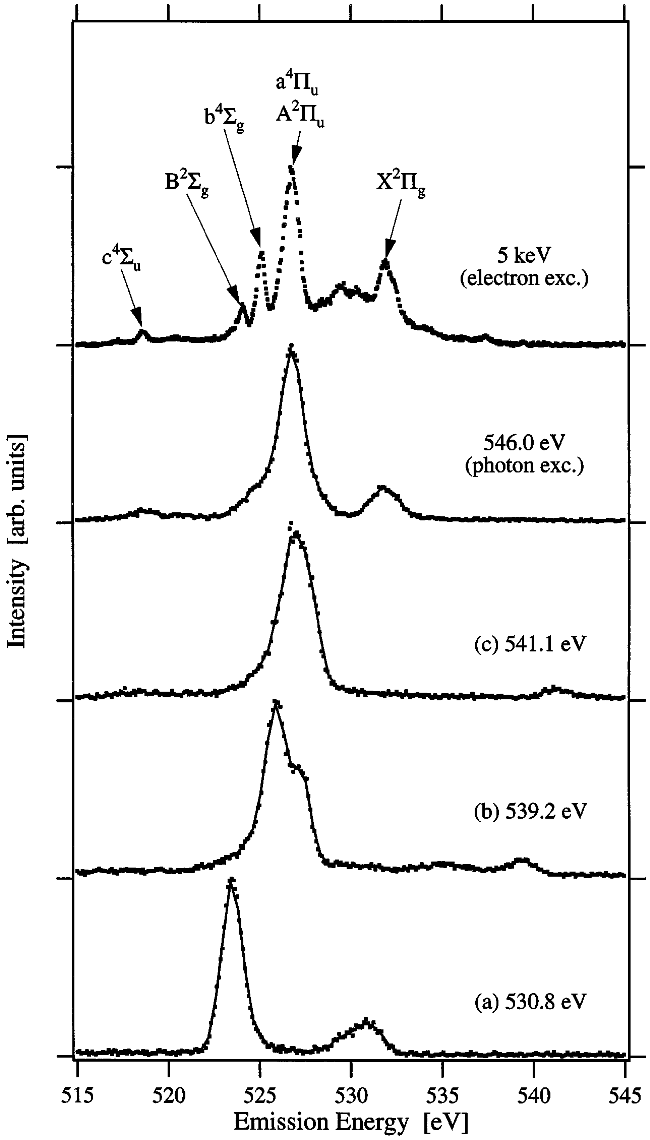

FIG. 1. X-ray emission spectra of O_2 excited at various photon energies and with 5 keV electron impact.

discerned at 503 eV in the spectrum generated at 530.8 eV). Summarizing, in the symmetry-restricted case, strict dipole selection implies only $^3\Pi_g$ and $^3\Sigma_g^-$ final states and in the one-particle approximation only one excited state, the $3\sigma_g^{-1}1\pi_g^3\,{}^3\Pi_g$ state. From the simple relation

$$E_{\mathrm{XES}} = E_{\mathrm{XAS}} - E_{\mathrm{OPT}}\,, \tag{1}$$

XAS and OPT denoting x-ray and optical absorption energies (here 530.8 [19] and 7.5 eV [20]), we can place this transition at 523.3 eV. In the symmetry unrestricted case both gerade and ungerade final states are allowed and transitions involving all occupied orbitals are possible. The spectrum would resemble the nonresonant spectrum excited above the ionization threshold. In particular, the $1\pi_u^{-1}1\pi_g^3\,{}^3\Sigma_u^-$ state would be represented close to 524.6 eV, using the value of E_{OPT} given in [21]. The fact that only one band apart from the recombination peak is observed in the SXES spectrum generated at 530.8 eV, and the fact that it is centered around 523.4 eV can be taken as a conclusive evidence that the parity selection rule is valid and that the symmetry is not broken.

We now turn to SXES spectra recorded at higher excitation energies. Transitions within two multiplet systems are observed in nonresonant spectra, the doublet and the quartet systems. In the upper part of Fig. 1 one can compare a recently published electron beam excited SXES spectrum [22] with a spectrum recorded at 546.0 eV excitation energy, just a few eV above the doublet and quartet ionization limits of 544.48 and 543.37 eV, respectively [23]. In Fig. 1 the diagram transition lines are assigned by their final states. The resolution in the electron beam excited spectrum is approximately a factor of 4 better, and, therefore, more features are resolved. There is an intense satellite contribution in this spectrum around 529 eV. In the spectrum recorded with selective excitation, on the other hand, these satellites are not observed. The satellite lines are mainly due to the creation of additional vacancies in the core-ionization process. The possibility of removing these types of satellites demonstrates the advantage of selective excitation.

Figure 2 shows an x-ray absorption spectrum of molecular oxygen measured in high resolution in another gas cell at the same beam line. The spectrum resembles recently published absorption data of O_2 [24]. The arrows indicate the excitation energy positions at which SXES spectra were recorded. Three main peaks are observed below the ionization limits. These peaks are labeled (a), (b), and (c). Peak (a) corresponds to an excitation of a core electron to the initially half-filled $1\pi_g$ orbital, discussed previously. High resolution electron energy loss spectra [25] and x-ray absorption spectra [24] show that peak (c) consists of a vast number of Rydberg lines. Peak (b) is primarily due to excitations to the $3\sigma_u$ molecular orbital (σ^* resonances), but there are also some Rydberg states contributing. A number of articles have recently been devoted to the exchange splitting of the σ^* resonances, discussing whether both resonances contribute to peak (b) or if they contribute one each to peaks (b) and

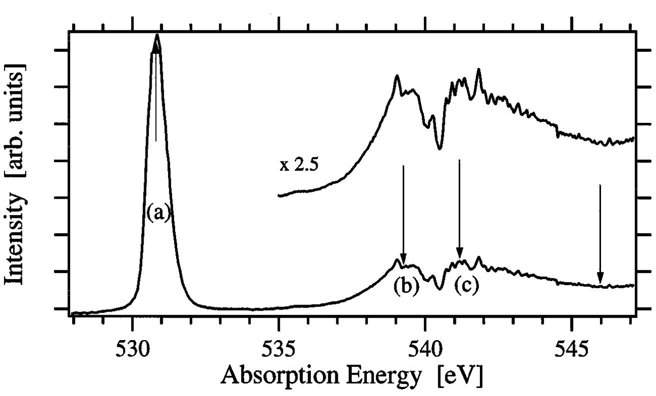

FIG. 2. X-ray absorption spectrum of O_2 recorded in high resolution. Indicated with arrows are the excitation energies where the resonant x-ray emission spectra were recorded.

(c). The σ^* resonance with a ${}^2\Sigma^-$ ion core has the lowest energy and contributes to absorption peak (b), but the question remains whether the σ^* resonance with a ${}^4\Sigma^-$ ion core contributes to peak (b) or (c). There are several recent measurements which strongly indicate that both the σ^* resonances contribute to peak (b) [26,27]. However, the alternative assignment has also been suggested [28].

As shown above, resonant excitation to the $1\pi_g$ orbital leads to final optically excited states with vacancies in gerade valence orbitals. Since the parity selection rule is valid, excitation to the $3\sigma_u$ orbital leads to vacancies in ungerade occupied orbitals. We denote these final states as $|g^{-1}, g^*\rangle$ and $|u^{-1}, u^*\rangle$, respectively. Hence, we obtain only $|g^{-1}, g^*\rangle$ states when the excitation energy is tuned to $1\pi_g$, and we expect only $|u^{-1}, u^*\rangle$ states from core excitations to the $3\sigma_u$ orbital. Ignoring the recombination lines, we observe in Figs. 1(a), 1(b), and 1(c) a single band, a composite band, and a single but broader band, respectively.

The band at 523.3 eV in spectrum (a) corresponds to the $3\sigma_g^{-1}1\pi_g^3\,{}^3\Pi_g$ final state as noted above. Spectrum (c) has a salient feature at 527 eV, and a weak line at 518 eV. In this case the strongest transitions in the absorption spectrum are to Rydberg states with $np\ \sigma_u$ and $np\ \pi_u$ symmetry [24]. We therefore assign the features to $|u^{-1}, u^*\rangle$ states. This assignment is supported by the fact that the $1\pi_g^{-1}x_g\,{}^3X_g$ band, which corresponds to the $1\pi_g^{-1}\ X^2\Pi_g$ band at 532 eV in the nonresonant spectra, is missing in spectrum (c). There are no indications of $|g^{-1}, g^*\rangle$ states.

The broad band in spectrum (c) has turned into a doublet structure in spectrum (b). The shift of the latter band and its high-energy shoulder can be taken as signatures of a core-excited $3\sigma_u$ state decaying to a $1\pi_u^{-1}3\sigma_u\,{}^3\Pi_g$ state, i.e., of a $|u^{-1}, u^*\rangle$ final state. Most of the known potential energy curves for the core [28] as well as the valence [29] states are steeply repulsive leading to strong vibronic excitations and possibly interference effects. Nevertheless, the differences in features of the (b) and (c) spectra point to different character of the core-excited states in the corresponding energy regions. This supports the interpretation [26,27] that both the paramagnetically split σ^* resonances contribute to peak (b) in the x-ray absorption spectrum.

In conclusion, we have shown that it is now experimentally feasible to perform SXES studies of free molecules using energy selective, synchrotron radiation excitation. Resonant x-ray emission spectroscopy is the photon emission analog of resonant Auger spectroscopy. It can provide information about core excited, intermediate, and final states. The dipole selection rules which apply to the resonant SXES process simplify the analysis of the spectra.

The resonant SXES spectra presented for molecular oxygen show that the parity selection rule applies, which proves that the inversion symmetry of the core-excited states involved in the x-ray scattering process is retained.

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