Amplitude of the Extended-X-Ray-Absorption Fine Structure in Bromine Molecules

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The discrepancy between the measured and calculated extended-x-ray-absorption fine structure amplitude in Br_2 molecules, the best documented case, is found to be due to an error in the experimental result. New measurements show good agreement with single-particle calculations at low energies near the K absorption edge and a value about 20% below the calculated one at high energies in agreement with the expected multielectron correction to the single-particle calculation.

The extended-x-ray-absorption fine-structure (EXAFS) technique has matured greatly in the last few years, to the extent that it is becoming a standard method of atomic-structure determination.[1,2] The availability of rather accurate calculations[3,4] of the various parameters entering into the effect has made it feasible to determine structures with reasonable accuracy based on the calculations alone,[4] although empirical comparisons with known structures to determine the parameters is still a more accurate method.

However, the nagging problem has remained of a discrepancy of a constant factor of about 2 between the magnitude of measured EXAFS and the calculated values.[5] It has been proposed to explain this discrepancy by multielectron effects due to Coulomb-Coulomb interactions between the electrons in the absorbing atom,[4,6,7] but the experimental decrease is about a third larger than can be explained in this manner, and is independent of energy, again in disagreement with the expected behavior of the multielectron effects.

The best documented case of this amplitude discrepancy is that of the Br_2 molecule.[5] We have made careful EXAFS measurements on Br_2 vapor and liquid and find that the original experimental data are too small by about a third. The new experimental results are consistent with the theory as corrected by multielectron effects, and, thus, this nagging discrepancy has been resolved. The new experimental results show that the multielectron effect has an energy dependence which is consistent with that expected. One can now have full confidence in EXAFS as a technique since there are presently no significant remaining uncertainties between the theoretical understanding and experimental measurements.

To obtain accurate EXAFS amplitudes it is important to eliminate the effects of several possible experimental difficulties. These are as follows: (a) characterizing and protecting the sample to confirm its initial state and to avoid deterioration; (b) contamination effects of the x-ray beam with higher harmonics or tails in the monochromator transmission function which became more important at greater sample thicknesses; (c) sample inhomogeneity including leakage of x rays around the sample; (d) preferred orientation of the sample; (e) correcting for the disorder-induced Debye-Waller factor. Bromine gas is particularly well suited for eliminating factors (c)–(e) since it is easy to obtain a uniform randomly oriented sample by employing a gas, and the rms disorder of the Br-Br distance is well known. The magnitude of effect (b) can be checked several ways. One is by measuring samples of different thicknesses, since the effect is largest for highly absorbing samples. Another is to use different gases in the ionization chambers used to detect the x rays. This changes the relative sensitivity of the detector to the fundamental and contamination x-ray energies. A third is to detune somewhat the double-crystal monochromator attenuating more the higher harmonics relative to the fundamental. If effect (b) is important, then when these checks are made a difference in the amplitude should be found.

Since bromine is a highly corrosive gas, elimination of effect (a) is most important in obtaining accurate results. Reaction of the Br_2 gas with its container, particularly the x-ray windows, can result in a breakdown of the molecules and a large reduction of the EXAFS amplitudes. This effect was seen in our early measurements using composite Teflon-Kapton x-ray windows. The bromine slowly reacted with the Kapton resulting in a gradual amplitude reduction of about 30%. This problem was solved in our later measurements by using an all glass cell with Teflon windows sealed with inert fluorocarbon grease. As a further check two cells were made at the same time identical in all respects except for a factor of 2 difference in length. If the Br_2 is reacting with the windows then the effect should be largest for the shorter cell. No differences in the data from the two cells were found. Since the original

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measurement of the Br_2 amplitude used a cell with Kapton x-ray windows[5] we suspect that reactions of the Br_2 with the windows caused the erroneous amplitude result.

The measurements were made at the Stanford Synchrotron Radiation Laboratory on EXAFS line II using a silicon (400) double-crystal monochromator. As mentioned, measurements were made on a thick and a thin sample to check for reaction with the windows and thickness effects. The thick sample was measured using both argon and nitrogen in the rear ionization chamber. The double-crystal monochromator was also detuned to almost 30% of its maximum and the EXAFS measured. Also measured at the same time were a thick and a thin liquid-bromine samples. These were sealed in all quartz cells with windows milled directly into the quartz. Again the effect of ionization-chamber gases was checked, and in this case possible preferred orientation was checked for by rotating the samples. In all cases there were no significant differences in the EXAFS amplitudes, and we are confident that all spurious amplitude effects have been eliminated.

The EXAFS from a randomly oriented Br_2 molecule can be written as[8]

$$\chi(k)=\frac{\mu-\mu_0}{\mu_0}$$
$$=\frac{F(k)}{kR^2}e^{-2\sigma^2k^2}e^{-2R/\lambda}\sin[2kR+\varphi(k)],$$

where μ is the absorption coefficient, μ_0 the smooth background, k the electron wave number, R the interatomic distance, σ^2 the rms deviation of R, λ the electron mean free path, and $\varphi(k)$ is the total phase shift of the photoelectron. The theoretical calculations give the amplitude function $F(k)$ and $\varphi(k)$. In Fig. 1 the experimental and theoretical $F(k)/k$ are compared. To obtain the experimental curves, the data were analyzed using standard techniques[8] to obtain $\chi(k)$. This $\chi(k)$ was corrected for the change in μ_0 using the fits of McMaster *et al.*[9] and the Debye-Waller factor removed using[10] $\sigma^2=0.0021$ Å^2. Comparison of the gas and liquid showed that the liquid had an additional contribution to σ^2 of 0.0002 Å, and this was included in the liquid σ^2 correction. These data were then smoothed and any residual background removed by filtering over an r-space range of 0.8–3.2 Å with a Hanning cutoff applied to 0.8–1.2 and 2.8–3.2 Å. This filtering distorts the amplitude slightly. However, this distortion can be corrected for by filtering the theoretical $\chi(k)$ in the same manner and comparing the resulting amplitude with the original. Also, various filtering ranges were tried to further check that this technique does not significantly alter the experimental amplitudes. The $k=0$ energy was taken as the maximum of the $4p$ white line for the gas and liquid data. For the theory the $k=0$ energy was then chosen such that the Fourier transforms of the two sets of data had the same

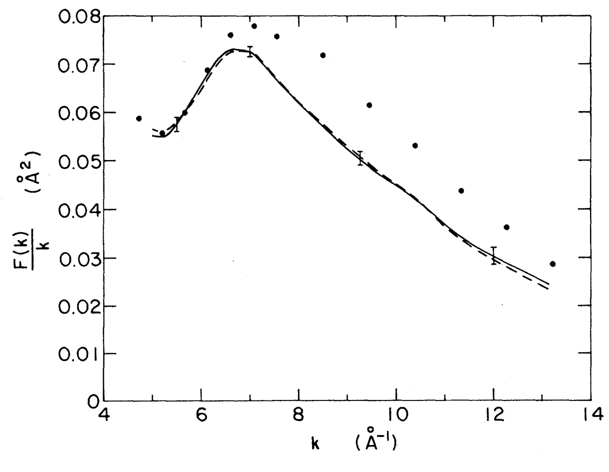

FIG. 1. A plot of $F(k)/k$ vs k for bromine atoms. The points are the single-particle theoretical calculation, the solid line is the measured value in Br_2 vapor, and the dashed line is the measured value in Br_2 liquid.

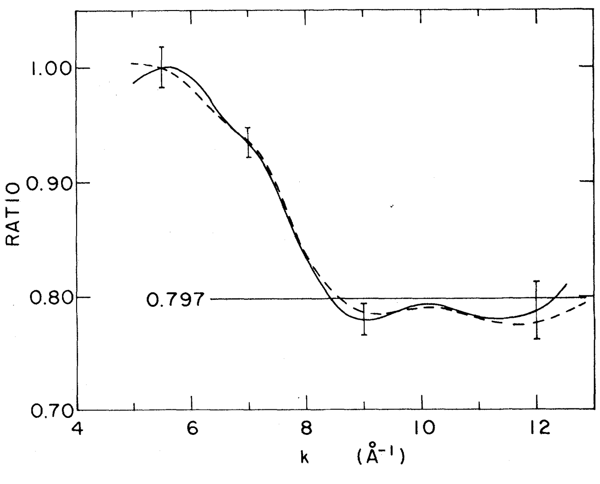

FIG. 2. The ratio of the measured $F(k)$ divided by the single-particle theoretical calculation as a function of k. The solid line and dashed line show this ratio for the Br_2 vapor and Br_2 liquid, respectively. The thin horizontal line shows the multielectron corrections at high k to the single-particle calculation.

phase. The curves in Fig. 1 represent an average of all the data taken. The error bars were determined from the scatter of the individual files.

As seen in Fig. 1, both the liquid and gas data are in good agreement at low k and fall significantly lower than the theory at high k. A more detailed comparison is shown in Fig. 2 where the ratios of the experimental to the theoretical amplitudes are plotted.

Multielectron effects[4,6,7] are expected to cause the experimental curves to deviate below the one-electron theoretical calculation at high k values, as observed. The multielectron effect causes a reduction in the one-electron dipole matrix element because of relaxation of the wave functions of the passive electrons (those not directly excited by the dipole operator) in the final state. The final-state core hole increases the attractive potential felt by the passive electrons, causing their states to relax to a lower energy. They therefore no longer have 100% overlap with their initial states. Since the many-electron matrix element includes a factor S_0^2 of the overlap between the initial and final states of the passive electrons, this relaxation effect will decrease the matrix element below that given by the one-electron theory which neglects the effects of the passive electrons.

As has been shown,[7] the EXAFS at high k is affected only by the relaxation within an atom and is not appreciably affected by the additional relaxation that occurs in the molecule which introduces charges only at low-excitation energies. The overlap factor S_0^2 in a Br atom[11] is 0.797, which, as indicated in Fig. 2, agrees with the experimental value at high k. This calculated value neglects correlation effects. There is experimental evidence from x-ray photoemission spectroscopy that correlation effects may decrease S_0^2 about (4–12)% further.[12] Since this is not well documented we do not include such possible correlation effects in the theoretical estimate but it may be invoked in explaining the possible few percent lower value of the experimental result.

The relaxation factor S_0^2 accounts for multielectron effects only when the creation of the core hole can be described in the sudden approximation and correlation effects can be neglected. Neither of these approximation are valid near the edge. In addition, multielectron excitations from atoms are experimentally found to reach their high-energy value only above excitation energies several times the threshold energy for the excitations.[13] The EXAFS is decreased by the multielectron effect only in the energy range where multielectron excitations are occurring. Thus, at energies near the edge one expects no decrease in EXAFS due to the multielectron effects and agreement with the single-particle calculation. Near the edge, the escape of the photoelectron may be slow enough as to be described by the adiabatic approximation which predicts that the overlap factor is 1 and again no decrease in the EXAFS. Although the transition between low-k and high-k behavior has not yet been calculated in detail, the qualitative behavior expected from the multielectron effect on EXAFS is the single-particle result at low k, decreasing to a factor S_0^2 of the single-particle result at high k. The experimental results of Fig. 2 agree with these theoretical expectations.

In summary, the previous experimental result for the amplitudes of Br_2 EXAFS was found to be too small by a significant amount. The new measurements compared to the single-particle calculation show the variation in Fig. 2 which is in agreement with that expected from multielectron effects. This agreement settles the one remaining disturbing discrepancy between our theoretical understanding of EXAFS and the experimental results, reinforcing confidence in the use of EXAFS as a technique in structure determination.

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Dispersion and Symmetry of Oxygen-Induced Bands on Al(111)

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Using polarized light and angle-resolved photoelectron spectroscopy, we have shown that oxygen is bonded in an ordered (1×1) configuration on Al(111). For this model system, we have determined the symmetry and dispersion of the threee oxygen derived bands. We find two even and one odd band with respect to the $(1\bar{1}0)$ mirror plane. A disordered oxide film shows no dispersion and different oxygen binding energies.

Oxygen adsorbed on Al is theoretically one of the simplest adsorption systems. There are no *d* bands in the metal to complicate the calculation, so that the bonding is *s*-*p* in nature. As a consequence, several *ab initio* calculations exist for this system[1-4] and different theoretical approaches can be compared. Experimentally, this system has proven to be much more difficult because of the formation of an oxide layer instead of a chemisorbed monolayer. We report in this Letter the first observations of the two-dimensional band dispersion of a chemisorbed layer of oxygen on Al(111). These data will furnish a definitive test for *ab initio* calculations for oxygen bonding on Al and can, in fact, be used to distinguish bonding sites.

A few groups have studied the oxidation of Al single crystals. Work-function changes,[5,6] angle-integrated photoemission valence-band spectra, and Al $2p$ core-level spectra have been reported.[7,8] From these studies, the oxygen on Al(111) would seem to be the most profitable to study since it appears to form an ordered overlayer during the initial stages of adsorption. Flodström *et al.*[7] found that the (1×1) low-energy-electron-diffraction (LEED) pattern from Al(111) changed only in intensity during the initial stages of oxygen adsorption. This could be interpreted as indicating the formation of an (1×1) ordered overlayer of oxygen or a discovered oxygen layer. Our angle-resolved photoelectron spectra show that the oxygen levels in this coverage range exhibit the symmetry and dispersion expected from a (1×1) ordered overlayer. Specifically, we find three oxygen-$2p$-derived bands in the $(1\bar{1}0)$ mirror plane, one odd and two even with respect to reflection about the mirror plane. The largest dispersion (~2.7 eV) is observed for the oxygen p_x, p_y-derived bands. Our results show that the dispersion is mainly determined by the oxygen-substrate–oxygen interaction via the $p_{x,y}$ orbitals. This favors the threefold hollow position. Also, the periodicity of the dispersion proves the oxygen unit cell has the same dimension as the surface unit cell; i.e., we have an ordered (1×1) overlayer.

The experiments were performed at the Synchrotron Radiation Center of the University of Wisconsin. We used two different spectrometers. One was a two-dimensional–display spectrometer.[9] *P*-polarized light with an angle of incidence of 55° was used in the photon energy range $12\ \text{eV} \leq h\nu \leq 35\ \text{eV}$. The second system was a 180°-deflection–type analyzer[10] which is fully rotatable about two orthogonal axes. The polarization of the incident light is continually variable, allowing us to separate orbitals of different symmetry.

The Al(111) surface was prepared by sputtering-annealing cycles with Ne ions. The surface was characterized and oriented *in situ* by LEED and photoelectron spectroscopy. The cleanliness of