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Study of the diffraction mediated selective adsorption through the close-coupling and diabatic distorted wave formalisms. Application to the ^4He -Cu(110) system^{a)}

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Two different formalisms, one based on close-coupling equations and other on the distorted wave approximation, have been applied to the low energy elastic scattering of ^4He atoms by a corrugated copper surface, Cu(110). Diffraction intensities and energetic positions and half-widths (selective adsorption resonances) have been obtained and compared with experimental and previous theoretical results, respectively. For this trapping process, and within the close-coupling framework, a plot of the diffraction channels (open and closed) has turned out to be very useful and a good guide in order to know the disposition of them at each interesting angular region. Also, a very accurate method, already employed successfully to treat resonances in the vibrational and/or rotational predissociation of van der Waals molecules, has been found to be also adequate here.

I. INTRODUCTION

In the past 20 years, gas-surface dynamical studies have grown very rapidly. Progress in technological problems and development of theoretical and computational methods have motivated this increasing interest. All this huge work has been widely gathered in many excellent reviews.¹

In this paper, we are concerned with low energy elastic scattering of light particles by single-crystal surfaces. Here the attractive physical interaction (physisorption) arises from the van der Waals forces due to electronic fluctuations in the gas-phase particle and the solid. However, very few attempts² to calculate this interaction from *ab initio* calculations are found. Diffraction experiments, in resonance conditions or not, provide an adequate method in order to propose model interaction potentials. In this way, information about corrugation parameters of the surface is obtained. The magnitude of this parameter is responsible for the coupling strength among diffraction channels through the Fourier components of the interaction potential. Thus, observance of minima or maxima in the specular intensity as a function of the initial conditions (energy and angle of incidence) is a direct consequence of this fact. Since the coupling is by means of diffraction channels, it is called this diffraction mediated selective adsorption.¹

From the theoretical point of view, trapping of atoms or molecules at highly corrugated surfaces can be treated within a quantum scheme. Most of approximations or methods used come from nuclear and atomic physics and have been widely developed in the field of molecular dynamics. In particular, weakly bound molecular systems such as van der Waals molecules have represented a good test of quantum schemes. Thus, different theoretical formalisms have been applied to this elastic scattering: close-coupling formalism,³⁻⁶ eikonal approximation,⁷ perturbative methods (Born or distorted wave Born series),⁸⁻¹⁰ semiclassical or

classical *S*-matrix method,¹¹⁻¹³ time-dependent wave packet approach,¹⁴ semiclassical trajectory method,^{15,16} sudden approximations,^{17,18} and more recently complex coordinates method.¹⁹ In general, one of the main goals of this variety of theoretical treatments, apart from its intrinsic interest, is to overcome the severe time limitation of the close-coupling calculations due to the high number of required channels in order to achieve numerical convergence. This number depends not only on the corrugation amplitude but also on internal states of the gas-phase particle. Very close results to the corresponding "exact" ones have been obtained by means of these formalisms for weak or medium corrugation amplitudes of the surface, when close-coupling calculations have been possible.

The system chosen in this work,⁴ $\text{He} + \text{Cu}(110)$, is a good candidate for carrying out a comparison among results produced by our close-coupling calculations and those obtained by two different formalisms, in particular, a general method based on high order distorted wave perturbation theory^{9(b)} and the complex coordinates method.¹⁹ Also, a great deal of experimental data²⁰ has been reported for the low energy scattering of helium atoms by the close-packed (110) copper surface. This face displays a roughness or corrugation which may be assumed to be only significant in the $\langle 100 \rangle$ direction and, therefore, all diffracted intensity goes in-plane except for the smallest incident angle. The model potential used is a corrugated Morse potential depending only on two variables (the perpendicular and the parallel one to the surface plane) which was considered by the other two calculations. At the same time, we present two new decoupling schemes, already applied successfully to study rotational predissociation of van der Waals molecules,²¹ based on the Golden Rule framework within a diabatic distorted wave approximation without (zero-order approximation) or with^{21(c)} configuration interaction (first-order approximation). This configuration interaction must be applied when the corrugation amplitude increases and the spacing

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among strongly coupled diffraction channels is close to the well depth of the model potential assumed for the lateral average of the gas-surface interaction or main term of the Fourier series.

Any application of the close-coupling formalism requires, first of all, a detailed study of the numerical convergence in order to know which are the relevant channels of the physical process treated. In the scattering that we are interested here, it is also necessary to know the disposition of diffraction channels since their asymptotic energies are functions depending on the energy and angle of incidence and of the $\mathbf{G}$ vector of the lattice. A plot of the kinetic energy of each diffraction channel vs the angle of incidence has turned out to be very useful in our convergence calculations as well as a good guide for choosing the angular regions of interest, that is, those crossing regions where quasisuperpositions of pairs of diffraction channels occur. Thresholds and bound state resonances calculated from the kinematic condition are also shown in this plot. Similar plots can be shown varying the azimuthal angle with the initial energy and polar angle kept constant. As concerns energetic positions and widths of these resonances, these ones are usually calculated by fitting a Lorentzian function of the energy to the modulus squared of the scattering S matrix. However, a more accurate way has been proposed and applied by ourselves elsewhere²² and used in this work. This method implies two scattering calculations at each sampled energy, one for obtaining the scattering S matrix and other for the corresponding background S_{bg} matrix, i.e., with only open channels. This method holds in the isolated narrow resonance approximation and assumes a very weak dependence on energy. Both conditions are fulfilled here. At low incidence energies and weak corrugations, this extra calculation is not a serious handicap.

II. THEORY

A. Close-coupling formalism

Consider the elastic scattering of a gas atom from a statically corrugated periodic solid surface. If the atom is a structureless particle of mass M and incident wave vector $\mathbf{k}$ the corresponding Schrödinger equation can be written as

$$\left[-\frac{\hbar^2}{2M} \nabla^2 + V(\mathbf{r}) - \frac{\hbar^2}{2M} \mathbf{k}^2 \right] \psi(\mathbf{r}) = 0. \quad (1)$$

Following the notation of Cabrera *et al.*,³ the z direction is chosen as the outward normal to the surface and, vectors in three-dimensional space are denoted by lower case letters

and capital letters for vectors which are to be parallel to the surface. Thus,

$$\begin{aligned} \mathbf{r} &= (x, y, z) = (\mathbf{R}, z), \\ \mathbf{k} &= (k_x, k_y, k_z) = (\mathbf{K}, k_z). \end{aligned} \quad (2)$$

It is assumed in Eq. (1) the interaction potential $V(\mathbf{r})$ between the incident atom and the surface is well described as a function of $\mathbf{r}$. Due to the periodicity of the surface lattice, we can expand this potential function in Fourier series

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}}(z) \exp(i\mathbf{G} \cdot \mathbf{R}). \quad (3)$$

$\mathbf{G}$ being the two-dimensional reciprocal lattice vector. Analogously, the wave function, $\psi(\mathbf{r})$, can also be expanded in the same form

$$\psi(\mathbf{r}) = \sum_{\mathbf{G}} \psi_{\mathbf{G}}(z) \exp[i(\mathbf{K} + \mathbf{G}) \cdot \mathbf{R}]. \quad (4)$$

Now, after substitution Eqs. (3) and (4) into Eq. (1), premultiplying by $\exp[-i(\mathbf{K} + \mathbf{G}) \cdot \mathbf{R}]$ this equation and integrating over the unit cell, we obtain the usual set of coupled equations for the diffracted waves⁴

$$\begin{aligned} \left[\frac{d^2}{dz^2} + k_{Gz}^2 - \frac{2M}{\hbar^2} V_0(z) \right] \psi_{\mathbf{G}}(z) \\ = \frac{2M}{\hbar^2} \sum_{\mathbf{G}' \neq \mathbf{G}} V_{\mathbf{G}-\mathbf{G}'}(z) \psi_{\mathbf{G}'}(z), \end{aligned} \quad (5)$$

where

$$k_{Gz}^2 = \mathbf{k}^2 - (\mathbf{K} + \mathbf{G})^2 \quad (6)$$

and $V_0(z)$ is the so-called laterally and thermally averaged potential. Each $\mathbf{G}$ channel is represented by an effective potential of the form $[(2M/\hbar^2)V_0(z) + (\mathbf{K} + \mathbf{G})^2]$, where $(\hbar^2/2M)(\mathbf{K} + \mathbf{G})^2$ can be seen as the asymptotic energy of the $\mathbf{G}$ channel. This asymptotic energy depends on the lattice constants, the angles of $\mathbf{k}(\theta_i, \phi_i)$ are the standard polar and azimuthal incident angles, respectively; θ_i is measured from the z axis, normal to the surface) and the initial momentum of the free atom. The eigenvalues of the $V_0(z)$ potential are the surface adsorbed states. The occurrence of selective adsorption resonances is due to the coupling elements, $V_{\mathbf{G}-\mathbf{G}'}(z)$, of the different diffraction channels. These Fourier components are usually repulsive and increase very rapidly for small z . The effective range is short for all $V_{\mathbf{G}}(z)$ ($\mathbf{G} \neq 0$) and this range decreases with $|\mathbf{G}|$.⁵ The number of these channels involved in the calculations depends strongly on the corrugation of the surface.

Equation (5) is solved subject to the usual boundary conditions⁴

$$\begin{aligned} \psi_{\mathbf{G}}(z) &\xrightarrow{z \rightarrow 0} 0 \\ \psi_{\mathbf{G}}(z) &\xrightarrow{z \rightarrow \infty} \begin{cases} k_z^{-1/2} \exp(-ik_z z) \delta_{\mathbf{G},0} + k_{Gz}^{-1/2} S_{\mathbf{G}} \exp(ik_{Gz} z) & \text{for open channels } (k_{Gz}^2 > 0) \\ \kappa_{Gz}^{-1/2} S_{\mathbf{G}} \exp(-\kappa_{Gz} z) & \text{for closed channels } (k_{Gz}^2 < 0) \end{cases}, \end{aligned} \quad (7)$$

where $\kappa_{Gz} = (-k_{Gz}^2)^{1/2}$. The amplitude $S_{\mathbf{G}}$ is related to the observable diffraction probability by $P_{\mathbf{G}} = |S_{\mathbf{G}}|^2$, starting from the specular channel ($\mathbf{G} = 0$).

B. Selective adsorption resonances and thresholds

The intensities of the specular and diffracted beams are functions, for a given static corrugated solid surface, of the

incident energy and θ_i and ϕ_i . Thus, the variation of these parameters seems to be very adequate in order to investigate selective adsorption resonances. In this way, we can obtain that⁴

$$k_{G_z}^2 = \frac{2ME_\alpha}{\hbar^2} < 0. \quad (8)$$

E_α being one of the bound states of the $V_0(z)$ potential (bound state resonance) or $E_\alpha = 0$ (threshold or surface resonance) where a diffraction channel becomes open or closed.

In order to calculate the bound state resonances, we have to study the behavior of the specular intensity around the critical values of these parameters [kinematic values obtained from Eq. (8)]. Alternatively, we can take into account the formal expression of the S matrix in the neighborhood of an isolated resonance depending on energy²³

$$S(E) = S_{bg}(E) \left[1 - \frac{iA}{E - \bar{E} + i\Gamma/2} \right], \quad (9)$$

where S_{bg} is the background S matrix, i.e., that obtained in the absence of closed channels, $\bar{E}$ and Γ are the position and width of the resonance, A a complex matrix that can be expressed as

$$A = \mathbf{g} \cdot \mathbf{g}^\dagger, \quad (10)$$

$\mathbf{g}$ being a complex vector that fulfills the condition

$$\sum_{i=1}^N |g_i|^2 = \Gamma \quad (11)$$

and where N accounts for the number of open channels at the energy E considered.

From the numerical point of view, two scattering calculations at each sampled energy are required in order to calculate the relevant quantities $\bar{E}$ and Γ . Thus, since S and S_{bg} are unitary matrices, the following Lorentzian functions are obtained

$$\begin{aligned} R(E) &= \text{Re}\{\text{Tr}[S_{bg}^\dagger(E)S(E)]\} \\ &= N - \frac{\Gamma^2/2}{(E - \bar{E})^2 + \Gamma^2/4} \end{aligned} \quad (12a)$$

$$\begin{aligned} II(E) &= \text{Im}\{\text{Tr}[S_{bg}^\dagger(E)S(E)]\} \\ &= -\frac{(E - \bar{E})\Gamma}{(E - \bar{E})^2 + \Gamma^2/4}, \end{aligned} \quad (12b)$$

where $\text{Re}\{z\}$ and $\text{Im}\{z\}$ are the real and imaginary part of the complex quantity z respectively, and Tr stands for the trace. At resonance conditions, these two functions take the particular forms

$$\begin{aligned} R(\bar{E}) &= N - 2, \\ II(\bar{E}) &= 0, \\ R(\bar{E} \pm \Gamma/2) &= N - 1, \\ II(\bar{E} \pm \Gamma/2) &\text{ is an extremum.} \end{aligned} \quad (13)$$

This method of calculating resonances was proposed by ourselves in other context.²² Deviations of the predicted behavior of the R and II functions must be attributed to a failure of the “isolated narrow resonance” approximation or the assumption concerning the S_{bg} calculations, i.e., to be a

smooth function of its argument. Very good estimates of angular positions and widths can be given from the two functions varying the incidence angle (polar or azimuthal) at fixed energy. Any angular variation presents a certain energetic disposition of the relevant channel and, therefore, different values of these two functions

C. Approximate selective adsorption resonances

A zero order approximation²¹ for obtaining positions and half-widths of these resonances could consist of neglecting all the coupling elements, $V_{G-G'}(z)$, and solving the uncoupled equations (adiabatic D distorted wave approach)

$$\left[\frac{d^2}{dz^2} + k_{G_z}^2 - \frac{2M}{\hbar^2} V_0(z) \right] \psi_G^{(0)}(z) = 0, \quad (14)$$

where $k_{G_z}^2$ has already been defined in Eq. (6). Equation (14) has discrete as well as continuum solutions. Discrete solutions are obtained by solving

$$\left[\frac{d^2}{dz^2} + \frac{2M}{\hbar^2} (E_\alpha - V_0(z)) \right] \psi_{0\alpha}^{(0)}(z) = 0, \quad (15)$$

α being the quantum number associated to each state of energy of the $G = 0$ channel. Now, the energy positions of the selective adsorption resonances for the diffraction channels will be given by $E_\alpha + (\hbar^2/2M)(\mathbf{K} + \mathbf{G})^2$ and the corresponding wave functions by $\psi_{G\alpha}^{(0)}(z) = \psi_{0\alpha}^{(0)}(z)$. On the other hand, continuum solutions are obtained from equation

$$\left[\frac{d^2}{dz^2} + \frac{2M}{\hbar^2} (\epsilon - V_0(z)) \right] \psi_{G\epsilon}^{(0)}(z) = 0 \quad (16)$$

with $\epsilon = E_\alpha + (\hbar^2/2M)[(\mathbf{K} + \mathbf{G})^2 - (\mathbf{K} + \mathbf{G}')^2] > 0$, ϵ represents the relative kinetic energy between two diffraction channels, $\mathbf{G}$ and $\mathbf{G}'$.

Thus, within the simplest Golden Rule formalism, the half-width associated to the α -quasibound state is estimated using the following expression:

$$\Gamma_\alpha^D = \pi \sum_{G'} |\langle \psi_{G\alpha}^{(0)}(z) | V_{G-G'}(z) | \psi_{G'\epsilon}^{(0)}(z) \rangle|^2 \quad (17)$$

and where each contribution must be calculated “on-shell energy.”

As will be shown later, this diabatic decoupling scheme provides very good estimates whenever the corrugation parameter of the surface lattice is small and, therefore, the coupling between the closed channel sustaining the resonance and the first open diffraction channel is also very small. Moreover, a large spacing between these two channels also contributes advantageously to the application of this scheme according to the so-called “energy-gap law.”²⁴ In fact, not only the weakness of the coupling but also rapid oscillations of the continuum wave function are important factors for obtaining small values of half-widths. This situation has been widely studied in the context of the predissociation of the van de Waals molecules. However, this approach will be no longer adequate in those surfaces presenting high corrugation parameters. Even more, if the spacing among strongly coupled diffraction channels is less than the well depth of the $V_0(z)$ potential then discrete–discrete and continuum–continuum couplings can not be neglected in higher orders of approximation. In general, the first kind of coupling is much

more important than the second one. Thus, we can improve this diabatic scheme taking into account the discrete-discrete coupling through a configuration interaction (CI) to describe more properly the adsorption states. Thus, the corresponding half-width associated to the α -quasibound state is calculated now by means of

$$\Gamma_{\alpha}^{\text{CI}} = \pi \sum_{\mathbf{G}'} |\langle \psi_{\mathbf{G}\alpha}^{(1)}(z) | V_{\mathbf{G}-\mathbf{G}'}(z) | \psi_{\mathbf{G}'\epsilon}^{(0)}(z) \rangle|^2 \quad (18)$$

where $\psi_{\mathbf{G}\alpha}^{(1)}(z)$ is the first-order wave function issued from the CI calculation for the α state.

We have also developed other dynamical decoupling schemes^{21(c)} within a diabatic distorted wave framework for the study of the predissociation of van der Waals systems and these schemes could be straightforwardly applied to this process. However, for the elastic scattering treated here, these zero- and first-order approximations have been sufficient.

D. The model potential

For atom-surface scattering problems, Armand and Manson^{9(b)} proposed a corrugated Morse potential which is defined by

$$V(\mathbf{r}) = D \{ \exp[2\chi(\phi(\mathbf{R}) - z)] / a_0 - 2 \exp(1 - \chi z) \} \quad (19)$$

a_0 being the surface average of $\exp(2\chi\phi)$, on the unit cell, D and χ the well depth and stiffness parameter of the Morse potential, respectively, and $\phi(\mathbf{R})$ the so-called shape or corrugation function. Its general form can be obtained by expanding this function in Fourier series, like Eqs. (3) and (4). The parameters of the shape function and D and χ have been varied in order to fit the calculated intensities to the experimental ones. Unfortunately, the different parameters

necessary determining this model potential are very dependent on the whole experimental energy range. However, this will be the potential used here in order to compare with previous works.

Following the ideas of Lapujoulade *et al.*,²⁰ the corrugation may be assumed to be only significant in the $\langle 100 \rangle$ direction. In other words, diffraction occurs mainly in plane and so it is assumed that the shape function is (independent of y)

$$\phi(x) = ha \cos(2\pi x/a), \quad (20)$$

where a is the unit cell length and h the dimensionless corrugation parameter. Therefore, the $\mathbf{G}$ vectors will take the following form $(2\pi n/a, 0)$. The same values of the potential parameters of Ref. 19 have been used in our calculations, that is, $a = 3.6 \text{ \AA}$, $D = 6.532 \text{ meV}$ and $\chi = 1.05 \text{ \AA}^{-1}$.

With this simplification, the potential of Eq. (19) depends on two variables (x, z) and its matrix elements have been analytically calculated by expanding the function $\exp[2\chi\phi(x)]$ in a cosine series. That is,

$$e^{2\chi\phi(x)} = \sum_{l=0}^{\infty} a_l \cos\left(\frac{2\pi l}{a} x\right). \quad (21)$$

The coefficients resulting from integration over the unit cell have the following expression:

$$a_0 = I_0(\beta), \quad (22a)$$

$$a_l = 2I_l(\beta) \quad (22b)$$

with $\beta = 2\chi ah$ and $I_0(\beta)$ and $I_l(\beta)$ are the modified Bessel functions. Each coefficient is, then, a power series in β and only five terms have been retained. The corresponding error introduced is to be $< 0.1\%$ for a maximum value of h equal to 0.1. Finally, the matrix elements of this model potential are expressed by

$$V_0(z) = D [\exp(-2\chi z) - 2 \exp(-\chi z)], \quad (23a)$$

FIG. 1. Kinetic energy (expressed in a.u.) of each n diffraction channel versus incident angle and for a total energy of 21 meV. The three horizontal lines represent the threshold, the ground state and the well depth of the $V_0(z)$ potential, respectively.

$$V_{G-G'}(z) = \frac{a_{|n-n'|}}{2a_0} D \exp(-2\chi z). \quad (23b)$$

Before any calculation, it is interesting to know the asymptotic behavior or the disposition of the diffraction channels (effective potentials) as a function of the incident angle, θ_i . For this purpose, a plot of the kinetic energy vs the incident angle θ_i is presented in Fig. 1, for a total energy of 21 meV (and $M = 4.0026$ amu). In our case, the kinetic energy is given by

$$E_k(n, \theta_i) = \frac{\hbar^2}{2M} \left[k^2 - \left(|k| \sin \theta_i + \frac{2\pi n}{a} \right)^2 \right] \quad (24)$$

and the double regularity found (along the two axes), in the crossings of these curves are easily understood from Eq. (24). The crossing of two n and n' diffraction channels occurs for an angle

$$\theta_i^{n,n'} = \arcsin \left[- \frac{\pi}{|k|a} (n + n') \right] \quad (25)$$

and at the kinetic energy

$$E_k^{n,n'} = \frac{\hbar^2}{2M} \left[k^2 - \left(\frac{\pi}{a} \right)^2 (n - n')^2 \right]. \quad (26)$$

This situation is drastically different to that found in atomic and molecular collisions. At $\theta_i = 0$ (normal incidence), the two $|n|$ and $-|n|$ diffraction channels are degenerated and they come apart, the negative one increasing in energy and the positive one decreasing in energy as θ_i increases. Also the crossing angles are obtained for values of $(n + n')$ equal to $-1, -2, \dots$, respectively, with n and n' of different sign. Analogously, the crossing kinetic energies decrease as the order of the coupling $|n - n'|$ increases from 1 to infinity, increasing at the same time the distance between two consecutive orders. Last, an oscillation between seven or eight open channels is found along the whole angular range and for this total energy. The $n = 0$ —channel is always open since it is the specular channel and its kinetic energy is zero for $\theta_i = \pi/2$. This is the first of the three horizontal lines drawn in Fig. 1 and represents the threshold at which a given n diffraction process becomes open or closed (bound or attenuated). The other two lines represent the ground state and the well depth of the $V_0(z)$ potential, respectively. In this way, all the kinematic aspects of the problem are displayed in this figure.

It would be noticed that this figure also gives an account of the interesting angular regions. In the crossing of two closed channels, each energy level supported by one of them is degenerated with the corresponding one of the other channel. Then, if the coupling between these two channels is strong enough (mixing resonant scattering),⁵ the two levels will split apart. A similar situation will take place if only one of the energy levels of both channels is degenerate. From the kinematic condition, Eq. (24), it is easy to show that the adequate disposition of channels will be given by

$$\theta_i^{n,n'} = \arcsin \frac{\Delta_{\alpha\gamma} - (4\pi^2/a^2)(n'^2 - n^2)}{(4\pi/a)|k|(n' - n)} \quad (27)$$

with $\Delta_{\alpha\gamma} = (2M/\hbar^2)(E_\alpha - E_\gamma)$, E_α and E_γ being two energy levels of the $V_0(z)$ potential. Obviously, this equation reduces to Eq. (25) for $\Delta_{\alpha\gamma} = 0$. The magnitude of these

TABLE I. Coupling strengths, $a_{|n-n'|}/a_0$, for different corrugation values, h .

h	0.008	0.04	0.1
Ratios			
a_0	1.0009	1.0230	1.148
a_1/a_0	6.045(−2)	2.990(−1)	7.067(−1)
a_2/a_0	9.139(−4)	2.252(−2)	1.305(−1)
a_3/a_0	9.211(−6)	1.133(−3)	1.625(−2)
a_4/a_0	6.964(−8)	4.277(−5)	1.525(−3)

splittings depends on the order of the coupling, $|n - n'|$, and no mixing resonant scattering is found due to the high orders of coupling given in this system. This is the reason why a high order configuration interaction has not been implemented for this problem.

III. RESULTS AND DISCUSSION

The set of coupled equations (5) has been solved with the boundary conditions (7) and using the Numerov–Cookey algorithm. Numerical convergence is reached with 3000 points of integration, starting at $z = -5$ a.u. and with a step of 0.01 a.u. In all the angular range studied, the $n = -3$ diffraction channel is the lower open channel. Thus, with these integration parameters and for a total energy of 21 meV, a description of 160 points per oscillation of the corresponding continuum wave function is obtained in the well region of this channel.

The number of diffraction channels required in these calculations depends on the magnitude of the corrugation parameter. According to Eqs. (22) and (23b), the ratio $(a_{|n-n'|}/a_0)$ is h dependent and gives us the strength of the coupling. In Table I, we present some of these ratios for several corrugation values used in our calculations. Whereas the a_0 coefficient, i.e., the surface average of $\exp(2\chi\phi)$ on the unit cell, presents slight variations, important changes in the coupling strengths are observed for increasing values of h .

In Table II, a study of convergence in diffraction channels is presented for $h = 0.008$, total energy of 21 meV and $\theta_i = 55.5^\circ$ (nonresonant angle). For this weak corrugation, the convergence is quickly reached in the specular intensity. Four open channels and only two closed channels ($n = 2$ being an attenuated channel; see Fig. 1) are relevant in this calculation in order to obtain six significative figures for this intensity (the computer time for a six-channel calculation is of 33 s in a CYBER 855). The same result is observed for the

TABLE II. Convergence in the specular intensity. The scattering angle is 55.5° and the total energy 21 meV.

Opened channels	Closed channels	1	1,2	1,2,3
0, −1		0.949 537	0.949 536	0.949 536
0, −1, −2		0.949 443	0.949 443	0.949 443
0, −1, −2, −3		0.949 445	0.949 444	0.949 444
0, −1, −2, −3, −4		0.949 445	0.949 444	0.949 444

FIG. 2. Diffraction intensities as a function of the corrugation parameter, h . I_n ($n = 0, \dots, -6$) denotes the n -order diffraction intensity. Total energy of 21 meV and scattering angle of 55.5° .

-1 , -2 , and -3 order diffraction intensities. From Fig. 1, for this angle and total energy, there are only seven open channels ($n = 0, \dots, -6$) and with the following distribution: the lower one is $n = -3$ after, decreasing in kinetic energy, three pairs of quasidegenerate channels, $(-4, -2)$, $(-5, -1)$, and $(-6, 0)$, respectively. Analogously, for the closed channels, the pair $(-7, 1)$, $(-8, 2)$, etc. are distributed with increasing negative kinetic energy. Thus, for this very weak corrugation, $h = 0.008$, one channel of the pair is transparent in the calculation. In particular, the channels $n = -4, -5, -6, -7, -8$. As the value of h increases, the coupling strengths also increase (see Table I) and the number of diffraction channels grows very rapidly since this transparency is little by little broken. For example, for $h = 0.04$, 11 channels ($n = -7, \dots, 3$) and, for $h = 0.1$, sixteen channels ($n = -10, \dots, 5$) are necessary in order to reach convergence in the different order diffraction intensities. In Fig. 2, we show these intensities as a function of the h parameter. Increasing h , the specular intensity decreases whereas the higher-order diffraction processes acquire more importance. A new increasing of the specular intensity as well as the other orders (after passage for a maximum) is found for very strong corrugation values. Similar behavior is reported by Wolken.⁴

Also, further calculations have been made for total energies of 21 and 63 meV with $h = 0.008$ and 0.012 , respectively, in order to compare with experimental and theoretical results already reported elsewhere. Experimental results²⁰ were obtained by extrapolation to zero temperature and renormalizing the sum of in-plane diffraction intensities to unity. The corresponding theoretical results were calculated by a least squares adjustment (of experimental data) of the parameters of the model potential chosen. The corrugated Morse and the modified corrugated Morse potentials are the

most convenient for describing the He-Cu(11 α) interaction.²⁰ As was pointed out by Goodman^{3(b)} and confirmed later by Wolken,⁴ the model potential used determines mainly the scattering with the surface. In fact, using a high order distorted wave perturbation theory^{9(b)} and a close-coupling formalism (for a set of potential parameter given), very close results are found. As expected, discrepancies will appear for high corrugation amplitudes.

With regard to the resonant elastic scattering, we must start from the knowledge of the eigenvalues of the $V_0(z)$ potential. Four bound states are found using the analytic form of the eigenvalues for a Morse potential: -4.74 , -2.01 , -0.43 , and -0.01 meV. Because this model potential is not suited to represent levels near the dissociation limit, the last bound state has been ignored. With the parameters of the numerical integration already indicated at the beginning of this section, we were able to reproduce only the three lowest ones. A first approximation to the selective adsorption resonances is obtained by adding to these eigenvalues the asymptotic energy of each diffraction channel. From the kinematic condition, Eq. (24), the kinematic angle can be calculated which is a good first estimate of the resonance angle. In the close-coupling formalism, two routes are open now. The first one is based on the location of an extremum value of the specular intensity (usually a maximum) when it is considered as a function of the angle of incidence for a given total energy. After energetic position and width of the corresponding resonance is found varying the total energy at the resonance angle. The second one is based on the method of the background S matrix (mixed S matrix method). Several calculations of the two S matrices are performed as a function of the incidence angle (at a fixed total energy) and by means of Eqs. (12a) and (12b), considered as angularly dependent, the angular position (resonance angle) and width are obtained. At this resonance angle, a scanning in

TABLE III. Resonance angle ($\bar{\theta}_i$) in degrees, energetic positions ($\bar{E}$) and half-widths ($\Gamma/2$) in atomic units for the first metastable level of the $n = 1$ -diffraction channel, (1_0^0), calculated from diabatic approach (D), configuration interaction-diabatic approach (CI), the two methods of close-coupling, CC(1) and CC(2) (see the text), and complex rotation method (CRM).

	D	CI	CC(1)	CC(2)	CRM
$(\bar{\theta}_i)$	56.286 7	56.283 6	56.281 1	56.280 8	56.280 8
$\bar{E}$	0.771 729(−3)	0.771 728(−3)	0.771 729(−3)	0.771 729(−3)	0.771 732(−3)
$\Gamma/2$	0.475(−7)	0.474(−7)	0.474(−7)	0.474(−7)	0.455(−7)

energy around the incidence energy is also performed in order to calculate the energetic position and width through Eqs. (12a) and (12b). Within the diabatic distorted wave formalism, the calculations are carried out starting from the kinematic conditions. In the diabatic approach, it is assumed the resonance position is the total energy and the resonance angle, therefore, the kinematic angle. The desorption process occurs because the bound state is embedded in the continua of the diffraction channels, the total width being the sum of contributions of each continuum [according to Eq. (17)]. When the configuration interaction is considered, starting also from the kinematic angle, we diagonalize a Hamiltonian matrix of maximum dimensions 18×18 (three bound states associated to each one of the six diffraction channels necessary to reach numerical convergence of the S matrix) and the position is found from the minimum difference between the total energy and the eigenvalue closest to the corresponding one of zero order. Its associated width is calculated according to Eq. (18).

In Table III we present the results obtained with these four ways: specular intensity method, CC(1); mixed S -matrix method, CC(2); diabatic approach without or with interaction of configurations, D and CI, respectively. Also we present those reported by Ref. 19 using the complex rotation method, CRM. $\bar{E}$ and $\bar{\theta}_i$ represent the energetic and angular position of the resonance (1_0^0), that is, the first level of the

$n = 1$ -diffraction channel. The agreement of the results is very good since the corrugation in this case ($h = 0.008$) is very weak. In an attempt to reproduce the CRM results (obtained for three channels: 0, 1, 2; one open and two closed), we performed a somewhat similar calculation with the same $\bar{\theta}_i$ value, $\bar{\theta}_i = 56.2808^\circ$, and applying the mixed S -matrix method. The results were: $\bar{E} = 0.771 729(−3)$ ($= 21$ meV) and $\Gamma/2 = 0.468(−7)$. The number of channels taken was four ($n = -1, 0, 1, 2$), one open more, due to the impossibility in this method of taking only one open channel.

Finally, angular widths can also be calculated with the mixed S -matrix method. In Fig. 3, we display the real and imaginary part functions of Eqs. (12a) and (12b) for the angular resonance (1_0^0). The angular position is at 56.2808° with a width of 0.0057° . These values are practically the same than those of Armand and Manson,^{9(b)} and Moiseyev *et al.*¹⁹ The behavior of the imaginary part is just the opposite to that predicted by Eq. (12b). This can be easily understood if the angular scale is transformed to a kinetic energy scale. If the angle of incidence is increased, the diffraction channels are shifted in such a way that their corresponding kinetic energies are smaller and, therefore, the sign of the numerator of Eq. (12b) changes from negative to positive passing through the resonance.

As a word of conclusion, the formalism based on the distorted wave approximation, widely developed in the predissociation of van der Waals molecules,²¹ has turned out to be also adequate in this problem for low corrugation surfaces. Higher order approximations within this formalism would be also convenient for surfaces with more corrugated faces. Thus, crystal faces like Cu(113) and (115), which are essentially corrugated in one dimension, will be good candidates in order to obtain a good comparison between these approximations and the close-coupling formalism and/or the complex coordinates method. Closer results to the experimental ones should be obtained using the modified corrugated Morse potential proposed by Armand *et al.*^{20(b)} Also, temperature dependent close-coupling studies for simulating more realistic problems are very important. It would be interesting to examine the incorporation of the temperature in the dynamical calculations through a modification of the potential parameters according to Ref. 3. Work in this direction is now in progress.

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FIG. 3. Real part (—) and imaginary part (---) of the angular resonance (1_0^0) calculated by means of the mixed S -matrix method.

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