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Angle-resolved high-resolution C(*KVV*) Auger spectra of CO were taken in the vicinity of the C(1*s*) σ^* shape resonance. These spectra show clear evidence for the theoretically predicted anisotropic *K*-shell Auger emission in molecules. Complementary results from angle-resolved photoion spectroscopy show that the small size of the observed effect is, besides the varying intrinsic anisotropy of the Auger decay, also due to a smaller anisotropy in the primary absorption process than originally predicted but in good agreement with more recent calculations. Contrary to this, satellite Auger transitions show unexpectedly large anisotropies.

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Atomic *K*-shell vacancies are isotropic and hence Auger decay of these vacancies is also isotropic. Molecules are different in this respect; they are supposed, for symmetry reasons, to exhibit anisotropic behavior. This Auger anisotropy is the direct result of anisotropic absorption, i.e., the exciting radiation in the $\sigma \rightarrow \pi^*$ excitation selects molecules with an axis oriented preferentially perpendicular to the electric vector because the electrons excited in this process are finally in a state of π symmetry. In contrast, a $\sigma \rightarrow \sigma^*$ transition prefers parallel orientation due to the σ symmetry of the excited electrons. This behavior turned out to be the key aspect for a wide field of applications such as near edge x-ray absorption fine-structure (NEXAFS) and symmetry-dependent molecular spectroscopy.

However, since the prediction of those anisotropic *K*-shell Auger angular distributions in the 1*s* σ^* shape resonances originating from intramolecular scattering in the 1*s* continuum of CO and N_2 by Dill and co-workers [1,2] more than a decade ago, all experimental results obtained for continuum resonances seemed to contradict this general prediction [3,4]. The question arose whether this was due to insufficient alignment of the molecules by the photoabsorption process above threshold or a result of vanishing intrinsic anisotropy of the subsequent Auger decay. Both possibilities seemed to be somewhat unlikely because the alignment creation is the result of very general physical properties of a molecule—potential behavior and symmetry—in conjunction with the dipole selection rules, whereas the intrinsic anisotropy had shown up to vary over all allowed values, particularly in atoms, but without showing any tendency to center around zero. Therefore, independent direct alignment measurements were undertaken and the situation became even more puzzling after strong molecular alignment within the 1*s* σ^* shape resonances of N_2 which was confirmed via angle-resolved photoion spectroscopy [5] according to the prediction of Dill *et al.* [2].

Measurements of the corresponding alignment in the core-level shape resonances of CO were not performed until very recently [6] and even these measurements were not absolutely calibrated. Therefore it was the objective of this study to determine in a first step the molecular alignment β_m of the core excited state and afterwards to examine the intrinsic anisotropy c_a of the Auger decay. The latter can be extracted from the Auger angular distribution which is given by [2]

$$\frac{d\sigma(h\nu)}{d\Omega} = \frac{\sigma_0}{4\pi}[1 + \beta_m(h\nu)c_a P_2(\cos\theta)] . \quad (1)$$

The help of the knowledge of the molecular alignment in searching for Auger anisotropies is twofold. First, it gives an estimate on the size of the effect expected, and second, it gives information about the optimal photon energies for taking high-resolution spectra to trace the photon energy dependence within the shape resonance.

In this Letter we report on the first combined studies of excitation and emission anisotropies of *K*-shell excited molecules showing evidence of the so far unobserved anisotropic *K*-shell Auger emission in a core-level shape resonance where the "excited" electron is indeed in the continuum and not in a bound state. Furthermore, we show that some satellite Auger transitions in a shape resonance exhibit different angular-distribution behavior than diagram lines, depending on whether they originate from shakeup or conjugate shakeup transitions.

The experiments were performed at the Berliner Elektronenspeicherringgesellschaft für Synchrotronstrahlung mbH (BESSY). Photons from the high-energy toroidal grating monochromator (HE-TGM) [7] were employed to ionize CO molecules from an effusive molecular beam. Two types of experimental setups were used to determine both the angular distribution of the fragment ions as well as of the Auger electrons. In the first experiment, which determines the degree of molecular alignment in the excited state, a time-of-flight ion spectrometer was used in a special operating mode. In this mode, a decelerating field is pulsed in order to keep the thermal ions, which are isotropically distributed, out of the drift tube. Using a very short time of less than 10 nsec, only the fast ionic fragments enter the drift tube where they became accelerated. The corresponding Auger measurements were also

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performed at the HE-TGM of BESSY but using a time-of-flight electron analyzer instead of the ion spectrometer. This instrument has been used in several related studies and is described in more detail elsewhere [8]. Here, we only want to point out the fact that the relatively high kinetic energy of the Auger electrons under study required a high retarding potential in order to achieve the necessary resolution.

The ionic fragment pattern of the dissociating CO molecules photoexcited in the π^* resonance and the σ^* shape resonance were recorded by measuring the angle-dependent intensity at several angles as shown in Fig. 1. The π^* fragmentation pattern shows clearly $\beta = -1$ expected from symmetry arguments mentioned in the beginning. Because the bound states are of definite symmetry, this selection rule is strict. In contrast to this behavior is the situation in shape resonance which is a continuum resonance. Both amplitudes for σ and π waves are present in the continuum, the σ wave in the σ^* case, becoming enhanced in the shape resonance region due to the centrifugal barrier seen by the scattered electron. The fraction of π to σ wave contribution depends critically on the shape of the potential chosen by the theoretical models. Whereas the continuum multiple scattering method (CMSM) reproduces the position of the shape resonance quite accurately, it overestimates the maximum of the induced alignment [2]. In contrast, calculations based on the relaxed core Hartree-Fock method (RCHF) [9,10] describe the maximal alignment correctly, whereas the position of the resonance is off by about 2 eV. Figure 2 shows our alignment points taken at two distinct photon energies along with the different theoretical curves illustrating this situation. The maximal alignment reached in the shape resonance is indeed nearly a factor of 2 smaller than originally expected from the CMSM results. Because of the difficult experimental procedure necessary to determine the complete fragmentation pattern, this method is not well suited to follow the variation of the alignment along the photon energy. Rather, it is suitable to measure accurate absolute alignment values at selected energies. The study of the photon energy dependent alignment behavior is much more effectively performed via the symmetry-resolved photoabsorption spectroscopy developed by Shigemasa *et al.* for O_2 [11]. Their CO results [6], converted into the molecular anisotropy parameter β_m via the relation

$$\beta_m(h\nu) = 2(D_\sigma^2 - D_\pi^2)/(D_\sigma^2 + 2D_\pi^2)\,, \qquad (2)$$

with $D_{\sigma,\pi}$ being the dipole transition matrix elements for a σ or π transition, respectively, are shown in Fig. 2 as a solid line. Using our data point at 305 eV their curve can be renormalized. The result supports the arguments presented here in a very convincing way.

From this basis concerning the behavior of the molecular alignment or anisotropy parameter β_m, we now turn to the behavior of the Auger angular distributions. To study this behavior high-resolution angle-resolved Auger spectra were measured under different angles at the π^* and σ^* resonance. Figure 3(a) shows two spectra taken under 0° and 54.7° with respect to the electric vector on the π^* resonance, whereas 3(b) shows the corresponding spectra, but in the vicinity of the σ^* shape resonance. The bars in the 54.7° spectra show line components used to obtain a reasonable fit of the whole spectrum, whereas the bars underneath the spectra give the β values of these components along with the average β values for specific line groups.

The resonant Auger spectrum shows quite distinct Auger asymmetries towards negative β values as expected from the results of earlier work [5]. However, this high-resolution measurement reveals that the anisotropy of the different Auger lines, including participator transitions, varies considerably, even changing sign. This may give rise to nearly isotropic electron emission if one considers the unresolved intensity of all transitions. Nevertheless,

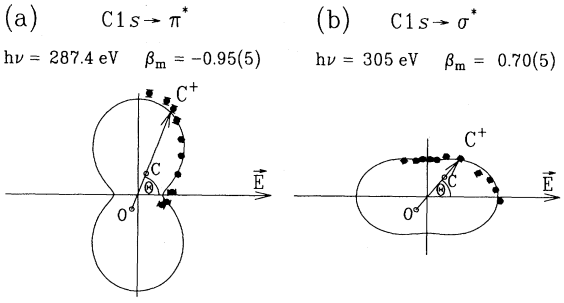

FIG. 1. Fragmentation pattern of dissociating core-excited CO in (a) the π^* resonance and (b) the σ^* resonance. The solid line represents a fit curve using Eq. (1).

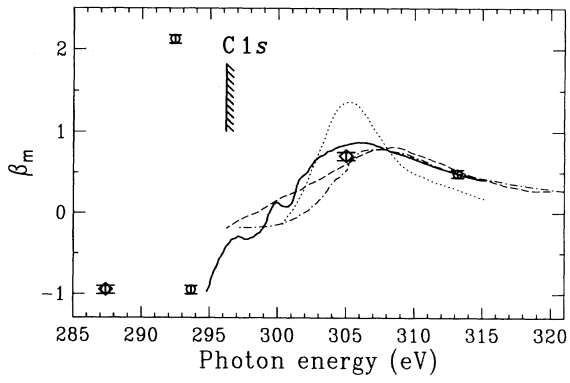

FIG. 2. Molecular alignment points (open diamonds) determined from the fragmentation pattern in Fig. 1 along with an experimental curve and data points (open circles) derived from the symmetry-dependent absorption spectra of Shigemasa *et al.* [6]. The experimental results are compared to theoretical calculations using the CMSM [2] (dotted line) and RCHF methods (dash-dotted [9] and dashed lines [10]).

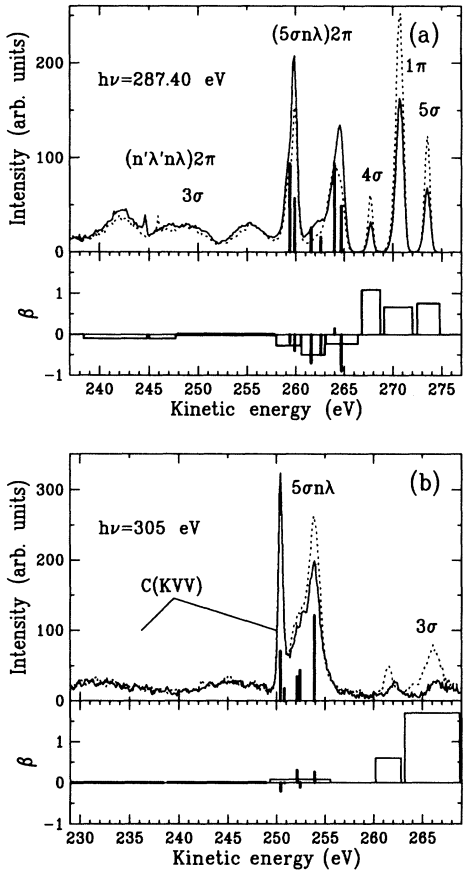

FIG. 3. C(*KVV*) Auger spectra of CO in the vicinity of the (a) π^* and (b) σ^* resonance. The solid curve represents the angle-independent spectrum taken under the "magic angle" of 54.7° in Eq. (1), whereas the dotted line shows for comparison the spectra taken under 0° with respect to the electric vector of the incoming soft x-ray radiation. The bars underneath the spectra represent line components of a fit which were based on the calculation of the regular Auger spectrum [shown in (b)] by Cederbaum *et al.* [13]. The angular-distribution asymmetry parameters β derived for these components are shown underneath each figure in the form of a separate bar diagram.

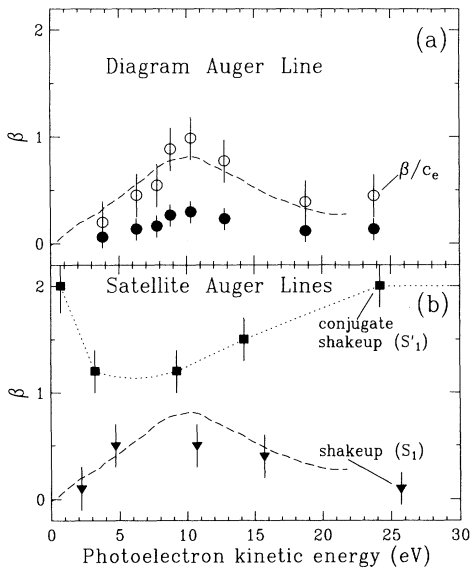

FIG. 4. Angular-distribution asymmetry parameters β (filled circles) and derived molecular alignment parameters β_m (open circles) for (a) the $5\sigma^{-2}$ diagram line along with the theoretical β_m curve of Lynch [10] (dashed line) as shown in Fig. 2, but shifted by 2 eV to lower photoelectron kinetic energies in order to make a direct comparison of the shape dependence. (b) The same curve together with the angular distribution of two satellite Auger lines, one originating from the decay of a shakeup line, the other identified as transition from a conjugate shakeup state. The latter data points are connected by a dotted line to guide the eye. Note that all primary hole states have different ionization potentials.

the observed variation in the intrinsic anisotropies is in good accord with corresponding observations in the decay spectra of core excited atoms (see, e.g., Ref. [12]). The surprising result, asymmetries seen in the regular C(*KVV*) Auger spectrum, is shown in Fig. 3(b). There is clear evidence that these Auger spectra exhibit nonisotropic emission behavior as predicted by Dill *et al.* [2].

The main factor preventing the unambiguous measurement of this effect was the insufficient resolution and statistics in all former measurements. Now, the higher resolution allows us to see the variation of the intrinsic anisotropy parameters across the different Auger transitions, as discussed for the π^* resonance. Therefore, high-resolution Auger spectra were necessary to observe the predicted anisotropy effect. The C(*KVV*) Auger spectra taken with a resolution of better than $E/\Delta E = 500$ revealed lines with anisotropies in the angular-distribution parameter β up to 0.3–0.5. However, not only the maximal Auger asymmetry on top of the σ^* resonance could be observed, but also the variation of this asymmetry with the photon energy could be examined. Figure 4 shows, for example, the behavior of the $5\sigma^{-2}\,{}^1\Sigma^+$ diagram line within the σ^* shape resonance. It clearly follows the predicted enhancement towards positive β values in accord with the molecular alignment which causes this effect. Similar enhancement, but less pronounced, is shown by several other transitions. These β values reflect in more general terms the Auger angular distribution of the oriented molecule [13] convoluted by the alignment pattern seen in Fig. 1.

Both of the shifted RCHF curves [9,10] are in good agreement with the observed data—the curve of Lynch is shown as an example—if one takes the intrinsic anisotropy of $c_a = 0.37$ derived from our ion yield measurement. The resulting data points are shown in Fig. 4 by the open circles. Because the intrinsic anisotropies for the strongest transitions vary between 0.37 and -0.30, the net value for the sum of the diagram lines $5\sigma^{-1}n\lambda^{-1}$ is, with

a maximal value of 0.1, very close to zero, explaining the results obtained in the former low-resolution measurements.

While solving this long-standing σ^* anomaly of vanishing asymmetry for the Auger diagram lines, a further surprise came when the Auger satellite lines were more closely examined. These lines, which should be more precisely designated as satellite Auger lines, originate not from the decay of the $1s$ main-line core-hole state but from the decay of $1s$ satellite lines, i.e., of two-hole one-electron states [14] as discussed below. Their alignment behavior reflects both characteristic features of the primary satellite line as well as of the decay transition. Figure 4(b) shows the behavior of two prominent satellite Auger transitions, one of them belonging to a $2\sigma^{-1}1\pi^{-1}2\pi$ shakeup satellite. The overall asymmetry of the shakeup satellite is somewhat larger than the asymmetry observed for the diagram line; however, it mimics the behavior of the diagram line. This fits well into the physical picture of overlap dependent satellite intensity, $\langle 1\pi|2\pi\rangle$, resulting from the shakeup model. Contrary to this, the other satellite Auger transition shows strong asymmetry ($\beta=2$), particularly outside of the shape resonance, with a tendency to weaken inside the shape resonance.

We explain this unexpected behavior by the occurrence of a conjugate shakeup line in the primary photoionization process leading to a strongly aligned intermediate state of the molecule. This state with an excited π^* electron, most likely a $2\sigma^{-1}1\pi^{-1}2\pi$ state, decays via a participator transition to $5\sigma^{-1}1\pi^{-1}$ taking along the angular momentum deposited in the core excited molecular ion via the $2\sigma\rightarrow 2\pi$ core excitation, a process known from atoms [15] but so far, to our knowledge, unobserved in molecules. This results in the observed strong decay anisotropy. Within the shape resonance π^* and σ^* excitations interact with each other, thereby causing a reduced alignment of the intermediate state as seen in the angular distribution of the corresponding Auger electrons. This behavior of the β parameter of the conjugate shakeup satellite Auger line is clearly depicted in Fig. 4(b). In addition to the general importance of showing the similarity between atoms and molecules in core-level photoionization, such studies may also help to identify conjugate shakeup transitions and differentiate them from other satellite transitions.

In summary, we have studied the long-standing anomaly that the *KVV* Auger electrons of CO seemed to be isotropically emitted in the presence of the C($1s$) shape resonance, in contrast to very general theoretical predictions. We have shown that this anomaly was the result of a smaller molecular alignment than originally expected, on the one hand, and insufficient resolution of the electron measurements, on the other hand. Our high-resolution measurements clearly show that the predicted *K*-shell Auger asymmetry does exist for continuum resonances above threshold and that it closely follows the more recent RCHF calculations of this process. Moreover, unexpected strong alignment of satellite Auger transitions turned out to be a sensitive tool in tracing the origin of molecular core-level satellite states.

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