21. F. W. Benz, J. Feeney, G. C. K. Roberts, *J. Magn. Reson.* **8**, 114 (1972).
22. B. L. Tomlinson and H. D. W. Hill, *J. Chem. Phys.* **59**, 1775 (1973).
23. A. G. Redfield and R. K. Gupta, *ibid.* **54**, 1418 (1971).
24. B. R. Reid, N. S. Ribeira, L. McCollum, J. Abbate, R. E. Hood, *Biochemistry* **16**, 2086 (1977).
25. P. C. Lauterbur, *Appl. Spectrosc.* **24**, 450 (1970).
26. A. Allerhand, D. W. Cochran, D. Doddrell, *Proc. Natl. Acad. Sci. U.S.A.* **67**, 1093 (1970).
27. E. Oldfield, R. S. Norton, A. Allerhand, *J. Biol. Chem.* **250**, 6368 (1975).
28. S. J. Opella, D. J. Nelson, O. Jardetzky, *J. Am. Chem. Soc.* **96**, 7157 (1974).
29. D. T. Browne, E. M. Earl, J. D. Otvos, *Biochem. Biophys. Res. Commun.* **72**, 398 (1976).
30. W. E. Hull and B. D. Sykes, *J. Mol. Biol.* **98**, 121 (1975).
31. J. Horowitz, J. Ofengand, W. E. Daniel, M. Cohn, *J. Biol. Chem.* **252**, 4418 (1977).
32. J. Seelig and W. Niederberger, *J. Am. Chem. Soc.* **96**, 2069 (1974).
33. H.-U. Gally, W. Niederberger, J. Seelig, *Biochemistry* **14**, 3647 (1975).
34. B. D. N. Rao and M. Cohn, *J. Biol. Chem.* **252**, 3344 (1977).
35. W. Niederberger and J. Seelig, *J. Am. Chem. Soc.* **98**, 3704 (1976); R. G. Griffin, *ibid.*, p. 851; S. J. Kohler and M. P. Klein, *Biochemistry* **16**, 519 (1977).
36. A. Pines, M. G. Gibby, J. S. Waugh, *J. Chem. Phys.* **56**, 1776 (1972).
37. J. Urbina and J. S. Waugh, *Proc. Natl. Acad. Sci. U.S.A.* **71**, 5062 (1974); S. J. Opella, J. D. Yesinowski, J. S. Waugh, *ibid.* **73**, 3812 (1976).
38. C. T. Burt, T. Glonek, M. Bárány, *Science* **195**, 145 (1977).
39. R. B. Moon and J. H. Richards, *J. Biol. Chem.* **248**, 7276 (1973).
40. I. D. Campbell, C. M. Dobson, R. J. P. Williams, A. V. Xavier, *J. Magn. Reson.* **11**, 172 (1973).
41. P. C. Lauterbur, *Nature (London)* **242**, 190 (1975); A. Kumar, D. Welti, R. R. Ernst, *J. Magn. Reson.* **18**, 69 (1975).
42. W. P. Aue, E. Bartholdi, R. R. Ernst, *J. Chem. Phys.* **64**, 2229 (1976).
43. W. P. Aue, J. Karhay, R. R. Ernst, *ibid.*, p. 4226.
44. M. W. Hunkapiller, S. H. Smallcombe, D. R. Whitaker, J. H. Richards, *Biochemistry* **12**, 4732 (1973).

# Geometry of Adsorbates on Solid Surfaces

## Angle-resolved photoemission spectroscopy is a promising tool for obtaining structural information.

E. W. Plummer and T. Gustafsson

The last decade has witnessed a tremendous surge in the growth of surface science, with every indication that this growth will continue for many years (*1*). The interest and activity in the gas-solid interface can be attributed to the coincidence in time of at least three complementary factors. First, the last few years have witnessed the development of several experimental techniques potentially capable of characterizing a surface on a microscopic level. Second, societal pressures have forced many scientists to attempt a closer coupling between basic research and practical problems. Surface science seems at face value easier to relate to the needs of society than many other areas of basic research. For example, it is often argued that the concepts and information obtained from work on well-characterized, idealized surfaces can and will have an impact upon technologically important areas such as corrosion, catalysis, fabrication of microelectronic devices, and lubrication. Third, from a purely conceptual point of view a surface can be seen as a distinct phase of matter, with unique properties differing both from a three-dimensional periodic solid and from free gas molecules (*2*). Many scientists in solid state physics and molecular chemistry have been willing to try to apply the concepts and expertise they have developed to understand surface phenomena.

Among the many questions that one can ask about a surface, one seems important with respect to the motivation outlined above: "How does a foreign atom or molecule interact with and bond to a surface?" This question is far ranging since it encompasses both static bonding and the dynamics of adsorption and desorption. It is obviously the question most relevant to practical surface problems. At the heart of this question is the experimental determination of the geometrical arrangement of the atoms. The present dearth of structural information is, in our view, what is currently impeding progress in this field. Theory is of little help in this regard; it is the exception and not the rule that a calculation can predict the structure of a molecule or bulk solid. Even the calculational schemes that successfully pass this test may not work at a surface. Yet if one knows where the atoms are, many less sophisticated theories can be used, in conjunction with experimental data, to elucidate chemisorption mechanisms.

When a gas phase molecule strikes a surface it may bounce off, maintaining its molecular identity or it may interact more strongly, either bonding or undergoing a chemical reaction induced by the surface and reemerging in the gas phase as a different species. If it bonds to the surface we want to know where it bonded and then how it is bonded. Figure 1 illustrates schematically some possibilities for a carbon monoxide molecule. The molecule may stand straight up on either end, bend over or dissociate into one carbon and one oxygen atom. Either of these two atoms (or possibly both), may penetrate the metal surface, forming the initial stage of an oxide or a carbide. If we are going to understand the interaction of an atom or molecule with the surface we must develop experimental techniques to measure the geometrical configuration of the atoms.

For determining the geometrical structure of surfaces conventional techniques such as x-ray diffraction or high-energy electron scattering are of little use. The power of these techniques arises from the weak interaction of the probe with the sample, which makes analysis relatively simple. For surface problems we face a very different situation. If a single layer of atoms is adsorbed on a single crystal of dimension 1 cm by 1 cm by 1 mm, then the ratio of the number of adatoms to substrate atoms is less than one to a million. This means that we need a probe that is only sensitive to the surface. Such a probe must not penetrate more than a few tens of angstroms, a situation which occurs only when it interacts strongly. Neutrons or x-rays are weakly interacting, whereas low-energy electrons are strongly interacting. The price for these surface-sensitive probes is a much higher degree of complexity in the data analysis. Much of the theoretical effort in surface science has been devoted to calculating the response of the system to experimental probes (*3*).

---

Dr. Plummer is professor and Dr. Gustafsson is an assistant professor in the Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia 19104.

The early attempts to determine the geometry at a surface employed low-energy electron diffraction (LEED). This technique never quite lived up to the early expectation that it would become a routine analytic tool, that is, the surface analog of x-ray diffraction for determining structure. The reason for this has already been mentioned. The LEED technique is surface sensitive because the low-energy electrons strongly interact with the surface atoms. This makes the analysis of LEED very difficult. We should not forget that whatever structural information that has been obtained about surfaces has come almost exclusively from LEED. In the last few years we have learned to expect rather little from a single technique and to live with the fact that analysis of data to obtain geometrical information will be difficult. The information obtained from a variety of techniques may eventually be synthesized to place all the pieces of the surface together.

In this article we briefly describe the application of angular resolved photoelectron spectroscopy to the determination of the geometrical configuration of molecules and atoms adsorbed on a surface (*4*). The technique is still new and only a few systems have been studied. We nevertheless are optimistic about the possibilities of applying it to a wide range of systems. The results obtained so far are not astonishing; they have not in any way revolutionized our understanding of surfaces. Their importance is that they illustrate a procedure which can obtain detailed, and perhaps otherwise inaccessible, information about the bonding geometry of adsorbed molecules or atoms.

The origin of photoelectron spectroscopy is Einstein's famous 1905 paper explaining the photoelectric effect. The technique is in principle quite simple. The sample under study is illuminated by a beam of ultraviolet light (*5*) or x-rays (*6*). A photon is absorbed from this beam by the excitation of an electron in the sample. The photon gives up all of its energy to this electron. If the energy of this electron is high enough, it may escape from the sample, leaving behind a positive ion. This event is referred to as photoionization or photoemission. The incident light penetrates far into the solid, but the strong inelastic scattering of the excited electron by the sample limits the escape depth of the electron to ~ 10 Å or less. This means that the experiment observes only those electrons originating near the surface. If the incident beam of photons all have the same energy (monochromatic radiation), the kinetic energy of the photoemitted electron (photoelectron) can be related to the energy spectrum of the quantum states in the sample. Usually the electrons emitted over a large solid angle are collected so as to increase the signal strength. The quantity that is most often studied is the energy of various electronic states on clean or adsorbate covered surfaces. We can, for example, compare the spectrum of a molecule in the gas phase with the spectrum of the same molecule when it is adsorbed on a surface. If the two spectra are very different we may be confronted with a case where the molecule has lost its molecular identity and is dissociated.

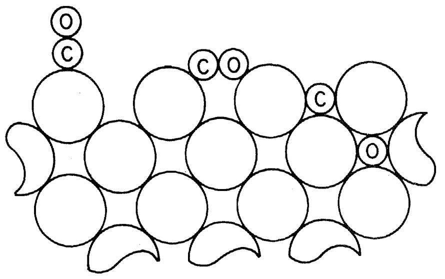


Fig. 1. Hard sphere model showing possible bonding configurations of CO bound to a surface. The sizes of the spheres were chosen to represent a nickel surface. This figure is a cross-sectional view perpendicular to the surface.

In angular resolved photoelectron spectroscopy only those electrons emitted in a given direction with respect to the sample and the direction of the photon beam are collected. By varying the photon energy and the angles, a set of spectra are obtained. This procedure is more difficult than the angle integrated one since the detector must be movable and the signal level is lower. Obviously, there is more information contained in a set of angular resolved photoemission spectra than in a single-angle integrated spectrum. This information has been used successfully to deduce the symmetry properties of quantum states of well-ordered solids (*7*) as well as randomly oriented gas phase molecules (*8*). It is clear that, if this technique is of value when studying randomly oriented molecules, it should yield much more useful information about the bonding symmetry of a molecule whose orientation has been fixed when it is bound to a surface.

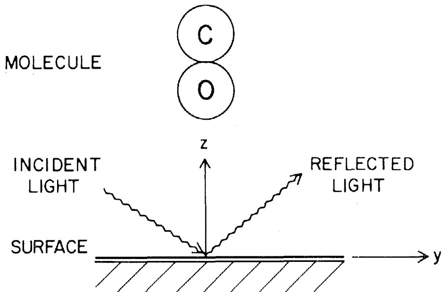


Fig. 2. Model of photoemission from a molecule of fixed orientation near a surface.

The problem is that we must have a realistic model that we can use to theoretically analyze the angular resolved photoemission data. At first glance this would seem to be even more difficult than the LEED problem. We must first understand the quantum state of the surface plus the adsorbed molecule from which we will photoeject the electron. Next, we must investigate the quantum state of the excited electron. Finally, we must know the strength of the coupling between these two states. However, we will show that we can simplify the analysis by singling out those components of the photoemission process that are most crucial and treating the others in an approximate manner.

We will begin by considering molecular (nondissociative) adsorption, using the simple model shown in Fig. 2 to analyze the data. In this model we assume that the surface plays only two roles. (i) It fixes the orientation of the molecule. Some of the quantum states of the molecule will be changed on adsorption, but others will not. We have to be able to isolate those states that do not take part in the bonding. (ii) The surface partially reflects the incident light beam, creating a standing wave field at the surface. This picture of photoemission from an adsorbed molecule (Fig. 2) places all of the emphasis on understanding the photoemissive properties of the isolated molecule. An advantage is that calculations can be checked in detail by comparison with gas phase data before they are applied to the adsorbed configuration. We believe that this model is a reasonable starting point because molecules maintain a substantial part of their photoemission identity when adsorbed on a surface. There is growing theoretical and experimental evidence that the chemisorption bond at a surface is very localized (*1*), which implies that our simple localized model could be expanded to include a few of the surface atoms in the molecule and then possibly yield detailed information about the bonding.

Adsorption of carbon monoxide (CO) on transition metal surfaces has been used as a test case to evaluate the validity of the model shown in Fig. 2. The photoionization cross sections from several quantum states of CO have been measured (*9*) and calculated (*10*) as a function of photon energy. It suffices for the purpose of this article to say that the calculations (*9*) for randomly oriented CO molecules were in remarkable agreement with the experimental data for gas phase CO. Given the fact that we now have some confidence in the theoretical procedure, we can, in the calculation, freeze out the molecular rotation and calculate the angular dependent emission from a molecule with a fixed orientation. It is this angular distribution from a molecule of fixed orientation on the surface that we will use to determine the orientation of the molecule. Figure 3 shows the photoemission pattern for two different quantum states of the CO molecule for three different orientations of the molecule relative to the direction of the exciting electric field. We have chosen these two quantum states because they are not involved in the bonding of CO to the surface. The differential photoionization cross section is just the probability that a photon will be absorbed and an electron will be emitted in a specific direction with a kinetic energy appropriate for the quantum state being considered. Therefore the plots, which we have labeled "the photoemission pattern," illustrate the relative intensities one would measure as the angle of detection is changed.

The $1\pi$ molecular orbital of neutral CO contains four electrons and is partially responsible for the bonding between the carbon and the oxygen atoms in CO. Row 3 of Fig. 3 shows the angular distributions for removing one of these four electrons from the $1\pi$ state of CO using 21-ev photons. The minimum energy required to remove an electron from this state is approximately 17 ev; therefore in this case, the outgoing electron has approximately 4 ev of kinetic energy. The photoemission pattern for the randomly oriented gas phase molecule is shown in column a. It is nearly isotropic with a slight elongation in the $y$ direction, that is, along the electric field direction. When the orientation of the molecule is fixed, the photoemission patterns become quite anisotropic and very dependent on the orientation of the molecule with respect to the direction of the exciting electric field. For the $1\pi$ state of CO at a photon energy of 21 ev, the largest signal would be measured when the exciting electric field is perpendicular to the axis of the molecule and the electrons are being collected in the same direction. The cross section in this geometry of collection is approximately 3.5 times larger than for the corresponding case of a randomly oriented molecule. On the other hand, when the molecule is rotated so that the electric field is parallel to the molecular axis (column c) the probability for exciting an electron from the $1\pi$ state is diminished considerably. Symmetry arguments show that for this geometry the emission is identically zero along the molecular axis.

The emission patterns for another quantum state of CO are shown in row 4 of Fig. 3. This molecular orbital of CO is called the $4\sigma$ state. The electrons in this state are mainly centered on the oxygen end of the molecule. A minimum energy of approximately 20 ev is required to remove one of the two electrons from this state. The emission patterns shown in Fig. 3 are for photoexcitation of an electron using 41-ev photons, so these electrons leave the molecule with a kinetic energy of $\sim$ 21 ev. There is a striking difference between the emission patterns for this $\sigma$ state compared to the $\pi$ state. The (angle averaged) gas phase cross section for the $\sigma$ state is approximately five times smaller than the equivalent cross section for the $\pi$ state and is slightly more anisotropic. Yet, even with the large overall decrease in average cross section the emission for one specific geometry can be as large as any from the $1\pi$ state. For a $\sigma$ state, in contrast to a $\pi$ state, this maximum emission occurs when the exciting electric field is parallel to the axis of the molecule (column c). One remarkable property of this state is that the emission is not equally shared between both ends of the molecule. Five times more emission originates from the oxygen end than from the carbon end. One final feature of the emission from a $\sigma$ state of a diatomic molecule should be pointed out here, since it will prove useful in determining the orientation of a CO molecule bound to a surface. Simple symmetry arguments show that, when the exciting electric field is perpendicular to the axis of the diatomic molecule, there can be no emission in the plane perpendicular to the electric field (*11*). Column b for the $4\sigma$ state illustrates this effect.

In Fig. 3 we have illustrated two important effects: the angular dependent emission depends (i) on the symmetry of the initial quantum state of the electron ($\sigma$ as compared to $\pi$) and (ii) on the orientation of the electric field. A third factor is described more fully below: when we change the photon energy, we also change the kinetic energy of the outgoing electron. This can have extremely dramatic effects on the angular patterns.

The identification of the quantum states of CO adsorbed on a surface as well as the determination of the bonding geometry would seem to be straightforward when angle resolved photoemission data and the calculations shown in Fig. 3 are used. For example, we could conceive of fixing the collection angle at 90° with respect to the exciting electric field (polarized light) and moving the surface with respect to the collector, look-

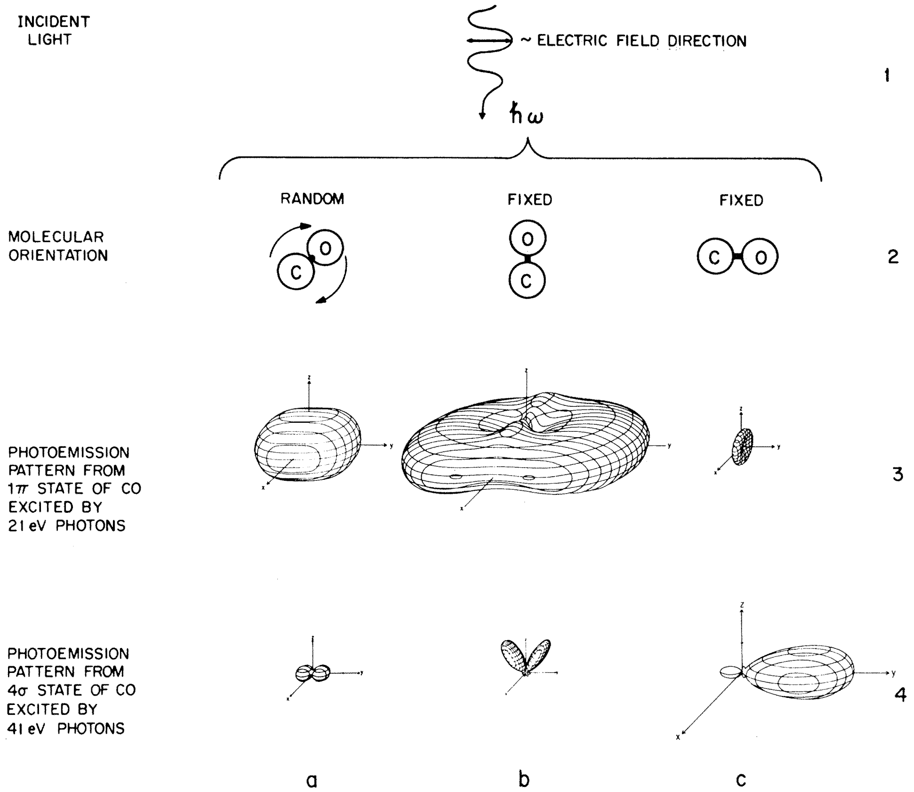


Fig. 3. Differential photoemission cross sections for excitation from two different quantum states of the CO molecule for various orientations with respect to the exciting electric field. Row 1 shows the field direction, row 2 the orientation of the molecule, while rows 3 and 4 are the resulting "photoemission patterns" for the $1\pi$ and $4\sigma$ quantum states, respectively.

ing at the 4σ level, until we find the null predicted when the electric field is perpendicular to the molecular axis. Alternatively, we could fix the detector parallel to the electric field and again move the surface orientation until one sees a maximum in the signal. This would correspond to having the electric field parallel to the axis of the molecule, with the oxygen end pointing at the detector (Fig. 3, row 4, column c).

Some caution should be exercised. There are many reasons why such a simple procedure is unsuitable and may even lead to erroneous results. One such reason is shown schematically in Fig. 2. The surface reflects and transmits the incident light, creating a standing wave field at the surface. The direction and magnitude of the field at the surface is given by the optical properties of the material in combination with the direction and magnitude of the incident electric field. This means that the experimenter does not have full control over the direction and the intensity of the exciting electric field. Another complication arises from the neglect in the calculations of another role that the surface plays. While some electrons from the molecule will go directly toward the detector, others will first be heading away from the detector into the surface. Here they may be back-reflected. This backscattered beam may interfere with the direct beam. While, as mentioned above, the agreement between theory and experimental result is considered good for the angle-averaged gas phase cross sections, it is hardly perfect. This means that one cannot put too much credence on small features in the angular cross sections.

What we should be looking for is, then, some particular feature in the angular distribution from a molecule which is so strong that it can be safely assumed to relegate these complications to second-order effects, which are interesting but not crucial to a determination of the geometry. Such strong features can arise as a result of what are commonly referred to as shape resonances. The cross section is a strong function of the kinetic energy of the electron. The most drastic effects occur when the kinetic energy of the emitted electron coincides with the energy of a scattering resonance in the molecule. This occurs when the excited electron has the correct energy to be temporarily trapped in a virtual bound state of the molecule. These virtual bound states in the continuum have a specific symmetry, and thus there are selection rules that dictate which initial quantum states of the molecule can be excited by a photon into them.

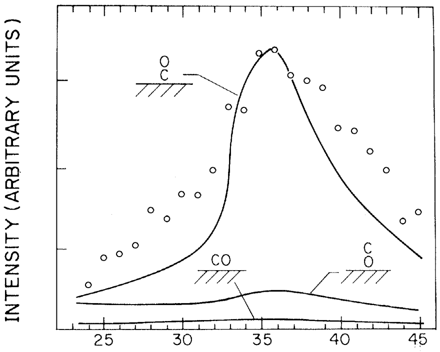


Fig. 4. Comparison of the photon energy dependence of the emission from the 4σ quantum state of CO adsorbed on Ni (100) (*13*) with calculations of molecules with different orientations (*10*). The data are for normal emission.

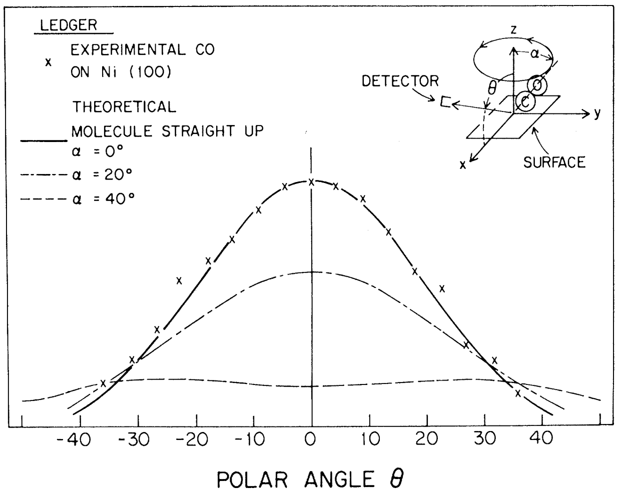
For CO, these resonance effects are dramatic and specific to the alignment of the molecule with respect to the surface. Such a resonance occurs in CO at ~ 15-ev kinetic energy (*10, 12*). It is a shape resonance, meaning that it is a virtual bound state in an angular momentum barrier. This virtual state has σ symmetry (*12*). Therefore, the 4σ state can be excited to the resonant state only by an exciting electric field parallel to the molecular axis. This means that the effects of the resonance will only be seen in the photoemission pattern with the molecular orientation shown in Fig. 3, row 4, column c. The calculation for the resonance shows that the increased emission is strongly axial in nature, focused out of the oxygen end of the molecule (*10*). This beam of extra intensity hence acts almost like a searchlight.

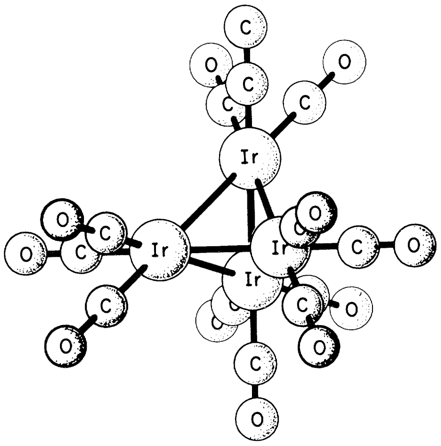
In Fig. 4 the measured intensity from the 4σ level of CO adsorbed on a nickel (100) surface with the detector normal to the surface is plotted as a function of photon energy (*13*). The resonance state produces a four- to fivefold increase in the photocurrent for photon energies near 36 ev. The three solid curves are the calculated cross sections for this detection geometry assuming the CO molecule is (i) standing straight up, with the carbon end down, (ii) lying flat on the surface, and (iii) standing straight up, with the oxygen end down. The comparison of these calculated cross sections with the experimental data determines the bonding configuration as carbon end down. Figure 4 shows how easy it is to determine that the oxygen end of the molecule is sticking out from the surface. The argument that the resonance only occurs when the exciting field is parallel to the molecular axis can be used as another check to prove that the molecule is standing straight up. If the exciting electric field is in the plane of the surface, the resonant emission from the 4σ level should vanish for all collection angles. Therefore, if any sign of the resonance is seen with this orientation of the field, the molecule is bent with respect to the surface normal (*14, 14a*).

Having established that the molecule is bound with the carbon end down, we then try to determine more accurately the angle between the molecular axis and the surface normal. In Fig. 5 we show the measured intensity from the 4σ level as a function of the angle of collection with respect to the surface normal. The incident light is 45° from the surface normal and the electric field is in the *yz* plane (the plane of incidence) in Fig. 2. The plane of the measurement is carefully chosen to be the plane perpendicular to the plane of incidence. The calculation shows that this plane is very sensitive to the detailed alignment of the CO molecule. In Fig. 5 the data (*13*) are compared with the calculation (*10*) for a CO molecule with various angles of bend (α) with respect to the surface normal. Since there is no reason to believe that the molecule should prefer to be tilted in a specific direction, the theoretical curves were obtained by averaging over all molecular orientations on a cone of angle α. For this collection geometry, the cross sections will be symmetric about the normal to the surface. It is immediately obvious from Fig. 5 that the predicted angular profile for a molecule with a 40° bend is qualitatively different from the data. Conversely, the predictions for a molecule with no bend at all are in excellent agreement with the data. It seems clear that the molecule is bound with its axis along the surface normal. The uncertainty in the determination can be estimated by comparing the full width at half maximum (FWHM) of the experimental curve with the calculated ones. The measured FWHM is 45° ± 2°, while the corresponding theoretical numbers are 44.5° for $\alpha = 0°$, 46.4° for $\alpha = 10°$, 53° for $\alpha = 20°$, and 73° for $\alpha = 30°$. With the present data we can say that the molecule is within 10° of the normal. This result is quite reasonable on chemical grounds. Indeed, by applying simple chemical reasoning it has for a long time been assumed that this is the bonding geometry of CO on transition metals. The data discussed above provide direct physical evidence for these plausibility arguments.

The adsorption of CO on a nickel surface has been used as a test case for this localized approach to photoemission from a surface molecule. It is not surprising that we concluded that the geometry was what chemical intuition would have suggested. The adsorption of nitric oxide

Fig 5 (left). Comparison of the measured angular dependent emission from the 4$\sigma$ quantum state of CO adsorbed on Ni (100) with calculations for various orientations. The angle is measured from the surface normal in a plane perpendicular to the incident light direction. Fig. 6 (right). Model of a multimetal carbonyl complex, $Ir_4(CO)_{12}$.





(NO) on a nickel surface is quite a different case. The NO bonds to metal atoms in organometallic complexes in a variety of ways. In the cases where NO is terminally bonded, the angle of the NO axis with respect to the nitrogen metal bond axis ranges from 0° to 60°. Therefore, this is an example where "chemical intuition" does not give the answer prior to the measurements. Nitric oxide is similar to CO in that the initial states have the same symmetry notation and approximately the same excitation energies. Experimental data and theoretical calculations show that a final state scattering resonance of $\sigma$ symmetry exists in NO, just as it did in CO (*15*).

The determination of the bonding orientation of NO adsorbed below −100°C on Ni (100) followed the same procedure as outlined above for CO adsorbed on a nickel surface (*15*). The first measurement was the photon sweep with the exiting electric field parallel to the surface. If the molecule is standing straight up with respect to the surface, symmetry arguments prohibit the excitation of a 4$\sigma$ electron into the $\sigma$ symmetry final state resonance, and consequently no resonance should be observed. Experimentally a strong resonant peak in the cross section for the 4$\sigma$ state of NO is observed near 35-ev photon energy. Consequently, we can conclude immediately that the molecular axis of NO is bent with respect to the surface normal. We are still comparing theoretical predictions with data for this system, but the present determination is that the angle is approximately 30°.

So far very little consideration has been given to the technical aspects of these experiments. The orientation of the sample should be adjustable relative to the direction of the light beam. It is clear that a movable photoelectron detector of great flexibility is necessary. Since only a small fraction of all photoelectrons are emitted into the angle of observation, a source of ultraviolet light of high intensity is also required. This wavelength range is beyond the reach of lasers. The most common light source is instead resonance radiation from noble gas discharge lamps. But only a few strong lines are available in the photon energy range between 20 and 100 ev. The last few years have, however, seen a very large surge in the utilization of synchrotron radiation for various spectroscopic experiments (*16*). This is the radiation emitted from relativistic electrons when they are accelerated. For our purpose this light source is almost ideal; not only is it intense, it is also continuous in wavelength and, if the accelerating device is an electron storage ring, very stable. In addition, this radiation is polarized, providing great advantage in these studies (Fig. 3). Its disadvantage is that a storage ring, which is obviously costly, and a monochromator are needed. The experimental flexibility provided by the continuous and polarized light source more than offsets these drawbacks; for example, the resonance shown in Fig. 4 could not have been detected with conventional sources. In our opinion, synchrotron radiation is indispensable for these types of measurements.

There are three remaining questions about the applicability of angle resolved photoelectron spectroscopy for determining the geometrical structure of adsorbed species: (i) How general is the approach for determining the orientation of other and bigger molecules? (ii) Can this approach be applied to determining the geometrical arrangement of the adsorbed species with respect to the substrate atoms? (iii) Will the analysis of angular resolved photoelectron spectra become so straightforward that the technique can be applied routinely?

The answer to the first question is that this approach seems applicable to any molecule. The limitation is that we must understand the photoemission properties of the isolated molecule, and this may become more difficult for larger molecules. Angular resolved spectra from CO adsorbed on several transition metal surfaces have been reported (*13, 14a, 17, 18*), and these data have been interpreted in terms of a localized molecular model. We have already discussed the case of NO adsorption, and presumably the molecular orientation of molecules like $H_2O$ and $CO_2$ can and will be determined.

We cannot at this time give a definitive answer to the second question concerning the determination of the bonding geometry of the adsorbed species with respect to the substrate. Yet the preliminary prognosis would appear to be quite optimistic as discussed below.

If angular resolved photoemission is to be used to determine the site geometry of an atom or molecule with respect to the surface atoms, we must look at those quantum states of the system that depend on the geometrical arrangement. In the photoemission process, this could arise either from the involvement of the initial state in the bonding or from the fact that the excited electron is scattered from the substrate atoms before reaching the detector. Let us consider first the case of the bonding orbitals of an adsorbed atom or molecule. In our localized picture of photoemission, it is necessary to ascertain whether a molecule containing only a few of the substrate atoms with the foreign atom or molecule bound to them will be an appropriate model for the semi-infinite solid. This question is amenable to experimental resolution, especially for CO adsorption. Various multimetal transition metal complexes are available, and their geometries are known from x-ray diffraction studies (*19*). One such multimetal carbonyl, namely $Ir_4(CO)_{12}$, is shown in Fig. 6. The metal-metal and metal-CO

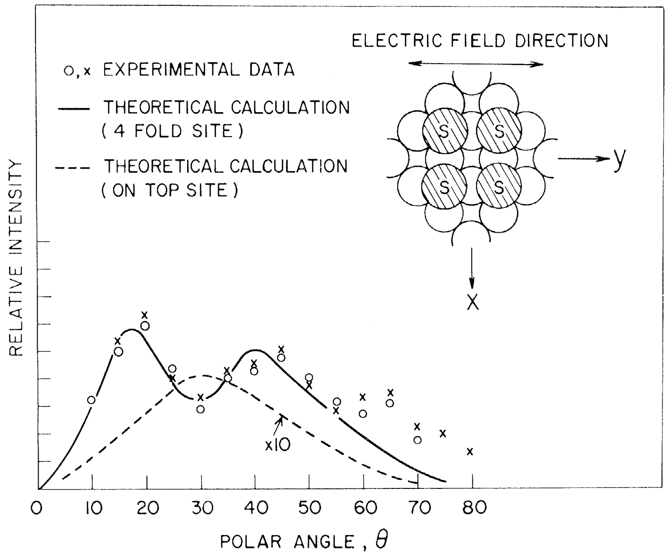


Fig. 7. Calculated and measured photocurrent from the sulfur-derived $p_z$ orbital as a function of the polar collection angle for sulfur adsorbed on Ni (100) in a $c(2 \times 2)$ configuration. The exciting photon energy is 21 ev and the electric field is in the $y$ direction. The inset shows the known bonding configuration for sulfur on Ni (100). The solid theoretical curve is for the correct geometry while the dashed curve is for a sulfur atom bound directly above the substrate Ni atom.

bonds in these complexes are believed to be very similar to the bonds that are encountered when CO is adsorbed on a corresponding metal surface (*14a*, *17*).

A comparison of both the ultraviolet and x-ray induced photoelectron spectra obtained from a large variety of transition metal carbonyl complexes with the spectra obtained from CO adsorbed on a transition metal surface supports the localized picture of the bonding (*20*). The photoelectron spectrum of a three- or four-metal atom complex is almost identical to the spectrum of CO adsorbed on a surface. This statement applies both to the quantum states of CO that are involved in the bonding to the metal, as well as to those states like the $4\sigma$ state, that are not involved in the bonding. These findings are very encouraging and indicate that, if we can theoretically understand the photoemission from these complexes, we can use this information to determine how and where a molecule is bound to the transition metal surface. The major reservation about the implication of the carbonyl results is that, even though the energy of each quantum state is the same for a multimetal carbonyl complex as for CO adsorbed on a surface, the details of the angular dependent emission may not be the same. The scattering effects on the photoexcited electron may not be so localized. Since the escape depth of this excited electron is only ~ 10 Å, there is good reason to believe that the localized model may work.

The best evidence available that illustrates the capabilities of determining the bonding configuration of atoms adsorbed on a surface is for the adsorption of sulfur on the (100) face of a nickel crystal. This system has been extensively investigated by means of low-energy electron diffraction (*21*) so that the geometry is now known. Sulfur is bound in the fourfold site shown by the inset in Fig. 7. Therefore, we view this system as a test case for angular resolved photoelectron spectroscopy. The measured intensity from the $p_z$ derived sulfur orbital when sulfur is bound to a nickel crystal (*22*) is shown in Fig. 7. Two theoretical curves are also shown in Fig. 7 (*23*). The solid curve is for the known geometry, and the dashed curve is for a geometry where the sulfur atoms are bound directly on top of the nickel surface atoms. The solid curve is compared to our measurements as a function of the collection angle with respect to the surface normal in the $yz$ plane. The incident light is 21 ev and polarized in the $y$ direction. The initial state was calculated from a localized cluster of five nickel atoms and one sulfur atom, while the final state was calculated by use of the formalism developed for calculations of dynamical low-energy electron diffraction. The agreement between the calculation and data for the proper geometry is excellent, and the calculation for the incorrect geometry clearly illustrates the sensitivity of this technique to the site geometry. Still unresolved is the question of whether a localized final state (excited electron) would produce such good agreement between theory and experiment.

We now address the third question concerning the routine applicability of this technique. On the basis of the experience we already have it seems safe to assume the next few years will be very exciting. We undoubtedly will learn many new details about the bonding of foreign atoms and molecules to a surface. The problem is that at present each adsorbed species has to be treated separately; a very close coupling between theory and experiment is essential. What is needed are generalized rules based on the symmetries of the initial state and the electric field with respect to the direction of detection. We illustrated several of these rules for diatomic molecules and new rules are emerging for adsorbed atoms (*24*). Once such rules have been developed, determination of site geometry should become a nearly routine experimental operation, without the need for detailed numerical calculations. Determination of bond lengths, however, will always rely on comparison to such calculations. The ultimate accuracy will have to be tested on systems like sulfur on Ni (100), where the bonding geometry is known. Finally, it should be pointed out that, if the essential features of the angular resolved photoemission patterns are dictated by the local geometry, then this technique will not be restricted to systems with long-range order.

### References

1. For an overview, see, for example, the April 1975 issue of *Phys. Today*.
2. H. D. Hagstrum, *Science* **178**, 275 (1972).
3. P. J. Estrup in (*1*), p. 1; T. N. Rhodin and D. S. Y. Tong, *Phys. Today* **28**, 23 (1975); F. Jona and P. M. Marcus, *Comments Solid State Phys.* **8**, 1 (1977).
4. A. L. Robinson, *Science* **196**, 1306 (1977).
5. D. E. Eastman and M. I. Nathan in (*1*); C. N. Berglund and W. E. Spicer, *Phys. Rev. A* **136**, 1030 (1964).
6. K. Siegbahn *et al.*, *Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy* (Uppsala, 1967).
7. N. V. Smith and M. M. Traum, *Phys. Rev. B* **11**, 2087 (1975) and numerous other papers by the same authors.
8. T. A. Carlson, G. E. McGuire, A. E. Jonas, K. L. Cheng, C. P. Anderson, C. C. Lu, B. P. Pullen, in *Electron Spectroscopy*, D. A. Shirley, Ed. (North-Holland, Amsterdam, 1972), p. 207.
9. E. W. Plummer, T. Gustafsson, W. Gudat, D. E. Eastman, *Phys. Rev. A* **15**, 2339 (1977).
10. J. W. Davenport, *Phys. Rev. Lett.* **36**, 945 (1976); personal communication.
11. A. Liebsch, *Phys. Rev. B* **13**, 544 (1976).
12. J. L. Dehmer and D. Dill, *Phys. Rev. Lett.* **35**, 213 (1975).
13. C. L. Allyn, T. Gustafsson, E. W. Plummer, *Chem. Phys. Lett.* **47**, 127 (1977).
14. Symmetry rules can be quite powerful in photoemission, see for example, H. Becker, E. Dietz, U. Gerhardt, H. Angermuller, *Phys. Rev. B* **12**, 2084 (1975); J. H. Hermanson, *Solid State Commun.* **22**, 9 (1977).

14a. G. J. Lapeyre, R. J. Smith, J. Anderson, *J. Vac. Sci. Technol.* **14**, 384 (1977).

15. G. Loubriel, personal communication.
16. E. M. Rowe and J. H. Weaver, *Sci. Am.* **236** (No. 6), 32 (1977); I. Lindau and H. Winick, *Comments At. Mol. Phys.* **6**, 133 (1977); E. E. Koch, C. Kunz, B. Sonntag, *Phys. Rep.* **29**, 155 (1977).
17. R. J. Smith, J. Anderson, G. J. Lapeyre, *Phys. Rev. Lett.* **37**, 1081 (1976); G. Apai, P. S. Wehner, R. S. Williams, J. Stöhr, D. A. Shirley, *ibid.*, p. 1497.
18. D. E. Eastman and J. E. Demuth, *Jpn. J Appl. Phys.* (Suppl. 2, part 2) (1974), p. 827; J. C. Fuggle, M. Steinkilberg, D. Menzel, *Chem. Phys.* **11**, 307 (1975); G. Broden and T. N. Rhodin, *Solid State Commun.* **18**, 105 (1976); P. M. Williams, P. Butcher, J. Wood, K. Jacobi, *Phys. Rev. B* **14**, 3215 (1976); D. R. Lloyd, C. M. Quinn, N. V. Richardson, *Solid State Commun.* **20**, 409 (1976).
19. E. L. Muetterties, *Science* **196**, 839 (1977).
20. E. W. Plummer, W. R. Salaneck, J. S. Miller, personal communication.
21. J. E. Demuth, D. W. Jepsen, P. M. Marcus, *Phys. Rev. Lett.* **31**, 540 (1973).
22. E. W. Plummer *et al.* in preparation.
23. S. Y. Tong, C.H. Li, A. R. Lubensky, *Phys. Rev. Lett.* **39**, 498 (1977).
24. M. Scheffler, K. Kambe, F. Forstman, *Solid State Commun.*, in press.