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Anion-yield spectroscopy using x rays is shown to be a selective probe of molecular core-level processes, providing unique experimental verification of shape resonances. For CO, partial anion and cation yields are presented for photon energies near the C *K* edge. The O⁻ yield exhibits features above threshold related *only* to doubly excited states, in contrast to cation yields which also exhibit pronounced structure due to the well-known σ^* shape resonance. Because the shape resonance is completely suppressed for O⁻, anion spectroscopy thus constitutes a highly selective probe, yielding information unobtainable with absorption or electron spectroscopy.

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Core-level measurements, in the form of electron, photon, or ion yields as a function of photon energy in the region of an inner-shell threshold, are powerful probes of molecular spectroscopy, symmetry, and photoionization dynamics [1–6]. Photoexcitation of a core electron in a molecule yields an unstable state which may decay radiatively by photon emission or nonradiatively by ejection of one or more electrons. Quite often, in conjunction with the electron rearrangement accompanying decay, the molecule fragments. Especially important for core-level spectroscopy is resonant excitation, which provides a well-defined (in energy and symmetry) intermediate state [7–9]. Of the resonant processes inherent to molecular core photoexcitation, perhaps the most commonly studied and utilized are the so-called shape resonances, one-electron effects in the continua just above core-level ionization thresholds. Their apparent simplicity, large energy widths, and well-defined symmetries have made shape resonances a popular area of study in molecular science [10–14] and a common tool for probing condensed-phase systems (e.g., adsorbates) [15–17].

The study of molecular shape resonances has not been without controversy (see, e.g., [13]). One central topic of debate concerns the detailed assignment of spectroscopic features above a core-level ionization threshold, especially the discernment of shape resonances from other resonant or nonresonant processes. A key point feeding the controversy is the lack of a direct experimental method to unambiguously distinguish shape resonances from either doubly excited states or (simply) the natural variation of the photoionization cross section; indirect experimental evidence and theory usually must be relied upon [13]. For example, a core-level shape resonance is generally considered to be a one-electron process enhancing *only* the mainline (e.g.,

1s) photoionization cross section, thus providing a convenient method (i.e., 1s core-level photoemission) to distinguish them from other phenomena. However, doubly excited states have been shown to influence the mainline cross section as well [18], so there is no clear-cut experimental approach to distinguish shape resonances from other phenomena using absorption, total-yield, or electron-spectroscopy measurements.

In this Letter we describe an experimental approach that directly distinguishes between shape resonances and doubly excited states in the region just above a molecular core-level ionization threshold. For the measurements, we used CO as a prototypical molecule in which the σ^* shape resonance above the C *K* edge is well known and well understood; CO thus provides an excellent "laboratory" in which to test the new approach. In particular, partial yields of all cations detectable following core-level photoexcitation were measured. In addition, the production of oxygen anions (O⁻) was measured as a function of photon energy in the vicinity of the C *K* edge. Although anions have been observed previously following core-level excitation [19–21], the improved photon-energy resolution and signal of the present results provide sufficient detail for careful spectroscopic comparisons. The measurements show a clear enhancement of the anion yield at doubly excited resonances above the *K* edge, but *no* detectable anion production due to the σ^* shape resonance. As a result, anion-yield measurements above an inner-shell threshold provide a powerful new tool to verify shape resonances in molecules.

The measurements were performed on undulator beam line 8.0.2 at the Advanced Light Source with a monochromator resolution of approximately 70 meV at 300 eV photon energy. This resolution was chosen to allow a

reasonable anion signal while being able to resolve some of the higher Rydberg states near the K edge. Photon energies were calibrated using the well-known $2\pi^*$ resonance at 287.40 eV ($\nu' = 0$) [22] and checked using the C-1s ionization threshold at 296.08 eV. The experimental apparatus has been described previously [23]. In short, it consists of a 180° magnetic mass spectrometer with a lens to focus ions created in the interaction region onto the entrance slit of the spectrometer. An effusive-jet gas cell containing push and extraction plates moves the ions from the interaction region into the lens. Ions are detected with a channel electron multiplier (CEM) at the exit slit of the spectrometer. The polarities of the lens, magnetic field, and CEM may be switched to allow measurement of either cations or anions produced by photofragmentation. An analog signal from a manometer was recorded simultaneously with the ion signal to monitor target gas pressure. Variation of the target pressure from 10^{-7} to 10^{-4} torr verified the anions were created and measured under single-collision conditions at the operating pressure of about 10^{-5} torr. Under these conditions, the anion count rate was $10\text{--}100\text{ s}^{-1}$, attesting to an anion-production cross section well below 1 kb.

The partial yield of O^- from CO near the C K edge is shown in Fig. 1. We observe a very low background, illustrating a lack of appreciable valence-shell-ionization processes leading to the creation of an anion. Below threshold, the $2\pi^*$ resonance shows the first four vibrational transitions seen in photoabsorption [22]. At higher photon energies, the $3s\sigma$, $3p\pi$, $3p\sigma$, $3d\pi$, and $4p\pi$ Rydberg states appear, and each shows three vibrational transitions. Immediately above threshold there is an exponential-like decay in the O^- yield attributable to postcollision interaction (PCI). While PCI is relatively well understood in atoms [24–29], few quantitative PCI studies have been done in molecules [30]. Detailed analysis of these PCI effects in anion production will be presented elsewhere.

Further above threshold, Fig. 2 shows an expanded view of the O^- yield and compares it to three representative

FIG. 1. Partial ion yield of O^- at the C K edge of CO.

cation-yield curves. All detectable cations from CO were measured in the experiment and will be presented and analyzed in detail elsewhere. Total and partial cation yields have been reported previously, in particular, below threshold [31–33]. In this Letter, we concentrate on new information provided by the O^- yields.

Dramatic differences between the anion and cation yields in Fig. 2 are evident; while features associated with doubly excited states are visible in the anion spectrum, we observe no anion signal above background at the maximum of the shape resonance near 305 eV [22,31,33–37]. In contrast, the shape resonance is pronounced in all the cation yields, including those not shown in Fig. 2 (the sole exception is CO^+ , which shows neither the shape resonance nor the doubly excited states). This striking difference between anion and cation yields can be explained by considering the decay modes of resonant processes in the core-level region, and the explanation ultimately leads to the conclusion that anion-yield spectroscopy provides a unique experimental tool to identify shape resonances.

Considering first the production of cations following core-level photoexcitation, there are, in general, many mechanisms for their production. Below threshold, resonant-Auger decay to singly charged two-hole/one-particle final states (so-called spectator decay) can produce copious amounts of positive ions. Above threshold, ionization of a $1s$ electron leads to Auger decay and doubly charged positive ions, which usually fragment. Specifically, at the shape resonance, which is presumed to enhance *only* photoionization of a C- $1s$ electron, we expect at least two electrons (the photoelectron and Auger electron) to be removed. The consequence for partial-cation-yield experiments will be a clear enhancement of positively charged ions at the shape resonance above the C K edge in CO, as has been observed [33].

FIG. 2. Partial ion yields of C^+ , O^+ , CO^{2+} , and O^- at the C K edge of CO. Plots are arbitrarily scaled for comparison purposes.

In contrast, possibilities for anion production following core-level photoexcitation are much more circumscribed. To satisfy charge conservation following photofragmentation of CO under single-collision conditions, there are only three possible “final states” yielding O^- as a product, distinguishable by the amount of positive charge on the atomic-carbon fragment: (1) $C^+ + O^-$, (2) $C^{++} + O^- + e^-$, and (3) $C^{+++} + O^- + 2e^-$. Final state (3) is ruled out immediately because C^{+++} was barely detectable in the cation measurements, having a yield at least 2 orders of magnitude lower than O^- . However, the dominant decay mode for shape-resonance-enhanced $1s$ photoemission is Auger decay, leading to a doubly charged CO^{++} molecular ion, which must fragment to final state (3) in order to yield O^- . Therefore, the lack of anion yield at the shape resonance in CO is related to the unlikelihood of a doubly charged molecular ion fragmenting to a triply charged positive ion (C^{+++}) and an anion (O^-).

However, about 0.1% of C- $1s$ core holes decay radiatively to a singly charged molecular ion, which, in competition with many other fragmentation pathways, could yield O^- via final state (2). By this mechanism, a shape resonance could still be apparent in the O^- yield. But we do not observe any enhancement of the anion yield at the shape resonance, forcing us to conclude radiative decay followed by formation of a cation-anion pair does not provide a significant contribution to O^- production above threshold. Core-hole radiative decay is not expected to differ much for excitation above or below threshold; therefore, it is likely radiative decay following $1s$ excitation is unimportant to the production of O^- throughout the core-level region. Thus, final state (1), which can be reached *only* via radiative decay of a core-excited molecule to a neutral valence-excited state followed by ion-pair formation, also can be ruled out as a significant contributor to the yield of O^- .

Based on these arguments, the primary pathway yielding O^- after core-level photoexcitation is emission of one electron followed by fragmentation to final state (2). Below threshold, the core-level spectrum consists of either molecular excitations (e.g., $2\pi^*$) or Rydberg states. In both cases, the dominant decay mode is via spectator transitions (emission of one electron) leaving a singly charged ion which occasionally may fragment to C^{++} and O^- . As a result, the anion-yield spectrum is dominated by below-threshold resonances. Above threshold, only non-radiative decay modes which lead to emission of just one electron will contribute to the anion yield. This criterion rules out direct $1s$ photoemission, including the shape resonance, as noted above, but does not rule out doubly excited states lying above the $1s$ threshold because they sometimes decay via spectator transitions. Thus, we conclude core-level production of anions is tied almost exclusively to excitation of discrete Feshbach resonances, as opposed to shape resonances or nonresonant photoionization.

Looking more closely at the doubly excited states above the C K edge (Fig. 1), the 299–305 eV region contains

several doubly excited Rydberg series leading to C K -edge satellite thresholds [33]. The primary transitions are due to simultaneous excitation of a $1s$ electron to the $2\pi^*$ molecular orbital and shakeup of a valence electron (5σ or 1π) to an $n\lambda$ Rydberg level. In CO, the C $1s^{-1}5\sigma^{-1}2\pi^*n\lambda$ doubly excited series, which appears weakly in the cation spectra, is also very weak in the anion spectrum. The broad feature in the 302–305 eV region, due to the doubly excited C $1s^{-1}1\pi^{-1}2\pi^*n\lambda$ series, is more prominent in the anion yield than in the cation yields above 303 eV. Throughout this region, the relative intensities of the doubly excited states are different in the anion and cation spectra. As an interesting point, we note the shape-resonance position appears to move to lower energy for the C^+ fragment compared to the other cations. We attribute this result to a larger influence of the highest-lying doubly excited states, seen here clearly in the anion spectrum, on the yield of C^+ .

Having established anion-yield spectroscopy as a unique approach to isolate shape resonances from doubly excited states, we apply it to a slightly more ambiguous case: the O K edge of CO. The yield of O^- in this region is shown in Fig. 3. In contrast to the C K -edge yield, there is little evidence of vibrational transitions at the O K edge due to the limited monochromator resolution of about 200 meV at 550 eV photon energy. However, there is close agreement with positions of spectroscopic features from previous results [31,36]. We note the yield of O^- is roughly an order of magnitude less at the O K edge than at the C K edge.

Looking at the O K -edge anion yield in more detail, there are strong similarities between the anion spectra at the C and O K edges; both are dominated by the $2\pi^*$ resonance, exhibit features attributable to Rydberg states just below and PCI just above threshold, and suppress the shape resonances in the continuum regions. A notable difference is the position of the shape-resonance maximum does not correspond to a minimum in the O^- yield at the O K edge, as it does at the C K edge. Based on the anion-yield

FIG. 3. Partial ion yield of O^- at the O K edge of CO.

results at the C K edge, we can attribute this result to O $1s^{-1}5\sigma^{-1}2\pi^*n/\lambda$ doubly excited states coincidentally being at the same energy as the shape-resonance maximum. It is very unlikely the peak near 551 eV is related to the shape resonance because it is much narrower than the shape-resonance feature seen in photoabsorption [36]. At higher energy, near 555 eV, we observe for the first time the doubly excited resonance due to a $1s \rightarrow 2\pi^*$ transition accompanied by a $1\pi \rightarrow 2\pi^*$ shakeup, predicted by Ågren and Arneberg some time ago [38].

In conclusion, core-level anion-yield spectra provide a unique tool to experimentally distinguish shape resonances from other phenomena because effects of shape resonances are completely absent in the anion yields. Compared to photoabsorption or absorptionlike measurements, such as total-electron or total-ion yield (including near-edge x-ray-absorption fine structure for gas-phase and adsorbed species), there is a clear advantage in monitoring a channel (i.e., O $^-$ partial yield) highly selective with respect to different types of resonances. Moreover, partial anion yield is more selective than other single-channel measurements. For example, with partial cation yields or core-level photoemission as a function of photon energy it is generally impossible to directly distinguish shape resonances from doubly excited states. Even the newer and more-elegant applications of these techniques, symmetry (i.e., angle-) resolved total cation yields and vibrationally and ligand-field-resolved photoemission at high resolution, while providing very useful information on symmetry and dynamics, cannot distinguish shape resonances from other features above threshold. Anion yield as a function of photon energy thus constitutes a new and valuable method for core-level spectroscopy and the study of photodissociation dynamics of small molecules. Finally, there is nothing special about CO; this new approach should be applicable to a variety of small molecules, providing a unique look at core-level resonant processes.

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