

Vibrational Bands in the Photoemission of an Adsorbate: O₂ on Graphite

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(Received 18 August 1981)

Photoemission spectra of O₂ physisorbed at 10 K on graphite exhibit vibrational structure in the 2 π band. With the assumption of a Morse potential the potential for the physisorbed ion can be calculated, which is slightly steeper than in the gas phase resulting in a higher vibrational frequency. The difference in equilibrium distance between the ion and the neutral molecule is reduced by about 20% compared to the free molecule.

PACS numbers: 79.60.Gs, 34.20.-b, 73.90.+f

We here report the first measurements showing vibrational structure in the photoemission of an adsorbate. The observation of vibrational structure in photoemission differs qualitatively from other techniques usually used like electron energy loss or infrared spectroscopy for two reasons. First, we gain information about the vibrational excitation of the corresponding molecular ion on the surface that is created in the photoionization process and second, we observe strong multiple-phonon excitations, an analysis of which allows us to calculate the vibrational potential for the adsorbed ion directly from the spectroscopic information.

Phonon contributions to the linewidth of core levels in bulk solids have been discussed theoretically earlier,¹⁻³ and recently theory has been extended to adsorbates.⁴ Experimentally, we here present the first data where vibrational structure can be observed in the photoemission of an adsorbate. Earlier experimental work only explains in general the much larger width of adsorbate levels compared to gas-phase molecules as being partially due to a smeared-out Franck-Condon envelope of the vibrational spectrum.^{5,6} From these earlier measurements it is, however, impossible to gain any specific vibrational information.

The experiments were performed at the Synchrotron Radiation Center of the University of Wisconsin using a toroidal grating monochromator⁷ and a commercial double-pass cylindrical-mirror electron analyzer (PHI model 15-255). O was adsorbed onto highly oriented pyrolytic graphite (HOPG) cleaved *in situ* in UHV and directly glued onto a He Dewar. The temperature of the HOPG was less than 10 K during the mea-

surements and the adsorption. This was verified by the fact that we were able to adsorb a thick layer of molecular hydrogen onto the surface. The pressure of the system during the experiment was around 5×10^{-11} Torr, except during gas exposure. Thus we were able to keep our sample free of contaminants for more than 1 h even at these low temperatures.

The phase diagram of O₂ on graphite is rather complicated and the data are controversial as deduced from neutron scattering,⁸ specific-heat studies,⁹ and x-ray diffraction.¹⁰ At our sample temperatures and coverages we essentially encounter only two different phases. The transition occurs when more than one monolayer is adsorbed, which is at a nominal coverage of 1.7 to 1.9 measured in $\sqrt{3} \times \sqrt{3}$ monolayers since O₂ is not in registry with the substrate.^{8,10} Moreover, besides the existence of a phase boundary there is still some disagreement about the exact nature of the phases.

Figure 1 shows photoemission spectra for the low- and high-coverage phases of O₂ on graphite compared to a gas-phase x-ray photoemission spectroscopy (XPS) spectrum.¹¹ Graphite is a rather weak photoemitter and the photoelectron energy distributions shown in Fig. 1 resemble essentially the adsorbate-derived signal. Only the structure at an initial-state energy of about 3 eV and the generally broad, relatively weak structural background are attributed to the intrinsic graphite emission. The gas-phase spectrum has been shifted in energy to give the best alignment of the observed peaks. For exposures of less than 2.5 langmuirs (1 L = 10^{-6} Torr sec) we observe photoemission characteristic of the emission of a single layer of oxygen molecules.

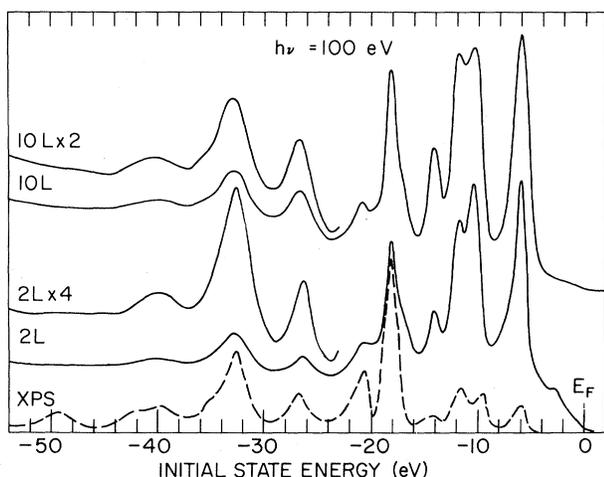


FIG. 1. Photoemission of O_2 adsorbed onto graphite at 10 K for monolayer (2 L) and higher coverage (10 L). The spectra are compared to a gas-phase XPS spectrum (Ref. 11).

O_2 is clearly physisorbed as judged from the similarity between gas phase and adsorbate spectrum. Especially, the O_2 2π level does not show any bonding shift as could be expected for a chemically bound species. The levels display an extramolecular relaxation shift of 1.1 eV,^{12, 13} or 1.9 eV,¹¹ comparing the adsorbate level binding energies to the gas-phase ionization energies. The thick O_2 layer (10-L exposure) shows a uniform reduction of the extramolecular screening by 0.4 eV and therefore a higher observed binding energy for all levels. This was not unexpected and has been observed for different adsorbate-substrate systems earlier.¹⁴ The peaks are also broadened compared to the single-layer adsorption. Certainly these photoemission results cannot distinguish at present between the subtle differences of the phase-diagram measurements. Also the differences between the gas-phase spectrum and the adsorbate spectrum will be discussed elsewhere.¹⁵

Figure 2 shows a high-resolution scan in the region of the O_2 2π emission. The combined resolution of monochromator and analyzer is better than 100 meV. We have chosen to fit the experimental spectrum with five Gaussian or Lorentzian functions because the spectra obtained from free O_2 molecules also show five distinct vibrational excitations.¹² These five peaks result from an electronic transition from the O_2 ground state ($X^3\Sigma_g^-$) into the ground state of the O_2^+ ion ($X^2\Pi_g$), which corresponds to a removal of a 2π electron, and simultaneously a

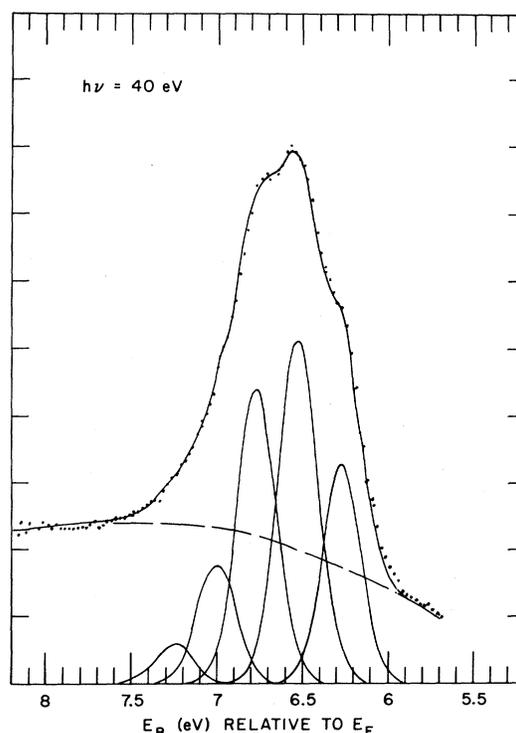


FIG. 2. High-resolution O_2 2π photoemission for sub-monolayer coverage on graphite. The actual data points are shown together with a convolution into five Gaussian functions of equal half-width [full width at half maximum (FWHM) = 280 meV] and a smooth background polynomial (dashed). The sum of the background functions plus the five Gaussian curves gives the smooth line going through the data points.

vibrational transition into one of the five lowest vibrational levels of O_2^+ ($X^2\Pi_g$). In the initial state only the $v=0$ vibrational level is occupied at our temperatures (10 K). The 2π electron is anti-bonding; therefore the equilibrium distance of the O nuclei is reduced from 1.21 Å for O_2 to 1.13 Å for O_2^+ .¹⁶ Vibrational sidebands in photoemission can only be observed when the equilibrium internuclear distance changes under the electronic transitions. Otherwise there is negligible overlap between the initial- and final-state vibrational functions for transitions different from $0 \rightarrow 0$. Therefore the relative intensity of the vibrational sidebands tells us the change in internuclear distance.

These relative intensities are independent of photon energy, unless the particular ionization channel is perturbed by final-state resonances or autoionization. For the electronic transition from the O_2 ground state $X^3\Sigma_g^-$ into the ionic ground state $X^2\Pi_g$ which we have studied here, there is

no indication of anomalies in the cross section between $h\nu = 20$ and 50 eV.^{17,18} Therefore we can compare the relative intensity of the vibrational sidebands of our spectra, taken at 40-eV photon energy, to gas-phase spectra, taken with 21.2-eV photons.¹² Qualitatively we can see directly that the 0-0 vibrational transition is more intense for the adsorbate than in the gas phase, whereas the higher transitions 0-3 and 0-4 are clearly weaker in the adsorbed layer. This leads us to the conclusion that the internuclear equilibrium distance changes less for the adsorbate.

We have calculated the Franck-Condon factors for two harmonic oscillators of different vibrational frequency as a function of the change of the internuclear equilibrium distance. The choice of harmonic oscillators instead of anharmonic ones, which would be more accurate, allows us to integrate the overlap matrix elements analytically rather than numerically. From a comparison between our calculated Franck-Condon factors we conclude that the internuclear equilibrium distance changes by about 20% less in the case of the adsorbed molecule than in the gas phase. In absolute numbers this means that the equilibrium distance decreases by 0.08 \AA for O_2 in the gas phase upon removal of a 2π electron, whereas on the graphite surface the corresponding change is only 0.065 \AA . Naturally this could mean that either the neutral molecule has a different equilibrium distance upon adsorption on graphite or the ion or both.

The second piece of information that we obtain from these data is the actual molecular potential of the adsorbed O_2^+ ion. Analyzing the energy separation of the vibrational sidebands, we get the basic vibrational frequency as well as the degree of anharmonicity. Assuming a molecular potential of the form

$$V(R) = D\{1 - \exp[-a(R - R_0)]\}^2 \quad (1)$$

as originally proposed by Morse,¹⁹ we get the exact solutions of an anharmonic oscillator with energy eigenvalues given by

$$E_n = \hbar\omega_0\left(n + \frac{1}{2}\right) - (\hbar\omega_0/4D)\left(n + \frac{1}{2}\right)^2. \quad (2)$$

D is the dissociation energy and $\hbar\omega_0$ is the basic oscillator frequency related to the parameter a in the potential by

$$\omega_0 = (a/2\pi)(2D/\mu)^{1/2}, \quad (3)$$

where μ is the reduced mass of the system. Using Eq. (2) and the energy values of the vibrational bands we can calculate the molecular potential for the adsorbed O_2^+ ion. Depending on whether we fit our data by Gaussian or Lorentzian functions we get a slightly different answer, the details of which are summarized in Table I. We list the extreme parameter values given by a fit with either Gaussian or Lorentzian functions. Since the actual line shape should be a composition of both we get a feeling for the error limits of our fitting procedure. We were not very successful in determining the dissociation energy D .

TABLE I. Parameters of the vibrational structure observed in the O_2 2π photoemission.

	v	Measured intensity ^a	Energy ^a (meV)	D (eV)	$\hbar\omega_0(\text{O}_2^+)$ (meV)	Peak width (meV) FWHM
Gas phase	0	1	0			
	1	2.3	220			50
	2	2.1	440	6.48	221	(resolution limited)
	3	0.9	655			
	4	0.3	865			
Adsorbed (Gaussian)	0	1	0			
	1	1.6	250			
	2	1.4	500	6.5	254	278
	3	0.54	740			
	4	0.16	980			
Adsorbed (Lorentzian)	0	1	0			
	1	1.6	240			
	2	1.4	470	8.4	241	318
	3	0.46	690			
	4	0.15	930			

^aRelative to 0-0 peak.

Observing only the five lowest vibrational states, we are only sensitive to the potential around its minimum. Typical values obtained are 6.5 to 8.5 eV, but also in one attempt we got a much higher value. The significantly higher basic oscillator frequency of the adsorbed ion compared to the gas-phase ion (247 vs 220 meV), however, clearly indicates that the potential of the adsorbed ion has to be steeper, which can be attributed to the additional interaction with the substrate.

If we deposit more than a monolayer we are unable to detect any vibrational substructure in the photoemission of O₂ adsorbed on graphite. Moreover, the peaks are substantially broader than for the adsorbed monolayer. This additional broadening could be caused by inhomogeneities in the layers or by a shift of the binding energy in the second or third layer due to the different screening. Also the vibrational spectrum of the O₂ molecule should change into the phonon spectrum of solid O₂, which might be unresolved.

The linewidth of the vibrational sidebands is surprisingly large (280 meV) for the adsorbed monolayer. In the gas phase the 2 π hole has essentially infinite lifetime since it is in the highest occupied orbital. This is not so for the adsorbed layer. Here the hole can decay via an interatomic Auger process involving two graphite electrons. This results in a larger lifetime broadening. Slight inhomogeneities in the layer also could cause a broadening, especially since the adsorbate layer is not in registry with the substrate.^{8,10}

We would like to thank Dr. J. Davenport for many useful discussions, and Professor J. E. Fischer for supplying the HOPG samples. We also wish to acknowledge the support of the University of Wisconsin Synchrotron Radiation Center. Our beam line was constructed and is

maintained primarily by the National Science Foundation Materials Research Laboratory Program at the University of Pennsylvania under Grant No. DMR79-23647. This research was also supported by the U. S. Department of Energy under Contract No. DE-AC02-76CH00016.

¹J. J. Markham, *Rev. Mod. Phys.* **31**, 965 (1959).

²M. Sunjic and A. Lucas, *Chem. Phys. Lett.* **42**, 462 (1976).

³C. O. Almbladh and P. Minnhagen, *Phys. Rev. B* **17**, 929 (1978).

⁴J. W. Gadzuk, *Phys. Rev. B* **20**, 515 (1979).

⁵P. R. Norton, R. L. Tapping, H. P. Broida, J. W. Gadzuk, and B. J. Waclawski, *Chem. Phys. Lett.* **53**, 465 (1978).

⁶J. C. Fuggle and D. Menzel, *Surf. Sci.* **79**, 1 (1979).

⁷B. P. Tonner, *Nucl. Instrum. Methods* **172**, 133 (1980).

⁸M. Nielsen and J. P. McTague, *Phys. Rev. B* **19**, 3096 (1979).

⁹R. D. Eppers, Ru Pin Pan, and V. Chandrasekharan, *Phys. Rev. Lett.* **45**, 645 (1980).

¹⁰P. W. Stephens, P. A. Heiney, R. J. Birgeneau, P. M. Horn, J. Stoltenberg, and O. E. Vilches, *Phys. Rev. Lett.* **45**, 1959 (1980).

¹¹K. Siegbahn, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1970).

¹²D. W. Turner, *Proc. Roy. Soc. London, Ser. A* **307**, 15 (1968).

¹³J. A. R. Samson, *J. Opt. Soc. Am.* **56**, 769 (1966).

¹⁴G. Kaindl, T. C. Chiang, D. E. Eastman, and F. J. Himpsel, *Phys. Rev. Lett.* **45**, 1808 (1980).

¹⁵W. Eberhardt and E. W. Plummer, to be published.

¹⁶F. R. Gilmore, *J. Quant. Spectrosc. Radiat. Transfer* **5**, 369 (1965).

¹⁷T. Gustafsson, *Chem. Phys. Lett.* **75**, 505 (1980).

¹⁸A. Tabche-Fouhaile, I. Nenner, P. M. Guyon, J. Delwiche, to be published.

¹⁹P. M. Morse, *Phys. Rev.* **34**, 57 (1929).