PHYSICAL REVIEW B VOLUME 17, NUMBER 10 15 MAY 1978

Extended-x-ray-absorption-fine-structure study of the Br_2-graphite system

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(Received 12 December 1977)

Extended-x-ray-absorption-fine-structure (EXAFS) measurements have been made on 0.6- and 0.9-monolayer samples of Br_2 adsorbed on Grafoil, a form of graphite, and on an intercalated sample between 100 and 293 K. For both of the adsorbed samples the Br_2 molecule is found to lie parallel to the basal-plane surface with each atom aligned as well as it can be above adjacent hexagonal sites. The Br-Br distance increases about 0.03 Å to accommodate part of the lattice mismatch. The average Br-C distance is 2.9 A. Both of these coverages seem to be in the two-dimensional liquid phase seen in low-energy-electron-diffraction measurements, although analysis of the Br-Br internuclear vibrational amplitude suggests increased ordering for the 0.9-monolayer sample as the temperature is lowered. These two coverages are distinctly different from results previously reported for 0.2 monolayer, demonstrating the importance of Br_2-Br_2 interactions. In the intercalated sample the average Br-C distance decreases to 2.5 A, and the bromine seems to be mainly molecular with the Br-Br distance increasing to match the periodicity of the graphite lattice. There is also evidence that the intercalated sample is a mixture of two phases. Finally, the amplitude of the Br-Br EXAFS is found to exhibit puzzling deviations from that of the vapor.

I. INTRODUCTION

The extended-x-ray-absorption-fine-structure (EXAFS) technique has been shown to be very useful in determining the short-range order around a particular atomic species. This determination can be made even for systems with no long-range order. In a previous letter,[1] the successful application of the EXAFS technique to adsorbed systems was described for bromine adsorbed on Grafoil, a form of graphite. In this paper, we present a much more detailed description of the application of the EXAFS technique to adsorbed systems along with extensive new measurements of the bromine-Grafoil system.

A widespread and useful technique for studying adsorbed systems is low-energy-electron diffraction (LEED), which probes the long-range order of the adsorbed films. However, information about the short-range structural details near the adsorbed atom is difficult if not impossible to obtain. Also, when the adsorbed film has no long-range order, LEED has only limited usefulness. Thus, the EXAFS technique is seen to be a nearly ideal compliment to LEED in the study of adsorbed systems. In particular, EXAFS offers the possibilities of determining the following characteristics: (a) distances parallel and perpendicular to the substrate surface; (b) the average structural and thermal disorder associated with these distances from a Debye-Waller effect; (c) the chemical state of the absorbed atom from the study of the x-ray absorption edge shifts and near-edge structure; and (d) the number and type of the surrounding atoms which can be used to determine the adsorption site.

The system of Br_2 and graphite is well suited for study by EXAFS. The x-ray absorption K edge from bromine is at sufficiently high energies that absorption due to the carbon substrate is small. The linear nature of the Br_2 molecule makes the polarization dependence of the EXAFS easy to interpret. Also, it is easy to differentiate the EXAFS due to carbon neighbors from that due to bromine neighbors. The scattering amplitude from bromine characteristically peaks at a photoelectron wave number k of 6 to 7 Å^{-1} and extends to $k \sim 15$ Å^{-1}. However, the scattering amplitude from low-Z materials, such as carbon, peaks near $k = 0$ and drops off sharply with increasing k. Finally, complementary isotherm[2,3] and LEED[1] studies have been made.

The LEED studies of Lander and Morrison[1] found that there are at least five distinct adsorbed phases associated with different temperature and coverages. They are in order of decreasing temperature: (i) lattice gas; (ii) liquid; (iii) first solid phase; (iv) second solid phase; and (v) multilayer or bulk solid phase. In the previous letter,[1] data were reported for a coverage of 0.2 monolayer at room temperature. This coverage could be associated with the lattice-gas phase of Lander and Morrison, and a detailed description of the location of the Br_2 molecule with respect to the substrate was obtained. One Br atom of the molecule is bound to a basal-plane hexagon with a Br-C distance of about 2.4 Å. The other end of the molecule is free to flop around and the Br-Br distance is the same or slightly less than in the vapor.

In this paper, coverages of 0.6 and 0.9 monolayers are studied as a function of temperature between 100 °K and room temperature. We find that at room temperature the adsorbed configuration is identical for both coverages, and is much different from the 0.2-monolayer results. The molecules lie flat on the surface with each Br atom in the molecular unit centered as well as it can above adjacent basal-plane hexagonal sites which are 2.46 Å apart. The Br-Br distance is stretched slightly from its normal value of 2.28 Å to 2.31 ± 0.02 Å to accommodate part of the lattice mismatch, and the average Br-C distance is increased to about 2.9 Å. These coverages seem to be in the liquid phase described by Lander and Morrison. As the temperature is lowered, there is little change in these results except that the thermal disorder of the Br-Br distance in the 0.9-monolayer case has a larger than expected temperature dependence. This could indicate a transition to a solid phase, although further measurements seem necessary.

Measurements were also made on an intercalated sample at 100 °K and room temperature. Again, the bromine remains mostly molecular with the long axis parallel to the graphite basal planes. In this case, however, the Br-Br distance increases by 0.15 ± 0.02 Å to match the spacing between adjacent hexagons, and the Br-C distance decreases to 2.5 Å.

This paper is divided into six sections. Experimental details and results are presented in Secs. II and III. In Sec. IV, the analysis of the data to obtain interatomic distances, scattering amplitudes, and Debye-Waller factors is described. Like the data, Sec. IV is divided into three parts: Sec. IV A in which the Br-Br (high-k) part of the data is analyzed; Sec. IV B in which the more difficult problem of analyzing the Br-C (low-k) EXAFS is discussed; and Sec. IV C in which the near-edge structure is analyzed. In Sec. V the results of Sec. IV are interpreted in the light of previous measurements, and all of the results are summarized in Sec. VI.

II. EXPERIMENTAL DETAILS

In measuring adsorbed layers the problem that must be overcome is to discriminate between the signal from the adsorbed layer and that from the bulk. In ordinary samples the absorption of x rays will be dominated by the bulk. This problem is overcome here by employing a form of exfoliated graphite, called Grafoil, where the surface area is greatly increased to 22 m^2/g so that the x-ray adsorption is dominated by the adsorbed bromine. Grafoil has been well characterized by a variety of experimental techniques.[5,6] It is known to consist of two types of crystallites with approximately equal surface area.[6] The first type consists of small randomly oriented grains, while the second have a preferred orientation with their basal planes parallel to the macroscopic sheet surface with an rms deviation of 15°. The adsorbing surface is predominantly the basal plane, and the studies have shown Grafoil to have a reasonably uniform surface area.

The Grafoil was cut into rectangular sheets and cleaned by heating to 900 °C for one hour under a mechanical pump vacuum. The sheets were then packed under a He atmosphere into nickel plated copper cells with mylar x-ray windows. The nickel plating is necessary to avoid reaction with the bromine. The amount of Grafoil used was chosen such that the x-ray absorption at the bromine edge is about two absorption lengths. This corresponds to a Grafoil thickness of about 1 cm for the adsorbed samples and 0.5 cm for the intercalated sample.

Since bromine easily intercalates into the graphite lattice, care had to be taken in preparing the adsorbed samples. They were prepared by letting a measured amount of Br_2 gas into the cells at low pressure. Typically the pressure was kept at or below 10 Torr. At these pressures, adsorption took place slowly, and the cells were cooled slightly (~0 °C) to speed the process. The intercalated sample was prepared in the same fashion, except that more Br_2 gas was admitted to the cell and the pressure was kept near 20 Torr. Once x-ray absorption measurements confirmed that the correct amount of Br_2 had adsorbed, the cell was sealed off. After sealing, further x-ray absorption measurements revealed that about 24 h was required before the Br_2 was distributed homogeneously on the graphite surface. The actual EXAFS measurements were not taken until several days later.

The EXAFS measurements were made at the Stanford Synchrotron Radiation Laboratory (SSRL), using EXAFS line II with a Si (111) channel cut monochromator. The x-radiation at SSRL is almost entirely polarized in the horizontal plane. The Grafoil sheets are stacked with their normals horizontal, which means that the angle of the polarization vector with respect to the sheet surface can be varied by rotation of the cells about the vertical axis. For each coverage and temperature, measurements were made with the x-ray polarization both normal to (out) and parallel to (in) the graphite planes. When the polarization vector is normal to the planes, the contribution to the EXAFS varies as $\cos^2\theta$, where θ is the angle between the surface normal and the radial vector between the absorbing and scattering atom. Thus, the contribution of atoms lined up along the normal is emphasized. When the polarization is parallel to the planes, the EXAFS contribution varies as $\sin^2\theta$, and the scattering of atoms lying in the basal planes is emphasized.[7]

III. DATA

Three samples were measured: two adsorbed samples, and one intercalated sample. The amount of Br_2 was determined by measuring the magnitude of the absorption step at the Br K edge. This was done with an accuracy of about 2%. The coverages could then be determined from the measured amount of Grafoil in the cell if the average area occupied by a Br_2 molecule at the completion of a monolayer is known. For graphitized carbon blacks, Hooley[3] found that each Br_2 molecule occupied 24 Å^2 at monolayer completion. For graphite Reyerson *et al.*[2] reported a value of 21 Å^2/molecule. The LEED[4] studies found that the densest phase (the first solid phase) corresponded to a 2×2 pattern. This means that there is one molecule for every four basal-plane hexagons, or again about 21 Å^2/molecule. In this paper, we will use the value of 21 Å^2/molecule and take the specific surface area of Graphoil to be 22 m^2/g. These values give coverages of 0.58 ± 0.01 and 0.87 ± 0.02 of a monolayer for our adsorbed samples where the error is due to the x-ray absorption measurements only. Considering the various other systematic errors possible, these coverages will be referred to as 0.6 and 0.9 monolayers, respectively. The intercalated sample had 0.27-mole%Br_2 which would correspond to an adsorbed coverage of 1.3 monolayers.

The 0.6-monolayer sample was measured at room temperature, and 105 °K for both polarizations, and at 200 °K with the polarization in the planes. The 0.9-monolayer sample was measured at room temperature, 160 and 100 °K for both polarizations, and at 210 °K with the polarization in the planes. The intercalated sample was measured at room temperature for both polarizations and at 100 °K for the polarization in the plane. In all cases, at least two runs were taken for each given polarization and temperature, and the results averaged before further analysis. The temperatures were held constant to about ±5 °K. Finally, a solution of CBr_4 in ethyl alcohol was measured for use as a standard.

The 100 °K data for the 0.9-monolayer sample are shown in Fig. 1 along with data for Br_2 vapor taken at room temperature.[8] It is clear that a large anisotropy in the EXAFS exists. When the polarization is out of the planes, the oscillations at large energies due to Br-Br scattering are reduced, while the low-energy Br-C oscillations are enhanced. This immediately indicates that the Br_2 molecules tend to lie flat along the basal planes. This fact is confirmed by the behavior of the sharp peak just below the edge, which is most obvious for the Br_2 vapor data. This peak is due to transitions to unfilled $4p$ states, and we will refer to it as a "white line." These states are associated with σ antibonding orbitals and are composed of p states directed along the direction between the two Br atoms. The magnitude of this $4p$ peak should, therefore, show the same angular dependence as the Br-Br EXAFS, as it does in Fig. 1. On the scale of these plots, all of the other adsorbed data are very similar to that shown, except that at room temperature the Br-C oscillations are somewhat reduced.

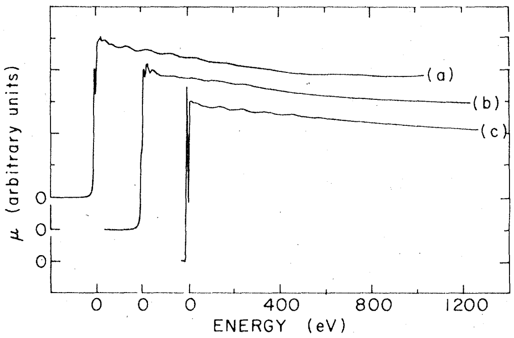

FIG. 1. X-ray absorption coefficient μ for the K edge for Br_2 adsorbed on graphite and Br_2 vapor. For comparison, each has been normalized to an edge step of one and the energy scales for (b) and (c) have been shifted 200 and 400 V to the right, respectively. (a) 0.9-monolayer, 100-K, x-ray polarization parallel to the Grafoil sheets. (b) 0.9-monolayer, 100-K, x-ray polarization perpendicular to the sheets. (c) Br_2 vapor at room temperature.

The data for the intercalated sample at room temperature are shown in Fig. 2. In this case the

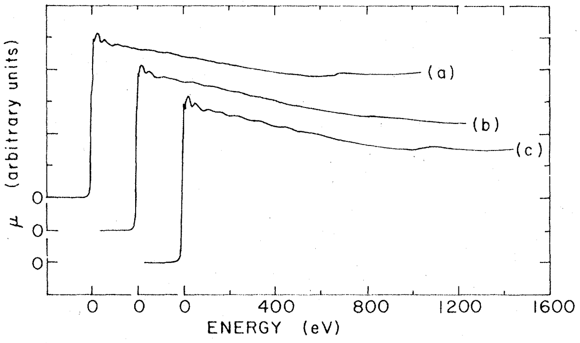

FIG. 2. X-ray absorption coefficient μ for the K edge for 0.27-mole% Br_2 intercalated with graphite. All edges have been normalized to an edge step of one. (a) 293°K, x-ray polarization perpendicular to the Grafoil sheets. (b) 293°K, polarization parallel to the sheets. (c) 100°K, polarization parallel to the sheets.

while line is much reduced, and the Br-C oscillations are different from the adsorbed data. Not as obvious on this scale is the fact that the period of the Br-Br oscillations is significantly different from that of Br_2 vapor or adsorbed Br_2. However, the existence of the Br-Br oscillations is direct evidence that at least part of the bromine remains molecular when it intercalates, a fact which could only be indirectly inferred from previous measurements.[9,10] Finally, there is little anisotropy in either the Br-Br or Br-C scattering. This will be discussed further in Sec. V.

IV. DATA ANALYSIS

A. Br-Br EXAFS

To interpret the results of the EXAFS measurements we will make use of the result that if there is only a single shell of N identical atoms located at a single distance R then the in- and out-polarization EXAFS are proportional to one another, independent of k. This follows immediately from the EXAFS theory for the K shell and for this case[11]:

$$\chi(k) = (N/R^2)B(k)e^{-2(k^2\sigma^2-R/\lambda)} \times \sin[2kR+\delta(k)] \sum_i \cos^2\theta_i , \qquad (1)$$

where $B(k)$ is a backward scattering function which depends on the type of scattering atom, σ^2 is the mean-square amplitude of the deviation of the relative distance between the center and scattering atoms, $\delta(k)$ is the phase, λ is the photoelectron mean free path, and θ_i is the angle between the x-ray polarization and the radial vector to the i^{th} atom. In our experiment, we expect more than one shell of atoms since we expect Br-Br and Br-C distances to appear. However, as we will show, it is possible to separate the Br-Br and Br-C distances and treat each separately.

The first step in a quantitative analysis of the data is to isolate the EXAFS from the background absorption. This was done using standard techniques of background subtraction and Fourier filtering.[11] The EXAFS from the data in Fig. 1 is shown in Fig. 3. The clear separation of the data into Br-Br and Br-C scattering is obvious. The oscillations at low k which decrease rapidly with k are due to Br-C scattering, while the high-k oscillations are due to Br-Br scattering. In this section, we will be concerned with the analysis of the Br-Br scattering for $k \gtrsim 6$.

A check was made of the proportionality of the Br-Br data for in and out polarization. To do this, the larger amplitude in-polarization results were multiplied by an appropriate factor and subtracted from the out-polarization data. It was found that the two polarizations are indeed proportional since only low-k oscillations due to the Br-C scattering, which has a different proportionality factor, remain. The proportionality factor is a measure of the degree of orientational anisotropy of the molecules, and it was found that the anisotropy increases as the temperature is lowered. This indicates that the molecules become more aligned with the Grafoil sheets at low temperatures. These results will be presented in Sec. IV C with similar results from the near-edge structure.

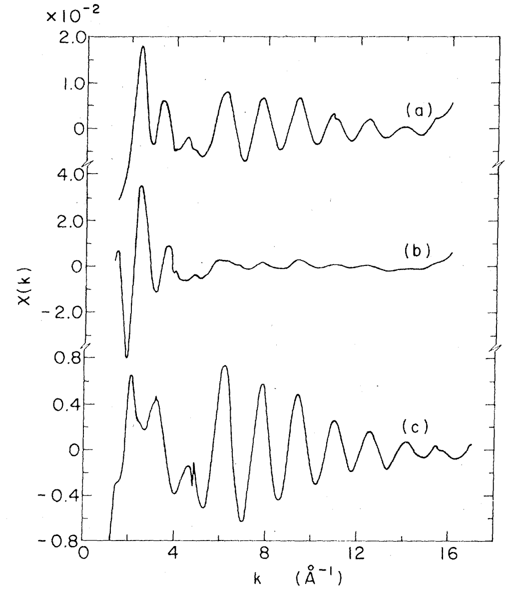

FIG. 3. $\chi(k)$ for the data in Fig. 1.

To determine the Br-Br distance, Fourier transforms were taken of the EXAFS for the range $k = 6$–15 Å^{-1}. Some examples are shown in Fig. 4 along with the same transform for Br_2 vapor. In both, the peaks are shifted to smaller R from the true interatomic distance by phase-shift effects. However, since the distance for Br_2 gas is known to be 2.283 Å, it can be used as a standard to accurately correct for the peak shift. For the transforms in Fig. 4, this peak shift is 0.27 ± 0.01 Å. Finally, there is no evidence for a distance at larger R which would be an intermolecular distance. This is in spite of the fact that the example shown in Fig. 4 represents the highest coverage and lowest temperature of the adsorbed phase data and is thus most likely to show evidence for higher shells.

The same analysis was carried out for the intercalate data, and the isolated EXAFS is shown in Fig. 5. An analysis of the Br-Br in-out proportionality again found that the data for the two polarizations is proportional, but in this case there

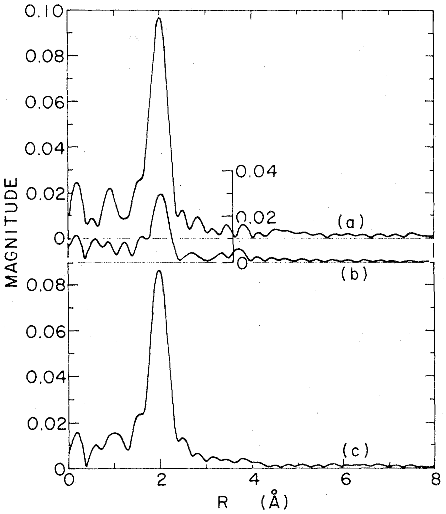

FIG. 4. Fourier transforms of k times the data in Fig. 3. Only the range $k = 6–15$ Å^{-1} was transformed and the peaks represent the Br-Br distance shifted to lower R by phase-shift effects. For ease of comparison, the magnitude scales are the same for all three transforms.

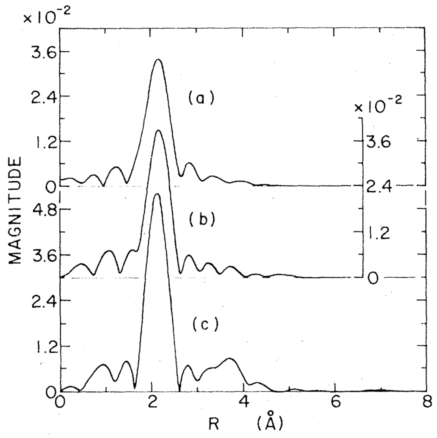

FIG. 6. Fourier transforms of k times the data in Fig. 5. Only the range $k = 6–15$ Å^{-1} was used and the peaks represent Br-Br distances shifted by phase-shift effects. In (c) note the appearance of a small second peak indicative of next-nearest-neighbor Br atoms. For ease of comparison, the magnitude scales are the same for all three transforms.

is no anisotropy. This indicates that the bromine molecules present are randomly oriented with respect to the macroscopic Grafoil sheets. The transforms of these data are shown in Fig. 6. The Br-Br distance has increased approximately 0.15 Å from that of the vapor and closely matches the graphite hexagon spacing of 2.456 Å. Also, for the 100 °K data, there is now evidence for a second shell appearing near 3.8 Å which would correspond to 4.1 Å when the peak shift is taken into account. Since the transforms were taken over only the large-k region, this has to be due to second-neighbor bromine, and not a Br-C distance.

Table I summarizes the Br-Br distances for all of the data taken. The errors given include contributions from both noise in the individual transforms and the uncertainty in the peak shift corrections. For the adsorbed phase the in-plane polarization results are more reliable since the amplitude of the oscillations is much larger. In Table I, we see that to within experimental error there is no dependence of the distance on coverage or polarization for the adsorbed phase data. It could

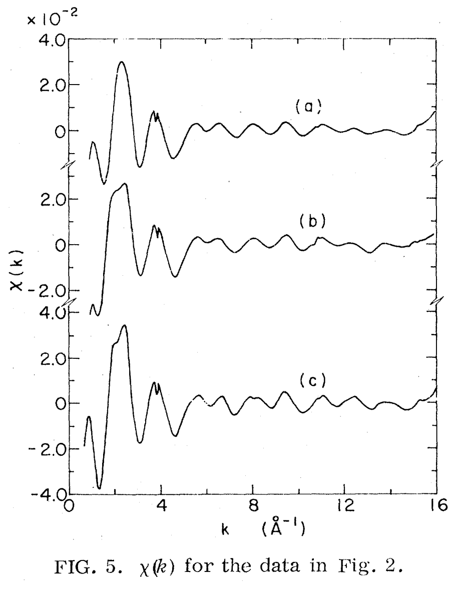

FIG. 5. $\chi(k)$ for the data in Fig. 2.

TABLE I. Br-Br distances. "pol. in" refers to data taken with the x-ray polarization vector parallel to the graphite basal planes and "pol. out" refers to data taken with this vector perpendicular to the graphite planes. The only second shell observed was for the low-temperature intercalate data.

T (°K)	R (pol. in)	R (pol. out)	R (2nd shell)
	0.9 monolayer		
293	2.29 ± 0.02 Å	2.30 ± 0.03 Å	
210	2.31	• • •	
160	2.30	2.31	
100	2.30	2.32	
	0.6 monolayer		
293	2.31	2.33	
200	2.31	• • •	
105	2.31	2.34	
	0.27 mole % intercalate		
293	2.44 ± 0.02	2.45 ± 0.02	
100	2.41	• • •	4.1 ± 0.1 Å

be argued that the 0.6-monolayer out polarization results are a possible exception. However, it should be mentioned that for the 105 °K data some leakage of the x-rays between the Grafoil sheets is indicated by a reduced absorption step at the edge. Such leakage can result in some distortion of the EXAFS, and increases the noise in the data.

The next step in the analysis of the data is the determination of vibrational amplitudes of the Br_2 molecules. For the adsorbed phase, Table I shows that R is temperature independent which means that there are two principle sources of temperature dependence in Eq. (1). The overall amplitude can be changed if the $\cos^2\theta_i$ term changes due to a change in molecular orientation, or σ^2 can change giving rise to a k-dependent amplitude change. To determine the temperature dependence, the envelope of the oscillations must first be isolated. This is done by making a Fourier transform back to k space using only a range of data centered on the first shell R-space peak.[11] An envelope can then be determined. The log of the ratio of envelopes for different temperatures is then plotted versus k^2 as in Fig. 7. The change in σ^2 can then be determined from the slope of the line, and the intercept is the log of the overall amplitude ratio. More details, including the smoothing effect of the size of the range in R space, are discussed in Ref. 11.

The mean-square vibrational amplitude for a free Br_2 molecule is well known,[12] which means comparison of the adsorbed data with Br_2 vapor can be used to determine absolute values for σ^2. These results are shown in Fig. 8. The error bars were determined from the scatter in the results using different transform windows for isolating the envelope. Also, intercomparisons between the different adsorbed phase data directly gave results in agreement with the differences shown in Fig. 8. Only the in-plane polarization results are shown, since the low amplitude of the out-plane oscillations rendered those results unreliable. They are, however, in qualitative agreement with the values shown.

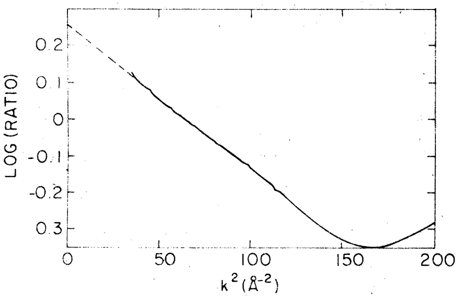

FIG. 7. Ratio of the envelope for the Br-Br EXAFS at 293 °K and a coverage of 0.9 to a similar envelope for the 100 °K data in Fig. 3(a) plotted versus k^2. The slope of the line gives the change in σ^2 and the intercept determines the amplitude ratio. The deviation at high k^2 is due to noise in the data. A range in R space of 1.37–2.74 Å was used for determining the envelopes.

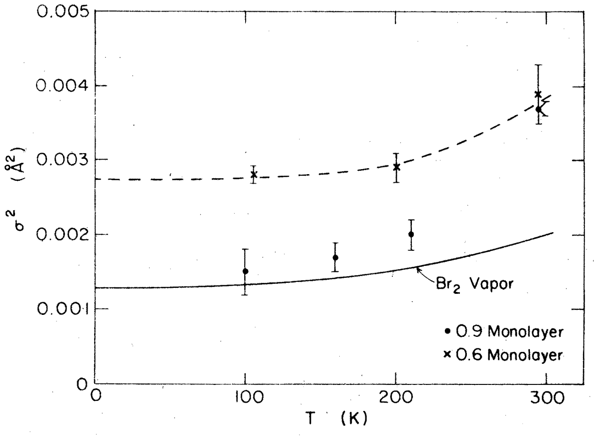

FIG. 8. Mean-square vibrational amplitudes (σ^2) of the Br-Br distance for adsorbed Br_2 compared with Br_2 vapor. The dashed line was drawn by eye through the 0.6-monolayer points to illustrate the different temperature dependence of the 0.9- and 0.6-monolayer results.

In Fig. 8, the 0.6-monolayer values are higher than, but have much the same temperature dependence as σ^2 for Br_2 vapor. The 0.9-monolayer values, on the other hand, have a larger temperature dependence. The room-temperature value is the same as the 0.6-monolayer result, but a low temperatures σ^2 is close to the values for Br_2 vapor. This could indicate a phase transition and will be discussed further in Sec. V.

Turning now to the overall amplitude of the oscillations, there is an apparently strange result in Fig. 7. The amplitude at low temperatures is less than at room temperature. From the anisotropy of the data it was found that at low temperatures the molecules better align themselves with the surface. Thus, one would expect a larger amplitude for the in-plane low-temperature results shown in Fig. 7.

To better understand the origin of the temperature dependence of the EXAFS amplitudes, a comparison with Br_2 vapor is useful. Since the molecules in the vapor are randomly oriented, while the adsorbed molecules have a preferred orientation, an average of the in and out polarization amplitudes must be taken. A simple calculation using the $\cos^2\theta_i$ dependence given in Eq. (1) shows that the appropriate average is

$$A_{\text{rand.}} = \tfrac{2}{3}A_{\text{in}} + \tfrac{1}{3}A_{\text{out}} . \qquad (2)$$

Using this average amplitude, effects due to

TABLE II. Ratios of the EXAFS amplitude as compared to that of Br_2 vapor. The combination of $\frac{2}{3}$ of the in polarization plus $\frac{1}{3}$ of the out polarization signals is insensitive to any orientational effects.

Temperature (°K)	$k=0$ amplitude ($\frac{2}{3}$ in $+\frac{1}{3}$ out)
0.6 monolayer	
293	0.99 ± 0.03
105	0.90 ± 0.04
0.9 monolayer	
293	0.97 ± 0.04
160	0.67 ± 0.05
100	0.71 ± 0.04
0.27 mole % intercalate	
293	0.20 ± 0.04

changes in the degree of orientation are removed, and the amplitude is that which would be measured for an equivalent set of randomly oriented molecules. Table II shows the results of the amplitude comparison. At room temperature, the adsorbed amplitude equals the amplitude of Br_2 gas. However, at low temperatures, the amplitude is reduced substantially with the higher coverage being reduced the most. Except for the low-temperature 0.6-monolayer out polarization data, which makes a small contribution to the average, the total absorption step at the edge is independent of temperature. This means the amplitude reduction can not be explained as an x-ray leakage effect.

The same analysis was carried out for the intercalate data. Because of the limited amount of data there is more uncertainty in the results, but again the amplitude seems to have unusual behavior. At 100 °K the value of σ^2 is found to be 0.0025 ± 0.0009 less than at room temperature, but comparison with the vapor gives the a value 0.0040 ± 0.0005 less than its corresponding value. However, for the vapor, $\sigma^2 = 0.0020$, and obviously the above result must be incorrect. What appears to be happening is that the amplitude function [$B(k)$ in Eq. (1)] is different for intercalated Br_2 as compared to free Br_2. Such a variation with chemical environment may be due to many electron effects.[13] Of course, this means the above analysis cannot be used to find differences in σ^2 between the intercalated Br_2 and the other forms. However, the temperature dependence of σ^2 can still be obtained by comparing the intercalated data at different temperatures. Thus, the change in σ^2 between 293 and 100 °K of $\Delta\sigma^2 = -0.0025 \pm 0.0009$ is meaningful.

B. Br-C EXAFS

The analysis of the Br-C EXAFS proceeds in the same fashion as for the Br-Br EXAFS except now there are additional complications. The most serious of these is the choice of the inner potential V_0. For the Br-Br analysis, the zero in energy was always taken as the point of maximum derivative on the portion of the edge above the $4p$ peak. The electron wave factor is then defined in the usual way: $k = [0.263(E - V_0)]^{1/2}$. For Br-Br EXAFS, E is large and the choice of V_0 is relatively unimportant, but at the low energies of the Br-C EXAFS a small change in V_0 can result in a large change in k.

The true zero in energy is approximately the point at which the photoelectron classically can just move freely between the atoms. For two isolated noninteracting atoms, this energy would be the continuum limit. However, when the atoms are bonded together this zero in energy is below the continuum limit. For example, in a crystal the appropriate energy for V_0 is the muffin-tin potential. For a Br_2 molecule, the situation is not as clear cut, but the zero should be near the $4p$ bonding state since at this energy electrons are being exchanged between the atoms. Thus, for the Br-Br analysis V_0 was chosen such that $k=0$ corresponds to the near-edge $4p$ peak. In the present case, we want to compare three different types of Br-C bonding: adsorbed Br_2, intercalated Br_2, and CBr_4. For the first two, the edge structure is due to bonding between bromine atoms and thus provides no clues as to the correct choice of V_0. For CBr_4, on the other hand, there is a small pip halfway up the edge which must be due to the Br-C bonding states. Thus, V_0 must be such that the $k=0$ energy is near this pip, and the problem is to consistently relate the other two cases to CBr_4.

In order to determine V_0 we make one main assumption, the phase function $\delta(k)$ in Eq. (1) is independent of the type of chemical bonding. Even though this assumption has been made previously in the literature,[14] it is, in our opinion hard to justify. Any breakdown in this assumption may introduce additional errors in our Br-C distance determination up to 0.1 Å. If the assumption is true, then when the correct $k=0$ energies are chosen, all three sets of data should be in phase. Accordingly, the $k=0$ point was taken as the pip for CBr_4, and V_0 was varied for the adsorbed and intercalated data until the Fourier transforms of all three had the same phase. In all three cases a nearly identical range in k space (approximately 1.5–6 $Å^{-1}$) was used. The peak shift for CBr_4 can then be applied to the other two cases to find the actual Br-C distance. There remains the possibility of a systematic error due to the choice of V_0 for CBr_4, but this procedure minimizes the effect of such an error.

Transforms of the Br-C EXAFS are shown in

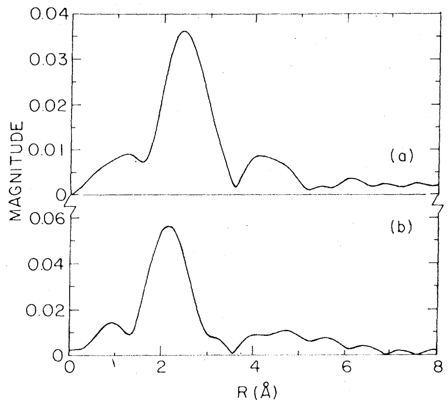

FIG. 9. Fourier transforms of k times the Br-C EXAFS for (a) 0.9-monolayer, 100 °K, out-plane polarization data minus 0.3 of the in polarization data; (b) 0.27-mole% intercalate, 100 °K, polarization parallel to the Grafoil sheets. For both, the range $k = 1-6$ Å^{-1} was used. In (a) the combination of in and out polarizations is used to eliminate the small contribution of the Br-Br scattering to this region.

Fig. 9. Since the structure due to Br-Br scattering is substantial in this low-k region, before transforming it was subtracted from the data using the proportionality of the in and out polarization Br-Br data as described in Sec. IV B. All of the Br-C data is summarized in Table III. For the adsorbed phase data, the above procedure gave $V_0 = 0$, while for the intercalate data $V_0 = -8$eV. These values are reasonable since the intercalated molecules are more tightly bound and, from the above arguments, would, therefore, have a lower V_0.

The peak shift as determined from the CBr_4 data is 0.46 ± 0.02 Å. The rest of the errors given in Table III are from the scatter in the data for slightly different transforms. This is substantial because of the large width of the transform peaks.

Table III also contains the results of a Debye-Waller analysis. In this case the small-k range makes the results uncertain, and it is only because the changes in σ^2 are large that they can be detected at all. The values of σ^2 are referenced to the lowest temperature point of each data set. The amplitudes obtained are referenced to the CBr_4 standard and used to determine the coordination number N. In view of the anomalous behavior of the Br-Br amplitudes, however, the possibility for similar anomalies in these amplitudes cannot be discounted. In fact, for the low-k region, chemical effects should be more important, increasing the likelihood of amplitude anomalies.

Finally, the proportionality between the in and out Br-C EXAFS is checked. For the adsorbed data, the Br-C structure is approximately proportional, but it is not for the intercalated form. This can be seen in Fig. 5 as additional structure in the first large peak of the in polarization data. The implication of this will be discussed in Sec. V.

C. Near-edge structure

Examples of the near-edge structure for the adsorbed phase and intercalate data are shown in Fig. 10. The near-edge structure can be qualitatively correlated with the electronic state of the atoms, and there is a distinct difference for the

TABLE III. Results from the analysis of the Br-C EXAFS. The Br-C distances, the relative mean-square vibrational amplitudes, and the $k = 0$ EXAFS amplitudes as compared to CBr_4 are given. The amplitudes are used to calculate the average carbon coordination number N_C.

T (°K)	R (Å)	$\sigma^2(T) - \sigma^2(LT)$ (Å^2)	Log of the $k = 0$ amplitude ratio (CBr_4 reference)	N_C
		0.9 monolayer		
293	2.81 ± 0.09	0.022 ± 0.010	0.6 ± 0.5	$4 \pm^{3}_{2}$
160	2.89 ± 0.10	0.011 ± 0.005	1.1 ± 0.5	$7 \pm^{4}_{3}$
100	2.92 ± 0.08	···	1.0 ± 0.3	6 ± 2
		0.6 monolayer		
293	2.85 ± 0.10	0.025 ± 0.019	0.8 ± 0.6	$5 \pm^{4}_{2}$
105	2.94 ± 0.08	···	1.2 ± 0.4	$7 \pm^{4}_{2}$
		0.27 mole % intercalate		
293	2.55 ± 0.07	0.003 ± 0.014	0.2 ± 0.2	$2 \pm^{0.6}_{0.3}$
100	2.56 ± 0.06	···	0.5 ± 0.2	$3 \pm^{0.6}_{0.5}$

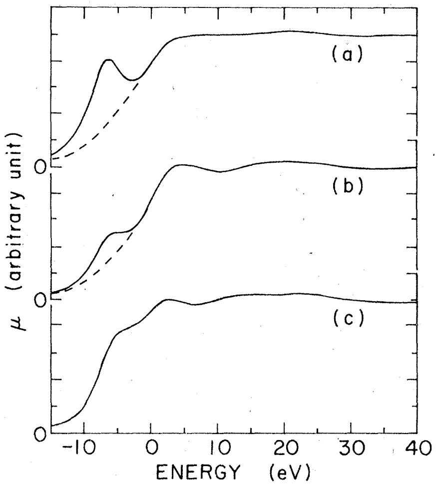

FIG. 10. Expanded plots of the near edge structure for the data in Figs. 1(a), 1(b), and 2(c), respectively. The dashed lines in (a) and (b) show the background used for determining the strength of the $4p$ peak.

intercalate data. This reflects the fact that the Br-Br bond has been stretched significantly, and the bromine is also more strongly bonded to the carbon atoms. For the adsorbed data, there is a definite anisotropy between in and out polarizations, and we have argued that this is related to the orientational anisotropy of the Br_2 molecules in the same fashion as the Br-Br EXAFS.

To qualitatively determine the anisotropy, the areas of the white line were determined. The smooth curve shown in Fig. 10 was used as the background. It was determined by eye from the out polarization data and was chosen to give a reasonably symmetric peak. The out-in anisotropy thus determined is given in Table IV along with similar results from the EXAFS amplitudes, and a comparison of the white line area with that in Br_2 vapor. The two anisotropy results are in reasonable agreement, and both indicate that the molecules are better aligned with the surface as the temperature is lowered. The low-temperature ratio for both coverages averages about 0.31 ± 0.02. The temperature dependence of the out-in anisotropy suggests that at low temperature thermal motion has frozen out. It is most reasonable to assume that at these low temperatures the molecules are lying perfectly flat and all of the out polarization signal is from the random oriented grains of graphite. From this, the fraction of random to oriented surface area can be calculated. If we assume that the oriented grains are perfectly oriented, then the calculated fraction is 0.67 ± 0.05. Neutron-diffraction measurements on Grafoil[6] found a ratio of 0.78. However, they also found that the oriented planes had an rms spread of about 15°. If this fact is also used, then our value for the ratio of random to aligned area becomes 0.61 ± 0.05, somewhat lower than the neutron-diffraction results. This variation is probably not unusual since Grafoil is an industrial product and its surface properties are incidental to its main uses.

TABLE IV. Ratios of the out polarization signal to the in polarization signal for both the $4p$ white line and the Br-Br EXAFS. The total white line area is also compared to that for Br_2 vapor.

T (°K)	White line area ($\frac{2}{3}$ in + $\frac{1}{3}$ out)	White line out-in ratio	Br-Br EXAFS out-in ratio
		0.9 monolayer	
293	0.58 ± 0.02	0.42 ± 0.02	0.43 ± 0.03
160	0.55	0.33	0.37
100	0.55	0.32	0.29
		0.6 monolayer	
293	0.65	0.36	0.42
105	0.67	0.30	0.33

The fact that the out-in ratio increases as the temperature rises suggests that the axis of the molecules is bouncing out of the plane due to thermal disorder. If the angle of the molecules with respect to the basal-plane surface is assumed to have a Gaussian distribution, then at room temperature the rms deviation from lying perfectly flat is about 25°. Calculations by Steele[15] indicate that a similar situation occurs for N_2 adsorbed on graphite. He finds a substantial rms tilt angle at finite temperatures.

The areas of the white line relative to the white line in Br_2 gas are also given in Table IV. Again an average of in and out polarizations was taken to eliminate orientational effects. The white line areas are significantly lower for the adsorbed bromine with the reduction greater for the highest coverage. This implies a filling of the empty $4p$ states. Since the amount of filling is dependent on coverage, the interactions between Br_2 molecules seems to be important. Transfer of electrons from graphite to intercalated bromine has been observed,[16] but it might be expected that charge transfer would be smaller for the more weakly interacting adsorbed system. Clearly it is desirable to separate the contributions of Br_2-Br_2 interactions and Br_2-C interaction to the reduction in the white line. Possibly this could be done by further study on the condensed phases of Br_2 to determine the role of Br_2-Br_2 interactions.

V. INTERPRETATION

The EXAFS measurements have provided a large number of physical parameters describing the bromine-graphite system. Using additional results from LEED and other work, a fairly complete description is possible. For coverages of 0.6 and 0.9 monolayers, the Br_2 molecules apparently lie flat above hexagonal sites. The fact that the molecules lie flat is obvious from the polarization dependence. It is not as obvious, however, that the atoms lie above adjacent hexagonal sites. The appearance of sharp Br-C EXAFS, especially at low temperatures, must mean that the molecules are predominantly on a particular localized site. Otherwise, there would be a whole range of Br-C distances and the EXAFS would be washed out.

Geometrical considerations, and the EXAFS measurements together with the LEED measurements of Lander and Morrison[4] determine the center of a basal-plane hexagon as the adsorption site in agreement with the earlier results for 0.2 monolayer. In the 0.2-monolayer case, the Br-C bond angle was determined by the in-out ratio of the Br-C EXAFS. For the present coverages, the bromine is farther from the surface and the in polarization signal is small. Since the contribution of the randomly oriented adsorption sites must first be subtracted off, the resulting ratio has a large uncertainty depending on the assumed fraction of random grains. Using our fraction of 0.61 ± 0.05 and the measured anisotropy, the angle of the Br-C bond is $70^{\circ}{}^{+20}_{-10}$ with respect to the basal plane. This is consistent with several kinds of adsorption sites including the hexagonal site. However, other aspects of the present measurements do rule out all other possible sites including the next most likely site which is in the middle of the bridge between two adjacent carbon atoms. In this case, the second-shell contribution would equal the first-shell contribution, and since it is at a distance of 0.5 Å larger than the first shell, the transform would exhibit considerable interference effects. For the hexagonal site, the second-shell amplitude is down by a factor of 3, and the distance is 1 Å larger. In fact, the Br-C transforms in Fig. 9 show a small second peak which is most likely the combined contribution of the second and higher shells. Probably the strongest evidence for a hexagonal site are the Br-C EXAFS amplitudes listed in Table III. These results greatly favor a carbon coordination of six. Finally, the fact that the in and out polarizations are approximately proportional indicates that the Br-C distances are dominated by only one distance, further confirming the hexagonal site.

From our EXAFS measurements, we obtain the location of the adsorbed Br_2 molecules as shown in Fig. 11. The molecule at low temperatures lies flat on the surface at a perpendicular distance of 2.53 Å from the center of the molecule to the center of the plane. The distances between each Br atom and the neighboring C atoms are $d_1 = 2.87$ Å, $d_2 = 2.90$ Å, and $d_3 = 2.94$ Å, where d_i are defined in Fig. 11. The absolute uncertainty in the distances is about 0.1 Å, but their relative values are accurate to better than 0.01 Å.

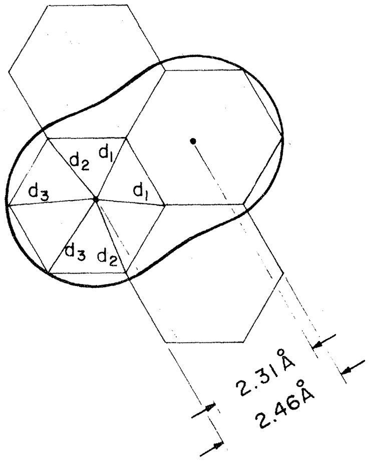

FIG. 11. Location of the Br_2 molecule on the graphite surface for coverages of 0.6 and 0.9 monolayers at low temperatures. A range of Br-C distances d_i are present because of the lattice mismatch. They are $d_1 = 2.87$ Å; $d_2 = 2.90$ Å; $d_3 = 2.94$ Å.

The adsorbed Br_2 molecule is slightly stretched from its relaxed value. This reflects the lattice mismatch of the adsorption sites. The centers of two adjacent hexagons are 2.456 Å apart compared to the normal Br-Br distance of 2.283 Å. For intercalated Br_2, the interaction with the substrate is much larger and the molecule is stretched to fit almost perfectly into the graphite lattice. This seems to be too great a coincidence to indicate anything other than having each bromine atom centered above a basal-plane hexagon.

The lack of orientation dependence of the Br-Br data and the lack of proportionality of the Br-C data for the intercalated sample deserves additional discussion. Since the Br-Br spacing indicates that the Br-Br distances are parallel to the planes, the lack of orientation dependence means the intercalated planes containing most of the bromine are unoriented. The randomly oriented grains in Grafoil, while contributing almost half the surface area, contains only a small part of the total mass. Thus, it is likely that most of the intercalate siganl is coming from regions for which the bromine concentration is considerably more than the nominal 0.27-mole%Br_2. On the other hand, the Br-C EXAFS shows a significant anisotropy. This indicates that some of the bromine is in the aligned planes. Since they do not seem to contribute to the Br-Br EXAFS, it is likely that this bromine is in atomic form.

Therefore, a two phase picture seems necessary to explain our intercalate results. It seems that intercalation takes place more easily in the small unoriented grains and the bulk of the bromine resides there. However, some bromine binds to the oriented planes in atomic form. These binding sites are most likely dangling carbon bonds located at imperfections in the lattice since the additional anisotropic signal occurs for the in polarization data. This indicates that the perpendicular distance between the graphite planes and the bromine atoms is small for these atomic binding sites. An attempt was made to isolate the anisotropic signal using the subtraction techniques described earlier. However, only a single peak could be isolated from which no structural information could be obtained.

The nature of the intercalated bromine in the unoriented planes is not completely clear. Other measurements[9] have indicated that intercalated bromine remains molecular. Our measurements tend to confirm this result, since in spite of the different k dependence of the Br-Br EXAFS, its overall amplitude for $k = 6-10$ Å^{-1} is roughly $\frac{2}{3}$ that of the vapor. This indicates that the average Br-Br coordination number is near one. However, we cannot rule out an atomic picture. The second-neighbor distance of 4.1 Å is close to the spacing of second-neighbor hexagonal sites of 4.26 Å. Such a distance could be observed for both an atomic or molecular picture.

From our results, the distance between the intercalated bromine and the adjacent graphite basal plane is 2.12 Å. This is considerably less than x-ray diffraction results for concentrated intercalates,[10,17] in which the distance between adjacent carbon and bromine planes was found to be 3.5 Å. However, this is probably not a fair comparison since our measurements indicate that the Br_2 is predominately intercalated in the small randomly oriented grains which probably contain a significant disorder. Other authors[9,16] have noted a similar tendency in bromine-graphite residue compounds for the bromine to be associated with lattice imperfections. For these residue compounds there is no increase in the c spacing of the graphite.[18]

Finally, we should point out that the measurements on intercalated bromine were aimed mostly at demonstrating that the adsorbed samples were not intercalated. This fact we have definitely shown. Also, the measurements show that once conditions for intercalation are reached, essentially all of the bromine intercalates, since our intercalated sample showed no evidence for a signal from adsorbed bromine. It is clear that Grafoil is less than ideal for studying the intercalated form, and further measurements should be done on a simpler form of graphite such as a single crystal.

We now turn to the question of the long-range order of these systems. In this case, comparison with LEED results is complicated by the fact that the coverages in the LEED experiments were not measured and varied as the temperature was changed. For our measurements at fixed coverage, it is likely that mixed phases will occur, making it more difficult to determine the location of phase boundaries. For example, the 4 × 4 solid phase observed by Lander and Morrison would correspond to a coverage of 0.75 in our notation. Therefore, neither of our coverages could be completely in this phase.

Since our coverage of 0.6 monolayer is substantially below that necessary for either solid phase and has a different short-range structure from the 0.2-monolayer lattice gas, it must be predominately in the liquid phase observed in the LEED measurements. In this phase, the molecules are again most of the time localized to specific sites, but interact with each other and hop randomly across the surface. At room temperature the 0.9-monolayer results are nearly the same as for 0.6 monolayer in all respects, and it seems likely that this coverage is also in the liquid phase. As the temperature is lowered, the larger decrease in the molecular vibration for 0.9 monolayer suggests that some sort of phase transition is taking place, but at present its exact nature is uncertain. The first solid phase seems to be excluded, however, since the data show no sign of the molecules assuming the tilted arrangement necessary for this phase.

The increased disorder at low temperatures found in the 0.6-monolayer Br_2 can only come from some structural disorder introduced by the interaction with the substrate, since reasonable temperature extrapolation to 0 °K as in Fig. 8 shows increased disorder remaining compared to the vapor. In contrast, the 0.9-monolayer data does not indicate any additional structural disorder at low temperatures. This structural disorder could occur because of the manner in which the 0.6 monolayer adsorbs onto the substrate, indicating that it is in the liquid phase and the 0.9 monolayer is in an ordered phase at low temperatures. The fact that the disorder becomes equal at room temperature for the two coverages could indicate a disordering of the 0.9 monolayer between 210 °K and room temperature. This conclusion should be checked by further measurements, especially in view of the puzzling behavior of the amplitude variation of the 0.9-monolayer EXAFS as a function of temperature. It is, of course, possible that the puzzling amplitude variation may be at the root of the temperature variation of σ^2 and not a phase transition.

The large differences between the microscopic structure of the liquid and gas phases and the large number of phases observed by LEED measurements makes it apparent that there is a complicated interplay of Br_2-substrate and Br_2-Br_2 interactions. For an isolated molecule it is evidently more favorable energetically for only one atom to be relatively tightly bound to the substrate. As the coverage increases, the interactions between molecules tend to line up the molecules in a plane. This same tendency of the molecules to line up in a plane is also seen in the 3-D solid form of Br_2. However, in order for the molecules to lie flat in the planes, they must move farther from the surface. This is necessary because of the lattice mismatch between the Br_2 molecules and the graphite substrate, and the overlap of the charge density between the Br atoms and that between the C atoms. In order for the molecules to lie flat and remain close to the surface, they would have to be stretched substantially as in the intercalated form.

The above picture also explains some other trends in our data. In Table III, the Br-C distance seems to be increasing slightly as the temperature is lowered. The increase is barely significant, but it does occur for both coverages. Also, both σ^2 and the amplitude show a similar temperature dependence with the amplitude increasing and σ^2 decreasing. From Sec. IV C, we know that the molecules lie flatter as the temperature is lowered and at room temperature have a significant rms angular deviation. It may be that when one end of the molecule bounces up, the other atom moves closer to the substrate in order to achieve a configuration closer to that of the low coverage lattice gas. As the temperature is raised and this occurs more frequently, the average distance would decrease and its rms deviation σ^2 would increase. Also, the overall amplitude would decrease because of a Debye-Waller factor and an increased probability of diffusion along the surface.

Finally, there remains the question of the anomalous Br-Br EXAFS amplitudes. In making the measurements, some care was taken to determine accurate amplitudes in order to determine the anisotropy ratios. Thus, the anomaly does not seem to be an experimental artifact, but rather the k dependence of the amplitude function seems to be changing. Because of this, some of our Debye-Waller results may be suspect, but the rest of our results are unchanged and the above interpretation still stands. Such an amplitude change might be expected between the intercalated and adsorbed bromine because of the significant change in chemical binding.[13] However, any change between the weakly interacting adsorbed system and the vapor, or especially between a given absorbed system as a function of temperature, is completely unexpected. Further measurements on this and simila systems are warranted.

VI. SUMMARY

In this paper we have shown how EXAFS is a very useful complement to LEED in the study of surface systems. EXAFS provides the short-rang structure, while LEED determines the long-range order of the system. For the 0.6- and 0.9-monolayer coverages studied, the location of the Br_2 molecule relative to the substrate has been essentially completely defined. The system studied in this paper, Br_2-graphite, is seen to be a rich one for looking at the interplay of adatom-surface and adatom-adatom interactions. In particular, this paper and a previous letter have provided the detailed structure for at least two adsorbed phases and a dilute intercalated phase.

It was found that there is a dramatic change in the short-range structure as the coverage increased. In the low coverage gas phase only one atom of a molecule is strongly bound to the surface; the other is free to flop around. As the coverage is increased and molecules start interacting with each other, they move farther from and align themselves with the surface. This occurs with a transition to a liquidlike phase and with increasing coverage two distinct solid phases also appear in the LEED measurements. The EXAFS measurements give some indications of a transition to a solid phase, but the results are far from conclusive. In any case, this points up another facet of the complementary nature of EXAFS and LEED. It is easy for LEED to measure transitions in the long-range order which are accompanied by subtle changes in the short-range order, while EXAFS can easily determine transitions which involve short-range changes, but where the long-range structure remains disordered.

We have also shown how EXAFS can be successfully applied to the study of graphite intercalation compounds. This is presently an active research field and no doubt one to which EXAFS will contribute extensively in the future.

Finally, we have found an unexpected strong dependence of the EXAFS amplitude function on temperature and physical state of these Br_2-graphite systems. This certainly indicates the need for further experimental and theoretical work to determine the origins of such behavior.

ACKNOWLEDGMENTS

We would like to express our sincere thanks to the staff at SSRL for their valuable help in making these measurements. We would also like to express our most sincere appreciation to Professor J. G. Dash for his invaluable guidance and advice. It is safe to say that without his help this work would not have been possible. We also thank Dr. B. Kincaid for supplying us with the Br_2 data reported in Ref. 8. This work was supported in part by the NSF in cooperation with the U.S. Department of Energy under Research Grant No. DMR73-02521 A02.

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