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Electron-Ejection Asymmetries by Molecular Orientation Following *K*-Shell Excitation of CO

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We report the first observation of electron-ejection asymmetries due to molecular orientation following *K*-shell photoexcitation in a free molecule. The angular distributions of electrons emitted by the decay of *K*-shell vacancies were measured in the vicinity of the π^* discrete and the σ^* shape resonance of CO. We see a sharp drop of the angular distribution asymmetry parameter to $\beta = -1$ at the π^* resonance as predicted by theory, but no comparable effect across the σ^* shape resonance. The results are discussed with respect to the intrinsic anisotropy of the *K*-shell vacancies.

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The excitation of a core electron in a molecule can occur into an unoccupied molecular orbital, into a Rydberg state, or into the continuum. Photoexcitation into discrete molecular orbitals produces neutral-molecular excited states with definite, characteristic orientations. Photoionization in the vicinity of a shape resonance produces molecular ions with energy-dependent orientations characteristic of each resonance.[1] Prominent examples of these two types of photoexcitations are the $2\sigma \rightarrow 2\pi^*$ discrete resonance and the $2\sigma \rightarrow \sigma^*$ shape resonance in CO. As a consequence of the dipole selection rules the excitation of the $2\pi^*$ resonance yields molecules preferentially excited perpendicular to the electric vector while photoionization within the σ^* shape resonance produces molecular ions preferentially excited parallel to the electric vector. These alternative orientations can be reflected by the angular distribution[2] of the electrons emitted in the decay of the *K*-shell vacancy.

The anisotropic behavior of the molecular photoabsorption process has been successfully utilized for the determination of molecular orientations on surfaces by polarization-dependent photoabsorption[3] and angle-resolved photoemission[4] measurements. Despite the success of these methods for oriented molecules[5] on surfaces, there was puzzling disagreement between the results of a gas-phase photoemission experiment[6] on CO and the theoretical predictions for free molecules.[1] In contrast to these predictions, Truesdale *et al.*[6] observed that the continuum shape resonance as well as the discrete $2\pi^*$ resonance showed nearly isotropic decay behavior. In this Letter we report the first measurements of electron-ejection asymmetries as a direct probe of the anisotropy of molecular photoabsorption in a randomly oriented gas-phase target. We show that the $2\sigma \rightarrow 2\pi^*$ absorption resonance follows the theoretically predicted behavior in contrast to former experimental work, whereas the $2\sigma \rightarrow \sigma^*$ shape resonance decays isotropically, unaffected by the anisotropy created by the excitation process.

The experiments were carried out at the new synchrotron radiation facility BESSY under single-bunch conditions with use of a high-energy toroidal-grating monochromator[7] with a resolution of about 0.5 eV at 300 eV. The relative photon flux was monitored by a sodium salicylate scintillator and an optical photomultiplier tube. The measurements were performed with two rotatable time-of-flight (TOF) analyzers in order to detect the entire electron spectrum simultaneously at two angles. The TOF photoelectron spectrometer is described in detail elsewhere.[8] In comparison to other TOF systems[6] our spectrometer shows improved performance regarding the following features: overall resolution (2% of the actual kinetic energy), high transmission at low kinetic energies, and high retarding capability without significant loss of transmission, the latter factor being crucial to the feasibility of the experiment described. The experiment was split into two parts: a high-resolution study with 210-V retarding potential in order to assign the electron spectrum at the $2\pi^*$-resonance position at 287.3 eV, and the angular distribution measurements, taken with somewhat lower resolution (170-V retarding voltage) but higher counting rate. The two TOF analyzers were placed at the quasimagic angle θ_{qm} and at "$\theta_{0°}$"$=\theta_{\text{qm}} - 54.7°$ relative to the polarization direction of the photon beam. The polarization determined by our rotatable analyzers with use of neon as calibration standard[9] was 88% at 290 eV with an axis parallel within 1° to the storage-ring plane.

Assuming the validity of the dipole approximation in the photon range under study and a randomly oriented sample of molecules, we were able to study the partial cross sections $\sigma(h\nu)$ and the angular distribution asymmetry parameters $\beta(h\nu)$ at the same time. Figure 1 shows the electron spectrum at the position of the $2\pi^*$ resonance after conversion from TOF to kinetic energy. The spectrum represents basically the decay channels of the $2\pi^*$ resonance because the nonresonant intensity is negligible compared to the inten-

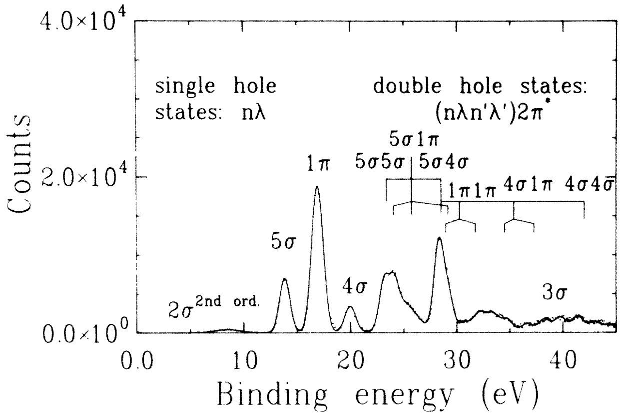

FIG. 1. TOF photoelectron spectrum of CO taken with 210-V retarding voltage at the $2\sigma \rightarrow 2\pi^*$ resonance position of 287.3 eV. The spectrum is converted from TOF to kinetic energy but not corrected for loss of transmission due to the retarding voltage. The fitted curves are Gaussian profiles used as the instrumental function for the data analysis. The additional structure seen in the double-hole peaks is attributed to further splitting of the hole-electron states.

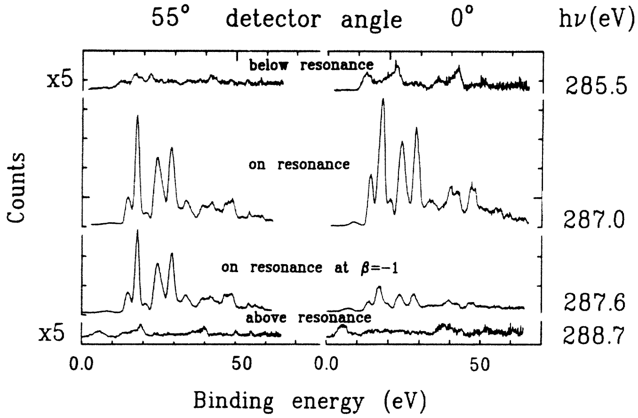

FIG. 2. A series of four photoelectron spectra taken at two different angles at photon energy positions below, near, and above the $2\sigma \rightarrow 2\pi^*$ resonance. The spectra taken with 170-V retarding voltage show peaks up to 60-eV binding energy. The 0° detector shows the sharp drop in intensity due to the molecular orientation created by the resonance process.

sity at resonance. The electron peaks correspond to final ionic states populated by autoionization of the excited CO $2\pi^*$ orbital into the photoemission main lines $n\lambda^{-1}$ and into the spectator satellite lines $(n\lambda^{-1}, n'\lambda'^{-1})2\pi^*$. The first process is also referred to as direct recombination of the core hole and leaves the ion in a single-hole state, whereas the second one, also referred to as resonant Auger decay, produces double-hole states. The different peaks were assigned according to their known binding energies[10] and with respect to expected energies of the double-hole states.[11] The latter are known in part from the valence satellite spectrum.[12] We assign the strongest spectator satellite peak to the $(5\sigma^{-1}4\sigma^{-1})2\pi^*$ and $(5\sigma^{-1}\pi^{-2}) \times 2\pi^*$ double-hole states. Our spectrum is directly related to the gas-phase Auger spectrum[13] above the C 1s threshold and can be compared to resonant photoemission spectra of CO absorbed on Pt(111).[14] In contrast to the adsorbate spectra, which are characterized by possible hybridization of the $2\pi^*$ electron with substrate states, the gas-phase spectrum reveals the effect of an undisturbed spectator electron on the decay of the C 1s hole.

The Auger angular distributions were measured in a series of electron spectra across the σ^* shape and the discrete $2\pi^*$ resonance in small steps. Four selected spectra are displayed in Fig. 2, one below and two close to the resonance position, and another one above the resonance. The two spectra near the resonance position are distinguished from each other by their angular distributions. While the 54° detector sees virtually no change in signal in these two resonant spectra, there occurs a dramatic drop in intensity in the corresponding 0° detector, reflecting rapidly changing angular distributions. The angular distribution variation across the narrow $2\pi^*$ resonance[15] was measured in small steps of 0.1 eV. Partial cross sections were determined from photon flux and bandpass-corrected peak intensities.

Figure 3 shows the result of this study for the discrete $2\pi^*$ and continuum σ^* resonance regions: partial cross sections and asymmetry parameters of ejected electrons which leave the ion in a double-hole state $(n\lambda^{-1}, n'\lambda'^{-1})$. The main difference between the two resonances with respect to their decay into double-hole states is the presence of a spectator electron in the case of the $2\pi^*$ resonance in contrast to the σ^* shape resonance which decays by conventional Auger decay. We see that the asymmetry parameter drops sharply to $\beta = -1$ at the $2\pi^*$-resonance position but shows no significant variation across the shape resonance, although both resonances are clearly exhibited in the cross section. The sharp decrease in the asymmetry parameter at 287.3 eV occurs in all electron channels in a very similar way, pointing to a common origin of this effect. Looking to the single-hole states $n\lambda^{-1}$ populated by direct recombination in more detail shows that the photoemission main lines exhibit a more asymmetric variation of their asymmetry parameters than the $2\pi^*$ spectator satellite peaks. This behavior can be understood as a change in the intrinsic β values due to the resonance. This effect, known from the decay of autoionizing levels in atoms[16] and molecules,[17] is superimposed on the asymmetry variation due to the anisotropy of the photoabsorption process.

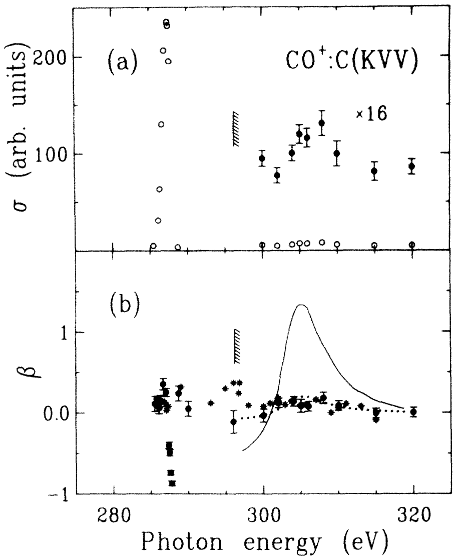

FIG. 3. (a) Partial cross sections and (b) angular distribution asymmetry parameters (circles) for ejected electrons below and above the C 1*s* threshold. The data points below this threshold represent the sum of the two double-hole-state peaks seen in Fig. 1 at 24- and 20-eV binding energy. The data points above this threshold are taken from the largest *KVV* Auger peaks in the spectrum and correspond to the same double holes as below threshold but without spectator electron. The β results of the former low-resolution experiment (Ref. 6) are shown with asterisks. The solid curve represents the orientation parameter β_m calculated by Dill *et al.*; the dotted line shows the corresponding electron asymmetry parameter β_e for an intrinsic anisotropy of $c_e = 0.15$.

Despite the excellent agreement between our results and the theoretical predictions[1] for the $2\pi^*$ resonance, there still remains a puzzling disagreement for the σ^* shape resonance, in this case corroborating the former TOF results[6] taken with lower resolution. The observed difference in the angular distribution behavior depends most likely on the character of the excited orbital: in one case a bound $2\pi^*$ orbital and in the other one a σ^* continuum state.

To understand this dependence in more detail we have to look at how the molecular orientation affects the angular distribution of the emitted electrons. Dill *et al.*[1] have shown that the molecular orientation along the direction Ω_m is described by an orientation parameter β_m in a formula analogous to the differential cross-section formula for photoelectrons[18] emitted by a randomly oriented target:

$$\frac{d\sigma(h\nu)}{d\Omega_m} = \frac{\sigma(h\nu)}{4\pi}[1+\beta_m(h\nu)P_2(\cos\theta_m)]. \quad (1)$$

Here $h\nu$ is the photon energy and $P_2(\cos\theta_m)$ is the second Legendre polynomial. The key aspect now is that the molecular orientation governs the angular distribution of the emitted electrons via the same orientation parameter β_m because the emission probability of an electron along the direction k can be written as

$$\frac{dP(h\nu)}{dk} = \left(\frac{P}{4\pi}\right)[1+\beta_m(h\nu)c_e P_2(\cos\theta_e)]. \quad (2)$$

This equation is equivalent to Eq. (1) despite the coefficient c_e which is characteristic of each electron channel and independent of photoexcitation energy. Equation (2) can be rigidly applied only to Auger electrons because it is based on the assumption of a two-step process describing the creation and the decay of the core hole. This assumption is a good approximation for the conventional Auger decay above threshold but is less well founded for the autoionization processes governing the decay of the bound $2\pi^*$ core-hole state. Nevertheless, one would expect that the resonant Auger channels behave similarly to the conventional Auger decay, despite the small shift in binding energy of about 10 eV due to the different screening of the core hole. Keeping in mind this approximation we interpret our results by application of Eq. (2) both to the continuum as well as to the discrete resonance. This equation tells us that the transfer of the molecular anisotropy to the electron asymmetries is weighted by the intrinsic anisotropy of each decay process via the characteristic constant c_e. This constant would always be zero for atomiclike *K*-shell vacancies as a result of the isotropic distribution of the 1*s* hole.[19] However, in molecules Dill *et al.*[1] expect the c_e to be nonzero in general because of their highly anisotropic charge distributions. Our results are in contrast to this expectation. They reveal a significant difference in anisotropy between core holes in the presence of an electron in a bound molecular orbital and without such an electron. The cross section of the outgoing *f* wave[20] enhanced by the shape resonance has no or much less effect on the core hole than the bound $2\pi^*$ electron. This screening electron in a molecular orbital seems to polarize the charge distribution of the *K*-shell vacancy strongly along the molecular axis, promoting resonant Auger emission in this direction. The similar β variation of the various decay channels indicates that the polarization effect is strong enough to affect all channels including direct recombination. On the other hand, the decay of the *K*-shell vacancy of the molecular ion takes much longer than the time during which the *f*-wave is trapped in the molecular potential. This preserves the intrinsic isotropy of the C 1*s* hole across the *f*-wave shape resonance. Such a vacancy decays in an atomiclike manner, showing isotropic behavior which is inherently unsuited as probe of molecular orientation.

This interpretation is supported by the observation of the same cancellation effect across the shape resonances[21] of N_2 and CO_2 which are more pronounced than in CO. This indicates that the observed electron dependence of the β effect is a general phenomenon in the K-shell photoexcitation of small molecules. However, this requires further study before general conclusions can be drawn.

To conclude, we have observed for the first time electron-ejection asymmetries arising from anisotropic K-shell photoexcitation of a free molecule. The transfer of the molecular anisotropy produced by the excitation process to electron-ejection asymmetries was shown to depend strongly on the character of the excited electron (bound versus continuum). Our results indicate that unscreened molecular K-shell vacancies are more atomiclike than expected. However, the presence of screening electrons in unoccupied molecular orbitals leads to a measurable intrinsic anisotropy which can be used in turn as a direct probe of the molecular symmetry of the excited state.

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