

Cross sections for He scattering from surface imperfections: Vacancies and CO adsorbates on Pt(111)

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Total cross sections for He scattering from isolated imperfections on surfaces are calculated using the Sudden approximation, and in some cases also by a numerically exact, time-dependent quantum-mechanical wave packet method. Systems studied include: CO adsorbates on Pt(111); mono-, di-, and trivacancies on Pt(111). The main results are: (1) the incidence angle and energy dependence of the cross section for He/[Pt(111) + CO] are very sensitive to the CO distance from the Pt plane. Interactions with the adsorbate image have little effect on the cross section. (2) The cross sections for clusters of vacancies are given within 10% or better, by the geometric sum of the monovacancy cross sections, the latter being treated as circles centered at each monovacancy. (3) The dependence of the cross section on the energy is sufficiently sensitive to distinguish between the “electron density hole” and “electron density hump” models for vacancies and vacancy clusters. (4) The Sudden approximation compares well with the exact quantum-mechanical results at typical experimental energies, when the incidence angle is not too far from the normal. These results indicate that experimental measurements of He scattering cross sections as a function of energy and incidence angle, combined with Sudden or wave packet scattering calculations, can provide detailed information on surface defects and their interactions with gas-phase atoms.

I. INTRODUCTION

The scattering of light atoms, long recognized and used as an important tool in the study of crystalline surfaces, has recently been applied as a probe of structure and properties of surface defects.¹⁻¹⁰ Studies of He scattering from imperfections on crystalline surfaces such as steps,^{6,9} isolated adsorbates,^{3,5,10} or vacancies,⁶ already provided considerable insight into the structure of such defects and the nature of interactions between them. A useful concept in the analysis of scattering data for such systems is the cross section for atoms scattering by a surface imperfection, a notion introduced and applied by Comsa, Poelsema, and co-workers.³⁻⁶ This quantity gives the effective area for scattering by a surface defect, and is defined in terms of the attenuation of the specular scattering peak as the concentration of the imperfections is increased. Using this quantity it was, for instance, possible to demonstrate that CO adsorbates in nearest-neighbor positions on Pt(111) repel each other,⁵ that vacancies on Pt(111) experience mutual attraction,⁶ and that Xe on Pt(111) undergoes a phase transition as the coverage is increased beyond some value.¹¹ Crucial in many applications of the cross section concept to the analysis of scattering data from surface imperfections is the assumption of geometric additivity for the cross sections⁶: That is, the cross section for atom scattering by several defects is assumed to be the combined geometric area covered by the cross sections for the individual defects, when the latter are viewed as circles centered at the imperfection sites.

Motivated by the above mentioned experiments, several

theoretical calculations of the cross sections for He scattering from adsorbates on surfaces were reported.¹²⁻¹⁵ Important as initial steps, these calculations employ, however, drastic approximations or models, e.g., treating the underlying surface as a hard wall. The quantitative accuracy of these methods has not been established yet. One may wonder if they can be used to assess or fit interaction potentials by comparison with experimental data. Also, the important assumption of “geometric additivity” of defect cross sections has not been tested yet in calculations.

The present study has several objectives. First, for CO adsorbates on Pt(111), we report here cross section calculations by the Sudden approximation and also, for some energies, by a numerically exact, time-dependent quantum-mechanical wave packet method. The “exact” calculations are used primarily to establish the validity of the Sudden approximation. The more extensive Sudden results lead to an assessment of the reliability of available potential functions for He interaction with CO on Pt(111). Second, we describe results on cross sections for He scattering from defects on Pt(111), calculations of which have not been hitherto reported. Third, and perhaps most important, we provide a test by calculation for a realistic model of the “geometric additivity” assumption for atom scattering from surface imperfections.

The structure of the article is as follows. In Sec. II we describe the potential functions used in the calculations for He scattering from CO on Pt(111) and from vacancies on Pt(111). Section III briefly outlines the methods used in the

scattering calculations. The results and interpretation of the cross section calculations are presented in Sec. IV. Concluding remarks are brought in Sec. V.

II. INTERACTION POTENTIALS

A. Interaction of He with CO on Pt(111)

We assume that a He atom colliding with the surface can be affected significantly by not more than one adsorbed CO molecule. This, obviously, is pertinent only to very low coverage, when the CO molecules are well separated, and because of their mutual repulsion, nonclustered. Throughout this study we ignore effects of energy transfer between the colliding atoms and the adsorbates, or the underlying crystalline surface. Experimentally, this assumption is supported by the finding that the measured cross sections exhibit no temperature dependence.⁷ Physically, the following justification can be given. There is considerable evidence from the work of Comsa, Poelsema, and their co-workers⁶ that the total cross sections for scattering by surface imperfections are determined by the long-range attractive forces between the colliding atom and the defect. Thus the cross section is dominated by collisions where the incoming atom has a large impact parameter with respect to the adsorbed molecule, and energy transfer to the latter is unlikely in this case. (Energy transfer to the adsorbate does occur in small-impact parameter hits upon the imperfection, but geometrically such collisions make a small contribution to the cross section.) The colliding He atom may transfer energy to the Pt surface upon impact on the latter, but this should be similar to the energy transfer taking place for a corresponding perfect Pt surface which contains no adsorbates. The operational definition used in the determination of the cross section from experimental data is such that it should be insensitive to energy transfer when the latter is the same for the "contaminated" surface as for the pure one. This picture is in accord with the experimental observation that the cross sections are insensitive to surface temperatures.⁷

Using thus a rigid nonvibrating model for the surface and the adsorbates, we assume the interaction for He/[CO + Pt(111)] to be of the form

$$V(X, Y, Z) = V_S(Z) + V_{AD}(X, Y, Z), \quad (1)$$

where Z measures the distance of the He atom from the surface and (X, Y) are the coordinates parallel to the surface plane. $V_S(Z)$ represents the interaction between He and a perfect Pt(111) surface. The corrugation of that surface is very weak and was thus neglected. In the calculations we used both a Morse and a Lennard-Jones model for $V_S(Z)$ ¹⁶:

$$V_S^{(\text{Morse})}(Z) = D_S [e^{-2\alpha(Z-Z_m)} - 2e^{-\alpha(Z-Z_m)}], \quad (2)$$

$$V_S^{(\text{LJ})}(Z) = D_S \left[\frac{1}{2} \left(\frac{Z_m}{Z+Z_0} \right)^9 - \frac{3}{2} \left(\frac{Z_m}{Z+Z_0} \right)^3 \right]. \quad (3)$$

While the LJ has the theoretically justifiable long-range asymptotic behavior, $V_S(Z) \propto Z^{-3}$, $Z \rightarrow \infty$, the Morse potential may well be more realistic for the shorter ranges, in particular in being less stiffly repulsive. The cross sections obtained with the two potentials differed only slightly. The

limited available knowledge on He/Pt interactions does not justify the use of more extensively parametrized $V_S(Z)$ potential functions. We used the value of $D_S = 4.0$ meV, taken from Harris *et al.*¹⁷ The steepness parameter of the Morse potential was taken to have the value of $\alpha = 0.6$ bohr⁻¹, rather typical of He interactions with metal surfaces. The center-of-mass position of the adsorbed CO was defined at $Z = 0$. The value of Z_m in the potentials (2) was then adjusted to yield a specified distance of the CO c.m. from the surface plane of Pt. This was obtained when the Z_m was chosen so as to give a turning point of 0.5 bohr for He reflected from the Pt surface at incident wave vector of $k_z = 2.5$ bohr⁻¹ normal to the surface. This corresponded to choosing $Z_m = 2.3$ bohr in this case of a Morse potential. As for the LJ 9-3 potential, the parameter Z_m was taken as 7.87 bohr, and $Z_0 = 5.42$ bohr. With these values, the LJ potential of Eq. (3) also yields, as in the case of the Morse potential, a turning point of 0.5 bohr for the He reflected from the Pt surface. In both cases the implication is that our model corresponds to a CO molecule partly immersed in the low-density region of the outer metal electrons (it is from this density region that scattered He is reflected), in accordance with the suggestion in Ref. 18.

The interaction between the scattered atom and the adsorbed molecule is represented in Eq. (1) by $V_{AD}(X, Y, Z) = V_{AD}(\mathbf{r} - \mathbf{r}_{AD})$, where \mathbf{r} is the position vector of He, \mathbf{r}_{AD} the position of the CO c.m. Three different models for $V_{AD}(\mathbf{r} - \mathbf{r}_{AD})$ were employed in our calculations: (i) An isotropic gas-phase He/CO Lennard-Jones potential, determined from the experiments of Butz *et al.*¹⁹ This potential has a well depth of $\epsilon = 2.37$ meV, and a minimum distance of $R_m = 3.5$ Å. (ii) An adjusted Lennard-Jones potential (with $\epsilon = 1.38$ meV, $R_m = 4.3$ Å) obtained by Jonsson *et al.*¹² by fitting the measured energy dependence of the cross sections for He scattering from CO adsorbates on Pt(111).³ The modification of the gas-phase He/CO potential parameters can be viewed as representing empirically the effects of CO polarization by the Pt surface. However, the calculations of Jonsson *et al.* to fit the cross section data used the drastic assumption that the Pt surface is a hard wall.¹² It is essential to examine the validity of the fitted potential in a more rigorous calculation. (iii) A He/CO potential obtained theoretically by Liu and Gumhalter,²⁰ which includes the effects of the surface on the He/adsorbate long-range interaction. The potential of Liu and Gumhalter has the form

$$V_{AD}(\mathbf{r} - \mathbf{r}_{AD}) = V_{AD}^{(d)}(\mathbf{r} - \mathbf{r}_{AD}) + V_{AD}^{(\text{im})}(\mathbf{r} - \mathbf{r}_{AD}) + V_{AD}^{(\text{int})}(\mathbf{r} - \mathbf{r}_{AD}), \quad (4)$$

where $V_{AD}^{(d)}$ is the direct, gas-phase-like interaction between the atom and the adsorbed molecule. Its attractive, long-range part is given by²⁰

$$V_{AD}^{(d)}(\mathbf{r} - \mathbf{r}_{AD}) = -C_{ab} \frac{(2+4\mu)}{R^6} \left[1 + \frac{1-\mu}{1+2\mu} P_2(\cos \theta) \right] \quad \text{for } (R \rightarrow \infty), \quad (5)$$

where θ is the angle between $\mathbf{R} = (\mathbf{r} - \mathbf{r}_{AD})$ and the normal to the surface. For the repulsive part of V_{AD} , Liu and Gum-

halter employed the exponential potential function given by Gordon and McGinnis²¹ for gas-phase He/CO. In Eq. (5), μ is the ratio of transverse and longitudinal adsorbate polarizabilities. In the calculations we employed the values of C_{ab} , μ as given in Ref. 2. The second and third terms in Eq. (4) describe He/adsorbate interactions that are mediated by the surface, and are expected to be far more important at large distances than at short ones. $V_{AD}^{(im)}(\mathbf{r} - \mathbf{r}_{AD})$ represents the interaction of the He with the adsorbate image in the surface plane. The long-range behavior of this interaction is

$$V_{AD}^{(im)}(\mathbf{r} - \mathbf{r}_{AD}) = -C_{aMbM} \frac{(2 + 4\mu)}{R_*^6} \times \left[1 - \frac{1 - \mu}{1 + 2\mu} P_2(\cos \theta_*) \right], \quad (6)$$

where \mathbf{R}_* is the distance vector between the atom and the center of the adsorbate image, $R_* = |\mathbf{R}_*|$, and θ_* is the angle between \mathbf{R}_* and the normal to the surface. An expression for C_{aMbM} was derived in Ref. 20. Finally, $V_{AD}^{(int)}$ represents an interference term between the interaction of the atom with the adsorbate and its interaction with the pure image²⁰

$$V_{AD}^{(int)}(\mathbf{r} - \mathbf{r}_{AD}) = 2 \frac{C_{abM}}{(RR_*)^3} [(4 - 3 \cos^2 \theta - 3 \cos^2 \theta_*) - (1 - \mu)(4 - 6 \cos^6 \theta - 6 \cos^2 \theta_*) + 9 \sin \theta \cos \theta \sin \theta_* \cos \theta_* + 9 \cos^2 \theta \cos^2 \theta_* + 1]. \quad (7)$$

The coefficient C_{abM} was taken from Gumhalter and Liu (0.841 eV Å⁶).²⁰ The role of the surface-mediated potentials $V_{AD}^{(im)}$, $V_{AD}^{(int)}$ between the colliding atom and the adsorbate is of fundamental interest in the field of gas/solid interaction dynamics.

B. Interactions of He with vacancies on Pt(111)

We consider first a potential model for the interaction between a monovacancy and the incoming atom. In this study the following potential function was employed:

$$V(X, Y, Z) = D_s \left[\left(\frac{Z_m}{Z + Z_s(X, Y)} \right)^9 - 3 \left(\frac{Z_m}{Z + Z_s(X, Y)} \right)^3 \right] / 2 - \frac{C_6}{R^6}. \quad (8)$$

Here $\mathbf{r} = (X, Y, Z)$ are the coordinates of the He atom, $R = [(X - X_D)^2 + (Y - Y_D)^2 + (Z - Z_D)^2]^{1/2}$ is the distance between the He and the position (X_D, Y_D, Z_D) of the vacancy. The parameter Z_m was taken as $Z_m = 7.87$ bohr, since it is analogous in role to the corresponding parameter used in Eq. (3) for He/[CO on Pt]. $Z_s(X, Y)$ has the meaning of a shape function, determining the form of the repulsive potential wall at the vacancy site. We took

$$Z_s(X, Y) = 0 \quad \text{for } \rho > a/2, \quad (9)$$

$$Z_s(X, Y) = \frac{b}{2} \cos \left(\frac{2\pi}{a} \rho \right) + \frac{b}{2} \quad \text{for } \rho \leq a/2, \quad (10)$$

where $\rho(X, Y) = [(X - X_D)^2 + (Y - Y_D)^2]^{1/2}$, and a is the nearest-neighbor distance of the Pt lattice, 5.2381 bohr. b

was so fitted that the depth of the defect, measuring in terms of the turning point for He scattering at incident wave number $k_z = 2.0$ bohr⁻¹, was on the order of the depth of the Pt layer. This leads to $b = 0.97$ bohr. This places the bottom of the defect "well" at a depth of half a width of a Pt layer. It is reasonable to have a value less than one full layer, because our belief is that the metal electrons fill in part of the space created by the vacancy.

Zaremba, in developing a model for He interaction with a vacancy on a metal, chose Z_D to lie on the plane defined by the undamaged Pt surface.²² In this case, the potential function (8) leads to numerical difficulties, since the point $R = 0$, which is an attractive singularity of the potential, is accessible to the scattered particle. To eliminate this difficulty, we modified his model by placing Z_D underneath the defect, as shown in Fig. 1. The value of the coefficient C_6 was obtained by fitting an experimental cross section of Poelsema *et al.*¹⁸ by the quantum wave packet calculations, giving $C_6 = 55$ a.u.

It should be stressed that present-day knowledge of atom/vacancy interactions is questionable even on the qualitative footing. The main model we used, Eq. (8), is based on Zaremba's treatment of the vacancy as introducing an additional surface polarization and hence an increased attraction between the He atom and the surface. An alternative model has been proposed by Lapujoulade and Levi²³. They suggest that a missing Pt atom could lead to a restructuring of the metal electron density so as to create an "electron density hump" on top of the vacancy, giving rise to repulsive polarization forces. Differently put, this view holds that if the long-range van der Waals interaction between a crystalline Pt solid and a He could be described as a sum of effective, pairwise $-C_6/R^6$ attractive potentials, then an atom "hole" might be treated as adding a repulsive $+C_6/R^6$ to the perfect surface interaction with the He atom. This view could be quantitatively modeled, e.g., by a potential of the form of Eq. (8), but with a positive $+C_6/R^6$ instead of the attractive term. We report here also results of calculation with this model, in the hope that scattering experiments, combined with calculations may be able to determine which picture is

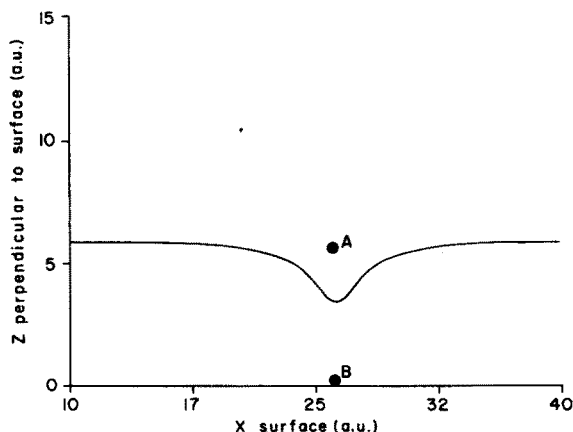


FIG. 1. He/Pt equipotential near monovacancy site. Equipotential shown is the locus of classical turning points for He scattering at wave number $k_z = 2.0$ bohr⁻¹. A is the origin of the attractive vacancy potential in Zaremba's model. B is the origin used in the present calculation.

more realistic. The coefficient C'_6 for the repulsive case was determined by fitting as well as possible the data of Ref. 18. This gave $C'_6 = 9.6$ a.u. In this case we took Z_D to lie in the (perfect) surface plane, since a repulsive singular term in the potential poses no difficulties in the scattering calculations.

We now proceed to consider He interactions with small clusters of vacancies. We adopted the following model for constructing an interaction potential for such systems. The shape functions Z_i , representing the form of the atom/monovacancy repulsive walls were geometrically superposed for all the vacancies in the cluster, as shown in Figs. 2 and 3. The combined shape of the repulsive walls was then smoothed, to round off the sharp potential corners, which seems intuitively a physically reasonable behavior. This gives rise to a numerically determined shape function $Z_c(X,Y)$ for the vacancy cluster, as indicated in Figs. 2 and 3. Finally the potential function between He and the vacancy cluster was constructed in the form

$$V(X,Y,Z) = \frac{D}{2} \left[\left(\frac{Z_0}{Z + Z_c(X,Y)} \right)^9 - 3 \left(\frac{Z_0}{Z + Z_c(X,Y)} \right)^3 \right] - \sum_i \frac{C_6}{R_i^6}, \quad (11)$$

where R_i is the distance between the He atom and the center of the i vacancy in the cluster. We note that the "shape rounding" of the repulsive equipotential has only a minor effect on the cross sections calculated, although the sharp edges of the simple, unrounded superpositions of monovacancy potential may lead to artifacts in the behavior of more detailed aspects of the collision dynamics (structures in non-specular scattering). Note that in the case of a trivacancy, both a linear and a triangular isomer are possible, and cross section calculations were carried out for both isomers. Our assumption in this case is that the experimentally relevant cross section is a (statistical) average of the results for the two forms.

III. METHODS OF CALCULATION

A. The Sudden approximation

The Sudden approximation has been used for some time to obtain diffraction intensities for atomic or molecular

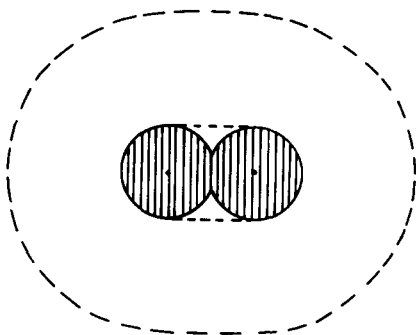


FIG. 2. Shape function of He interaction with divacancy on Pt. The shaded area is the superposition of the two monovacancy shape functions. The "rounded" tube form used in the calculation is indicated by ---. Shown also is the geometric superposition of the two monovacancy cross sections, and its considerable proximity to the "tube" form.

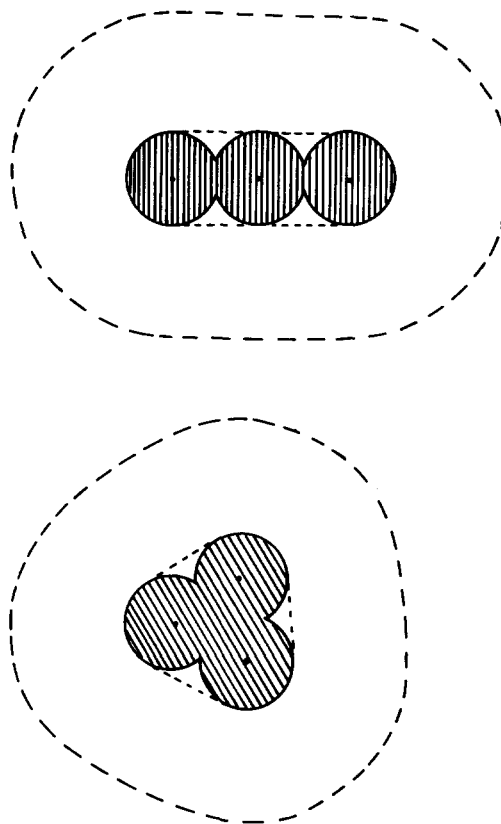


FIG. 3. Shape function of He interaction with trivacancies on Pt. The shapes are shown for a linear and for a triangular trivacancy. The shaded area is the superposition of the three monovacancy shape functions. The smoothed shape function is shown in each case by broken lines. The geometric sum of the monovacancy cross section is also shown, and its proximity to the trivacancy form is indicated.

scattering from crystalline surfaces.²⁴ Application of the method to scattering from disordered surfaces was more recently proposed by Gersten *et al.*²⁵ The approximation was employed to study the off-specular angular intensity distribution in atom scattering from adsorbates²⁶ and from several models of disordered surfaces.^{26,27} Numerical tests have shown that the Sudden method gives results of good accuracy for the angular intensity distribution for models of adsorbates and scattering energies not very different from those considered in the present study.²⁶ This article provides, however, the first application of the Sudden method to the quantitative calculation of cross sections for scattering by surface imperfections.

The condition for the validity of the Sudden approximation is that the momentum transfer in the collision in the direction normal to the surface (due to reflection by the surface potential wall) be much greater than the momentum transfer in parallel to the surface plane (due to surface corrugation). Denote the incident wave vector by $\mathbf{k} = (\mathbf{K}, k_z)$, where \mathbf{K} is the component parallel to the surface and k_z is perpendicular to this plane, the condition for the Sudden to be applicable is

$$|\mathbf{K}' - \mathbf{K}| \ll 2k_z, \quad (12)$$

where \mathbf{K}' is any final or intermediate wave vector that contributes significantly to the scattering. We focus here on the

calculation of total cross sections, and the latter quantities are determined mainly by collisions that have large impact parameters with regard to the defect. One expects the Sudden to be valid for such collisions which lead to low momentum transfers in parallel to the surface, provided that k_z in Eq. (12) is not too small. At typical experimental energies this excludes only scattering with incidence direction far from the normal.

The Sudden approximation for scattering from an isolated defect located on an otherwise smooth surface can be formulated as follows. Consider a defect placed at the center of a square surface segment of areas $A = L \times L$. The linear extension of the surface segment L is taken large enough so that when the He atom is placed at the edge of the segment, the interaction between it and the surface defect is already completely negligible (typically in the calculations carried out, has the length of 15 unit cell constants of the underlying surface). The probability of scattering into final wave vector component \mathbf{K}' parallel to the surface is given in the Sudden approximation by^{24,25}

$$P_{\mathbf{K}-\mathbf{K}'} = \left| \frac{1}{A} \iint e^{i(\mathbf{K}' - \mathbf{K}) \cdot \mathbf{p}} e^{2i\eta(\mathbf{p})} d\mathbf{p} \right|^2, \quad (13)$$

here $\mathbf{p} = (X, Y)$ are the coordinates in parallel to the surface and the integration in Eq. (13) is over the surface segment used. The phase shift $\eta(\mathbf{p})$ is given in the WKB approximation by

$$\eta(\mathbf{p}) = \int_{Z_0}^{\infty} dZ \{ [k_z^2 - 2\mu V(X, Y, Z)/\hbar^2]^{1/2} - k_z \} - k_z Z_0. \quad (14)$$

Here V is the interaction potential between the atom and the surface (including the defect), μ the mass of the scattered atom, and Z_0 the classical turning point pertaining to the integrand in Eq. (14). For a finite surface segment the spectrum of allowed \mathbf{K}' values is, in principle, discrete (as seen, e.g., by imposing boundary conditions at the edges of the surface segment), but the grid of allowed \mathbf{K}' values is so dense for large L that this is not of practical importance. If the adsorbate has cylindrical symmetry about an axis normal to the surface (e.g., a monovacancy or a CO adsorbate) the integral in Eq. (13) can be simplified by transforming to polar coordinates. Note however that defects such as di- or trivacancies have no such symmetry. The calculation of the cross section Σ is based on the experimental definition of that quantity,⁶ namely Σ is determined from

$$I_{\text{imp}} = I_0 e^{-\Sigma n_s \theta}. \quad (15a)$$

Here I_{imp} is the specular scattering probability for the surface having coverage θ of defects, n_s is the number of sites that can accommodate a defect per unit surface area, and I_0 is the specular intensity for the corresponding perfect surface. The experimental specular scattering intensity is proportional to the normalized specular scattering probability given by Eq. (13), hence

$$P_{\mathbf{K}-\mathbf{K}'} = e^{-\Sigma n_s \theta} \quad (15b)$$

since the probability for specular scattering from a perfect rigid flat surface is one. Note that Eqs. (15) hold only for

very low coverages.⁶ n_s , the concentration of sites available for defects, is taken in our case as the number of Pt(111) surface unit cells per unit area, while the coverage θ corresponds to a single defect for the surface segment used in the calculation. Several authors have used a modified definition of Σ , where the latter quantity is divided by $\cos \theta_i$, θ_i being the angle of incidence,²⁰ and this must be kept in mind when comparing with their results. The Sudden evaluation of Σ , using the integrations (13), (14), and (15b) is computationally straightforward. It must be checked, however, that the Σ obtained does not vary when A , the surface segment area used, is increased. This requires using large surface segments having linear extensions of the order of 50 Å.

B. Time-dependent wave packet calculations

Time-dependent wave packet methods are being increasingly used in quantitative studies of scattering from surfaces.²⁸ One advantage of these methods is they are applicable also in cases of a continuum of channels, unlike, e.g., the coupled-channel method and several other rigorous computational techniques of time-independent scattering theory. Scattering from an imperfect or disordered surface, when there is no lattice periodicity to dictate a discrete set of momentum changes, is such a continuum channel problem. Both semiclassical^{2a} and rigorous quantum-mechanical time-dependent wave packet algorithms^{30,31,26} were recently applied to atom scattering from defects or from disordered surfaces, although they were not as yet used to calculate cross sections from imperfections.

In the present study we apply the numerically exact algorithm for solving the time-dependent Schrödinger equation due to Kosloff and Kosloff.³² The method has been extensively described in the literature,³² also in the particular context of surface scattering.²⁸ We briefly mention here only some of the main points.

In solving the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \left[-\frac{\hbar^2}{2\mu} \nabla^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}, t), \quad (16)$$

a major computational effort is invested in evaluating the second spatial derivative of the wave function at each time t and for all \mathbf{r} , which is a necessary step for the time propagation of the solution. The procedure of Kosloff and Kosloff³² deals with this by using the very efficient fast-Fourier transform (FFT) algorithm: The wave function is transformed into \mathbf{k} space by the FFT procedure: In \mathbf{k} space the action of ∇^2 becomes multiplication by $-k^2$. A second FFT operation applied to $-k^2 \Psi(\mathbf{k}, t)$ then yields the desired $\nabla^2 \Psi(\mathbf{r}, t)$. Symbolically

$$\Psi(\mathbf{r}, t) \xrightarrow{\text{FFT}} \tilde{\Psi}(\mathbf{k}, t) \xrightarrow{\times -k^2} k^2 \tilde{\Psi}(\mathbf{k}, t) \xrightarrow{\text{FFT}} \nabla^2 \Psi(\mathbf{r}, t). \quad (17)$$

The propagation in time of $\Psi(\mathbf{r}, t)$ can then be carried out by expanding the formal solution of Eq. (16):

$$\Psi(\mathbf{r}, t) = \exp(-iHt/\hbar) \Psi(\mathbf{r}, 0), \quad (18)$$

in Chebychev polynomials³³:

$$e^{-iHt/\hbar} \approx \sum_{n=0}^N a_n \Phi_n \left(-\frac{iH}{\Delta E} \right), \quad (19)$$

where ΔE is a parameter having the interpretation of the energy range of the wave packet generated in the calculation (the larger ΔE , the greater the accuracy), Φ_n are the complex-valued Chebychev polynomials, $a_0 = J_0(\Delta E t / \hbar)$; $a_n = 2J_n(\Delta E t / \hbar)$ where J_n is the Bessel function of order n . Starting from the initial state $\Psi(r, 0)$, the expansion (19) is used to generate the time propagation. The actual implementation of the method is described in Ref. 33.

In application to surface scattering one begins with a wave packet outside the atom-surface interaction range, then propagates in time using the above method until the collision process is over and the projectile again no longer experiences a significant force.²⁸⁻³⁰ The numerically exact wave packet method is computationally far more expensive than the Sudden approximation. We therefore applied it only at several energies and for one of the defects, to provide a rigorous test on the accuracy of the cross sections provided by the Sudden.

IV. RESULTS AND ANALYSIS

A. He scattering from CO on Pt: Comparison with experiment

Figure 4 compares calculated cross sections for He scattering from an isolated CO molecule adsorbed on Pt(111) with the corresponding experimental values of Poelsema *et al.*¹⁸ The cross sections are plotted as a function of the collision velocity. The theoretical cross sections shown were obtained in the Sudden approximation, using the following potentials (discussed in Sec. II): (i) An isotropic He/CO potential from gas-phase data,¹⁹ with a Morse potential from He/Pt(111). (ii) The modified He/CO potential given by Jonsson *et al.*¹² combined with a Morse interaction for He/Pt(111). (iii) The He/CO potential of Jonsson *et al.*,¹² with a [9,3] Lennard-Jones model for the He/Pt(111) interaction. As noted in Sec. II the potential of Jonsson *et al.* was fitted to data of He scattering from [CO + Pt(111)] under

the assumption of a hard-wall repulsive interaction between He and Pt(111).

As seen from Fig. 4, the results obtained with the He/CO potential of Jonsson *et al.*¹² are in very good agreement with the experimental cross sections. The gas-phase He/CO potential yields much poorer results. It is interesting to note that there is a small but nonnegligible difference between the two results obtained using the same He/CO potential, but different soft wall He/Pt(111) interactions. On this basis one must conclude that the use of hard-wall interaction between He and the metal is questionable, and the success of the potential fitted by Jonsson *et al.* using this model may be partly accidental. The results with the Morse potential for He/Pt seem in somewhat better agreement with experiment than those for the Lennard-Jones interaction. This may be due to the fact that the cross sections, while determined by collisions with large impact parameter (large $X^2 + Y^2$) with respect to the adsorbate, are mainly sensitive to Z values near the He/Pt turning points: It is the competition between the noncorrugated potential field of the metal, and the long-range potential due to the CO at the impact point, which determines if the He is scattered specularly or nonspecularly. The slightly softer Morse potential is probably a more realistic model in the pertinent region than the stiffer Lennard-Jones one, although the differences are not large.

Figure 5 shows the dependence of the cross section for He scattering from CO on Pt(111) on the angle of incidence, for a fixed collision energy. Only crude agreement is found between the measured cross sections and the calculated ones. The results for the He/CO potential of Jonsson *et al.*¹² (used with a Morse interaction for He/Pt) are substantially better than those obtained using the gas-phase atom-molecule interaction, but even the modified potential does not yield cross sections in adequate quantitative accord with experiment. In part this is undoubtedly due to inaccuracy of the Sudden approximation used in the calculation of the cross section, which is unreliable for the higher (further from nor-

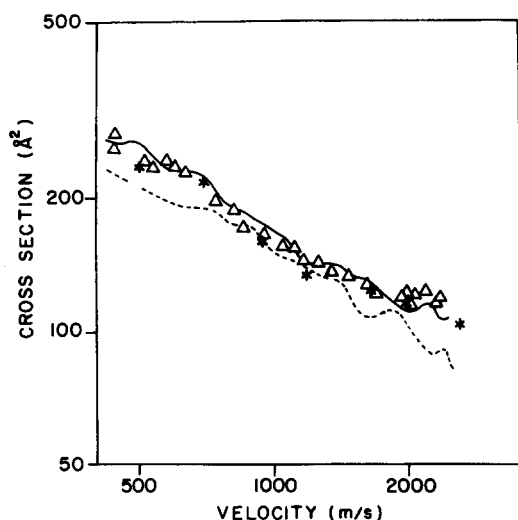


FIG. 4. Cross sections for He scattering from CO on Pt vs collisions velocity. Δ Experimental results (Ref. 18). — Potential of Jonsson *et al.* (Ref. 12) for He/CO, with Morse for He/Pt. * Potential of Jonsson *et al.* for He/CO, with Lennard-Jones for He/Pt. ---- Gas-phase He/CO potential with Morse for He/Pt.

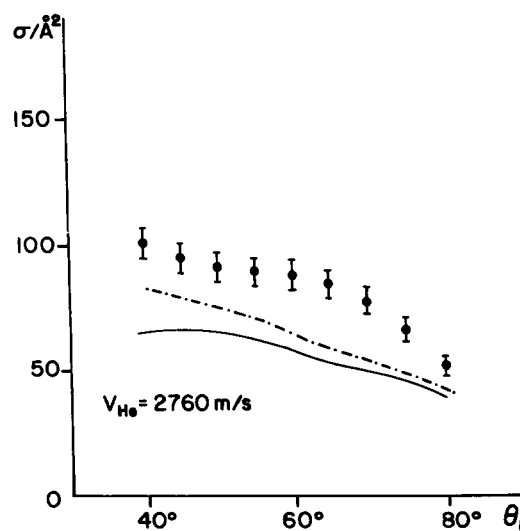


FIG. 5. Cross section for He scattering from CO on Pt vs incidence angle θ_1 . Results are for collision velocity of $v = 2760$ m/s. Φ Experimental results (Ref. 18). - - - Calculations using He/CO potential of Jonsson *et al.* (Ref. 12) (with Morse for He/Pt). — Calculations using gas-phase He/CO.

mal incidence) θ_i values. It seems, however, most unlikely that the entire discrepancy between the calculated and experimental values can be due to Sudden approximation errors, especially that the deviations at small and at large θ_i are roughly of the same magnitude. Figure 5 thus appears to indicate an inadequacy of the potentials when tested on a quantitative level.

We note that we carried out calculations also with an anisotropic He/CO potential, where the dependence of the interaction on the orientation of the CO molecule with respect to the atom was taken from gas-phase data. The results, not shown here, do not indicate any significant improvement of the agreement with experiment in Figs. 4 and 5.

B. Importance of adsorbate position and of image and interference interaction terms

Figure 6 shows the velocity dependence of the cross section calculated from the potential of Gumhalter and Liu,²⁰ and from several modifications of that potential. The Sudden approximation was used in these calculations. Comparison with the experimental results of Poelsema *et al.*¹⁸ is shown. The main interest here is in testing the long-range, surface-mediated interactions between the adsorbate and the scattered atom, calculated by Gumhalter and Liu (see Sec. II). In the test calculations we employed the He/adsorbate potential given by Gumhalter and Liu in combination with a Morse potential for He/Pt(111). The scattering calculations by the above authors used the less satisfactory hard-wall model for the underlying surface.

Consider first the comparison between the cross section for the full potential of Gumhalter and Liu and the corresponding results for that potential when the terms due to image and interference interactions induced by the surface are omitted. As Fig. 6 shows, the two cross section curves are very close over the entire range of experimental collision

velocities. We conclude that *interactions with the surface image of the adsorbate are of negligible importance for atom scattering*. A more refined treatment of image and interference effects due to the jellium-like metal electrons is unlikely to alter this conclusion. This, of course, does not exclude the possibility that surface-mediated He/CO interactions, involving mechanisms that are not modeled in the potential of Gumhalter and Liu may play a much more important role. Comparing now the cross sections from the potential of Gumhalter and Liu with the experimental data, a large deviation is found. This potential is thus in serious error. In their modeling of the [CO + Pt(111)] system, Gumhalter and Liu²⁰ assume a relatively large distance between the CO center of mass and the repulsive wall of the Pt(111). We attempted therefore to use the same potentials as in Ref. 20, but to modify the CO location to the shorter distances from the surface as advocated by Poelsema *et al.*¹⁸ As seen from Fig. 6 this improves considerably the agreement between the calculated and the experimental results. This shows *that the cross sections for scattering by an adsorbate are very sensitive to its location with respect to the surface plane*. In fact, the role of this geometric factor is seen to far outweigh the relatively minor contribution of image interactions. Note that even with the improved position for the CO adsorbate, the potential of Gumhalter and Liu still gives cross sections that deviate considerably from the experimental data, and the potential of Jonsson *et al.*¹² seems better as seen from Fig. 4.

C. Assessment of potentials for He/[CO + Pt(111)]

The results of Figs. 4–6 show that none of the available model potentials for He/[CO + Pt(111)] offers a quantitatively adequate description of the interaction pertinent to the real system. Even the best of these in terms of comparison with experiment, the potential of Jonsson *et al.*,¹² can be viewed only as a first approximation. This suggests *that a necessary approach to obtaining atom/defect interactions in the present state of the art should be to determine these potentials by fitting measured cross section data*. Clearly the experimental velocity and incidence-angle dependencies of the cross section are sufficiently sensitive to the interaction potential that fitting these observable quantities will result in considerable improvement of present-day knowledge.

The calculations discussed in the previous subsections demonstrate that the cross sections are very sensitive to the position of the adsorbate with respect to the underlying surface plane. Combination of experiments and theoretical calculations of cross sections should thus be useful in obtaining a sensitive determination of the location of the adsorbed imperfections. The distance between the adsorbate and the supporting surface plane is one of the most critical aspects affecting the interaction potential $V(X,Y,Z)$ in Eq. (1). On the other hand, it appears that interactions due to the adsorbate surface image are virtually of no quantitative importance for $V(X,Y,Z)$. It is of interest to speculate as to what are the important missing and incorrect features that affect the available He/[Pt(111) + CO] potentials. One aspect may be surface induced effects of types different from the image and interference terms included in the potential of Gumhalter and Liu.²⁰ If the location for the CO position

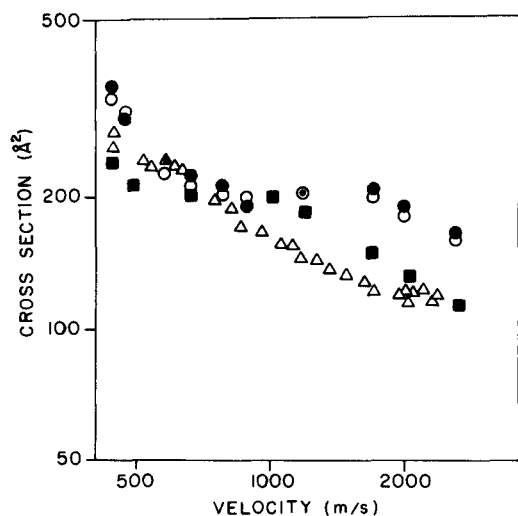


FIG. 6. Cross section for He scattering from CO on Pt vs collision velocity. Δ Experimental results (Ref. 18). \bullet Potential of Gumhalter and Liu (Ref. 20). \blacksquare Potential of Ref. 20 with corrected distance between CO and surface. \circ Potential of Ref. 20 without image and interference terms.

accepted in this article is correct, the molecule is immersed in a nonnegligible density of outer metal electrons: While this density region lies outside the jellium edge, it may suffice to affect significantly the electronic states of the adsorbate, and the polarizability to which the latter contribute. Charge transfer from metal states to CO orbitals is also likely in this "immersed" configuration. *Ab initio* studies which allow for these effects should be of interest. Note that this mechanism should lead to a reduction of the effective He/CO attractive well depth compared with one in the gas phase, as the relative success of the Jonsson *et al.*¹² potential suggests. Another point where refinement of the present interaction may be important pertains to the He/Pt(111) component of the potential $V(X,Y,Z)$. The "corrugation" that leads to non-specular scattering of the He is a consequence of competition between the He/CO potential, and the flat, purely z -dependent He/Pt interaction. As the difference between calculations with a Morse and with a Lennard-Jones He/Pt potential shows, the shape of the surfaces "soft wall" may affect the results.

D. Comparison between Sudden calculations and exact results

The above results were obtained using the Sudden approximation, and it is essential to assess its limitations. An unsatisfactory aspect of the approximation is that the cross sections it yields depend only on the velocity component normal to the surface, which is clearly not true in general. A simple test of Sudden approximation errors is shown in Table I. The calculations are for He scattering from a monovacancy on Pt(111), using the potential discussed in Sec. II. Presented in Table I are cross sections for given incident wave vector components normal to the surface $k_z = 2.2445$ bohr⁻¹, but for three different incidence angles. The "exact" cross sections from the time-dependent wave packet calculations fall from 77.9 Å² for normal incidence to 66.50 Å² for $\theta_i = 19.1^\circ$, and to 67.04 Å² for 40.9°. The Sudden result is, of course, the same in all cases. Nevertheless, we note the error in the Sudden results is not more than 10% for the unfavorable high incidence angle, and less than 5% for normal incidence. The aspect tested here, dependence on θ_i for fixed k_z , is an aspect particularly unfavorable for the Sudden. The results show that the Sudden provides a good approximation ($< 10\%$ error) for the magnitude of the cross section at low or intermediate incidence angles.

E. "Geometric additivity" principle for the cross section of scattering from a cluster of vacancies

As noted in the introduction of this article, the assumption of "geometric additivity" of cross sections,⁶ is extremely

TABLE I. Cross section for the scattering from a monovacancy on Pt(111). (Results are for collisions with $k_z = 2.2445$ bohr⁻¹.)

θ_i	Σ (Å ²) (Sudden)	Σ (Å ²) (exact)
0°	73.76	77.9
19.1°	73.76	66.50
40.9°	73.76	67.04

useful for studying interactions between defects by He scattering. This assumption states that the cross section for scattering by a cluster of defects is the geometric area covered when the cross sections for each of the defects is described as a circle centered at the defect.

Figure 7 provides a computational test for this assumption in the case of di- and trivacancies on Pt(111). The interaction potentials between the vacancy systems and He, and the geometries of the vacancy clusters were described in Sec. II and in Figs. 1–3. The cross sections were calculated in the Sudden approximation, for normal incidence energies up to 58 meV. The results show excellent agreement between the calculated cross sections for the di- and trivacancies and the corresponding predictions of the "geometric sum" assumption. The intuitively based relation is thus found completely justified. Figure 8 gives results of calculations of cross sections from mono-, di- and trivacancies using a very different potential than that employed in obtaining the values of Fig. 7. In Fig. 8 the cross sections were obtained using the electronic density hump assumption, which implies a repulsive He/vacancy interaction (see Sec. II). Note that also this very different potential shows excellent agreement between the scattering calculations for the di- and trivacancies, and the values given by the geometric additivity principle.

F. "Hole polarization" versus "electronic hump" model for He/vacancy interaction

As noted in Sec. II, two very different models have been proposed for He interaction with a vacancy on a smooth metal face. The model of Zaremba²² associates a polarizability with the hole corresponding to the vacancy, and gives an estimate for a long-range increased attractive force (over that in the case of a flat surface) due to such a hole. A very different model by Lapujoulade and Levi²³ argues for a repulsive long-range He/vacancy potential. Specific potential functions representing each of the two models were described in Sec. II. A free parameter in each of these potentials

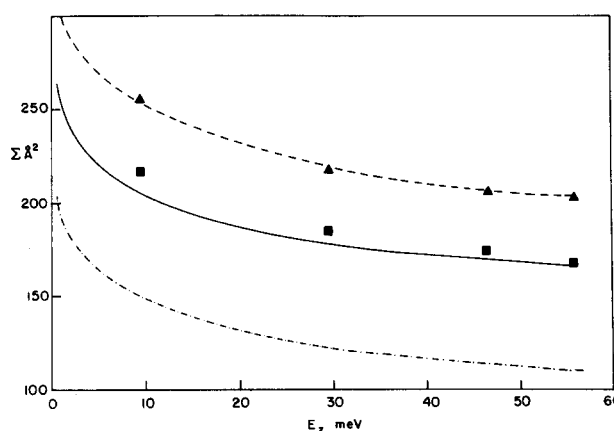


FIG. 7. Cross sections for He scattering from mono-, di-, and trivacancies on Pt(111). The calculated cross sections are shown as a function of the incidence energy normal to the surface. The calculations are for the Zaremba-type potential (see Sec. II). — Sudden results for monovacancy. --- Sudden results for divacancy. - · - Sudden results for trivacancy (averaged over geometric isomers of defect). ■ -- Geometric additivity result for divacancy. ▲ -- Geometric additivity results for trivacancy.

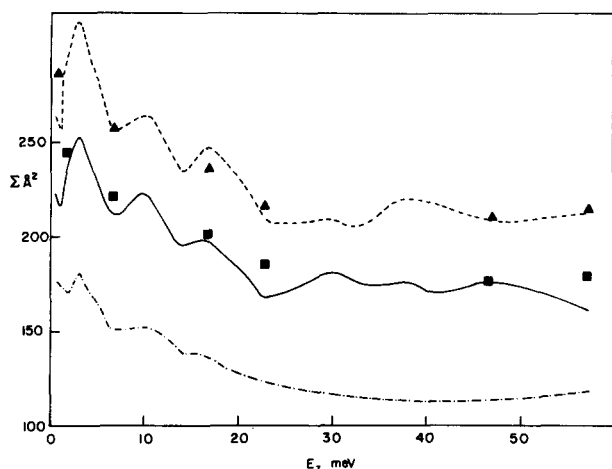


FIG. 8. Cross sections for He scattering from mono-, di-, and trivacancies on Pt(111). --- Sudden results for monovacancy. — Sudden results for divacancy. --- Sudden results for trivacancy (averaged over isomers of the defect). ■-- Geometric additivity result for divacancy. ▲-- Geometric additivity results for trivacancy.

was fitted so as to reproduce a value of 150 Å^2 (experimental) for the cross section for He/[Pt(111) + vacancy], for incidence wave vector component normal to the surface $k_z = 2.2445 \text{ bohr}^{-1}$. Comparison of the calculated cross section for the Zaremba model, Fig. 7, and the electronic hump model, Fig. 8 shows a very different behavior for the cross sections in the two cases, especially for the di- and trivacancies. The Zaremba model gives a smooth energy dependence, while the electronic hump model gives rise to oscillations: In the latter case, the fitted repulsive vacancy potential corresponds to such a large hump that substantial interference arises between scattering from the top of the repulsive potential hump and from the smooth part of the Pt surface. The fitted vacancy "hole" is too shallow to produce interference effects in this energy range. The point is that *energy dependence measurements of the cross sections should be able to distinguish between the two models by the above theoretical predictions.*

V. CONCLUDING REMARKS

In this article we reported calculations of cross sections for He scattering from several types of surfaces defects: mono-, di-, and trivacancies Pt(111), and CO adsorbed on Pt(111). The calculations were mostly carried out in the framework of the Sudden approximation, the accuracy of which was confirmed by comparison against numerically exact, quantum-mechanical time-dependent wave packet results in a few test computations. Several interesting results were obtained with regard to the properties of the cross sections, and on the effect of various features of the He/defect interaction on these quantities.

Perhaps the most important result obtained in this study is a confirmation of the "geometric additivity" postulate for cross sections of scattering from a cluster of defects. This postulate⁶ states that the cross section for scattering from several defects is the net geometric area covered by the cross sections for scattering from the individual defects (when

these quantities are described as circles centered at the imperfection site). The role of this assumption in applying He scattering to the mutual interaction between defects is a major one, so the successful test of this principle here, in the case of vacancies, lends support to several interesting experimental conclusions in this area.

Another interesting result on scattering from vacancies has been the prediction that measurements of the energy dependence of the cross sections should make it possible, although not trivial, to test experimentally two alternative, very different current models for the He/vacancy interaction: The electronic hump model, resulting in repulsive long range He/vacancy potential, and the polarizable hole model that estimates a long-range attraction in this case.

In studying He scattering from CO adsorbed on Pt, it was found that the calculated cross sections are sensitive to the distance of the adsorbate from the Pt plane. Thus, this suggests that cross section measurements for adsorbates, in particular of the variation with energy and incidence angle, when interpreted with corresponding calculations, may throw light on the positions of such imperfections. On the other hand, the effect of interactions with the adsorbate image on the He scattering was found to be negligible. The main conclusion here must be viewed as a negative one: None of the existing potentials for He/[CO + Pt(111)] can adequately reproduce the incidence energy and angle dependence of the measured cross sections. This suggests that a very fruitful approach to the study of He/defect interactions may be by trying to fit detailed cross section measurements for such systems. The demonstrated sensitivity of the cross section to the interaction between the He and the defect, provided both energy and incidence angle are varied in a substantial range, offers hope for the quantitative determination of the potentials for such systems.

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