

Determination of the Exchange Splitting of the Shape Resonance of O₂ Using the Core Hole Decay Spectrum as a "Fingerprint"

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We have determined the exchange splitting of the $1\sigma_g^{-1}3\sigma_u$ shape resonance excitation of gas phase O₂, which cannot unambiguously be identified using conventional absorption spectroscopy. By identifying the electronic decay spectrum of the shape resonance excitation we could separately monitor the decay of the σ^* shape resonance and the Rydberg states. Using this fingerprint method we measured the pure core to $3\sigma_u$ bound state absorption spectrum in partial secondary electron yield spectroscopy.

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Spectroscopy of deep-lying electronic levels of small molecules gives unique insight into the electronic and geometric structure as well as the dynamics of the electronic interactions. Additionally, inner-shell absorption measurements provide a testing scheme for various molecular calculations. The understanding of the x-ray absorption spectra of small gas phase molecules and the excited states involved is also a challenge in chemistry and physics with regard to understanding the interactions of molecular adsorbates on surfaces.

In this context a longstanding debate is going on about the interpretation of the *K*-shell near-edge x-ray-absorption fine-structure (NEXAFS) spectra of gas phase and adsorbed O₂. Because of the overlap of the σ^* shape resonance with various Rydberg transitions [1,2] it is not possible to definitely assign the conventional NEXAFS spectrum. Therefore the exact location and the determination of the magnitude of the magnetic exchange splitting of the σ^* shape resonance cannot be unambiguously given. Wurth *et al.* [3] argued that the double structure in the NEXAFS spectrum [Fig. 1(a)], between 538 and 544 eV exhibiting an energy difference of about 3 eV, arises due to the large exchange splitting of the σ^* shape resonance. The interpretation of Ruckman *et al.* [4] is based on a much smaller calculated exchange splitting (0.4 eV) of the shape resonance locating both components in one of the features. The two interpretations lead the two groups to contradicting conclusions about the electronic interactions upon adsorption and in different chemical environments. Changes in the NEXAFS spectra were interpreted as a quenching of either the exchange splitting [3] or the Rydberg states [4]. Both groups base their interpretation on theoretical results. The different theories, however, reveal contradicting values for the splitting, ranging from 0.4 to 2.75 eV [3-5].

Here we present a method leading to the direct interpretation of the NEXAFS spectrum of free O₂. To solve this problem we identified and separated the substantially different σ^* and Rydberg core excited states in deexcitation electron spectroscopy (DES) [6]. We offer a simple interpretation of the complex structured deexcitation

spectra excited between 538 and 544 eV distinguishing between the decay of the excited σ^* shape resonance and of the Rydberg states. Upon identification of the unique decay spectrum of the shape resonance excitation we then monitor the transition to the σ^* shape resonance separately using partial electron yield measurements. Thus we are able to give an unambiguous interpretation of the NEXAFS spectrum of O₂.

All spectra were taken at the high resolution X1B undulator beamline [7] at the NSLS of Brookhaven Nation-

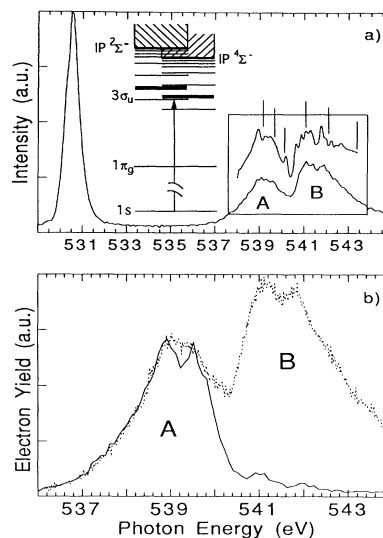


FIG. 1. (a) *K*-shell NEXAFS spectrum of gas phase O₂, together with a schematic level scheme indicating the exchange split Rydberg series and the $1\pi_g$ and $3\sigma_u$ orbitals. The energy region of the Rydberg transitions and the σ^* shape resonance is boxed by A and B. The high resolution NEXAFS spectrum in the top region of the boxed area is taken from Ref. [8]. The six lines are representing the excitation energies for the DES spectra in Fig. 2. (b) The partial (full line) and total electron yield spectra (dashed line) of the Rydberg transitions and the σ^* shape resonance. The partial yield spectrum is taken at a final state energy of 510.3 eV.

al Laboratory. The spherical grating monochromator (SGM) was set to a photon resolution of 0.5 eV for the accumulation of the deexcitation spectra by a commercial double pass cylindrical mirror analyzer (DPCMA) with the energy resolution set to 1 eV. The electron yield spectra were measured with a kinetic energy window of 2 eV. The kinetic energy scale was calibrated by comparison with the O₂ Auger spectrum of Moddeman *et al.* [8].

The complex high resolution NEXAFS spectrum of gas phase O₂ [9] in the energy region between 538 and 544 eV is shown in Fig. 1(a) in the top region of the enclosed area. The Rydberg-type core excitations which converge to the $^4\Sigma^-$ (543.1 eV) and $^2\Sigma^-$ (544.2 eV) ionization thresholds [10] appear in the energy region of the two broad features which are labeled A and B. The exchange splitting between the Rydberg levels in the two dipole allowed Rydberg series is assumed to be close to the multiplet splitting of the ionic states [10] since the interaction between the Rydberg electron and the remaining electrons is insignificant for the spin interaction. As already mentioned, these structures A and B are also interpreted as transitions into the antibonding molecular $3\sigma_u$ orbital. As given by the dipole selection rules there are, as in the case of the Rydberg transitions, two possible spin state configurations in this σ^* shape resonance where the excited electron can couple to either a doublet ($^2\Sigma^-$) or a quartet ($^4\Sigma^-$) parental ion core. In both cases, to avoid a change of the overall multiplicity during the absorption step, the excited $3\sigma_u$ electron must possess the opposite spin direction compared to the remaining core electron in the $1\sigma_g$ orbital.

Below we show that the two exchange split states are not to be associated with the splitting between structure A and B, but are both contributing to structure A. With the help of the technique of DES, the difference between the molecular orbitals and Rydberg states becomes distinctly apparent. It was demonstrated for gas phase N₂ [11] that the shape of the decay spectra differs considerably if the excited state is of Rydberg or molecular orbital type. The multiplet coupling in N₂ is clearly different for the decay of the Rydberg state excitations in comparison with the π^* transition. The decay of various excited Rydberg orbitals are dominated by different $2h1p$ (two-hole one-particle) final states, where the excited electron takes part only as a passive spectator during the transition to the final state. The overall shape looks like a normal Auger spectrum, only shifted to higher kinetic energies in comparison with the double ionized Auger final state. This is due to the difference in the Coulomb screening of the Rydberg electron in the initial and final state. In contrast, a primary excited molecular state, as for example the π^* state of N₂, shows a completely different decay spectrum due to the strong interaction between the excited, comparatively compact valence orbitals and the rest of the electron system. The situation for O₂ is quite similar by inspection of the totally different

decay spectra of the molecular π^* resonance [Fig. 2(a)] and the Auger spectrum [Fig. 2(h)]. In contrast, the decay spectra excited in the energy range between the π^* and the ionization limit [Figs. 2(b)–2(g)] are very complex for O₂ due to the overlapping of different Rydberg states and the σ^* resonance, whereas in N₂ the σ^* shape resonance is located in the continuum.

In Figs. 2(b)–2(g) the measured decay spectra of O₂ are shown, which are excited at characteristic energies within feature A at 539.2, 539.7, and 540.1 eV and at three different photon energies of feature B at 541.4, 542.4, and 543.4 eV. The spectra are much more complex than the corresponding spectra of N₂ [10]. For example, the deexcitation spectra in Figs. 2(e) and 2(d) reveal four or even six major features in the kinetic energy range between 490 and 515 eV. In comparison, the Auger spectrum of O₂, shown in Fig. 2(h), is characterized by three major features between 490 and 501 eV kinetic energy and another peak at 476 eV. The deexcitation spectrum of the well separated π^* orbital is shown in Fig. 2(a) to demonstrate the quite different decay of a molecular excited state. The number of the observed structures and the overall shape of the deexcitation spec-

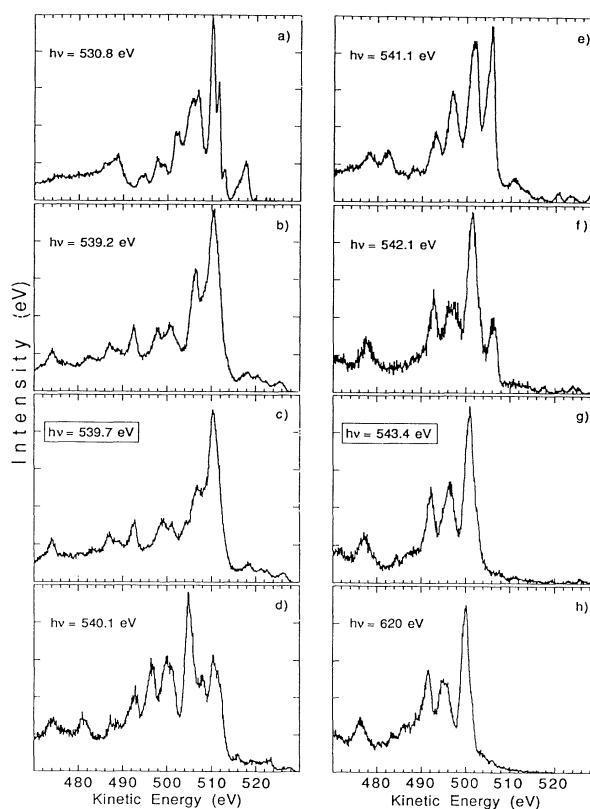


FIG. 2. Deexcitation spectra of O₂ taken at six different excitation energies depicted in Fig. 1(a). The spectrum of the π^* decay is shown in (a) excited at 530.8 eV and the Auger spectrum is seen in (h).

tra excited between 538 and 544 eV all vary quite remarkably upon only small changes of the excitation energy.

Below we propose an interpretation of the main features observable in the deexcitation spectra without attempting a full assignment of these spectra, which will be left as a challenge to the theorists. We start our discussion with the deexcitation spectrum excited most closely to the doublet ionization limit in Fig. 2(g). This deexcitation spectrum excited at the photon energy of 543.4 eV is very close in overall shape to the Auger spectrum in Fig. 2(h). It is only shifted 1 eV to higher kinetic energy and the second high kinetic energy peak at 495 eV is somewhat higher in intensity. Following the above discussion we can safely assume that this deexcitation spectrum represents the electronic decay of an excited Rydberg state.

Going to lower excitation energies we observe in Fig. 2(f) and particularly in Fig. 2(e) increasingly more complex deexcitation spectra. Whereas the deexcitation spectrum excited at 542.1 eV shows a strong similarity to the Auger spectrum, the deexcitation spectrum in Fig. 2(e) is characterized by two additional peaks at 482 and 506 eV. This latter peak is already seen in Fig. 2(f) as a small rising component. In order to explain the complex deexcitation spectra of Fig. 2(e) we used the simple idea to describe it as a superposition of at least two of the identified single excited Rydberg deexcitation spectra in Fig. 2(g). As an indicator for the number of the simultaneous excited states we used the well separated triangular structure between 470 and 485 eV kinetic energy. By a combination of two of the representative deexcitation spectra of the purely excited Rydberg state in Fig. 2(g) we can easily construct the complex spectra seen in Fig. 2(e). This is graphically demonstrated in Fig. 3(a). Following this discussion the deexcitation spectrum shown in Fig. 2(f) is then mainly dominated by a single excited Rydberg state with a minor component at 506 eV arising due to a simultaneous excited second Rydberg level.

Before discussing the details let us try to use this quite simple model to also explain the spectrum excited at 540.1 eV within feature A. Because of the two triangular shaped peaks between 475 and 482 eV the complex spectrum seen in Fig. 2(d) could be a composition of two excited states. A combination of two Rydberg excited deexcitation spectra fails completely in reproducing the spectrum of Fig. 2(d). However, this can be achieved by a superposition of one Rydberg excited spectrum of Fig. 2(g) with the quite different deexcitation spectrum of Fig. 2(c). By adding these two spectra on the correct energy scale the decay spectrum shown in Fig. 2(d) is quite well reproduced. The artificially constructed decay spectrum is shown in Fig. 3(b).

To add the spectra on the correct energy scale we have to shift the Rydberg excited spectrum in Fig. 2(g) to the corresponding kinetic energy for all constructed spectra.

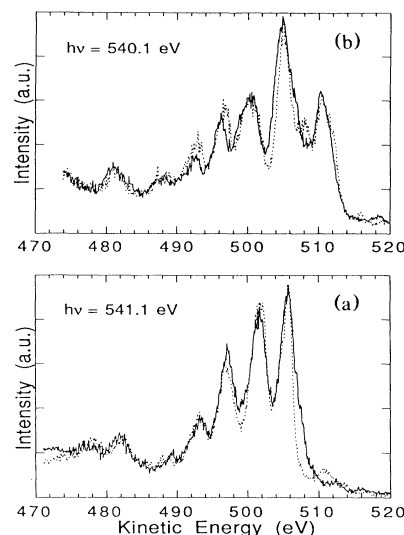


FIG. 3. The graphical constructed deexcitation spectra (line) of (d) and (e) of Fig. 2. The experimental spectra excited at 540.1 and 541.1 eV are shown as dashed lines.

This shift arises due to the Coulomb screening of the lower excited Rydberg states. To get the correct shift we assumed a linear approximation for the screening ability as a function of the binding energy of the spectator electron in the core excited state. This linearity was found out empirically for N_2 and various azabenzenes [12]. In a semiempirical calculation this was also shown for N_2O [13]. We assumed that the multiplet splitting of the Rydberg states is equal to the splitting of the core ionized states.

The deexcitation spectrum in Fig. 2(b) and particular in Fig. 2(c) brings forward no recognizable similarity to the Auger spectrum or to a Rydberg decay. As in the case of the π^* deexcitation spectrum in Fig. 2(a) it is not possible either to reproduce the spectrum in Fig. 2(c) by a simple superposition of different deexcitation spectra as it was described for the higher excited deexcitation spectra. This excludes the decay of an atomiclike state and we assign it to the decay of the σ^* shape resonance since no other molecular excitations are predicted in this energy region.

We see that all deexcitation spectra which are excited at a corresponding energy within feature B are resembled by a decay of one or more Rydberg states whereas the deexcitation spectra for the chosen excitation energies within feature A are always associated with the decay of the shape resonance.

Having identified the characteristic fingerprint of the decay of the σ^* shape resonance seen in Fig. 2(c) we can now come back to the question of the magnitude of the magnetic exchange splitting. To do this we monitored the absorption spectrum determined only by the excitation to the shape resonance. With the chosen specific final state

energy at 510.3 eV, which is characteristic for the decay spectrum of the σ^* shape resonance in Fig. 2(c), it is possible to measure such a characteristic partial yield spectrum. The final state energy of 510.3 eV for the decay of the σ^* shape resonance was the observed highest kinetic energy peak in all decay spectra, except of the transition energies corresponding to the lowest 1h final states. For this reason no decay signals resulting from any other excitation can be measured in the partial yield spectrum beside a small extent of inelastic scattered electrons originating from the weak participator transitions to the 1h states with the lowest binding energies. The partial electron yield spectrum shown in Fig. 1(b) reveals only the broad feature A. Therefore the shape resonance excitation unambiguously only contributes to the lower energy feature A of the NEXAFS spectrum. For comparison, the *total* yield spectrum taken under the same conditions is superimposed on the partial yield spectrum in Fig. 1(b).

The absorption spectrum in Fig. 1(b) clearly demonstrates that both components of the σ^* shape resonance are embedded only in structure A. We find that the partial yield spectrum has a pronounced double structure. We assign the splitting of 0.6 eV to the exchange splitting of the $1s^{-1}3\sigma_u$ state. Our experimentally determined splitting is significantly lower than the recently calculated values of 1.2 eV [3] and 2.75 eV [5] for gas phase O_2 . In comparison, the calculated splitting of 0.4 eV [4] is close to our value. The large variation in the predicted values partially reflects the theoretical difficulties in treating the Coulomb and exchange interaction in the core hole excited states. Biased by the theoretical values different assignments have been proposed, and this has led to the general confusion that we have resolved with our method.

Our result also implies that Rydberg excitations fully dominate structure B in the absorption spectrum. This supports the observation that this feature is attenuated in the absorption spectra of condensed O_2 [14]. Such a quenching should be expected for the Rydberg excitations but not for the σ^* shape resonance, which is much less affected by the interaction in the solid phase.

In conclusion, we have measured the exchange splitting of the $1\sigma_g \rightarrow 3\sigma_u$ state for gas phase O_2 to be 0.6 eV. This was done by partial secondary electron yield measurements at a specific final state energy. This energy

could be chosen after the identification of the electronic decay spectrum characteristic for the σ^* shape resonance. Therefore the line shape of the core to valence transition could be recorded in the yield spectrum without the influence of the overlapping Rydberg orbital excitations.

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