

Angle-Dependent Changes of Auger Line Shapes from Adsorbed Molecules

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Strong polar-angle dependence has been observed in *KVV*-Auger spectra of adsorbed molecules. These angular effects are caused by the anisotropy of the Auger matrix element and can be explained by simple symmetry arguments. It is shown with the example CO on Ni(100) that molecular Auger spectra can be largely understood with use of nothing but the present angular results and experimental one-electron binding energies. Information about the adsorbate orientation as well as about the screening mechanism can also be obtained.

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Auger spectra generally exhibit rather complex fine structures because of the many possible decay channels of the primary hole and because of the interaction of the two holes in the final state. While spectra of atomic species and of some metals are well understood, this is less true for molecules or adsorbates although several theoretical and experimental investigations on simple molecules¹⁻³ and on molecular adsorbates^{4,5} have recently improved the situation.

This Letter presents a new source of experimental information by employing angle-resolved, x-ray-induced Auger spectroscopy for adsorbed (=oriented) molecules. The observed strong angle-dependent changes of the Auger line shape have so far been neglected in adsorbate studies. They are due to the anisotropy of the Auger decay and are not markedly influenced by scattering effects. The changes can be explained by simple symmetry arguments and thus provide a direct indication of the symmetry character of the observed transitions. This facilitates the interpretation of molecular Auger spectra and the comparison between experiment and theory. It also sheds light on the role of the substrate particularly concerning the screening mechanism which is rather important for photoemission or photon-stimulated desorption, and which has been the object of lively discussion.⁶ In addition, angle-resolved Auger electron spectroscopy (AES) provides a new direct method to determine the geometry (e.g., the orientation) of molecular adsorbates. We emphasize that such drastic angular effects are important for Auger spectroscopy in general even if AES is only employed as an analytical method or as a probe for other techniques (e.g., surface extended x-ray

absorption fine structure, near-edge x-ray absorption fine structure).

We also mention that different angle dependences have been found in some previous Auger studies. In the gas phase the observed anisotropies are small ($\sim 5\%$)⁷ and are due to angular correlation between the initial excitation and the Auger electron. Some Auger lines of solid samples show azimuthal- and polar-angle dependences which are dominated by diffraction effects.⁸ In the present study diffraction effects can be excluded because only relative changes in the Auger line shape are considered, and the relative wavelength difference $\Delta\lambda/\lambda$ of the main peaks is only about 0.5%.

Most Auger studies are performed with electron excitation. For high-resolution experiments, however, excitation by x rays is preferable because these cause less background problems and less beam damage to molecular adsorbates.^{4,5} The major disadvantage of conventional x-ray sources is the need for long measuring times, but this can be overcome by the use of high-flux photon sources such as undulators or wigglers at a storage ring. This Letter reports the first experiment using radiation from the Stanford Synchrotron Radiation Laboratory undulator in the soft-x-ray range (450–1500 eV).⁹ Our experience with this synchrotron device clearly demonstrates that even its unmonochromatized radiation is ideally suited for such experiments because of its extremely high photon flux ($> 10^{15}/\text{sec}$) and its quasimonochromatic and partially tunable energy spectrum.^{9,10} Thus, Auger spectra with good signal-to-noise quality could be obtained within rather short measuring times (~ 15 min) at high angular ($\pm 2^\circ$) and energy (~ 0.2 eV) resolu-

tion with use of a conventional electron spectrometer. Experimental details will be given elsewhere.¹⁰

Figure 1 shows oxygen Auger spectra from molecularly adsorbed CO on Ni(100) at 105 K taken at various polar angles. Drastic changes of the line shape occur between 500 and 525 eV even for an angular variation of 10° or less. For instance, the peak at 505 eV (labeled 3) has negligible intensity at polar angles above 30° but increases more than 10 times for normal emission ($\theta \sim 0^\circ$). Peak 4, however, is hardly discernible at normal and grazing exit angles but reaches a strong relative maximum around 45°. Most other peaks or shoulders also show angle-dependent changes but these are less pronounced because of overlapping peaks or because of the symmetry of the involved transitions. The variation of relative peak intensities is seen more clearly in Fig. 2 which presents the quantitative evaluation of the spectra of Fig. 1.

These angular effects can be understood without calculational effort by simple symmetry consid-

erations. Following Siegbahn *et al.*¹ we can write the intensity I_{jk} of an Auger transition $c \rightarrow jk$ in terms of Coulomb, J_{jk} , and exchange, $K_{jk} = J_{kj}$, matrix elements of the form

$$J_{jk} = \langle \varphi_j \varphi_k | e^2/r | \varphi_c \varphi_e \rangle, \quad (1)$$

where c and e refer to the initial core hole and the emitted Auger electron, respectively, and where j and k represent valence orbitals. The proper symmetry group for chemisorbed linear molecules is $C_{\infty v}$ (C_{4v} would yield very similar results) if we assume that the surface mainly causes the alignment of the adsorbed molecules and that the symmetry of substrate and adsorption site is less important for most of the electronic transitions. On the basis of the knowledge that the integrand in Eq. (1) must belong to the totally symmetric representation Σ^+ for nonzero J_{jk} and K_{jk} , and that the operator as well as φ_c both belong to Σ^+ , we can determine the symmetry character of the emitted Auger electron φ_e for each decay channel jk . In our simple linear molecules there are three possible classes of double-hole final states: $\sigma\sigma$, $\sigma\pi$, and $\pi\pi$. According to group theory we can thus derive the symmetry of the wave function φ_e :

Final state	$\sigma\sigma$	$\sigma\pi$	$\pi\pi$
Symmetry of φ_e	σ	π	σ, Δ

For σ symmetry (quantum number $m = 0$) we expect emission along the symmetry axis; for par-

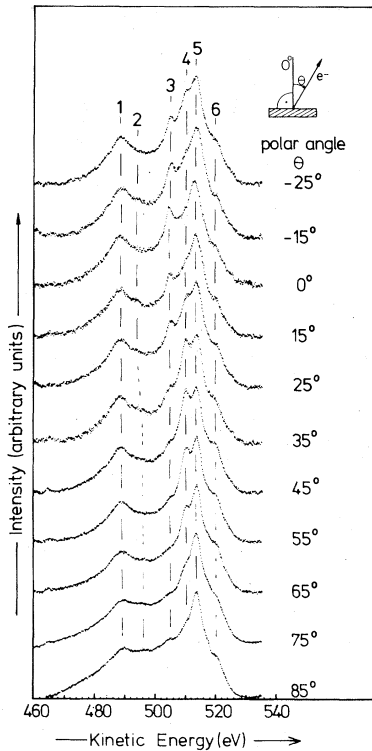


FIG. 1. O KVV spectra of molecular CO on Ni(100) taken at different polar angles as indicated. Spectra are shown as recorded in the $N(E)$ counting mode; only a linear background has been subtracted. Kinetic energies are referred to the Fermi level.

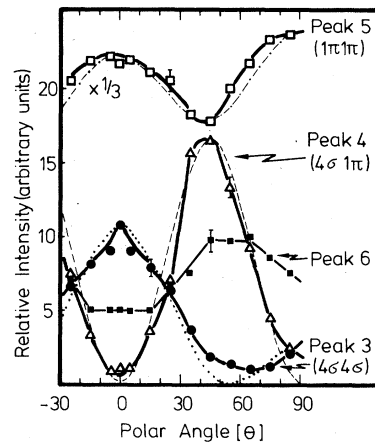


FIG. 2. Intensity variation of some peaks of Fig. 1 with polar angle. Full lines connect data points (symbols) which represent relative intensities (deconvoluted peak areas) referred to the total KVV intensity. Broken lines represent specific partial waves normalized to experimental data: $|Y_{20}|^2$ (dotted line), $|Y_{21}|^2$ (dashed line), and $C|Y_{00}|^2 + |Y_{20}|^2 + |Y_{22}|^2$ (dash-dotted line).

tial waves $l \geq 1$ the emission should even be strongly peaked in this direction. For π and Δ symmetry ($m = \pm 1$ and ± 2 , respectively), however, emission along this axis is forbidden. Hence we can unambiguously derive that peak 3 is dominated by a σ partial wave and, according to its energy position, that it must belong to the $4\sigma 4\sigma$ final state. Furthermore, it can be shown¹⁰ that $l \leq 2$ because only $2s$ and $2p$ atomic levels contribute to the molecular orbitals in these light molecules. Therefore peak 4 must belong to a π wave (mainly $l=2$) and can unambiguously be attributed to a $4\sigma 1\pi$ final state. Peak 5 apparently contains a mixture of σ as well as (π or) Δ partial waves and can thus be assigned to a $1\pi 1\pi$ final state in agreement with its intensity and energy position. Our qualitative interpretation is corroborated by the excellent agreement between the measured angular variation of peak intensities and "theoretical" curves indicated by broken lines in Fig. 2. These lines simply describe the polar-angle dependence of the square of spherical harmonics $|Y_{lm}|^2$ which represent the angular part of appropriate partial waves, m , belonging to the correct symmetry representation.¹⁰

Next we briefly discuss the interaction of the two final-state holes and the interpretation of CO Auger spectra based on a one-electron description. Therefore we consider the kinetic energy (E_K) of an Auger transition $c-jk$ which can be approximated by^{1,2}

$$E_K = I_c - I_j - I_k - U_{\text{eff}}(j, k; s), \quad (2)$$

where I_c , I_j , and I_k represent the one-electron binding energies of the respective levels which can be taken from photoemission measurements, and U_{eff} describes the spin-dependent interaction of the two-hole final state jk including Coulomb repulsion and static relaxation.¹ U_{eff} can be derived from experimental data by comparing the two-electron binding energy in the final state, $I_c - E_K$, with the sum of one-electron binding energies, $I_j + I_k$, as shown in Fig. 3 for representative O and C Auger spectra. The oxygen spectra had to be shifted by 2 eV ($\equiv U_{\text{eff}}'$) to align the main peaks ($1\pi 1\pi$ final state) with the bar at 16 eV representing twice the 1π binding energy; the C-Auger spectrum was not shifted ($U_{\text{eff}}' = 0$). The fact that most Auger peaks coincide with their bar counterparts, or deviate only slightly from them, corroborates our assignment based on the angular dependence. It also shows that U_{eff} is very small compared to the gas-phase value ($U_{\text{eff}}^{\text{gas}} = 15-20 \text{ eV}^{2-5}$) because of the very

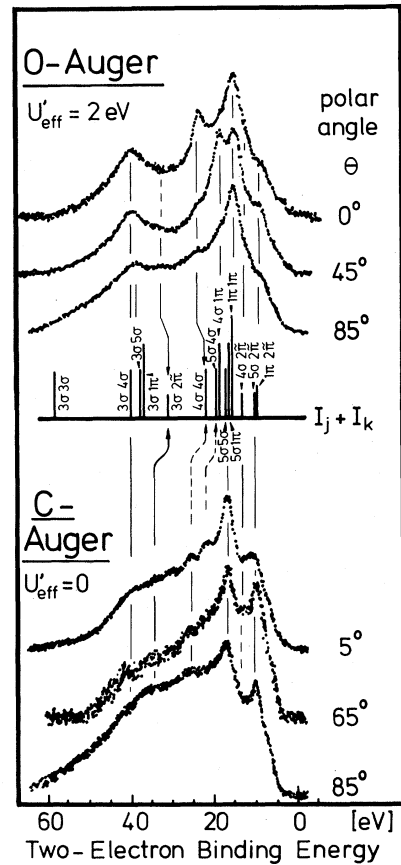


FIG. 3. Comparison of selected O and C KVV spectra from CO on Ni(100) with a bar graph representing possible two-hole final states derived from experimental one-electron binding energies (Ref. 4). Spectra are plotted on a two-electron binding energy scale $I_c - E_K - U_{\text{eff}}'$ according to Eq. (2).

effective screening which leads to a nearly complete delocalization of the two holes in the final state^{4,5} (nonzero U_{eff} values indicate some remaining hole-hole interaction, e.g., in the case of $4\sigma 4\sigma$ and $1\pi 1\pi$ final states). This screening process can be described by charge transfer from the metal to an unoccupied adsorbate orbital (e.g., the 2π level) which has been pulled down below the Fermi level by Coulomb attraction of a hole in the adsorbate.⁶ The present results support this model because it implicitly predicts a participation of this screening level in the Auger decay. Indeed we observe intense peaks or shoulders (peak 6) in the carbon or oxygen spectra, respectively, at high kinetic energies where transitions involving only 4σ , 5σ , or 1π orbitals are not expected. The assignment of peak 6 to $4\sigma 2\pi$, $1\pi 2\pi$, and $5\sigma 2\pi$ final states (2π denotes the screening orbital derived from CO 2π and Ni $3d$

levels) agrees well with the observed angular dependence (Figs. 2 and 3) and with conclusions derived by other authors.^{3,4} The interpretation of most other peaks or shoulders, or peak shifts, can be given in a similar way¹⁰ and is indicated in Fig. 3. It should be added that our interpretation is corroborated by the finding that different coverages, azimuthal angles, and x-ray polarizations did not result in a significant change of the polar-angle dependence of the O KVV spectra, and by the reasonable agreement with theoretical calculations of the CO molecule and of carbon-yls.^{2,3}

Finally we note that angle-resolved Auger spectra can be utilized for the determination of the orientation of adsorbed molecules with high accuracy (<5%) and with less ambiguity compared to other surface methods. For instance, the present results clearly prove that CO stands vertically on the Ni(100) surface because they are only compatible with the assumption that the molecular symmetry axis and the surface normal coincide. While this finding is not new for CO on Ni(100) the situation is less clear for other adsorbates. For instance, the question of whether NO is tilted or not on different metal surfaces has attracted some attention in the past. Our NO results unambiguously show that NO is also vertically adsorbed on the Ni(100) surface.¹⁰ The angular effects for NO, and also for N₂, on Ni(100) are similarly strong as for CO.

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