Selective adsorption resonances in the scattering of helium atoms from xenon coated graphite: Close-coupling calculations and potential dependence

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Selective adsorption resonances in the scattering of helium atoms from xenon coated graphite: Close-coupling calculations and potential dependence

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Accurate close-coupling calculations are carried out for the scattering of helium atoms from a monolayer of Xe on the (0001) face of graphite, using atom-surface potentials based on pairwise additivity and the (known) He–Xe pair potential. Good agreement is obtained with the selective adsorption data of Bracco et al. The potential dependence of the resonance spectrum is explored, and it is found that the data are very sensitive to small changes in the potential; two pair potentials which both reproduce the gas phase data well, give significantly different resonance spectra, and the contributions of three-body forces are also shown to be important. The resonance spectra are significantly affected by small changes in the corrugation strength as well as by the laterally averaged potential. The potential dependence becomes even more pronounced as the scattering energy is decreased.

I. INTRODUCTION

There has recently been much interest in the scattering of atoms from overlays of rare gas atoms on solid surfaces.1–6 Ellis et al.1–5 have measured diffusive scattering and selective adsorption resonances for scattering of hydrogen atoms from an ordered monolayer of xenon on the (0001) face of graphite, and Bracco et al.4,5 have performed similar experiments with a beam of helium atoms.

There are several reasons why scattering from overlays is of particular interest. First, atomic scattering can provide information on the structure and dynamics of the overlay itself, and this is of value in understanding the processes involved in physisorption. Secondly, since the pair potentials for the interaction of H and He atoms with rare gas atoms are well known, a good a priori estimate of the atom–surface potential may be made using pairwise additivity, so that atom–overlay systems provide an excellent testing ground for approximate dynamical methods, such as the eikonal7 and hard corrugated wall8 approximations. Thirdly, the deviations of the real gas–surface potential from that predicted on the basis of pairwise additivity may provide detailed information on the contributions of many-body forces to intermolecular potentials.8

The present paper will be mainly concerned with this last objective, and will set out to establish how much information on the gas–surface potential is contained in atom–overlay scattering data. We present converged close-coupling calculations for the scattering of helium atoms from a monolayer of Xe on graphite (He–Xe/C), using realistic models for the gas–surface potential, and investigate the sensitivity of the calculated scattering observables to small changes in the potential. This work is similar in spirit to recent calculations by Jonsson and Ware9 for the scattering of hydrogen atoms from a similar surface.

Section II describes the model of the He–Xe/C system used in the present work, and Sec. III discusses the computational method used. Sections IV and V present calculations of diffractive and resonant scattering, respectively, and compare the calculated quantities with the experimental data of Bracco et al. Section VI discusses the sensitivity of the experimental data to different aspects of the intermolecular potential, and investigates the role of many-body forces. Section VII considers the information content of lower-energy scattering experiments, for which no data are yet available.

II. THE MODEL

In the experiments of Bracco et al.,4,5 a monolayer of Xe was adsorbed on the (0001) face of graphite. The xenon appears to form an ordered (12×3)R30° lattice in registry with the substrate,4 with lattice constant 4.2965 Å.10 Figure 1 shows the conventions used in the present work for the direct space unit cell, the reciprocal space unit cell and the primitive reciprocal lattice vectors ̂ g1 and ̂ g2. The origin of the coordinate system is located on a xenon atom. An arbitrary direct space position vector is denoted r, and its projection onto the surface plane is R. An arbitrary reciprocal lattice vector is denoted

\[ G = (g_1, g_2) = \hat{g}_1 \hat{g}_1 + \hat{g}_2 \hat{g}_2 . \]  

Our choice of unit cell is not unique, and a different choice was made in Ref. 4; their reciprocal lattice vector \( (g'_1, g'_2) \) corresponds to \( (g_1 + g'_3, g'_3) \) in our coordinate system.

The dynamics of the system are determined by the potential energy for interaction of a helium atom with the surface. To a first approximation, the potential may be assumed to be a sum of He–overlayer and He–graphite interactions. The He–Xe interaction may be treated as a pairwise sum over surface atoms. If \( U(r) \) is the ap-
appropriate pair interaction, the total interaction energy between a He atom located at \( r \) and the layer of surface atoms, neglecting many-body contributions, is

\[
V(r) = \sum_j U(|r - r_j|),
\]

(2)

where \( r_j \) is the \( j \)th lattice site. This gives for the Fourier components of the atom–surface potential

\[
V_G(z) = a_d^2 \int \sum_j U(|r - r_j|) \exp(-iG \cdot R) \, d^2 R,
\]

(3)

where \( a_d \) is the area of the direct space unit cell. The summation may be eliminated and the integral evaluated numerically as described by Steele.\(^{11} \) The He–Xe pair potentials used in the present paper are summarized in the Appendix.

The xenon monolayer prevents helium atoms from approaching closer than about 6.0 Å to the plane of the graphite surface atoms, so that it is a good approximation to represent the He–graphite interaction by its limiting long-range behavior:\(^{12} \)

\[
V_00(z) = -C_2(z + d)^3,
\]

(4)

where \( d \) is a parameter specifying the effective origin of the interaction; \( d \) has been estimated to be 3.435a_0 for the He–Xe/C system.\(^1\) The coefficient \( C_2 \) may be treated as an empirical constant or calculated theoretically; in the present work the theoretical value of \( C_2 = 184 \text{ meV Å}^3 \) has been used throughout. It may be noted that this neglects any dielectric screening due to the xenon. Both the deviation of the He–graphite potential from Eq. (4) and corrugation terms involving the graphite lattice have been ignored in the present work, since they are much smaller than the corresponding quantities arising from the overlayer.

III. COMPUTATIONAL METHOD

The coupled equations that describe the scattering of an atom of mass \( m \) and incident wave vector \( k \) from a rigid periodic surface are\(^{14} \)

\[
\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{\hbar^2}{2m} (K + G)^2 + V_00(z) - E \right] \chi_0(z) = \sum_{G'} V_{G',G}(z) \chi_{G'}(z),
\]

(5)

where \( E = \hbar^2 k^2 / 2m \) is the energy of the incident beam, \( K \) is the projection of \( k \) onto the surface plane, and the polar angles of the vector \( k \) are denoted \((\theta, \phi)\) where \( \phi \) is measured relative to \( \hat{z}_1 \). The prime on the summation indicates that the term with \( G = G' \) is to be excluded. The appropriate boundary conditions for atom–surface scattering have been given by Wolken.\(^{14} \) In the present work, the coupled equations were solved using the \( R \)-matrix propagator algorithm of Walker and Light.\(^{15,16} \) This yields \( S \) matrices such that unit incoming flux in channel \( G \) results in outgoing fluxes \( \Sigma_{G'} |S_{G,G'}|^2 \) in the various outgoing channels \( G' \). The only important dynamical approximation is the neglect of inelastic effects; this may be crudely accounted for by multiplying the calculated intensities by a Debye–Waller factor.

Accurate calculations of resonant scattering require the inclusion of many closed channels in the coupled equations, but these are important only at relatively small values of \( z \) where the channels are classically accessible. It was therefore found advantageous to contract the basis set to exclude deeply closed channels in the long-range region. This was done by first transforming the local \( R \) matrix back into the primitive basis of Fourier components, truncating it to exclude the deeply closed channels, and then transforming back to the local eigenbasis. Each closed channel was removed from the basis when a WKB phase integral

\[
(2m/\hbar^2)^{1/2} \int_{z_1}^{z_2} |E - V(z)|^{1/2} \, dz'
\]

(6)

indicated that the wave function amplitude for that channel had dropped below \( 10^{-6} \). For channels which are classically accessible at some value of \( z \), \( z_1 \), is the outer classical turning point; for channels which are classically inaccessible everywhere, \( z_1 \) was taken to be \( 1.5z_2 \), where \( z_2 \) is the position of the inner turning point in the lowest channel.

For scattering at arbitrary incident angles, the symmetry of the Xe lattice does not simplify the calculations. However, for incident angles of \( \phi = 0^\circ \) or \( 30^\circ \) the Hamiltonian matrix is symmetric with respect to reflection in the reciprocal plane containing \( k \) and the \( z \) axis. Since close-coupling calculations use an amount of computer time proportional to \( N^3 \), where \( N \) is the number of basis functions included, it is highly desirable to take account of this symmetry. A symmetrized two-dimensional basis set is therefore introduced

\[
\Phi_0 = \exp[i(K + G) \cdot R] + \Phi_0 \exp[i(K + G) \cdot R],
\]

(7)

where \( \Phi_0 \) is the operator for the reflection referred to above. For \( \phi = 0^\circ \), the symmetrized basis functions are

\[
\Phi_{\psi_1,0} = \exp[i(K + (\psi_1, 0)) \cdot R],
\]

\[
\Phi_{\psi_1,\psi_2} = \frac{1}{\sqrt{2}} \left[ \exp[i(K + (\psi_1, \psi_2)) \cdot R] + \exp[i(K + (\psi_1 - \psi_2, \psi_2)) \cdot R] \right], \quad \psi_2 > 0
\]

(8)

and for \( \phi = 30^\circ \),

\[
\Phi_{\psi_1,\psi_2} = \frac{1}{\sqrt{2}} \left[ \exp[i(K + (\psi_1, \psi_2)) \cdot R] + \exp[i(K + (\psi_1, \psi_1 - \psi_2)) \cdot R] \right].
\]

(9)
Only the even combinations of the contributing functions need be considered, since the incident beam is even with respect to the reflection operator. Symmetrization of the basis set nearly halves the number of basis functions necessary for a given accuracy, and saves about a factor of five in computer time.

For an incident beam normal to the surface, even greater symmetry is present. The Hamiltonian is then symmetric with respect to any rotation of the reciprocal coordinate system by a multiple of 60°, so that the appropriate symmetrized basis spans the totally symmetric (A) representation of the group C₆:

$$
\phi_G = \frac{1}{\sqrt{6}} \sum_{g \in \mathbb{Z}_6} (\hat{C}_g)^n \exp(iG \cdot R), \quad G \neq (0, 0), \quad (10)
$$

where

$$
\hat{C}_g \exp[i(g_1, g_2) \cdot R] = \exp[i(g_2, g_2 - g_1) \cdot R]. \quad (11)
$$

Again, only the A representation need be considered because the incident beam has A symmetry. In this case, proper symmetrization of the basis set reduces the computer time required by a factor of at least 100.

### IV. DIFFRACTION DATA AT NORMAL INCIDENCE

Bracco et al.⁴ have measured the intensity of all diffracted beams for He–Xe/C scattering at normal incidence using an incident beam with \( k = 11.05 \) Å⁻¹, and have interpreted their results using the eikonal approximation with a corrugated hard wall model of the potential. We have performed close-coupling calculations for this system using a potential based on the postulate of pairwise additivity of intermolecular forces as described in Sec. III; the He–Xe pair potential used was the HFD-1 potential of Ref. 17, and the He–graphite C₃ coefficient was taken to be 184 meV Å⁻¹. The resulting gas–surface potential is referred to below as potential 1. The potential is quite strongly corrugated, with a peak-to-peak corrugation of about 0.9 Å; its Fourier components are shown in Fig. 2.

The results of our calculations for a 51-channel basis set, including all channels with \( |G| \leq 9|\hat{G}|_1 \), are compared with the experimental data in Table I; it may be noted that this calculation was feasible only because of the sixfold symmetry of the basis set, and is equivalent to a 301-channel calculation in an unsymmetrized basis. The S-matrix elements are converged to better than \( \pm 10^{-4} \) with respect to basis set size. The S-matrix elements given in Table I are those appropriate to an individual diffracted beam: the symmetrized S-matrix elements have been divided by six for non specular outgoing channels. The calculated intensities have been corrected for inelastic effects using a Debye–Waller factor with the Beeby correction:⁹

$$
I_{calc} = |S_{00}|^2 \exp(-\Delta E' \langle \omega^2 \rangle), \quad (12)
$$

where

$$
\Delta E' = \left( k^2 \cos \theta_i + \frac{2m\epsilon}{\hbar^2} \right)^{1/2} + \left( k^2 \cos \theta_d + \frac{2m\epsilon}{\hbar^2} \right)^{1/2}, \quad (13)
$$

\( \theta_i \) and \( \theta_d \) are the incident and diffracted beam angles and \( \epsilon = 7.4 \) meV is the average well depth of the atom–surface potential. The value of \( \langle \omega^2 \rangle \) was taken to be 0.0051 Å⁻² for a surface temperature of 17 K.³

The general features of the diffraction pattern are well reproduced by the calculations. The outgoing channels with \( \hat{G}_2 = 0 \) correspond to diffracted beams at \( \phi = 0° \), and this series shows rainbow maxima at \( G = (3, 0) \) and

---

**Table I.** Comparison of observed diffraction intensities for He–Xe/C with \( k = 11.05 \) Å⁻¹ at normal incidence with those calculated from potential 1. Note that the reciprocal unit cell used here differs from that of Ref. 4.

| \( G \) | \( 0_2 \) | \( 0 \) | \( |S_{00}|^2 \) | \( I_{calc} \) | \( I_{exp} \) |
|---|---|---|---|---|---|
| 0 | 0.0 | 0.0 | 0.00761 | 0.00047 | 0.00031 |
| 1 | 0.0 | 8.8 | 0.00267 | 0.00017 | 0.00008 |
| 2 | 0.0 | 17.9 | 0.00625 | 0.00044 | 0.00030 |
| 3 | 0.0 | 27.5 | 0.01711 | 0.00139 | 0.00087 |
| 4 | 0.0 | 38.0 | 0.00994 | 0.00020 | 0.00015 |
| 5 | 0.0 | 50.3 | 0.02343 | 0.00025 | 0.00020 |
| 6 | 0.0 | 67.3 | 0.00688 | 0.00011 | 0.00005 |

---

**Fig. 2.** Fourier components of potential 1 as a function of normal separation \( z \).
(5, 0) as observed experimentally. The channels with $g_1 = -g_2$, corresponding to diffracted beams at $\phi = 30^\circ$, show much less high-angle scattering, again in agreement with experiment. The relative intensities are not reproduced quantitatively, with discrepancies of around 50% in many cases, but it should be realized that small errors in the positions of the rainbow angle can cause quite large errors in the individual peak intensities.

V. CALCULATIONS OF RESONANCES

Bracco\textsuperscript{5} has also measured selective adsorption resonances in the specular intensity for a helium beam at $k = 6.5$ Å\textsuperscript{-1} scattered from a monolayer of Xe on graphite. In this experiment, the specular intensity was measured as a function of polar angle $\theta$ at constant azimuthal angle $\phi = 0^\circ$. We have performed calculations of resonances for these experimental conditions using potential 1 (described in Sec. IV). The basis set used included all functions satisfying the following three criteria:

\begin{enumerate}
  \item $|G| \leq 7 |\tilde{g}_1|$, 
  \item $\mu_2 \leq 4$, 
  \item $\frac{\hbar^2}{2m} (K + G)^2 < 75$ meV.
\end{enumerate}

The size of this basis set depends upon the angle of incidence $\theta$, but $N$ is typically between 50 and 60 after symmetrization. The calculations used approximately 50 min per angle on a VAX 11/750 with floating point accelerator.

The calculated specular intensity is shown in the middle trace of Fig. 3 as a function of $\theta$. Bracco's experimental data are reproduced in the bottom trace for comparison. The quantity plotted for the calculated points is

\begin{equation}
\frac{I}{I_0} = |S_{\theta_0}|^2 \exp(-\Delta E_0^2 \gamma^2) \cos \theta,
\end{equation}

where the additional factor of $\cos \theta$ was included to allow for the decreased area of the scattering surface normal to the beam for near-grazing incidence.

The agreement between theory and experiment is remarkably good, despite the fact that no attempt has been
made to convolute the theoretical spectrum with the experimental beam conditions. Nearly all the peak positions agree well, and the relative intensities of the peaks are moderately well reproduced. Nevertheless, there are points of disagreement which cannot be explained in terms of the finite experimental resolution, and which must be due to inadequacies in the potential surface used. The most striking of these features are the doubling of the theoretical peaks around \( \theta = 30^\circ \) and \( 64^\circ \), and the shape of the broad feature from \( 43^\circ \) to \( 49^\circ \). The assignment of the resonant features and the implications for the atom-surface potential will be discussed in the following sections.

The fully converged calculations described above are computationally too expensive to allow the detailed investigation of the effects of changing basis sets and potential parameters. We have therefore also performed "minimal basis" calculations for potential 1, using only the functions

\[
G = (-3,0) \quad (-2,0) \quad (-1,0) \quad (0,0) \quad (1,0) \quad (2,0) \\
(-2,1) \quad (-1,1) \quad (0,1) \quad (1,1) \quad (2,1) \\
(-1,2) \quad (0,2) \quad (1,2) \quad (2,2) \\
(0,3) \quad (1,3) \quad (2,3)
\]

properly symmetrized according to Eq. (7). This 18-channel basis set is equivalent to a 30-channel unsymmetrized basis, and gives the results shown in the top trace of Fig. 3. It may be seen that all the principal features of the full calculation are present for \( \theta > 30^\circ \), although there are some changes in the relative intensities of different features. Since these calculations took only about 180 s of CPU time per angle, the minimal basis set has been used throughout the following sections.

For a weakly corrugated surface, selective adsorption resonances occur at incident angles for which

\[
E = \frac{h^2}{2m} (K+G)^2 + E_n ,
\]

where \( E_n \) is the (negative) binding energy of the \( n \)th vibrational level supported by \( V_{\text{ad}}(z) \)

\[
-\frac{h^2}{2m} \frac{d^2}{dz^2} + V_{\text{ad}}(z) - E_n \chi_n(z) = 0 .
\]

The energies of the lowest five vibrational levels of the various potentials used here are given in Table II. The resonance positions implied by Eq. (17) for low-order \( G \) vectors using potential 1 are shown in Fig. 3.

According to the Weare-Wolfe rules for selective adsorption resonances, resonant channels which are strongly and directly coupled to the specular channel should produce minima in the specular intensity (rule 1), whereas those which are indirectly coupled should produce intensity maxima (rule 3). It may be seen from Fig. 2 that the (1,0) Fourier component of the potential is easily the strongest corrugation term, so that we expect the (1,0) and (1,1) channels to produce specular minima and all other resonant channels to give maxima. In order to investigate whether this actually occurs, we performed additional calculations using basis sets which selectively excluded individual resonant channels; an isolated resonance should disappear when the channel responsible for it is excluded from the calculation. For calculations excluding indirectly coupled channels this was sometimes the case, allowing the unambiguous assignment of a few features. It was not possible to obtain conclusive assignments of the overlapping resonances between \( 39^\circ \) and \( 50^\circ \) by this method, and it appears that the bound states involved are very strongly mixed.

The (1,2) channel is coupled to the specular by the moderately strong \((1,\pm 1)\) potential component (see Fig. 2), and might therefore exhibit either rule 1 or rule 3 behavior. A calculation excluding this channel is shown in Fig. 4; it may be seen that the large peak at \( 74^\circ \) is still present, but the shoulder at \( 72^\circ \) has disappeared. The multiplet structure between \( 61^\circ \) and \( 68^\circ \) has collapsed to a broad singlet. The \( 72^\circ \) shoulder should therefore be associated with the \( n=1 \) level of the \((1,2)\) channel. The peak at \( 74^\circ \), if it is a resonant feature at all, must be assigned to the \( n=0 \) level of the \( G=(1,1) \) channel, which the Weare-Wolfe rules predict will give rise to a minimum. It thus seems likely that the corrugation in this system is too high for the Weare-Wolfe rules to be reliable for first-order resonances. The peaks around \( 64^\circ \) apparently derive their intensity from

<table>
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<th>2</th>
<th>3</th>
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<td></td>
<td></td>
</tr>
<tr>
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<td>-5.019</td>
<td>-5.411</td>
<td>-4.645</td>
</tr>
<tr>
<td>1</td>
<td>-2.021</td>
<td>-2.365</td>
<td>-1.803</td>
</tr>
<tr>
<td>2</td>
<td>-0.071</td>
<td>-0.848</td>
<td>-0.572</td>
</tr>
<tr>
<td>3</td>
<td>-0.176</td>
<td>-0.237</td>
<td>-0.141</td>
</tr>
<tr>
<td>4</td>
<td>-0.031</td>
<td>-0.046</td>
<td>-0.022</td>
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</table>

TABLE II. Energies \( E_n \) of the lower vibrational levels supported by \( V_{\text{ad}}(z) \) for the potentials used in the present work. Energies are in meV.
VI. SENSITIVITY OF RESONANCE STRUCTURE TO POTENTIAL PARAMETERS

It has been suggested that measurements of selective adsorption resonances may provide information on many-body contributions to the atom–surface potential. The purpose of this section is to describe tests of the sensitivity of the data to small changes in the potential, in order to establish whether many-body effects will be significant compared to the uncertainties in the two-body potential. The characteristics of the various potentials used here are summarized in Table III.

A. Sensitivity to the pair potential

Smith et al.17 gave two He–Xe pair potentials which fitted the gas phase and molecular beam data; in addition to the HFD-1 potential used above, they recommended a Maitland-Smith potential with parameters $\kappa = 27.4 \text{ K}$, $R_m = 3.98 \text{ Å}$, and $\gamma = 5$. The well depth is about 1 K shallower than for the HFD-1 potential, and $R_m$ is 0.06 Å larger. The gas–surface potential obtained from this function, again assuming pairwise additivity and using a He–graphite $C_2$ coefficient of 184 meV Å$^3$, is designated potential 2.

The resonance spectrum obtained for potential 2 using the minimal basis set for the same experimental conditions as in the previous section is shown in the middle trace of Fig. 6. All the features are shifted to larger angles, as expected from the deeper bound state energies. The doublet at 64° collapses to a singlet, in agreement with experiment, and the shape of the feature between 34° and 49° is altered. The agreement between calculated and observed peak positions is significantly poorer than for potential 1, but there is little change in the overall intensity pattern. It is interesting to note that the surface scattering results can distinguish so clearly between the HFD-1 and MS pair potentials, while the gas phase data used in Ref. 17 cannot.

B. Sensitivity to three-body forces

The leading term in the many-body contribution to the atom–surface potential is the Axilrod–Teller triple-dipole term. As a first approximation, the many-body correction may be calculated by summing this over all pairs of surface atoms

$$V_3(r) = \sum_{i<j<k} \frac{\mu_{123} [1 + 3 \cos \theta \cos \theta_i \cos \theta_j]}{|r-r_i|^3 |r-r_j|^3 |r_i-r_j|^3},$$

where $\theta$, $\theta_i$, and $\theta_j$ are the angles of the triangle formed by $r$, $r_i$, and $r_j$. The coefficient $\mu_{123}$ is given by

$$\mu_{123} = (h/\pi) \int_0^\infty \alpha_i(\omega) \alpha_j(\omega) \alpha_k(\omega) d\omega.$$

In the present work, the three term upper bound Pade approximants of Tang et al.81 were used for the functions $\alpha(\omega)$, giving $\mu_{123} = 28470$ meV Å$^3$ for the He–Xe–Xe

<table>
<thead>
<tr>
<th>Potential</th>
<th>Pair potential</th>
<th>Comments</th>
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<tr>
<td>1</td>
<td>HFD-1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>MS</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>HFD-1</td>
<td>Axilrod–Teller</td>
</tr>
<tr>
<td>4</td>
<td>HFD-1</td>
<td>Corrugation × 0.9</td>
</tr>
<tr>
<td>5</td>
<td>HFD-1</td>
<td>Corrugation × 1.1</td>
</tr>
</tbody>
</table>
interaction. The corresponding lower-bound approxi-
mants give $\nu_{123} = 27520 \text{ meV } \AA^2$. These values may be
compared with $\nu_{123} = 31520 \text{ meV } \AA^2$, obtained by Klein
and Cole$^{22}$ using a single pole approximation to $\alpha(i\omega)$. No
attempt was made in either case to account for higher-
order multipole or repulsive contributions to the
many-body forces.

The Axilrod-Teller contribution to the He–Xe/C po-
tential was calculated from Eq. (19) by summing over
all surface atoms within ten lattice constants of $R$. The
integration over the unit cell to yield the Fourier com-
ponents was performed using the Cooley-Tukey fast
Fourier transform algorithm$^{23}$ on an $8 \times 8$ grid. The
$V_{oo}(z)$ component of the three-body potential is shown in
Fig. 7 as a solid line. The three-body term is repulsive
at all distances, in accordance with the usual result for
condensed phases.$^{24}$ The other Fourier components are
extremely small, generally at least a factor of $100$
smaller than the corresponding two-body components.

In order to test the effect of many-body forces on the
resonant scattering, we have repeated the minimal basis
calculations of Sec. V, using a potential constructed
from potential 1 (HFD-1) by adding the Axilrod–
Teller terms; this is referred to below as potential 3. The
lowest five bound state energies of $V_{oo}(z)$ for potential 3
are given in Table II, and the calculated selective ad-
sorption spectrum is shown in the bottom trace of Fig.
6. The spectrum differs significantly from that for po-
tential 1; here the vibrational levels are more weakly
bound than those of potential 1, and the peak positions
are shifted to smaller angle.

A change in the parameter $d$ of Eq. (4) can have an
effect on the potential similar to that of the Axilrod–
Teller term. The value of $d$ used in potential 1 was
given by

$$d = Z_1 - c/2,$$

(21)

where $Z_1$ is the separation between the xenon and graphite
planes and $c$ is the graphite interplanar distance. Equation
(21) is approximate; as noted by Zaremba and Kohn,$^{25}$
the first correction to Eq. (21) decreases the value of $d$.
In Fig. 7 we show the change in $V_{oo}(z)$ if $d$ is chosen in-
stead as

$$d = Z_1 - 2c/3.$$

(22)

This seems to be a reasonable upper bound to the possi-
ble variation in $d$. It may be seen that the effect of this

![FIG. 6. Resonances in the calculated specular intensity for
different atom-surface potentials. Top: potential 1; center:
potential 2; bottom: potential 3. All calculations used the mini-
imal basis set and are for the same experimental conditions as
Fig. 3.](image)

![FIG. 7. Axilrod-Teller triple dipole correction to the laterally
averaged potential (solid line) and the correction due to
changing the image plane (dashed line) as a function of $z$.](image)
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FIG. 8. Dependence of the specular intensity upon corrugation strength for the experimental parameters of Fig. 3. Top: potential 4 (corrugation × 0.9); center: potential 1 (corrugation × 1.0); bottom: potential 5 (corrugation × 1.1). Change would be similar in form but opposite in sign to the Axilrod-Teller contribution. Since the corrugation terms arising from the Axilrod-Teller term are negligible, it may well be that the good agreement between the observed resonance positions and those calculated from potential 1 arises from a cancellation of errors of this type.

A second source of uncertainty in the atom-substrate interaction is the value of the $C_3$ coefficient. A change in $C_3$ can also affect the potential in much the same way as the Axilrod-Teller term. Information on many-body forces could be extracted from resonant scattering data only if the atom-substrate potential is well known from theory or independent experiments. For the He-Xe/C system, the uncertainties in the He-Xe pair potential and the He-graphite surface potential are too great to allow any definite conclusions at present. However, it should be emphasized that we have considered only the Axilrod-Teller term, and other contributions to many-body forces may also be important.

C. Sensitivity to corrugation

The discussion above interpreted the resonance spectra solely in terms of the positions of the bound states of $V_{ot}(z)$, although the corrugation terms also differed for potentials 1 and 2. It is interesting to investigate how much the spectra change when the corrugation is altered but $V_{ot}(z)$ remains the same. We have therefore performed minimal basis set calculations on two potentials obtained from potential 1 by scaling the corrugation terms by 0.9 and 1.1; these are designated potentials 4 and 5, respectively, and their resonance spectra are compared with that for potential 1 in Fig. 8.

It may be seen that there are significant changes in the spectra when the corrugation is changed by 10%. The overall specular intensity drops as the corrugation is increased, and several peaks move appreciably. The peak at 44° for potential 4 coalesces with the structure on its high-angle side, and the relative intensity of the peak at 67° increases dramatically. The shoulder on the low-angle side of the 74° peak disappears as the corrugation is increased. It may be concluded that the resonance spectra are strongly sensitive to the corrugation as well as to the positions of the zeroth order bound states.

VII. PREDICTIONS FOR LOW-ENERGY SCATTERING

It is interesting to investigate whether the information content of atom-surface resonant scattering experiments increases as the scattering energy is decreased. Computationally, the problem becomes simpler at lower energies, since fewer channels are needed to obtain convergence of close-coupling calculations. We have therefore performed calculations for resonant scattering in

FIG. 9. Predicted specular intensity as a function of $\theta$ for very low energy scattering ($k=4.0$ Å⁻¹) and $\phi=0$ using potentials 1 (top) and 2 (bottom). In each case, the resonance angles obtained using Eq. (17) are shown as in Fig. 3.
the same geometry as used above, but for an incident wave vector of 4.0 Å⁻¹; this corresponds to a beam energy of 8.36 meV, which should be accessible using a supersonic beam of He with the source cooled to liquid He temperatures. The results obtained for potentials 1 and 2 using the minimal basis set of Eq. (16) are shown in Fig. 9, together with the zero corrugation estimates of the resonance positions.

As for the higher-energy resonance spectra, some features may be unambiguously assigned to individual resonances while others are strongly mixed. The principal difference between the spectra for the two potentials is that once again the peaks for potential 2 are shifted to higher angles, as expected from its deeper bound state energies. However, there are also considerable differences in the relative intensities of different peaks, particularly between 20° and 35°. It is clear that the low-energy scattering will be considerably more sensitive to details of the potential than the existing 6.5 Å⁻¹ data, and that it is highly desirable to perform low-energy experiments.

VIII. CONCLUSION

We have presented the results of accurate close-coupling calculations for both diffractive scattering and selective adsorption resonances for the strongly corrugated system He–Xe/C. The potential surfaces used were based on pairwise additivity of intermolecular forces and the (known) He–Xe pair potential. Calculations using a large (>50 channel) basis set agree well with experiment, and the principal features of the resonant scattering are preserved when a much smaller (18 channel) basis set is used.

The selective adsorption data are very sensitive to the details of the potential used. For example, the existing data can distinguish clearly between atom–surface potentials based on two different He–Xe pair potentials, both of which fit the gas phase data very well. The calculated resonance spectra are also strongly sensitive to corrugation terms in the potential. Three-body forces have a considerable influence on the resonant scattering, but experimentally it may be difficult to distinguish the effects of three-body effects from those of uncertainties in the atom–substrate interaction, particularly the effective origin of the interaction.

Predictions of resonant scattering for very low incident energies were made. Under these conditions, the scattering is even more sensitive to the atom–surface potential than for the existing data, and measurements of selective adsorption under these conditions would be very valuable.

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APPENDIX

The He–Xe pair potentials used in the present paper are those recommended by Smith et al.¹⁷ on the basis of differential cross sections and dilute gas properties.

1. The HFD-1 potential

This is a Hartree–Fock plus damped dispersion potential of the form

\[ U(r) = A \exp(-ar) - (C_g r^2 + C_q r^4 + C_{10} r^{15}) D(r), \]

where the damping function \( D(r) \) is

\[ D(r) = \exp[-(1.28 r_m/r - 1)^2] \text{ for } r '\text{<} r_m, \]

\[ D(r) = 1 \text{ for } r \text{'} \geq r_m. \]

2. The MS potential

This is a Maitland–Smith potential of the form

\[ U(r) = \epsilon/(n^2 - nx - x^2), \]

where \( x = r/r_m \) and the exponent \( n \) is allowed to vary with \( r \)

\[ n = 13 + \gamma(x - 1). \]

The parameters defining these potentials are listed in Table IV.