

Inverse-photoemission observation of the shape resonance

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We present the first observation to our knowledge of the molecular shape resonance in adsorbed CO using the technique of inverse photoemission. By comparison with earlier photoionization measurements we are able to examine the role of the final-state potential in determining the binding energy of the shape resonance. We find that screening of the photohole is more effective for valence-band photoionization than for the more localized core-level photoionization.

Molecular shape resonances or bound electron states in the continuum^{1,2} have now been observed either directly or indirectly using a variety of techniques. These resonances are generally considered to arise through multiple scattering of the electron within the molecular potential. The observation of such resonances in photoionization of both valence³ and core⁴ levels of adsorbed molecules has been used to obtain geometrical information on the adsorbate. In particular, dipole selection rules have been used to establish the orientation of the adsorbed molecules. It has further been proposed that the binding energy of the shape resonance is directly related to the intramolecular distance.⁵ Thus, in near-edge extended x-ray-absorption fine structure (NEXAFS) measurements, changes in the binding energy of the resonance from one molecular adsorption system to another have been used to establish the change in bond length of the adsorbed molecule.⁶ However, it has been noted that the continuum resonance observed in NEXAFS (core-level excitation) is more sensitive to these changes in intramolecular bond length than the equivalent resonance observed in valence-band photoionization.^{7,8} With such phenomena still not clearly understood it may be hoped that any new technique capable of observing these resonances will provide more information concerning the factors that influence their binding energies.

Recently, we proposed that the shape resonance should be observable in inverse photoemission spectroscopy (IPES) as an initial-state effect.⁹ Thus the cross section for observation of the unoccupied $2\pi^*$ level in adsorbed carbon monoxide should peak at incident electron energies corresponding to coupling into the shape resonance as an initial state. This would be a transition between a σ and a π level rather than the σ to σ transitions observed in photoemission. In this paper we report the first observation to our knowledge of this phenomenon for an adsorbed system, in particular, the adsorption of carbon monoxide on a Ni(001) substrate. The shape resonance in this adsorption system has also been studied in both valence¹⁰ and core-level⁴ photoionization experiments, which provide an excellent data base for comparison. Inverse photoemission represents the scattering of an electron by a neutral atom as opposed to the positive ion characteristic of photoemission.

Our results compared with earlier photoionization measurements clearly demonstrate the role of the final-state potential in determining the binding energy of the continuum resonance.

Our experiments were performed in an inverse photoemission apparatus that has been described in detail elsewhere.¹¹ Briefly, a normal incidence spectrometer allows the detection of photons emitted in the inverse photoemission process in the range from 10 to 30 eV. Using such an instrument, the cross-sectional behavior of the unoccupied orbitals is measured as a function of the incident electron beam energy. The Ni(001) surface was cleaned by repeated argon bombardments and anneals followed by annealing in an oxygen atmosphere. Surface cleanliness was monitored by low-energy electron diffraction and Auger electron spectroscopy. Following cleaning, the surface was exposed at room temperature to 10 L of carbon monoxide at a partial pressure of 10^{-8} Torr. No attempt was made to establish an ordered overlayer structure, as the sought-after effect is thought to be dependent only on the molecular potential of the carbon monoxide itself.

Figure 1 shows a series of inverse photoemission spectra recorded at room temperature from the Ni(001) surface with adsorbed carbon monoxide as a function of incident electron beam energy. The electron beam is incident along the surface normal for all experiments. The lowest spectrum is that recorded from the clean surface. Briefly we identify two features in this spectrum. The large peak immediately above the Fermi level we associate with transitions into the unoccupied part of the d band. The other peak, 4.65 eV above the Fermi level, we identify as the image state derived from the long-range image potential.¹² Surface-derived features show no dispersion with k_{\perp} and similar spectra are recorded from the clean surface at all the energies indicated. On exposure to CO the surface feature is completely quenched and replaced by a new broad feature. The peak associated with the d band remains but is quenched slightly. We identify the peak centered 4 eV above the Fermi level with the unoccupied $2\pi^*$ orbital of the carbon monoxide. The observation of this peak has already been reported for a number of different adsorption systems.¹³ It can be seen in Fig. 1 that the intensity or cross section for the observation of

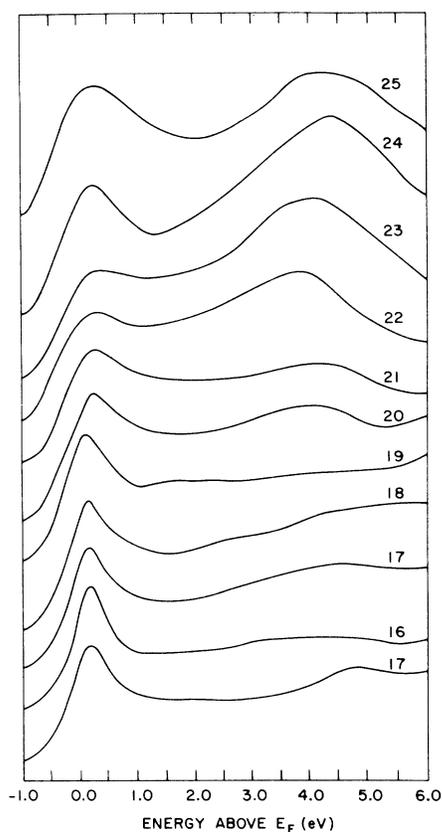


FIG. 1. Smoothed [ΔE (full width at half maximum)=0.5 eV] inverse photoemission spectra recorded from CO adsorbed on Ni(001) as a function of incident electron energy E_i with respect to the Fermi level. The lowest curve is a representative spectrum from the clean surface.

the $2\pi^*$ level clearly goes through a resonance at incident energies approximately 24 eV above the Fermi energy.

In Fig. 2(a) we plot the inverse photoemission cross section for observation of the CO $2\pi^*$ level as a function of the incident electron beam energy measured with respect to the Fermi level. A measure of this cross section in arbitrary units is obtained by integrating the area under the $2\pi^*$ peak in the spectra of Fig. 1. Because of the large width of the $2\pi^*$ orbital this measurement will be virtually independent of the resolution of the instrument. In Fig. 2(a) we also show the CO $2\pi^*$ level, observed as the final state in the inverse photoemission transition. For the purpose of this figure the experimentally measured $2\pi^*$ orbital in this present experiment has been scaled vertically to facilitate comparison with the NEXAFS result shown in Fig. 2(c).

We associate the peak in the cross section in Fig. 2(a) with the shape resonance serving as the initial state. An alternative explanation for such an increase in photon flux at a particular energy could be some form of resonant photon emission following an excitation of the system. Thus the adsorbed molecule is raised to an excited state by the incident electron beam and subsequently the molecule returns to its ground state with the emission of a pho-

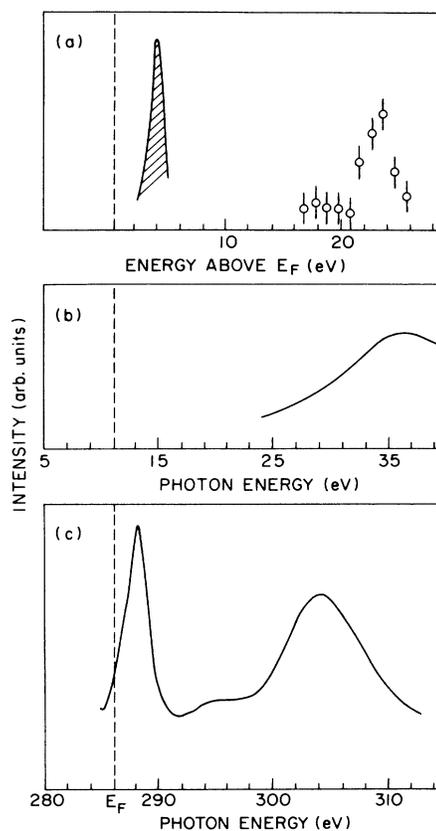


FIG. 2. CO adsorbed on Ni(001). (a) Cross-hatched peak shows the $2\pi^*$ orbital above the Fermi level E_F measured as the final state in inverse photoemission. Individual points ϕ show IPES cross section or integrated intensity of the $2\pi^*$ as a function of incident electron beam energy with respect to E_F . (b) Photoionization cross section of the CO 4σ molecular level from Ref. 10. (c) Near edge structure for carbon K -edge excitation from Ref. 4.

ton. However, if such a process were to occur the energy of the photon released might be expected to be similar to the characteristic energies observed in the electron-energy-loss spectroscopy of adsorbed carbon monoxide. Tabulations of these energy losses¹⁴ indicate that for the CO/Ni(001) system no loss occurs at 20 eV as would be required for transitions into the $E_F + 4$ eV peak at the $E_i = 24$ eV incident energy. Furthermore, such a fixed photon energy process would produce a series of peaks with final-state electron energies $E_f = E_i - 20$ eV marching through the spectra in Fig. 1, which is not observed. For comparison, we plot in Fig. 2(b) the measured photoionization cross section of the 4σ level of the adsorbed carbon monoxide¹⁰ and in Fig. 2(c) the carbon K -edge NEXAFS⁴ spectrum of the CO/Ni(001) adsorption system. Excitation from the 5σ valence level shows a shape resonance at approximately 1.8-eV lower binding energy than the resonance shown for the 4σ valence level in this figure. We observe from the figure that the shape resonance observed as a final state in 4σ valence-band photoionization lies closer to the inverse photoemission observa-

tion than does the core-level photoionization measurement.

As stated earlier, the shape resonance may be considered to be a bound state in the continuum, its binding energy reflecting the potential to which the electron is bound. The inverse photoemission process essentially represents the scattering of an electron from a neutral atom.⁹ Conversely, the photoionization measurements represent the scattering of the electron from a positive ion. In the event of perfect screening of the photo hole, the two should be indistinguishable. Thus, we clearly observe different types of screening in Fig. 2: We observe that the localized core hole in the NEXAFS measurement produces a larger perturbation of the neutral atom potential (which is characteristic of the IPES measurement) than does the 4σ hole in the valence-band photoionization.

This observation is confirmed if we compare the present observations for adsorbed CO with similar measurements for gas-phase CO. In Table I we show the measured binding energies of the shape resonance for CO gas-phase photoionization^{15,16} experiments and the binding energy measured in vibrational excitation studies of a molecular beam;¹⁷ we also tabulate the binding energies measured for the adsorbed CO case. Again we observe that the core-level photoionization serves as a larger perturbation (the shape resonance is pulled down closer to E_F) than the more delocalized valence-band photoionization, both in the gas phase and in the adsorbed phase. We observe that for the neutral atom the binding energy of the shape resonance changes slightly on moving from the gas phase to the adsorbed phase, possibly indicative of a change in the bond length.⁵ We finally note that when CO is adsorbed on the Ni(001) surface all of the photoionization measurements move closer to the neutral atom measurements, indicating increased screening of the photo hole.

Finally, we note that in Fig. 2 the energy width of the shape resonance is less in the IPES experiment than in photoemission. This is probably a reflection of the elec-

TABLE I. Binding energies of the shape resonance for CO measured in the gas phase and following adsorption on the Ni(001) surface. e^- CO refers to resonant electron scattering in the gas phase and to the present IPES study for the adsorbed system. The gas-phase binding energies are referred to the vacuum level; the adsorbed phase to the Fermi level. The CO/Ni(001) work function is approximately 6 eV. References are indicated.

	Gas phase	Adsorbed CO/Ni(001)
e^- CO	19.5 eV ^a	24.0 eV
$(4\sigma^{-1})\text{CO}^+$	12.3 eV ^b	24.8 eV ^c
$(1\sigma^{-1})\text{CO}^+$	7.7 eV ^d	17.2 eV ^c

^aReference 15.

^dReference 14.

^bReference 13.

^cReference 4.

^cReference 10.

tron lifetime in the resonant state for the two different transitions.

In summary, we have observed for the first time to our knowledge the molecular shape resonance in an inverse photoemission experiment. This resonance serves as an initial state rather than a final state as it does in photoionization measurements. Comparison of the inverse photoemission results with earlier photoionization studies clearly shows how the effective potential affects the measured binding energy of the resonance. Finally, we make the observation, based on the present study, that in calculations of the photoionization cross section into the shape resonance for adsorbed molecules a ground-state or neutral-atom potential would appear to be more appropriate for valence-band excitation, whereas a positive ion potential would be better for core-level photoionization.

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