Near-Threshold Measurements of the C 1s Satellites in the Photoelectron Spectrum of CO

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The cross sections and asymmetry parameters of the two π-π^* $^2\Sigma^+$ shakeup satellites on C 1s in the photoelectron spectrum of CO are found to differ significantly in the threshold region. The first satellite (due to triplet π-π^* coupling) shows intensity enhancement near threshold whereas the second satellite (singlet π-π^* coupling) decreases in intensity as expected for the adiabatic limit. Moreover, the data indicate that a shape resonance in the first-satellite channel is responsible for the observed effect rather than a conjugate shakeup process.

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Core-level photoelectron spectra of atoms and molecules are characterized by main lines, corresponding to single-hole states, and associated satellite structures.[1,2] At sufficiently high photoelectron kinetic energy, i.e., in the so-called sudden limit,[3,4] the photoelectron can be regarded as being removed instantaneously from the system. The other electrons do not adjust to the suddenly switched-on hole potential and there is then a finite probability of the resulting ion being left in an excited state, giving rise to a satellite in the photoelectron spectrum. On the 1s lines of simple molecules such as CO and N_2 about (30–40)% of the total spectral intensity is to be found in such "shakeup" and "shakeoff" satellite structures. Particularly dominant, and at lowest energy, are the shakeup states involving π-π^* excitations. Whereas molecular 1s photoelectron spectra have been measured for many years with Al $K\alpha$ radiation, for which the sudden-limit condition almost certainly applies, the availability of intense tunable synchrotron radiation now makes it possible to investigate the photon-energy dependence of the cross section and angular distribution of photoelectron lines over a wide energy range. For 1s shakeup states, this experiment is still, however, very difficult because of the very low cross sections. The only previous experiments of this kind on core-level satellites have been performed for adsorbates[5] and for the rare-gas atoms Ne and Ar.[6,7] Nor are calculations of satellite cross sections for molecules available, in contrast to the situation for single-hole states.[8] Instead, there exists only a generalized description of satellite intensities as a function of photoelectron energy[9]: As the threshold for photoionization is approached, the sudden approximation should at some point cease to be applicable. The photoelectron is removed so slowly that the new effective potential is turned on adiabatically and the satellites lose their relative intensity. Hitherto, it has not been clear how and at what energy above threshold the transition to adiabatic behavior takes place or, indeed, whether such a description applies at all.[5,10,11] In contrast to the adiabatic picture, a dramatic *enhancement* with respect to the sudden limit has recently been reported for the first π-π^* shakeup satellite on C 1s in CO by electron-electron coincidence measurements $(e,2e)$ in the corresponding Auger channel.[12] The effect has been attributed to conjugate shakeup involving the strong C 1s-π^* transition. In this Letter, we report a direct investigation of the π-π^* shakeup satellites on C 1s in CO over an extended energy range starting from close to threshold. Our experiment—the first study of its kind for free molecules—shows that the enhanced partial photoionization cross section of the first satellite near threshold is not due to a conjugate shakeup process, but rather due to a shape resonance. For the second satellite we find, however, the generally expected slow sudden-adiabatic transition over a range of several tens of electronvolts above threshold.

The experiments were carried out at the electron storage ring BESSY with use of the high-energy toroidal grating monochromator.[13] The measurements were performed under single-bunch conditions with two rotatable time-of-flight analyzers, thus providing information on both cross section and photoelectron angular distribution (asymmetry parameter β).[11] Figure 1 shows the C 1s photoelectron spectrum of CO at

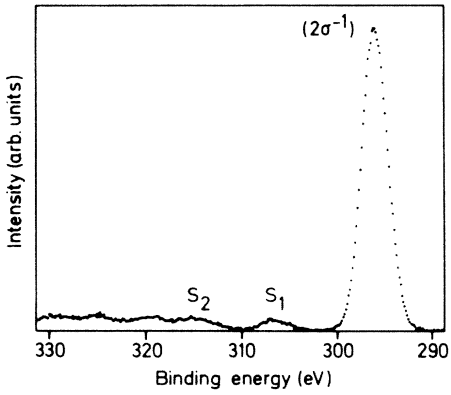

FIG. 1. Photoelectron spectrum of CO excited with 390-eV photons as observed at the magic angle (54.7°) with respect to vector **E**.

$\hbar\omega = 390$ eV. The main line, corresponding to the core-hole $(2\sigma)^{-1}$ state, has a binding energy of 296.2 eV. In addition, there are two prominent satellites at 8.3 and 14.9 eV (labeled S_1 and S_2, respectively), as well as others at still higher binding energy. Figure 2 shows the measured partial photoionization of the one-hole state and the satellite states between $\hbar\omega = 310$ and 400 eV. For the main line the high-energy wing of the σ-shape resonance located about 10 eV above threshold is observed in the cross section[15] and angular distribution.[14,16] The cross section of the S_1 state behaves similarly to that of the main state: It shows a broad resonancelike structure, but at ~ 20 eV above threshold. At its maximum, the cross section is about 10% of that of the $(2\sigma)^{-1}$ state, i.e., a factor of 5 higher than in the high-energy limit.[1] Although our measurements could not be extended any further, an extrapolation would indicate a relative cross section of (5–8)% at 2 eV above threshold, thus confirming, qualitatively, the result of Ungier and Thomas.[12] Towards higher proton energies the relative cross section decreases as it approaches the sudden limit [2.1% at $\hbar\omega = 1486$ eV (Ref. 1)]. A strikingly different picture is found for S_2: The cross section rises steadily until it reaches its high-energy asymptote at about 100 eV above threshold. At $\hbar\omega = 365$ eV, there is a crossover in the relative intensities of the two satellites. The different behavior of the cross section is also reflected in the photon-energy dependence of β (Fig. 3).

The satellites S_1 and S_2 are due to two distinct $^2\Sigma^+$ states associated with the configuration $(2\sigma)^{-1}$-$(1\pi)^{-1}(2\pi)^1$. They differ by the alternative possibilities of coupling the π and π^* electrons to form intermediate triplet (S_1) and singlet (S_2) states.[17] Apart from demonstrating the inadequacy of the simple concept associated with the so-called adiabatic limit, the data for the two satellites present other interesting features. In view of the fact that both satellites are associated with the same electronic configuration and differ only with respect to the coupling scheme of the π electrons, the differences in cross section and β, in particular the absence of a resonancelike feature for S_2, are unexpected.

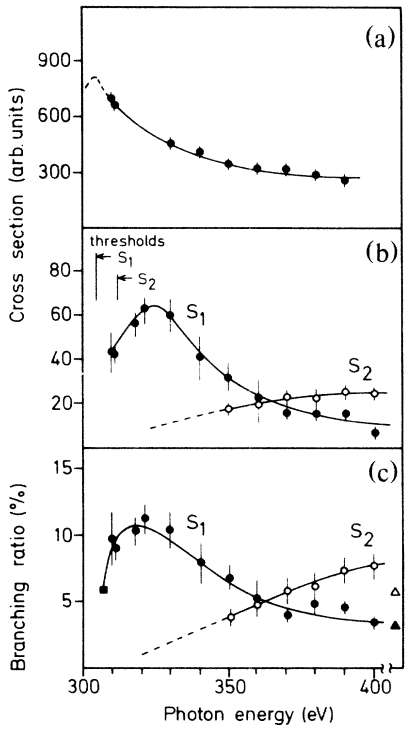

FIG. 2. Cross section of (a) the main line $(2\sigma)^{-1}$ and of (b) satellites S_1 and S_2. The dashed line in (a) is taken from Ref. 14 and has been scaled to coincide with our lowest datum point at 310 eV. In (b) and (c), full circles correspond to S_1, and open circles to S_2. The thresholds for the two satellites are indicated with arrows. The extrapolation of S_2 to lower energies is derived from data obtained with an ellipsoidal-mirror–retarding-field analyzer with very high luminosity. Part (c) shows the satellite to main-line branching ratios including the datum point at 1.4 eV from Ref. 12 (square) and the high-energy values from Ref. 1 (triangles).

Is there a simple explanation? A qualitatively satisfactory theoretical description of the one-hole $(2\sigma)^{-1}$ cross section has been achieved by use of both the frozen-core static exchange potential[8,15,18,19] and a so-called relaxed potential.[20] In particular, the nature of the shape resonance—a quasibound valence-type σ^* orbital in the potential of the molecular ion—has been clarified. To our knowledge, however, there has been no attempt to arrive at a similar theoretical description of the cross section of the satellite states. A starting point would be the derivation of the appropriate potentials for the two ionic states. Following the approach of Hunt and Goddard,[19] we have derived frozen-core static exchange potentials for the motion of the photoelectron in the field associated with the (zeroth or-

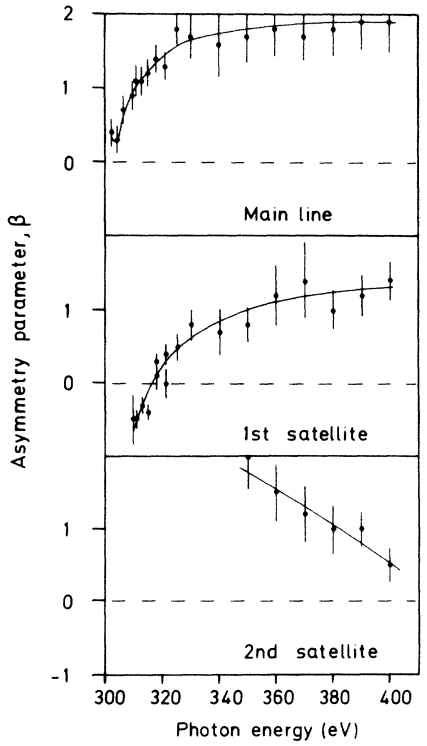

FIG. 3. Asymmetry parameter β of the $(2\sigma)^{-1}$ main line and satellites S_1 and S_2.

der) satellite states.[21] The interesting point here is that the exchange potentials $\hat{K}_{2\sigma}$, $\hat{K}_{1\pi}$, and $\hat{K}_{2\pi}$ for the three open molecular shells of the ion enter the expressions for the triplet coupled state $\hat{V}$ $(S=1)$ and the singlet coupled state $\hat{V}(S=0)$ differently:

$$\hat{V}(1)=\hat{V}-\hat{K}_{2\sigma}+\tfrac{1}{2}\hat{K}_{1\pi}+\tfrac{1}{2}\hat{K}_{2\pi},$$
$$\hat{V}(0)=\hat{V}+\hat{K}_{2\sigma}-\tfrac{1}{2}\hat{K}_{1\pi}-\tfrac{1}{2}\hat{K}_{2\pi}. \quad (1)$$

$\hat{V}$ is the potential associated with the nuclear frame and the electrons in the closed shells. Whereas exchange with the core level will only be of minor importance, there is likely to be a major effect on the scattering states arising from exchange with the 1π and 2π levels. Thus, a possible explanation for the differing cross sections and angular distributions are the different potentials experienced by the ejected electron in each case. As is well known, e.g., from scattering calculations in the multiple scattering model, already slight modifications of the scattering potentials and the corresponding potential barrier heights can be crucial for the existence of shape resonances. In the present case, there seems to be a delicate balance between appearance and nonappearance of a shape resonance depending on the specific character of the effective potential, in particular on the height of the corresponding barrier. This interpretation is corroborated by the variation of the angular distributions of the two satellites. Satellite S_1 shows the typical β variation induced by a shape resonance in contrast to the atypical β behavior of satellite S_2, which still needs theoretical explanation. The term dependence of a shape resonance is analogous to the term dependence observed in the collapse of the $4f$ orbital in Ba and the rare earths.[22] The higher the kinetic energy of the ejected electron, the lesser will be the effect of the exchange operators, so that in the high-energy limit, the scattering potentials for the two ionic states become identical. This is consistent with the observation that in this limit the satellite intensity ratios are determined by the spectroscopic factors.[4,9,23] Only actual calculations, however, will show whether the observed behavior can be explained on the basis of such a one-particle scattering description. It is possible that we will have to resort to a more general formulation which allows for interchannel coupling and bound-state–continuum correlation.

Ungier and Thomas[12] have suggested that the increased intensity of S_1 near threshold is due to a resonant enhancement caused by a conjugate shakeup process.[23] We briefly comment on this possibility. The expression for the partial photoionization cross sections of the two $^2\Sigma^+$ states contains a direct part and a conjugate, or nonorthogonal part. For high kinetic energy of the photoelectron, i.e., in the sudden limit, the conjugate part may be neglected since here the overlap integrals $\langle 2\sigma|\epsilon\pi\rangle$ are small compared to the dipole matrix elements $\langle 2\sigma|t|\epsilon\pi\rangle$. Furthermore, the dipole matrix elements for the main and satellite states will then differ only slightly, so that the ratios of the partial cross sections are determined by the spectroscopic factors. For low kinetic energy, in particular near threshold, the conjugate part could also become important. Moreover, as has been stressed by Ungier and Thomas,[12] the dipole matrix element $\langle 2\sigma|t|2\pi\rangle$ corresponding to the 2σ-2π excitation is large, so that the conjugate contribution could be considerable if the overlap integral $\langle 1\pi|\epsilon\pi\rangle$ is not too small. This argument should apply equally well to both satellites S_1 and S_2, which have similar conjugate shakeup contributions. This, however, is in contradiction to the observed behavior of the second satellite. Moreover, if conjugate shakeup should play a major role then—as a result of different selection rules—the shakeup states of $^2\Sigma^-$ and $^2\Delta$ symmetry should also appear in the photoelectron spectrum. On the assumption of the same spin-coupling scheme as for the $^2\Sigma^+$ states, the cross sections to the lowest order are $6\bar{\sigma}$, $2\bar{\sigma}$, $3\bar{\sigma}$, and $\bar{\sigma}$ for $^2\Delta(1)$, $^2\Delta(0)$, $^2\Sigma(1)$, and $^2\Sigma(0)$, respectively, where $\bar{\sigma}$ is of the form $|\langle 1\pi|\epsilon\pi\rangle\langle 2\sigma|t|2\pi\rangle|^2$. Energetically, these four states should be situated in a relatively small interval about 1–2 eV above S_1. As yet, and this includes the present investigation, they have

not been observed.

In conclusion, we have shown that the increase in the partial photoionization cross section near threshold for the first π-π^* satellite on C 1s in CO arises from a shape resonance in this channel, rather than from the conjugate shakeup process. The behavior of the second π-π^* satellite, in contrast, is in accordance with the simple model of the adiabatic-sudden transition. It is suggested that this difference in behavior may be explained on the basis of differing exchange potentials in the one-particle scattering model for the two differently coupled satellite states.

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