

Sticking coefficient of light particles on surfaces

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We consider a theoretical treatment of particle-surface scattering in which the sticking coefficient and scattered intensities are simultaneously calculated to arbitrarily high orders in perturbation theory. We present model calculations through third order in perturbation theory, including all two-phonon contributions, for the cases of H_2 and D_2 interacting with a Cu(100) surface and the case of Ne interacting with a Ru(001) surface. The direct scattering into the bound states gives rise to structure which can be observed both in the sticking coefficient and in the specular intensity.

I. INTRODUCTION

One of the most important processes occurring at a gas-solid interface is the capture and subsequent sticking of incident atoms or molecules. Recently, there has been considerable interest in both the experimental measurement¹⁻⁴ and theoretical interpretation⁵⁻¹⁰ of the sticking of very light atoms and molecules in which quantum-mechanical effects play a significant role.

If the gas molecules are massive, the theoretical treatment can be completely classical and the sticking, at least conceptually, is a straightforward process of energy loss upon collision or multiple collision with the surface.¹¹⁻¹³ For light atoms a quantum-mechanical approach must be used and the situation is not so simple. A problem arises because the sticking problem is unlike the usual scattering theory treatment of the collision process. In a typical scattering problem the particle is initially prepared in a continuum state of the unperturbed potential in the remote past. The perturbing potential is then adiabatically switched on, allowing the interaction with the scattering center to occur, after which the interaction is again slowly switched off. Consequently, after a large time has passed, the particle amplitude is typically described as a linear combination of all the states of the unperturbed potential. The fractional probability in each final state or the transition rate from initial to each unperturbed state can be readily calculated.¹⁴ In particular, one might assume that the probability of transition from an initial continuum state to a negative-energy bound state can be interpreted as the trapping or sticking coefficient for the given bound state. This implies that a "stuck" particle would be defined as one that remains an infinitely long time localized near the surface. However, in any situation corresponding to possible experimental conditions, the perturbing potential is always present near the surface, and a particle localized near the surface must continue to make further transitions. This can be viewed somewhat differently by considering the evolution of a particle initially prepared in a bound state of the unper-

turbed potential. The probability amplitude of such a particle near the surface should decay with time, and will eventually disappear from the neighborhood of the surface and go into the continuum states. Otherwise stated, there are no particles that remain in bound states an infinitely long time. Thus it is difficult to define unambiguously the quantum-mechanical sticking coefficient, and consequently its theoretical definition must be operationally defined in order to match the manner in which the sticking coefficient is measured experimentally.

Prompted by recent experiments measuring the sticking coefficient of H_2 , D_2 , and Ne on metal surfaces, we consider in this paper a general theory for the scattering of a particle from an incident beam into a negative-energy surface bound (adsorption) state. The theory developed can simultaneously be used to calculate the sticking and the elastic or inelastically scattered intensities, and all can be related by the unitarity relation. The theory is developed to all orders of phonon exchange, and model calculations are carried out that include not only the distorted-wave Born approximation but the higher-order single-phonon and double-phonon processes. The phonon distribution used is that of a Cu(100) surface, and the calculations for H_2 or D_2 beams at energies too small to excite molecular rotational states show structure similar to that seen in the measurements of sticking; this structure is also apparent in the specularly scattered intensity. The model potentials used in these calculations are ones that have been used previously to explain the elastic diffraction and thermal attenuation of beams of H, H_2 , and Ne scattered from a variety of clean copper surfaces. The calculations are extended to the case of sticking of Ne at a Ru(001) surface and the results agree favorably with recent experiments.

II. THEORY

For the theoretical description of atom-surface scattering we consider an incident particle of mass m and initial wave vector \mathbf{k}_i interacting with a potential $V(\mathbf{R}, z, \mathbf{u})$.

Using a standard notation, \mathbf{R} and \mathbf{z} label space coordinates parallel and normal to the surface, respectively, i.e., $\mathbf{r}=(\mathbf{R},\mathbf{z})$. The influence of the thermal vibrations of the crystal atoms on the interaction potential is taken into account through the phonon displacement operator \mathbf{u} . Anticipating a treatment based on distorted waves, or two-potential theory, we write the total interaction potential $V(\mathbf{R},\mathbf{z},\mathbf{u})$ as the sum of a static term and a term depending on the thermal displacement:

$$V(\mathbf{R},\mathbf{z},\mathbf{u})=v(\mathbf{R},\mathbf{z},\mathbf{u})+\langle\langle V(\mathbf{R},\mathbf{z},\mathbf{u})\rangle\rangle, \quad (1)$$

where the double brackets stand for the ensemble average over vibrational states of the crystal. We will also assume for the calculations done here that $\langle\langle V\rangle\rangle$ is spatially averaged over directions parallel to the surface and hence is a function of z only (i.e., $\langle\langle V\rangle\rangle$ is the zero spatial Fourier component of the vibrationally averaged potential). We adopt the two-potential formalism with $v(\mathbf{R},\mathbf{z},\mathbf{u})$ and $\langle\langle V(\mathbf{R},\mathbf{z},\mathbf{u})\rangle\rangle$ the perturbing and distorting potentials, respectively. Then the transition operator for this problem is

$$T=v+vG^+T, \quad (2)$$

with the Green function given by the distorting potential:

$$G^+=(E_i^p+E_i^c-H_0+i\epsilon)^{-1}, \quad (3)$$

where E_i^p and E_i^c are, respectively, the incident particle energy and the initial crystal energy, and the distorted Hamiltonian is

$$H_0=-\frac{\hbar^2}{2m}\nabla^2+\langle\langle V\rangle\rangle+H^c, \quad (4)$$

where H^c is the unperturbed crystal Hamiltonian. We denote the eigenstates of H^c corresponding to the eigenvalues E_n^c by $|n\rangle$. Then the eigenstates of the distorting Hamiltonian are simple products:

$$e^{i\mathbf{K}\cdot\mathbf{R}}\phi_{c,b}(z)|n\rangle, \quad (5)$$

where for the state $\phi_{c,b}(z)$ describing particle motion normal to the surface, the labels c or b signify continuum or bound states of $\langle\langle V\rangle\rangle$, respectively. The energy eigenvalue corresponding to the state of Eq. (5) is

$$(\hbar^2/2m)K^2+e_{c,b}+E_n^c, \quad (6)$$

where $e_{c,b}$ is the energy associated with normal motion in the potential $\langle\langle V\rangle\rangle$, and we note that e_b is both negative and discrete.

The transition rate between an initial state i and a final state f of the Hamiltonian H_0 due to scattering by the perturbation v is given by the usual expression

$$w_{fi}=\frac{2\pi}{\hbar}|T_{fi}|^2\delta(E_f^p+E_f^c-E_i^p-E_i^c). \quad (7)$$

The sum of w_{fi} over final crystal states and the ensemble average over initial crystal states gives the transition rate $w(\mathbf{k}_f,\mathbf{k}_i)$ between incident particle state \mathbf{k}_i and final particle state \mathbf{k}_f

$$w(\mathbf{k}_f,\mathbf{k}_i)=\langle\langle\sum_{n_f}w_{fi}\rangle\rangle$$

and clearly if \mathbf{k}_f is chosen to be a continuum state this is an experimentally measurable quantity. Using the Van Hove transformation, this averaged transition rate can be written as the Fourier transform of a time-ordered correlation function

$$w(\mathbf{k}_f,\mathbf{k}_i)=\frac{1}{\hbar^2}\int_{-\infty}^{+\infty}dt e^{i(E_f^p-E_i^p)t/\hbar}\langle\langle T_{fi}^\dagger(0)T_{fi}(t)\rangle\rangle. \quad (8)$$

Now let us consider the situation in which the final state is \mathbf{k}_b , a bound state of the potential. The third component of \mathbf{k}_b corresponds to the negative discrete energy in the bound state of $\langle\langle V\rangle\rangle$. In this case the reflection coefficient σ_{bi} obtained by dividing $w(\mathbf{k}_b,\mathbf{k}_i)$ by the incident normal flux $j_i=\hbar k_{iz}/m$ can be interpreted as the sticking coefficient or trapping coefficient into the bound state b for the given incident conditions. The problem with such a definition, as noted in the Introduction, is that for an exact calculation on a totally isolated system, σ_{bi} will be vanishing. This is because no particles will remain in the bound state for an infinitely long time.

What is needed is to tailor the calculation to the experiment so that their conditions match closely. For example, in the experiments of interest,²⁻⁴ the residence times in the bound states at low surface temperatures are long compared to the collision time, which is of the order of a phonon vibration period $\sim 10^{-13}$ s. The sticking coefficient is measured by monitoring the change in work function in the limit of low coverages,² or by thermal desorption measurements.³ Thus from an experimental standpoint, it is clear that the incident molecules may be captured in the attractive well at the surface, if not for infinite times, at least for times long compared to a typical experiment. This suggests that from the corresponding theoretical standpoint, the appropriate calculation would be to assume that a particle is captured (or stuck) once it has been scattered into a bound state. This assumption is certainly valid for situations in which the sticking probability is small, since if the probability of entering a bound state is small, according to detailed balancing arguments the probability of escaping is also small; hence the lifetime in the bound state is long, implying that subsequent desorption is a slow process.

In this work we calculate the sticking coefficient within the distorted-wave formalism by making the perturbation expansion of the T matrix of Eq. (2) to higher orders:

$$T=v+vG^+v+vG^+vG^+v+\dots \quad (9)$$

The Born approximation gives the direct transition from an initial continuum state to all the bound states through a single inelastic interaction with the potential. In this case the definition of the sticking is unambiguous. For the higher-order corrections to T we calculate the probability that the particle ends up in a bound state after several interactions with the potential in which energy can either be gained or lost. In actual calculations with the models described below, the expansion of T was

made through third order, and all terms involving single- or double-phonon exchange were included. Results for the distorted-wave Born approximation show that the sticking is small and comparable to the experimental values, and hence, according to the arguments above, the perturbation approach is valid. The higher-order corrections, although in some cases significant, as particularly in the scattering of neon, constitute a smaller correction to the Born approximation for very low crystal temperature.

We would like to point out that it is often useful to use the optical theorem, i.e., the statement of unitarity in the scattering process, in order to relate the elastic scattering, inelastic scattering, and the sticking. The optical theorem is usually stated in the following form, which can be obtained directly from the T matrix in Eq. (2):

$$T - T^\dagger = -2i\pi T^\dagger \delta(E_i^f - E_i^c - H_0) T. \quad (10)$$

In the present case, it is convenient to anticipate the fact that the repulsive molecule-surface potential is short ranged in space with a scale parameter χ . We can then define a dimensionless T operator according to

$$F = \frac{2m}{\hbar^2 \chi^2} T, \quad (11)$$

and after taking the diagonal matrix element of (10) with respect to the distorted states, the optical theorem takes the form

$$1 = \left\langle \left\langle \left| 1 - \frac{i\pi}{P_i} F_{ii} \right|^2 \right\rangle \right\rangle + \sum_{c \neq i} \pi^2 \frac{|F_{ci}|^2}{P_i P_c} + \frac{2\pi}{P_i} \sum_b |F_{bi}|^2. \quad (12)$$

This is clearly a statement of unitarity and the three terms on the right-hand side are, respectively, the reflection coefficient into the specular beam, into inelastic continuum channels (and other elastic diffraction channels if the perturbing potential is chosen to be periodic), and into the bound states. Following the above discussion, the last term is proportional to the sticking coefficient. Therefore, if the sticking has a maximum for a given set of incident conditions, the sum of intensities in the elastic and inelastic channels should be a minimum. Thus one can immediately link extrema found in the sticking coefficient to structure in the inelastic and elastic intensities.

III. CALCULATIONS

The potential that we have used for the actual calculations is a vibrationally corrugated exponential repulsion representing the repulsive exchange forces near the surface, together with an attractive part:

$$V = D \exp[-2\chi(z-u)] \exp(-2\chi^2 \langle u^2 \rangle) - f(z), \quad (13)$$

which has been used successfully for the calculation of the thermal attenuation of the specular beam intensity on flat metal surfaces.¹⁵⁻¹⁷ Note that although this potential is one dimensional in the sense that it does not contribute to the transfer of momentum parallel to the sur-

face, the scattering from it is fully three dimensional in the sense that the incident particles are scattered into a range of final angles, depending on the exchange of energy. Also, this potential exhibits phonon-associated resonances with the bound states.

As an example of a calculation, we present here the distorted-wave Born approximation, taking for the distorted potential the thermal averages of V in Eq. (13):

$$\sigma_i = (2\pi)^2 \frac{2m}{p_i M} \left[\frac{2mD}{\hbar^2 \chi^2} \right]^2 \sum_b |\langle \phi_b \exp(-2\chi z) \phi_i \rangle|^2 \frac{\rho(\Omega_b)}{\Omega_b} \times \langle \langle n(\Omega_b) + 1 \rangle \rangle. \quad (14)$$

Here M is the crystal atom mass and Ω_b is the dimensionless energy exchanged:

$$\Omega_b = \frac{2m}{\hbar^2 \chi^2} (E_i + |e_b|). \quad (15)$$

The phonon distribution function or spectral density $\rho(\Omega)$ is taken equal to that of four atoms belonging to the unit cell of the (100) face of an fcc crystal, with the force constants chosen to match those Cu. The attractive potential is usually taken to be $-2D \exp(-\chi z)$, which leads to a Morse potential for $\langle \langle V \rangle \rangle$, although we have also used attractive potentials with a $1/z^3$ asymptotic behavior consistent with the known form of the van der Waals force in order to ascertain that the short-range attractive force of the Morse potential does not give spurious results [an exponential attractive potential is convenient because it leads to an analytic form for the necessary matrix elements in (14)].

With these choices the model is of the same form as that which has been used to calculate the thermal attenuation of He and H₂ from smooth Cu surfaces,¹⁷ and the potential model is also identical to the zero-order Fourier component of the corrugated potential used to calculate diffraction peak intensities for He and H₂ scattered from Cu(110) and from vicinal stepped surfaces.¹⁸ The only remaining parameters are the well depth D and the range parameter χ , and these are chosen to be $D=30.9$ meV and $\chi=1.14 \text{ \AA}^{-1}$ for the case of H₂ and D₂ on Cu(100), as has been recently determined.¹⁹ Actually, two values for D were tested: the value 30.9 meV corresponds to the well depth given in Ref. 19, while a slightly larger value of 34.5 meV gives a closer match to the measured values of the lowest bound-state energies. This small difference in well depth made no significant change in calculated values for the sticking coefficient over the range of incident conditions of interest.

Although we have explicitly exhibited only the distorted-wave Born approximation in Eq. (14); with the potential of Eq. (13), all contributions of higher order in the perturbation series for σ_i can be thermally averaged, term by term. Detailed discussions together with calculations for inelastic scattering into the continuum states have been given elsewhere.²⁰ In the numerical calculations discussed in Sec. IV, we have carried the development far enough to include all single- and double-phonon transfers, regardless of whether the phonons are virtual (leading to no net energy transfer) or real (producing a

net exchange of energy between particle and surface). At large temperatures, this is equivalent to saying that we calculate all terms in σ_i proportional to T and to T^2 .

The temperature dependence can be seen, for example, from the distorted-wave Born approximation of Eq. (14), which is a process involving transfer of a single real phonon. The temperature dependence is contained in the Bose-Einstein factor $n(\Omega_b)$, which, for $k_B T \gg \hbar\Omega_b$, behaves as $k_B T / \hbar\Omega_b$. All single-phonon processes with a first-order dependence on T are contained in Eq. (14). Two real phonon processes proportional to T^2 come from both first- and second-order perturbation theory. Single-phonon processes of order T^2 arise from the interference between first-order and second- or third-order perturbation theory, and these contributions involve the exchange of a virtual phonon as well as the real phonon exchange.²⁰

IV. RESULTS

For molecular hydrogen scattered by the copper (100) face, Fig. 1 gives the variation of the sticking coefficient σ_i as a function of normal incident energy E_i and for a surface temperature of 10 K. The present calculations are shown in both the distorted-wave Born approximation and with all corrections due to double-phonon exchange.

Also shown in the same graph are the experimental points and two different calculations of Andersson *et al.*, the distorted-wave Born approximation (DWBA) and a forced oscillator model. The DWBA of Andersson *et al.* shows some sharp structure in σ_i at low energies, which arises directly from a sharp structure in their phonon spectral density. This structure is not apparent in our calculations because we use the phonon spectral density of four surface atoms, as has been shown to be necessary for describing scattering into the continuum.^{15,16,21} This structure also does not appear in the forced oscillator model of Andersson *et al.*

Our calculated curves lie somewhat below the experimental points. They could be made to lie much closer to the experimental points by decreasing the number of surface atoms over which the phonon spectral density $\rho(\Omega)$ is calculated; however, we have chosen to retain the same spectral density that has proven to be satisfactory for previous calculations.^{15,16}

A very interesting feature of our calculations is that, viewed as a function of increasing energy, σ_i initially has a maximum and then shows a globally decreasing behavior, but with some clearly superimposed oscillations of small amplitude. The origin of these oscillations is the fact that different bound states contribute most strongly to the sticking at different incident energies. Figure 2 demonstrates this behavior. A plot of the contribution of the individual bound states to the total sticking is shown. As a function of increasing energy each bound-state contribution rises to a single maximum and then decreases. The maximum contribution to σ_i comes from the bound-state levels in the middle, with the highest and lowest levels contributing very little. However, the position of the maximum for each bound-state contribution

increases in energy with the order of the state. The oscillations in the sticking coefficient of Fig. 1 can be directly related to the maxima appearing in the individual bound-state contributions in Fig. 2. The behavior of the individual contributions shown in Fig. 2 reflects the similar and well-known behavior of the matrix elements that couple bound states to continuum states. Our calculations show that this behavior persists in the transition matrix, even when it is calculated to higher order. We emphasize that the oscillations in these calculations are an effect of the matrix elements of the interaction potential. They are not due, as discussed above, to sharp peaks in the phonon spectral density, nor are they due to resonances with the bound states.

Figure 3 shows the behavior of the specular peak intensity for three different surface temperatures. The global behavior is a decrease in specular intensity with increasing incident energy, as would be expected from a crude Debye-Waller picture of the thermal attenuation. However, clearly superimposed on this global behavior is a series of oscillations that are the mirror images of the oscillations in σ_i , i.e., a maximum in σ_i corresponding to a minimum in the specular, and *vice versa*. This behavior is a direct result of unitarity as expressed by Eq. (12). Similar structure appearing in the elastic diffraction intensity due to bound-state transitions has been obtained by Goodman.²²

Figure 4 is similar to Fig. 1, except that it is for the sticking of D_2 on Cu(100) at $T=10$ K. Again we see that superimposed on the general decreasing behavior, as a function of incident energy, are the small oscillations due to the individual bound states. This behavior is similarly

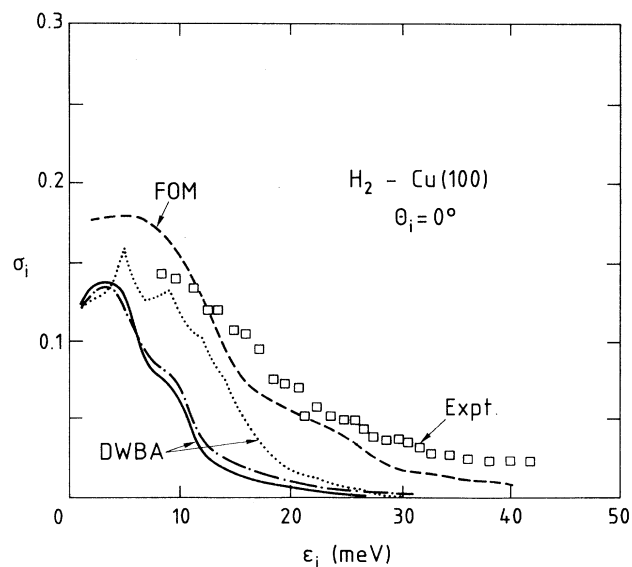


FIG. 1. The sticking coefficient as a function of incident energy for a beam of H_2 incident normally on a Cu(100) surface. The present calculations are the following: —, DWBA; - · - · -, with all two-phonon contributions. The experimental points and · · · ·, DWBA; - - -, FOM (forced oscillator model), are from Ref. 4.

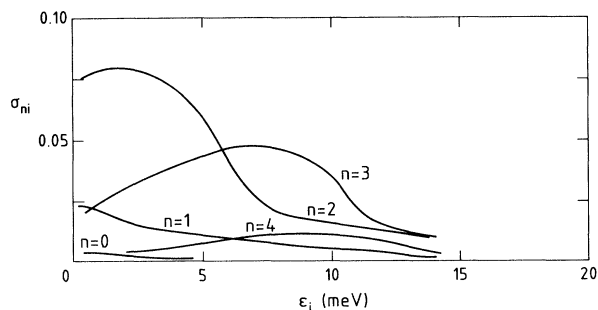


FIG. 2. The partial sticking coefficient contributions σ_{ni} from each bound state n of the potential, as a function of incident particle energy, for the double-phonon calculation of Fig. 1.

apparent in the specular intensities, as in the case of H_2 above.

The attractive part of the Morse potential used here is short ranged and does not describe well the correct surface van der Waals attraction. In order to check our results, particularly with respect to the oscillating structures, and show that there are no artifacts due to the Morse potential, we have carried out completely numerical calculations with two other potentials exhibiting the correct long-range dependence. One of these is the "shifted Morse hybrid potential,"²³ which smoothly joins a $1/z^3$ long-range tail into the Morse potential; and the other is the "saturated potential," which consists of the same exponential repulsion as Eq. (13) but with $f(z)$ a function with $1/z^3$ dependence at large z but saturating to a constant near the surface in such a way that gives bound states at the correct energies. Each of these potentials shows oscillating structure in both the specular intensity and in σ_i , which is very similar to that of Figs. 1,

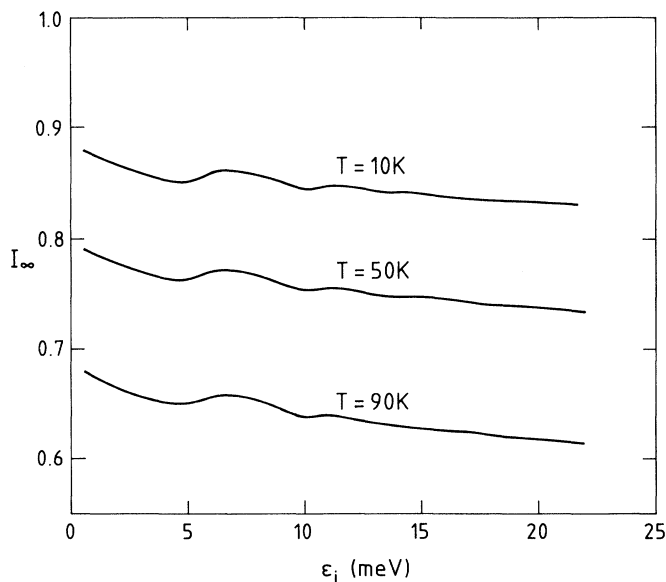


FIG. 3. The specular intensity for the double-phonon calculation of Fig. 1, as a function of incident particle energy, and for three different surface temperatures.

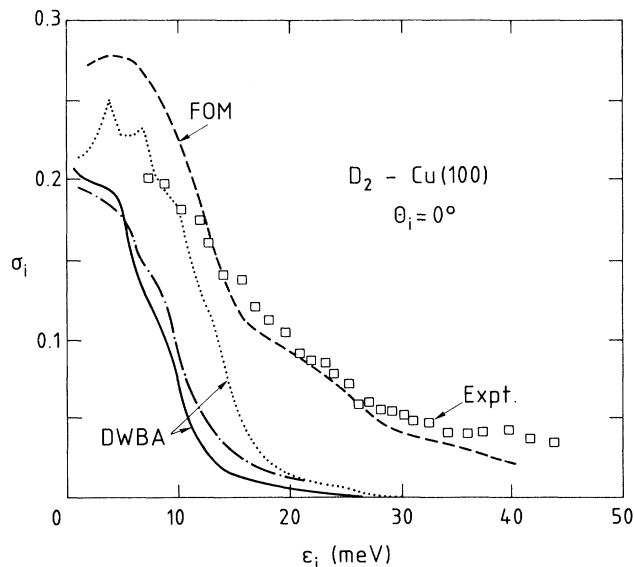


FIG. 4. Same as Fig. 1, except for D_2 incident on Cu(100).

3, and 4. Similar results have been obtained for a potential in which the repulsive part is generated by a pairwise summation of atomic potentials.²⁴

The importance of the multiquantum contributions can be seen in Figs. 1 and 4 by comparing the distorted-wave Born approximation to the two-phonon contribution. At very low incident energies, the two-phonon terms are relatively unimportant, while for increasing incident energies they can cause as much as a third of the total sticking. The multiphonon contribution is more important in the case of deuterium in Fig. 4, a direct result of the fact that the two-phonon contribution is proportional to the square of the mass ratio m/M . The calculations of Andersson *et al.*⁴ shown also on Figs. 1 and 4 indicate an even greater importance of multiphonon contributions. Their calculations are carried out using a semiclassical forced-oscillator model. The present calculations, although limited to two-phonon contributions, are fully quantum mechanical, as necessitated by the very low energies of the incident particles.

It is also of interest to consider the sticking of neon on the Ru(100) surface in view of the recent experiments of the Ne interaction with metal surfaces.³ In these experiments a beam of neon strikes a ruthenium (001) surface at a temperature of 7 K and the sticking coefficient is measured. The incident beam is not monoenergetic, but has a distribution in incident normal energy, with the interesting peculiarity that particles with velocity parallel to the surface, much larger than the perpendicular velocity, do not strike the surface. Consequently, the incident beam can be considered as a beam ensemble of particles moving normally to the surface with a distribution of normal kinetic energies that is well approximated by

$$\frac{n_0}{k_B T_G} [\exp(-E_{\perp}/k_B T_G) - \exp(-n_1 E_{\perp}/k_B T_G)] dE_{\perp},$$

with $n_0 = 2.44$, $n_1 = 1.69$. Then the exchange of parallel

momentum is certainly limited, a favorable circumstance in view of the comparison with the present calculation.

In the absence of a precise determination of the Ru-Ne potential, we take, in the calculation, the potential determined by neon scattering experiments on copper (110).²⁵ This leads us to ascribe to the Morse-potential¹³ parameters the following values: $D=12.2$ meV and $\chi=1.9 \text{ \AA}^{-1}$. We present in Fig. 5 the results of calculations of the sticking coefficient of a monoenergetic beam of Ne incident on both Cu and Ru surfaces. Figures 6 and 7 give a comparison with the experimental results for Ne sticking on Ru by including the energy distribution of the incident beam. For the phonon spectral density of the Ru(001) face we use that of the Cu(100) face corrected for the Ru bulk Debye temperature of 415 K and atomic mass of 101 a.u. For the scattering of He and H₂ from Cu(100) surfaces it has been found necessary to take the spectral density of four atoms, and we have done the same for Ru.

Figure 5 illustrates the evolution of the sticking coefficient as a function of normal incident energy when the surface atomic mass is increased from 64 a.u. (Cu) to 101 a.u. (Ru), and then when the Debye temperature is raised from 350 K (Cu) to 415 K (Ru). Also shown is the single-phonon contribution given by the distorted-wave Born approximation. At this very low surface temperature of 7 K the two-phonon contribution is relatively small, but at higher temperatures multiquantum contributions become much more important because of the large mass ratio m/M .

The calculated values are practically the same as the experimental data (Figs. 6 and 7) for incident energy greater than 60 K. Below this energy the calculated values are lower than the measured quantities and the difference increases as the beam temperature decreases. This discrepancy can be due to the shape of the copper spectral density in the low-energy phonon region, which

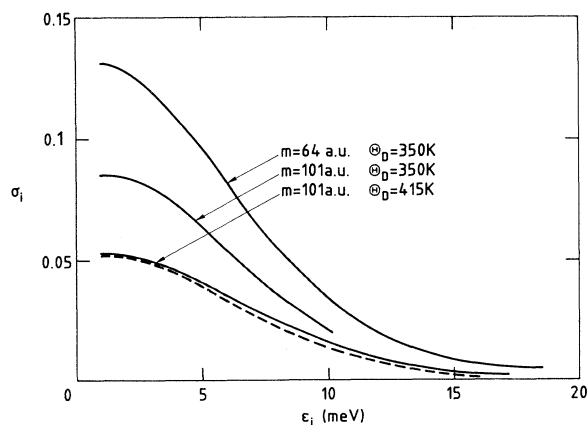


FIG. 5. The sticking coefficient as a function of incident energy for Ne on Cu(100), $m=64$ a.u., and $\Theta_D=350$ K; for Ne on Ru(001), $m=101$ a.u., and $\Theta_D=415$ K; and for Ne on an intermediate system with $m=101$ a.u. and $\Theta_D=350$ K. The surface temperature is 7 K. The dashed curve shows the DWBA single-phonon contribution for $m=101$ a.u. and $\Theta_D=415$ K.

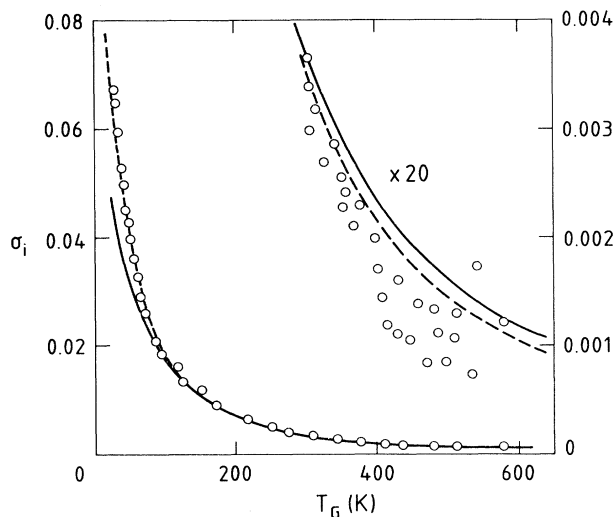


FIG. 6. The sticking coefficient of Ne on Ru(001) for the experimental conditions of Ref. 3 as a function of incident gas temperature. The points are a representative sample of the data, the dashed line is the calculation of Ref. 3, and the solid line is the present calculation.

certainly does not match correctly those of the ruthenium atoms of the (001) face. In this region the spectral density is proportional to the square of the frequency, and inspection of the transition-rate expression shows that this quantity is very sensitive to the proportionality coefficient. A more refined calculation would include the Ru spectral density calculation.

On the other hand, the observed discrepancy can be due to the chosen potential, which is well known for copper but could be slightly different for ruthenium. In particular, it is important to know the bound-state energies in the middle of the well with sufficient precision.

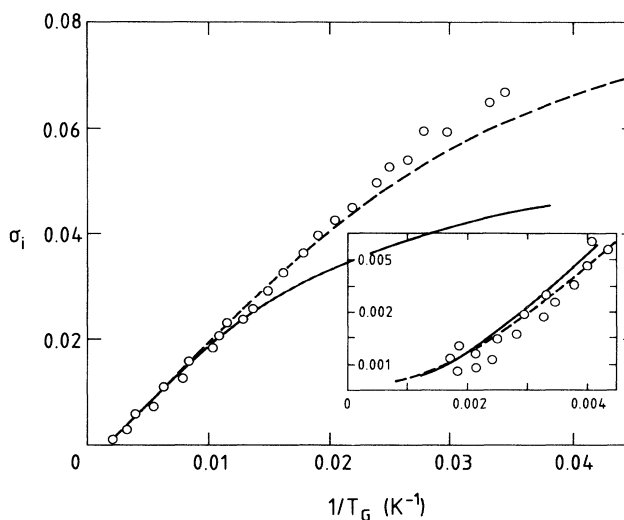


FIG. 7. Same as Fig. 6, except that the sticking coefficient is plotted as a function of inverse incident gas temperature. The inset is an enlargement of the region around the origin.

This is because in the low-incident-energy regime the transition rate is the highest for these bound states (see Fig. 2). A scattering experiment carried out in the same manner as those done on copper is certainly the best way to determine precisely all the bound-state energies.

Despite this discrepancy the present theory clearly confirms that the sticking of neon should be considered in the framework of quantum mechanics, as pointed out in previous work.³ As diffraction phenomena have been also observed in a scattering experiment,²⁵ it appears that in the range of low incident energy, neon atoms should be considered as quantum particles. In this way the sticking coefficient is obtained as the sum of transition rates over the bound-state energies of the potential.

Although not explicitly exhibited in the present calculations, the sticking coefficient vanishes at very low incident particle energies, as has been noted previously.²⁶ This predicted sharp decrease to zero in σ_i occurs typically at energies below 0.1 meV, well below the presently measured range.

V. CONCLUSIONS

We have considered the sticking of small molecules, on atoms in the quantum-mechanical regime. For several different potential models we have calculated the transition rates and sticking coefficients both in the lowest-order or distorted-wave Born approximation and to higher orders, proportional to the square of crystal temperature, including all double-phonon transfers, either real or virtual. The results are compared with experiments for the sticking of H₂ and D₂ on Cu(100) surfaces of Ne on Ru(001), and are compared with other calculations.

We find that the sticking coefficient is a relatively smoothly varying function of the incident energy of the particles, but for systems such as H₂/Cu or D₂/Cu in

which there are just a few bound states, there is some oscillatory structure in σ_i . This structure can be directly related to the strongly peaked energy dependence of the probability of transition from the incident beam into the different bound states. This structure, although not clearly resolved in the present experiments, should be equally observable in the energy dependence of the specular beam, as a result of the unitarity of the scattering process.

The observability in the specular intensity of structure arising from enhanced or decreased sticking is an interesting suggestion for future experiments. Because entry into the bound states is a phonon-mediated process, the probability of capture by a bound state increases with temperature. This implies that not only will the overall sticking probability increase with T , but also the structure in σ_i will be enhanced. Furthermore, at larger T higher-order effects become more important, and more channels for bound-state capture become probable. The major experimental problem is that at higher temperatures the residence time on the surface for a light-physisorbed molecule becomes too short to make accurate measurements of the sticking. The calculations presented here and the arguments based on unitarity seem to indicate that, at higher temperatures, capture into the physisorption bound states can be monitored through careful measurements of the specular beam, even under circumstances under which the residence time of a physisorbed particle is short.

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