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[11] No beats are predicted for linearly polarized D_1 broadband nonsaturating excitation in spontaneous fluorescence. In SF we observed the 400-MHz beats for linearly polarized saturating excitation.

Adsorbate and Substrate Characterization Using Extended X-Ray Absorption Fine Structure*

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We illustrate the usefulness of the extended x-ray absorption fine-structure effect for determining the chemical state, structure, and location of adsorbed species by a study of 0.2 monolayers of bromine adsorbed on graphite at room temperature. Bromine adsorbs as molecules with one atom fixed above the basal-plane hexagonal site while the molecular axis is free to flop around.

In this Letter, we illustrate the power of the extended x-ray absorption fine structure (EXAFS) technique[1-5] for determining the atomic structure and location of adsorbed species by studying bromine adsorbed on graphite.[6] The capabilities of EXAFS that make it particularly suited for adsorption studies are the following: (a) measurement of the short-range order around a particular species of atom in both periodic and nonperiodic arrangements: (b) discrimination between types of surrounding atoms; (c) distinction between distances parallel and perpendicular to the surface by use of polarized x rays; (d) measurement of the variation about its average value of a given bond distance through a Debye-Waller effect; (e) determination of the chemical state of the atom by edge shift and near-edge structure; and (f) relatively simple interpretation of EXAFS, since multiple scattering effects are precisely zero in a Fourier analysis of the first-neighbor shell and usually negligible for the next few shells.[5,7]

We find EXAFS to be an extremely useful complement to low-energy electron diffraction (LEED) and other scattering techniques that probe long- and intermediate-range positional order of monolayer films. On suitable systems, EXAFS can determine positions and orientations of adsorbate molecules with respect to neighboring molecules of both the adsorbate and surface atoms. As initial test system we chose Br_2 on graphite, which was studied by Lander and Morrison using LEED.[8]

We find several new features of relevance to this and other similar systems. The EXAFS pattern shows that the adsorbed bromine is definitely Br_2, although the molecular bond length is probably slightly less than that in Br_2 vapor. At room temperature and low coverage, the Br_2 is adsorbed with one Br atom localized above the center of a basal-plane hexagonal site. The molecular axis is randomly oriented with respect to the substrate plane, suggesting a novel mode of hindered libration. The measurements suggest that the carbon bonds in the neighborhood of an adsorbed Br_2 are perceptibly stretched, causing the top graphite plane to be dimpled locally.

For simple measurement of the EXAFS above the *K* edge of bromine by absorption, the graphite substrate used was Grafoil, which has a large surface area of 22 m^2/g.[9,10] With this substrate, the x-ray absorption in the vicinity of the bromine *K* edge can be dominated by the bromine even when it constitutes only a small fraction of a monolayer. Grafoil is an exfoliated conglomerate of small graphite crystallites in a preferred common orientation. The adsorbing surfaces are essentially pure basal-plane graphite facets; and many studies show Grafoil to be a very uniform adsorbent. 50% of the surface area is due to randomly oriented crystallites, while the remaining area is on crystallites with basal planes parallel to the macroscopic sheet surface with an rms deviation of 15°.

The sample consisted of 0.2 monolayer of Br_2 on the surface of 10 g of Grafoil. The Grafoil formed a 1-in. cube of parallel sheets in a Cu absorption cell fitted with Mylar windows for passage of x rays. The Grafoil was cleaned by heating in high vacuum and subsequently guarded in purified He atmosphere—a technique shown to produce uniform and reproducible surfaces. The bromine was introduced by placing a drop of liquid Br_2 into the cell; and then the cell was sealed with an In *O*-ring gasket. This method of dosing may have caused some local intercalation of Br_2, although we have no evidence that this occurred in the portion of the sample in the path of the x rays. The coverage of 0.2 monolayers was determined directly from the magnitude of the absorption step at the bromine *K* edge.

The x-ray measurements were made at the Stanford Synchrotron Radiation Project (SSRP) EXAFS facility.[11] Measurements were made at room temperature with the x-ray polarization parallel and perpendicular to the Grafoil planes by rotating about the vertical axis. Such a pair of measurements permits discrimination of the atom spacings perpendicular and parallel to the surface. The x radiation at SSRP is almost completely polarized in a horizontal plane. For polarization parallel to the Grafoil surface, the sensitivity of EXAFS to scattering from a given atom varies as $\sin^2\theta$, where θ is the angle between the surface normal and the line between the absorbing and scattering atoms. The atoms in a plane parallel to the surface and passing through the absorbing atom give the largest contribution, while those along a line normal to the surface give no contributions.

For polarization normal to the surface the sensitivity of EXAFS to scattering from a given atom varies as $\cos^2\theta$. In this polarization, atoms in a line normal to the surface are emphasized while atoms in the same plane as the absorbing atom parallel to the Grafoil planes are not detected.

Figure 1(a) shows the bromine *K*-edge absorption coefficient μ measured for Br_2 on Grafoil, with polarization normal to the surface. The background was subtracted off, showing only the contributions from the bromine *K* edge normalized to a step of magnitude one. On this scale there is no striking difference in the measured μ for polarization parallel to the planes.

Figure 1(b) illustrates the absorption for gaseous Br_2.[12] The most striking difference is the large sharp peak just below the edge, which is caused by transitions to the unfilled $4p$ states. One might be tempted to associate the peak at the edge in Fig. 1(a) with the $4p$ peak in Fig. 1(b). However, the inset in Fig. 1(a), which gives an expanded energy scale of the bromine edge for polarization normal to the surface, shows that such an association is not valid. The "pip" at the onset of the edge corresponds to the $4p$ transition. The interaction with the surface has made this transition less promenent. The location of this "pip" is shown by the arrow in Fig. 1(a) and corresponds to the peak at the arrow in Fig. 1(b).

Measurements on various carbon-containing compounds have shown that scattering from carbon atoms gives a characteristic EXAFS similar to the first few prominent oscillations in Fig. 1(a) —a rapidly decaying oscillation as the energy is increased past the edge. Scattering from bromine, as an analysis of Fig. 1(b) shows, gives oscillations extending to much higher energies and with an envelope peaking at about 150 eV. Figure 1(c) shows an expanded version of the EXAFS oscillation where the abscissa has been

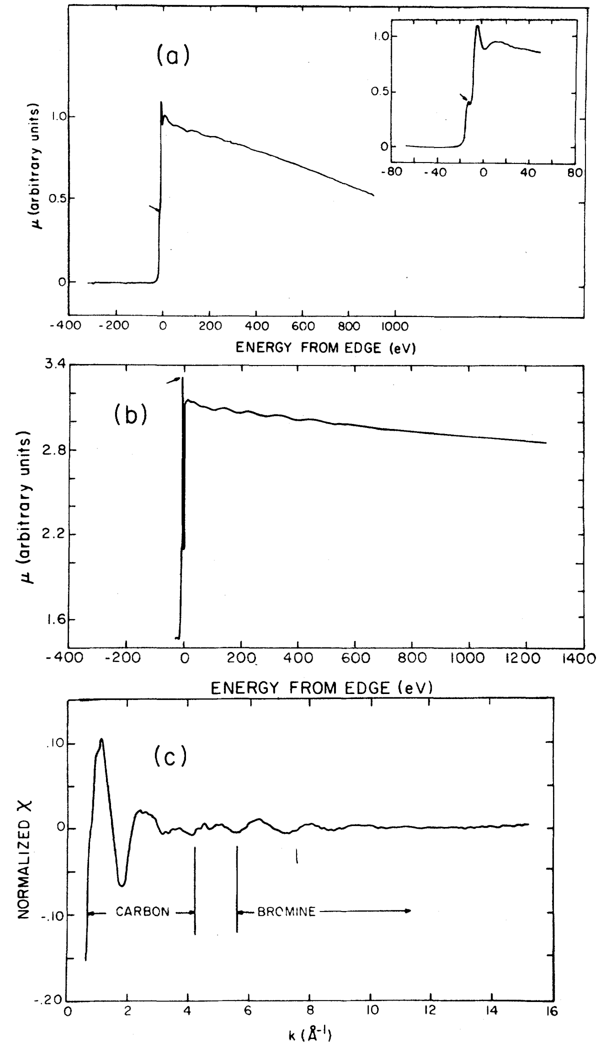

FIG. 1. The EXAFS at the K edge of bromine for (a) bromine adsorbed on graphite and (b) bromine vapor. In (c) the EXAFS of (a) is plotted as a function of photoelectron wave number k illustrating the contribution from the C and Br neighbors.

changed from photon energy to photoelectron wave number $k = (2mE/\hbar^2)^{1/2}$, where E is the photoelectron energy. The zero of energy was chosen at the point of maximum derivative of the edge. On this figure, the regions where the scattering from each type of atom dominates are indicated. There is a clear separation in this case between the Br-C scattering and the Br-Br scattering.

Fourier transforms of k times the EXAFS of both the Br_2 vapor and the bromine adsorbed on Grafoil are shown in Fig. 2. The single peak in Fig. 2(a) locates the Br-Br distance in the Br_2 molecule which is decreased by 0.29 Å because of phase shift effects.[4] The large peak in Fig. 2(b) is split in two because of the interference between the Br-Br and Br-C peaks which overlap one another. The atoms corresponding to each peak can be separated by the quite different k dependence of the EXAFS contributed by Br and C. Details will be given in a future publication, but it is important to emphasize here that the two main peaks shown in Fig. 2(b) are not located where each would individually because of the interference between them.

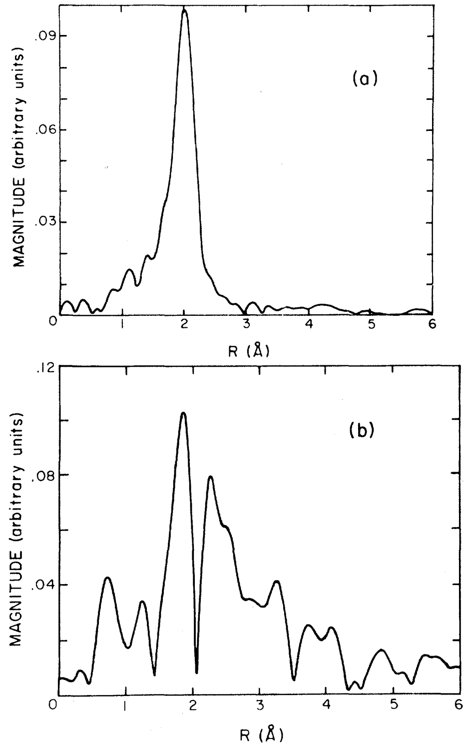

FIG. 2. The magnitude of Fourier transforms of k times the EXAFS for (a) bromine vapor and (b) bromine adsorbed on graphite with the x-ray polarization perpendicular to the basal planes of graphite.

The transforms of Br_2 on Grafoil with both polarizations are more striking by their similarities than by their differences. The data for each polarization were analyzed by standard techniques[3,4] and their results combined to discriminate between atom spacings perpendicular and parallel to the surface.

The picture that emerges is shown schematically in Fig. 3. Its quantitative details are as follows. The fixed end of the Br_2 molecule is 2.37 ± 0.10 Å from the nearest carbon atoms; and the Br-C bond makes an angle of 42° ± 3° with the normal to the plane. This implies a C-C distance in the graphite plane of 1.58 ± 0.12 Å, compared to

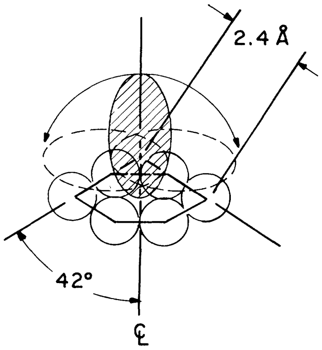

FIG. 3. Illustrating the location and configuration of Br_2 adsorbed on graphite. The circles are carbon atoms and the ellipses are the various positions of the Br_2 molecule as it flops around as indicated by the arrows.

the bulk value of 1.42 Å. The discrepancy is barely significant, but it suggests some expansion of the substrate C-C bond around the adsorption site. Improved data will permit a more reliable answer to this question.

The average Br-Br bond length in the adsorbed molecule is 2.25 ± 0.03 Å with the polarization normal to the surface and 2.22 ± 0.03 Å with parallel polarization. These are compared with the gaseous molecule distance of 2.283 Å. The Debye-Waller factor indicates that the atoms have a larger amplitude of motion relative to one another when adsorbed than they do in the vapor. The square of the amplitudes of the relative motion increases by 0.0025 and 0.0053 Å^2 for polarizations normal and parallel to the graphite basal plane, respectively, with an uncertainty of 0.0015 Å^2.

By comparison, LEED measurements detect four different phases as the vapor pressure and temperature are varied.[8] In the low-coverage lattice-gas phase, the Bragg spots of the graphite substrate are surrounded by a peculiar type of halo. The intensity of the halo is constant within its boundaries, and its extend in reciprocal space corresponds to a spatial length of 17 Å. It was concluded that the bromine is localized on sites because the halos are associated with each spot, but all other conclusions were speculative since there was no quantitative explanation of the intensity distribution. In fact, the EXAFS result shows that the speculation that the bromine adsorbs as atoms is wrong. The origin of the halos, which Lander and Morrison speculated as due to strong distortions of the electronic environment, now seems to be caused by local dimpling of the graphite surface.

In conclusion, we have illustrated the capability of EXAFS to supplement the more established techniques in characterizing substrates and films. EXAFS can completely define the configuration of the lattice-gas phase of Br_2 on graphite at room temperature. Future usefulness of EXAFS to surface studies can be broadened by detection schemes that emphasize the adsorbate, such as detection of Auger electrons.[13, 14]

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