Multiphonon Resonances in the Debye-Waller Factor of Atom Surface Scattering

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He atom surface scattering by dispersionless phonons is treated employing coupled channel (CC) calculations. At low energies, they predict a behavior opposite to perturbative Born or "exponentiated" Born approximation: strong resonant phonon stimulated elastic and inhibited inelastic scattering. The corresponding resonances have not been observed in earlier CC results since these have considered only the temperature dependence of the Debye-Waller factor at higher energy or omitted the attractive well. The resonances can be interpreted in terms of bound states in the attractive well with several excited vibrational quanta. They may be observable for, e.g., He scattering by a cold Xe/Cu surface.

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The scattering of helium atoms is an important tool for the investigation of structural and dynamical properties of surfaces [1–7]. In contrast to thermal neutron scattering by solids, the stronger coupling of atoms usually leads to strong multiphonon effects rendering the theoretical treatment more difficult. The theoretical interpretation of experiments therefore had to retreat to approximations and assumptions which have not been checked systematically in detail.

There are, e.g., the extensions of the distorted wave Born approximation (DWBA) [8] to higher orders [9,10]. In order to describe n-phonon processes properly, one has at least to go to nth order of perturbation theory. With increasing n, this becomes increasingly difficult and, hence, cannot be executed without introducing further approximations. Furthermore, unitarity is violated if one straightforwardly quits the calculation beyond nth order. Unitarity is crucial for a correct value of the Debye-Waller factor (DWF) (the portion of elastically scattered particles), in particular, if the number of excited phonons is large and, hence, the DWF is small.

A fully unitary approximation which allows one to treat an arbitrary number of excited phonons is the so-called "exponentiated Born approximation" (EBA). It is a quantum mechanical generalization of the "forced oscillator model" (FOM) in which the oscillator is subject to a *classical* force $F(t)$ [11–16]. The wave function of the FOM is a "coherent state": the oscillator ground state shifted in phase space [by an amount proportional to the Fourier component $F(\omega)$ at the oscillator frequency ω of the force $F(t)$]. In EBA the shift is proportional to the corresponding quantum mechanical force matrix element [17–19]. In FOM and EBA, the quantum effects associated with the *substrate phonons* are properly taken into account: There is a nonzero elastic scattering probability as measured by the DWF and a suppression of low energy sticking probability for light scattered particles [20].

In contrast to FOM, the EBA takes quantum effects associated with the motion of the *scattered particle* at least partly into account. Thus, for instance, the threshold behavior of the single-phonon scattering probabilities is correctly described: Below threshold the probabilities vanish and just above the threshold energy E_s one finds the correct behavior $\propto \sqrt{E - E_s}$. As a consequence, also the low energy limit of sticking probabilities [21] is properly described.

The EBA treatment of inelastic scattering probabilities has proven very useful for the interpretation of many scattering systems as well as adsorption [22] and accommodation [23] and, in particular, the He atom scattering (HAS) from phonons of various substrates [2].

A possibility to check the validity of EBA theoretically is, of course, to consider simple models which can be solved exactly (for instance, numerically) and to compare the exact results with approximations. A first step in this direction has been done for the temperature dependence of the DWF for H, He, and Ne scattering by Xe/graphite [24]. In this case, good agreement between EBA and exact coupled channel (CC) results were obtained for H and He at energies above 50 meV. There were small quantitative differences for He and bigger ones for Ne.

More recently, the dependence of DWF and one or two-phonon transitions for He and Ne scattered by Xe/Cu on initial energies (between 0 and 150 meV) was considered. Here the main emphasis was on differences between DWBA data for nonlinear coupling models as compared to EBA and exact ones for linear coupling [25]. The results indicated good agreement between EBA and exact CC data for He and acceptable agreement for Ne. DWBA for nonlinear coupling produces some multiphonon effects but differs strongly from exact and EBA results. To avoid problems with bound-state resonances, however, in these calculations the attractive part of the potential was omitted.

In this Letter, we consider the consequences of an attractive well in detail. At first sight, we expected only small effects: Possible bound-state resonances occur at low energies where only few phonons get excited. In EBA for Xe/Cu below 10 meV, for instance, mainly zero and one phonon excitations occur. Bound-state + single-phonon resonances, however, cannot be seen asymptotically below the one phonon threshold. So we expected some (weak) two-phonon peaks on top of a strong single-phonon continuum. Much to our surprise, something quite different occurred: There were strong two-phonon and three-phonon peaks in the DWF (and corresponding dips in the single-phonon continuum) and some three and four phonon peaks on top of the single-phonon probabilities (and corresponding *dips* in the two-phonon continuum). All these effects are absent in (straight) EBA. If bound-state transitions would be additionally taken into account, the CC results for He scattered by Xe/Cu indicate that at least 13 states would have to be considered in a secular equation treatment on top of EBA.

The two-dimensional model which we used in our studies is the same one as in [24,25]: It is applicable to He atom scattering (without parallel momentum transfer) from vibrating noble gas adsorbates weakly bound to metal or graphite surfaces, typically Xe adsorbed on Cu or graphite. The scattered atoms couple most strongly to the vertically polarized adsorbate phonons which show little dispersion and therefore can be accurately described by an Einstein model. The Hamiltonian then takes the form (z, Z the He,Xe coordinates)

$$H = \frac{p^2}{2m} + \frac{P^2}{2M} + \frac{M}{2}\omega^2 Z^2 + v(z - Z), \qquad (1)$$

with $m = 4m_p$, $M = 131m_p$ (m_p the proton mass), and $\hbar\omega = 2.7$ meV. For the He-Xe interaction, we take a Morse potential $v(z) = D(e^{-2\alpha z} - 2e^{-\alpha z})$ with $D = 6.6$ meV and $\alpha = 1.22$ Å^{-1}.

Xe/Cu has been investigated extensively—experimentally [26] as well as theoretically [2]—and, hence, may be used as a useful and simple testing ground for theoretical methods. For further systems compare [27]. The parameters quoted above are appropriate for Xe/Cu.

Together with the potential $v(z)$, we introduce the force $f(z) = -\partial v(z)/\partial z$ and its matrix elements $f_{n,0} = \langle p_n, \text{out}|f(z)|p_0, \text{in}\rangle$ between scattering states of the Morse potential with incoming (outgoing) momenta p_0 (p_n). We have used the labels $0, n$ to indicate that we consider initial (final) states with 0 (n) phonons. Energy conservation then says (E_i the initial kinetic energy)

$$E_i = \frac{p_0^2}{2m} = \frac{p_n^2}{2m} + n\hbar\omega. \qquad (2)$$

A key quantity in EBA is the number $N = |f_{1,0}|^2/(2M\hbar\omega)$ which is the single-phonon excitation probability in DWBA and the average number of excited phonons in EBA. The probability of excitation of n phonons in EBA is given by the well-known Poisson distribution $P_{n,0} = e^{-N}N^n/n!$. In particular, one has the following for the DWF: $P_{0,0} = e^{-N}$. Since we work only with the single-phonon matrix elements $f_{1,0}$, the threshold behavior of the two-phonon transitions is not correctly described. This is only a small error of EBA, and here we refrain from correcting it. In principle, this can be done by omitting the contributions below threshold and "unitarizing" the remaining terms.

In the coupled channels approach, the wave function is expanded in oscillator eigenfunctions (channels). The Schrödinger equation then becomes a system of coupled 1D differential equations. If the potential is replaced by a stepwise constant potential—with sufficiently many, e.g., 100 to 200, steps to ensure a good representation of the actual $v(z)$—one can use the transfer matrix method to solve these equations. We work with local reflection (LORE) matrices in order to avoid numerical instabilities due to closed channels. The LORE matrices (apart from normalization factors) approach the scattering matrices $S_{n,m}$ asymptotically [28] and, hence, directly yield the corresponding transition probabilities $P_{n,m}$ introduced above.

We use 100 equidistant steps for z to represent the potential between $z_i = -1.4$ Å and $z_f = 5.5$ Å, $N_v = 7$ channels, and 600 equidistantly spaced energies between $E = 0$ meV and $E = 12$ meV or $E = 60$ meV. The small energy spacing is necessary to resolve the resonance structure occurring at energies below 12 meV. Below 12 meV, actually $N_v = 5$ channels are sufficient to ensure convergence.

Figure 1 shows the transition probabilities $P_{n,0}$ for $n = 0$ to $n = 6$. For larger energies they agree well with the results of [25]. This can be expected since for energies well above $D = 6.6$ meV the attractive well should not play an important role. At energies below 10 meV, however, there is additional structure which shows up in neither EBA nor [24] or [25].

Figure 2 shows this structure in more detail on an expanded energy scale: There are various pronounced peaks or dips in the first three $P_{n,0}$. They can be associated

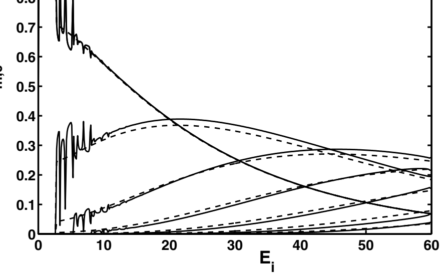

FIG. 1. Comparison of EBA and CC excitation probabilities $P_{m,0}$ of the first seven vibrational levels (including the ground state) as a function of the initial kinetic energy E_i measured in meV. Note the pronounced structure in the CC results which is absent in EBA and in the CC results of [25].

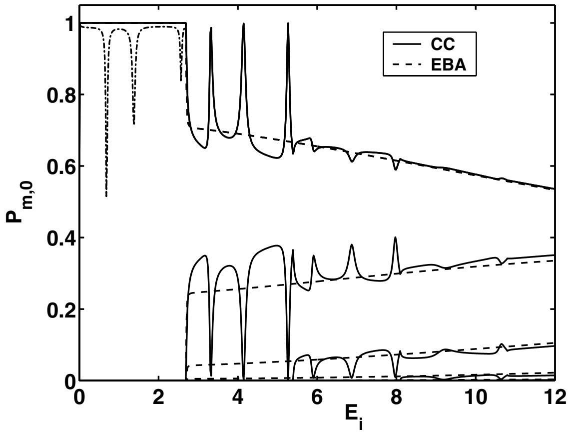

FIG. 2. The low energy structure of Fig. 1 in more detail. There are three peaks in the DWF and three more in the one phonon probability. The peak in the one phonon probability near the two phonon threshold is no resonance but a threshold anomaly. The weaker structures above 8 meV will not be discussed in detail. Below the single phonon threshold, there is additional structure, indicated by the dash-dotted line, which occurs if a small imaginary part is added to the potential. For more details, see the text.

with six energy levels of scattering resonances and may be considered as the upper six of all together 13 bound-state levels with up to four excited phonons.

There are three bound states in the Morse potential with energies $E_1 = -4.54$ meV, $E_2 = -1.57$ meV, and $E_3 = -0.14$ meV. Hence, there are 12 levels $E_{i,n} = E_i + n\hbar\omega$ with $i = 1, 2, 3$ and $n = 0, 1, 2, 3$. Four of these levels are below zero and, hence, cannot be seen in scattering states; three levels are above zero but below the one phonon threshold. They lead to elastic scattering resonances which, however, do not show up in the DWF since this exhausts the unitarity sum; the five remaining levels above the one phonon threshold are the ones seen in Fig. 2 together with the level near 6 meV which disappears in a four channel calculation but shows up from five channels on. This indicates a four phonon excitation superimposed on the ground state of the Morse potential.

It is interesting to note that near the resonances rather high phonon excitations occur although the *average* number of excited phonons is below 0.6 for energies below 12 meV. Obviously, the attractive well assists the excitation of phonons *inside the well.* On the other hand, *outside the well* and near the resonance energies, surprisingly enough the scattering becomes *more elastic* (at least for the first three peaks in DWF). It is also interesting to mention that these effects do not occur in a classical trajectory treatment. We will consider such effects in more detail in a subsequent publication [29].

The three levels in the DWF = 1 region can be seen as rapid changes in the phase of $S_{0,0}$ or more directly after adding a very small imaginary part to the Morse potential. This leads to a small reduction of the DWF which, however, is strongly enhanced near the resonance energies. Figure 2 shows the result for an imaginary part of 10^{-3} of the attractive well of $v(z)$. It leaves most of the excitation probabilities practically unchanged but leads to the surprisingly large dips in the DWF = 1 region, which we have indicated explicitly in Fig. 2 above.

Of course, all the "zero order levels" described above are slightly shifted by configuration interactions. These shifts could, in principle, be determined from a secular equation for the 13 levels described above neglecting the coupling to the continuum states. Such calculations will open up a possibility to determine interaction potentials in analogy to the procedures using selective adsorption resonances.

The resonance scattering processes all involve bound states in the attractive well and, hence, are related to sticking/desorption processes. Such processes, of course, require a continuum of phonons and nonzero temperatures and cannot be treated rigorously by CC methods. It

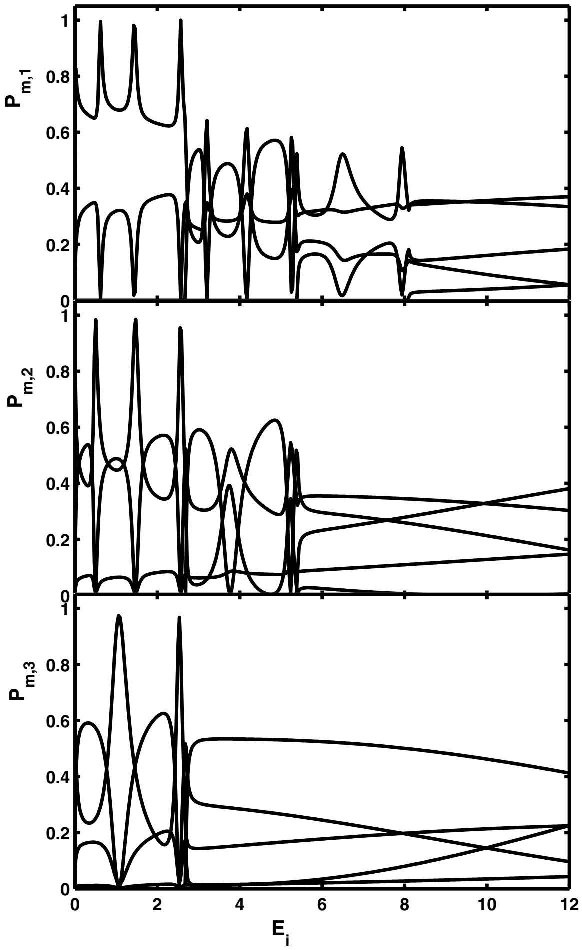

FIG. 3. Phonon excitation probabilities starting from the first three excited initial states. Note the symmetry $P_{m,0} = P_{0,m}$ which can be checked by comparison with Fig. 2. In doing this, one has to take into account that E_i is the initial *kinetic* energy which is total energy minus $m\hbar\omega$ for $P_{m,0}$.

may be interesting, however, to consider an increasing number N_p of coupled phonons and the evolving behavior of the resonances discussed above as function of N_p.

The predicted resonance structures will, of course, be broadened. Since, however, the observed broadening of the phonon peaks is only about 2 to 3 times bigger than the resonance peak width, the broadened peaks will still be visible. Initial energies of about 6 meV have been used experimentally. Specular scattering at angles of 45° would correspond to 3 meV vertical energies which is low enough to detect all resonances above the single-phonon threshold.

In an experiment at nonzero temperature, however, there will be initially excited states which have to be considered also. Figure 3 shows the transition probabilities $P_{n,m} = |S_{n,m}|^2$ starting from the first three excited states. They exhibit even more pronounced structures than the $P_{m,0}$ and would add on to them. In order not to mess up the situation too much, it will be desirable to freeze out excited initial states by using sufficiently low temperatures. The low energy and low temperature problems can be facilitated by using argon or krypton overlayers which have about 2 times bigger vibrational frequencies [27].

In conclusion, simple model calculations predict new types of resonances for He scattering by adsorbate overlayers with unexpected and interesting properties. From the energetic position of the resonances, the bound state as well as phonon energies can be determined.

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