Two-phonon assisted selective adsorption

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(Received 23 July 2010; revised manuscript received 12 October 2010; published 17 November 2010)

The bound-state-plus-two-phonon resonances in scattering of atoms by surface phonons are considered in detail. We compute the dependence of single phonon transition probabilities on the initial energy performing large-scale coupled channel calculations. It turns out that the resonances in this case are relatively strong and sharp. Furthermore, due to a new implementation we are able to consider two- and three-phonon resonances in the scattering in full detail. It turns out the two phonon resonances should be observable but three phonon resonances not.

DOI: 10.1103/PhysRevB.82.193407 PACS number(s): 68.49.Bc, 34.35.+a, 68.35.Ja

The coherent scattering of atoms or molecules from surfaces has been known as a tool for probing surface structures since the 1930s.[1–3] Based on diffraction patterns, information about the periodicity and lattice constant of the surface and surface excitations such as phonons can be derived.[4,5] Furthermore, at certain angles of incidence, resonances in the intensity of the scattered beams occur.[2,3] These so-called selective adsorption resonances occur when the scattered particle can make a transition into one of the discrete bound states of the adsorption potential. The energetic positions of the corresponding selective adsorption resonances yield important direct information about bound state energies of adsorbed particles.[6] New kinds of long-lived surface states can be obtained when a phonon is coupled to a bound state. The corresponding "phonon assisted selective adsorption resonances" were indeed observed in ionic crystals.[7] Similar effects can be found for Xe overlayers on Cu. In this case a simplification occurs since the corresponding relevant transverse phonons are practically dispersionless.[8] On the other hand their energy is quite low. So the single phonon-plus-bound states occur below threshold. But two, three, or more phonons show up as resonances in various scattering events (peaks in elastic or dips in inelastic scattering).[9,10] The resonances were found in coupled channel calculations (CCCs) of the scattering intensities of He atoms scattered by a Xe overlayer on Cu. Note that for He/Xe:Cu two energetically low-lying resonances were particularly strong so that they should be experimentally observable thus allowing for a validation of the theoretical predictions.

In a treatment of thermal adsorption/desorption by kinetic equations one has to consider processes where the incoming particles "fall down" the ladder of bound states to the ground state where they stay for a long time before they desorb again. Besides these processes there occur so-called *prompt* ones where the particles, classically speaking, just execute a few "round trips" in a single bound state and then desorb directly back into the gas phase. In a CCC treatment such prompt adsorption/desorption processes show up as resonance scattering as described above. This indicates a way to identify prompt processes as peaks (or dips) in scattering intensities as a function of the *initial energy* in surface scattering events.

Since Xe atoms are large, closely packed Xe overlayers are rather smooth. Hence parallel momentum transfer by diffraction can be expected to be small and selective adsorption processes will be strongly suppressed. The dominant He dynamics then is quasi-one-dimensional (1D), perpendicular to the surface. The adsorption processes then show up as sharp resonances in the elastic beam similar to the selective adsorption resonances.

In a recent paper[11] parallel momentum transfer was considered in more detail. It turned out that, indeed, the motion is largely 1D but there is some parallel momentum transfer. The He motion then has three dimensions (3D) (or two dimensions at least). This leads to two effects. (1) The dependence of kinetic energy of the He atoms on parallel momentum leads to additional broadening of the resonances. (2) Excitation strength is redistributed from the zero momentum resonance to higher (parallel) momenta, where the coupling strength is lower. Hence the inelasticity is reduced in general. This effect is quite strong for 3D motion. It leads to a large elastic background in the Debye-Waller factor (DWF) of about 95%. Any resonance then can be at most a 5% effect in the DWF.

Two further contributions[12,13] considered the effects in more detail. Both agreed that increasing the number of participating phonons in the basis and the energy resolution lead to more pronounced resonances. In Ref. 12 it was mentioned that the total inelastic scattering intensity exhibits about a 10% dip at the resonances which may be easier to observe than the corresponding peaks in the DWF. Gumhalter and Siber[13] however point out that for this one would have to scan larger portions of the hemisphere above the surface which makes these dips less accessible.

The purpose of this Brief Report is threefold: (1) we compute the single phonon excitation probabilities directly, which are known to be accessible experimentally;[14] (2) we discuss the technical issues necessary to cope with the huge number of phonons in the CCC; (3) as the main point of this Brief Report, we address the issue whether two- and three-phonon resonances are detectable.

ad (1) Using the same potential as in Ref. 11, we now compute the single phonon excitation probabilities directly. These are particularly strong at low momentum transfers

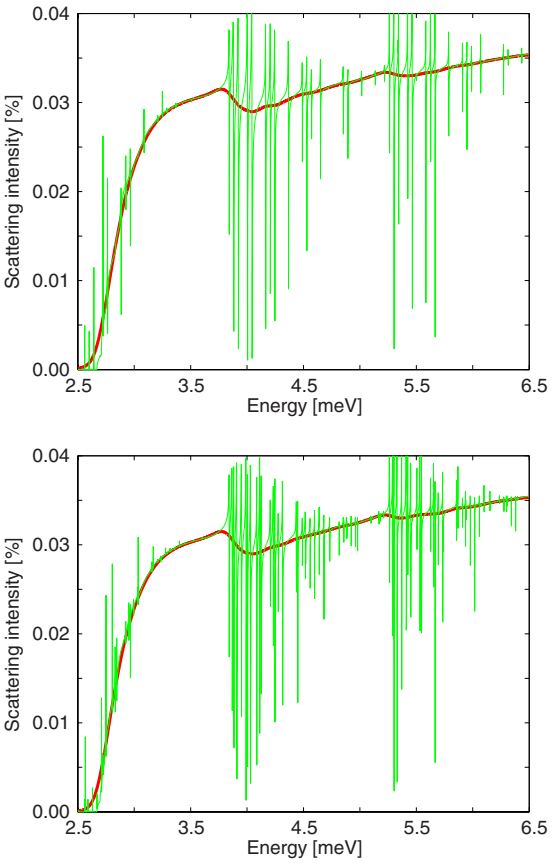

FIG. 1. (Color online) Single phonon inelastic scattering intensities for various final parallel momentum transfers (top: 9×9 and bottom: 9×11 phonons) together with Gaussian convolution to simulate a phonon continuum.

near specular scattering. In this region they show a dependence on the incident energy similar to the total scattering intensity but with somewhat more pronounced resonance dips (compare Fig. 1 with Fig. 1 of Ref. 12). So for an experimental measurement it is even better to consider the single phonon excitation probabilities instead of the total ones.

ad (2) In the coupled channel calculations we have increased the total number of phonons participating in the CCC. To cope with the resulting huge computational cost the code has been parallelized with respect to the energy loop. Since the energy points are independent, nearly 100% parallel efficiency can be obtained here. However the more phonons are involved the more time does the initial setup for the matrix elements require. Therefore the initial matrix elements, which are independent on energy, have been computed only once and stored to a file. To speedup the distribution of this huge file among the computational nodes, a binary treelike scheme has been utilized.

The resulting speedup is nearly linear with respect to the allocated cores and scales well up to several hundred nodes. It allows to compute the scattering intensities on a very fine energy grid which is essential due to the very narrow peak structure of the intensities in case of higher phonon momentum numbers. Convergence of the spectra required 4000 energy points between 2.5 and 6.5 meV.

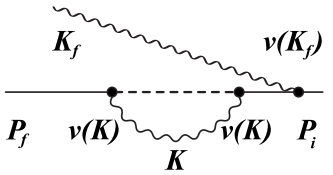

FIG. 2. Self-energy correction to single phonon scattering in third-order perturbation theory. Wavy lines: phonons and solid (dashed) lines: continuum (bound) He states.

Of course the resonance positions vary with the momentum vectors of the phonons, and the corresponding energy distributions of scattered He atoms vary correspondingly with the momentum vector grid in the Brillouin zone. Since for a phonon continuum this variation cannot be observed we have considered average energy distributions. Such averages also show better convergence with increasing phonon numbers. We considered a Gaussian convolution with 0.1 eV smearing width. It turns out that the averages depend on the grid up to 9×9 phonons in the Brillouin zone but from 9×9 to 9×11 there is essentially no change anymore (see Fig. 1). So one can say that convergence of the CCC calculations is reached for about 4000 to 5000 two-phonon states.

ad (3) In the 1D calculations[9,10] besides the two-phonon also three-phonon resonances were found. In fact the lowest resonance above the single phonon threshold is a three-phonon state. However, it is not clear whether these resonances are also prominent in 3D calculations.

The effects of linear versus nonlinear coupling were considered in detail in a paper by Šiber and Gumhalter,[15] compare also.[16] It turns out that the dominant contributions to multiphonon coupling originate from higher orders of perturbation theory and not from nonlinear terms in the coupling. In accordance with this in our 3D CC calculations we have considered only linear couplings. 3D calculations with nonlinear couplings become tedious and time consuming.

The three-phonon basis to consider the effect of parallel momentum transfer for this state in a CCC is prohibitively large. We have therefore restricted ourselves to an approximate treatment of three-phonon contributions using fifth-order perturbation theory. The diagrams in third order are shown in Figs. 2 and 3. In fifth order one more phonon line becomes linked to the He line leading to more complicated self-energy and vertex corrections. The diagrams are evaluated approximately by neglecting the dependence of vertices on vertical energy across the peaks. Details will be described in a separate paper. It turns out that the three phonon resonances, while they lead to sharp peaks in the 1D calculations,[9] become too much broadened in the 3D results to be observable.

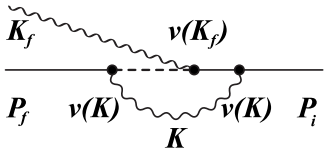

FIG. 3. Vertex correction to single phonon scattering in third-order perturbation theory.

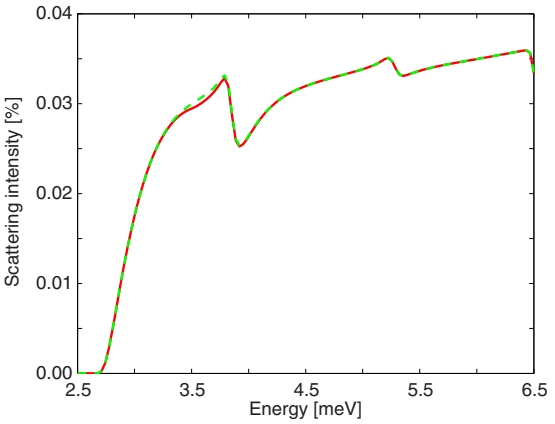

FIG. 4. (Color online) Single phonon scattering intensities for zero final parallel momentum transfer in third order, i.e., including only two phonon scattering resonances (dashed line) and fifth order, i.e., including three phonon resonances (solid line), perturbation theory (linear coupling).

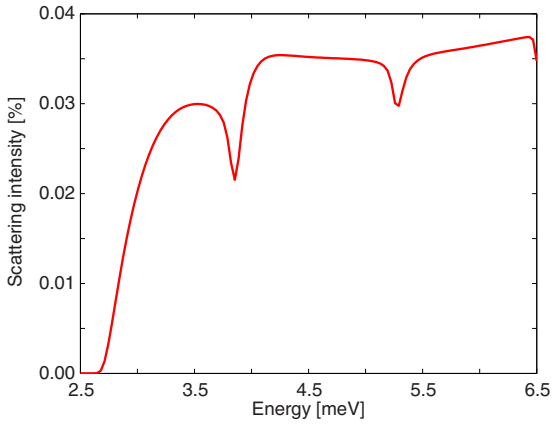

FIG. 5. (Color online) Single phonon scattering intensities for zero final parallel momentum transfer in fifth-order perturbation (nonlinear coupling).

The position and width of the two phonon peaks come out similar in the CCC (Fig. 1) and perturbative (Figs. 4 and 5) results but the intensities are bigger in perturbation theory. This is particularly important for the high-energy peak around 5.5 meV which looks observable in perturbation theory in contrast to the rather weak CCC result. Since both calculations are approximate no definite statement can be made at present.

Furthermore one should note that even the CCC results show distinct peaks around 5.5 meV. But in contrast to the Lorentzian-type dips of the perturbation results these peaks are strongly reduced by the averaging process due to their $\propto \tan(\epsilon-\epsilon_0)$-like shape. It may be of interest in this context to note that this behavior is to some extent connected with the linearization of the potential in the phonon amplitudes.

In 1D calculations, on the other hand, the full nonlinear coupling can be taken into account. In fact this was done in our original paper.[9] Figure 5 shows the shape of the resonance peaks for nonlinear 1D calculations: they are more or less Lorentzian and not tanlike. If these results are used as basis for a perturbation treatment the corresponding 3D peaks become more pronounced. We take this as an indication that even the high-energy two-phonon peak may be observable. In this case phonon assisted resonances would yield experimental information about the bound state excitation spectrum similar to selective adsorption processes.

For substrates other than Xe:Cu the stronger dispersion of phonon frequencies will lead to stronger broadening of the resonances, on the other hand the stronger corrugation will lead to more localized bound states and hence sharper resonances. Furthermore we point out again that heavier particles (e.g., Ne) instead of He lead to stronger inelasticities and hence to stronger resonances. It will be interesting to consider such situations altogether in more detail.

In conclusion, multiphonon resonances including parallel momentum transfer were considered using two different approximations. (1) For linearized phonon coupling and a discrete set of points in momentum space "exact" results for two-phonon resonances in single phonon scattering events were obtained using CC calculations. Results for a continuum of momentum states were simulated by a Gaussian average of the "discrete" results. (2) For linear *and* nonlinear coupling and a continuum of momentum states approximate results for two- and three-phonon resonances were obtained using perturbation theory.

The predictions are (1) three-phonon resonances will not be observable, (2) the lowest two-phonon resonance should be observable, and (3) the perturbation results (in particular, for nonlinear coupling) suggest that the second (higher) two-phonon resonance may also be observable.

The authors gratefully acknowledge interesting discussions with B. Gumhalter and A. Šiber. We also thank the BWGRID project (Ref. 17) for the computational resources.

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