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POTENTIALS AND SCATTERING CROSS SECTIONS FOR COLLISIONS
OF He ATOMS WITH ADSORBED CO

W.-K. Liu

and

B. Gumhalter

International Atomic Energy Agency

and

United Nations Educational Scientific and Cultural Organization

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

POTENTIALS AND SCATTERING CROSS SECTIONS FOR COLLISIONS
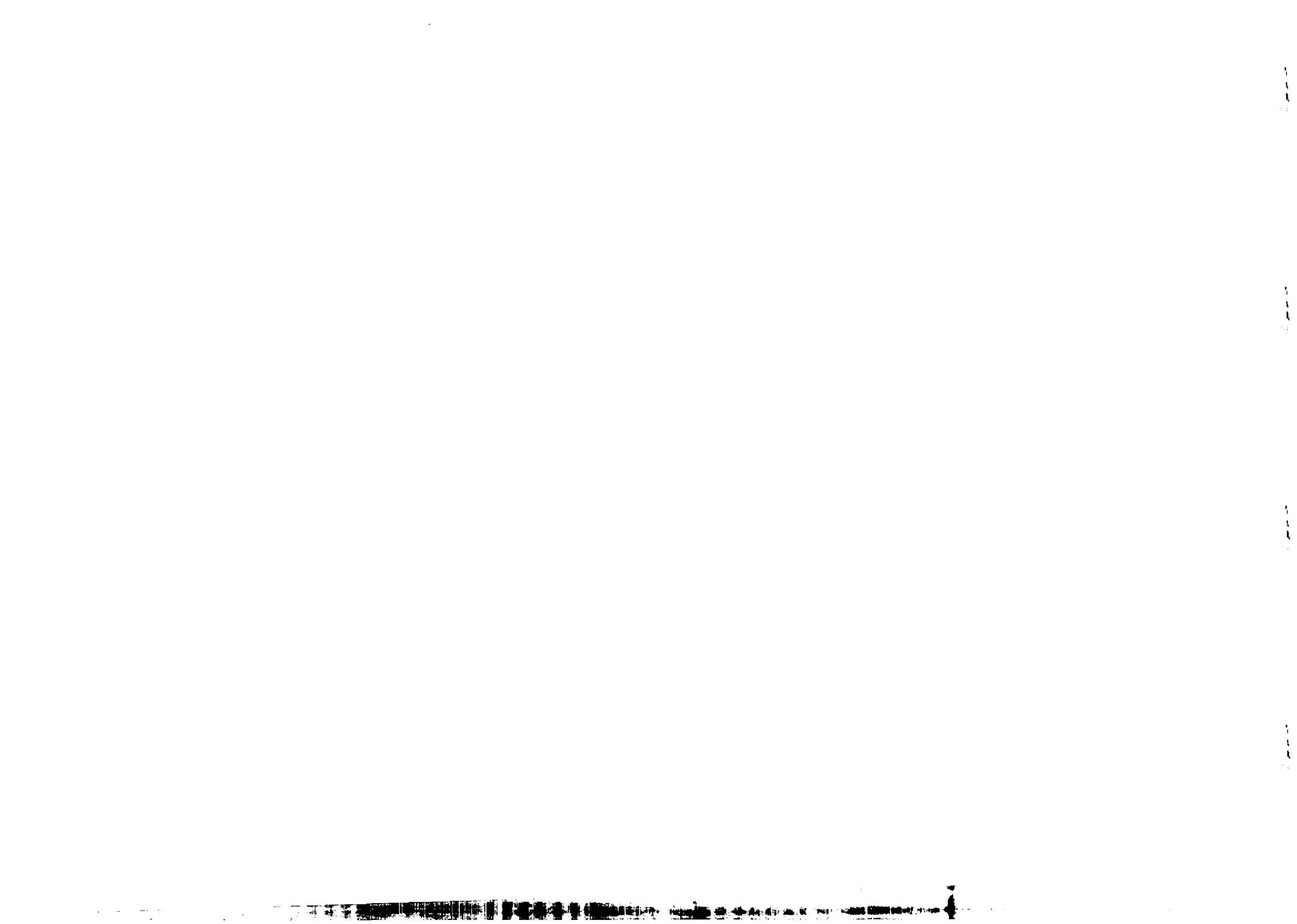OF He ATOMS WITH ADSORBED CO [†]

W.-K. Liu [*]
$(GWP)^2$ Guelph-Waterloo Programme for Graduate Work in Physics
and

Department of Physics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

and

B. Gumhalter
International Centre for Theoretical Physics, Trieste, Italy
and
Institute of Physics, University of Zagreb, 41001 Zagreb, Yugoslavia.[**]

ABSTRACT

Ab initio calculations of the total scattering cross section for
the collision system He → CO/Pt(111) within the renormalized distorted
wave Born approximation are reported. The interaction potential for this
atom-adsorbate system consists of the usual two-body gas phase-like
potential as well as two additional substrate mediated van de Waals
contributions, all with similar long range behaviour.   Comparison of
the calculated cross sections for various incident velocities and angles
with available experimental data is made without using any adjustable
parameters to fit the data, and the importance of including the substrate-
mediated forces is emphasized.

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1. Introduction

The technique of thermal energy atom scattering (TEAS) from
surfaces covered with adsorbates has become a powerful tool for the
investigation of adsorption of atomic and molecular species on various
substrates in the limit of low coverage. The nozzle beam technique, which
produces the beams of neutral atoms and molecules of kinetic energy down
to a few meV, proved as an ideal method in revealing the crystallographic
and electronic structure of clean and adsorbate covered metallic surfaces
[1], surface excitations [2], adsorbate-adsorbate interactions, adlayer
formation, island growth and structural phase transitions [3] and the
difference between TEAS in adsorbed and gas phase [4], etc. In this
respect the beams of thermalized He atoms turn out to be particularly
useful due to the closed shell (inert) electronic structure and small mass
of the scattered particles. Firstly, the inert structure of He atoms
rules out any chemical effects and diabatic transitions in their collision
with the surface [5] thereby leaving the interaction potential with the
target relatively simple. Secondly, the low kinetic energy and the mass
of the incoming He atoms make the wavelength associated with their motion
of the order of the substrate lattice spacing and therefore subject to the
diffraction effects at perfect monocrystalline surfaces [1].

The measurements of the intensity of the He beams reflected from
clean and adsorbate covered surfaces yield the information on various
adsorbate properties and on the adsorption process itself. In these
studies the adsorbate induced scattering cross section turns out to be of
particular interest because it is connected with other quantities

characteristic of the system such as, e.g., the adsorbate sticking
coefficient at low coverage [6], mutual interaction and distances between
adsorbates [1], He-adsorbate potential [9], etc. Hence, it appears
desirable that theoretical studies and model calculations could provide a
support and conceptual confirmation to the interpretation of the
experimental findings regarding the adsorbate induced scattering cross
section in TEAS, and this is the aim of the present paper.

A careful study of the He atom collision processes with
adsorbates requires a proper knowledge of the potentials which govern
these events. From the very beginning of the experimental activities in
this area, it has been realized that the long range potentials, which fall
off as an inverse power of the He-adsorbate separation $|\underline{R}|$, should play an
important role in the He-adsorbate collisions in the regime of low
incoming kinetic energies. Accordingly, due attention has been paid to
the role of the long range van der Waals (vdW) potentials in both
experimental [1,6] and theoretical [7-11] studies of these events.

In some earlier theoretical studies [7,8] of the He-adsorbate
scattering, the long range dispersive or vdW potentials have been treated
only on a phenomenological footing. A single interaction of the type
$-C/R^6$ reminiscent of the gas phase potential was employed in the
calculations of the scattering cross section $\sum$. Its strength parameter C
was fitted so as to obtain $\sum$'s which would agree with the experimental
data. It turned out that a realistic fit required the magnitude of C
about twice as large as the one appearing in the gas phase interaction.
This phenomenon was ascribed to the enhanced polarizability of the
adsorbate brought about by the image effects.

From the physical point of view we find such a fitting procedure
unsatisfactory mainly for two reasons. Firstly, it neglects entirely the
effects of the polarizability and the chemical activity of the surface,
reducing the latter to a mere geometrical object, and secondly, it ignores
the intrinsic anisotropy of the vdW potentials brought about by the
presence of a third polarizable body (here the surface). This anisotropy
exists even when both the adsorbate and the scattered atom are spherically
symmetric (c.f. refs. 9 and 11), as is for instance the case in He
scattering from adsorbed Xe [1,11].

Since the vdW potentials are of particular interest within the
context of low energy He-surface collisions we have already examined some
of their properties in connection with the He scattering from clean
[12,13] and adsorbate covered [9] flat low index surfaces of fcc metals
(typically Cu or Pt). A great number of experimental data presently
available for noble gas atom scattering from adsorbates and the attempts
to interpret them have motivated us to embark on an extensive programme of
ab initio calculations of various effects which contribute to the
scattering cross section for He-adsorbed CO collisions, as well as to
establish a proper formulation of the scattering dynamics when the spatial
symmetry of the system is somewhat lower than usual. Our aim has been to
make all the calculations essentially parameter-free in order to gain
insight into the physical situation in terms of some basic quantities
characteristic of the system considered. In a series of papers we have
derived the expressions for the atom-adsorbate surface induced or indirect
vdW potentials and collision dynamics within the distorted wave Born
approximation (DWBA) [9], effects of electronic backdonation on the vdW
forces between He atoms and adsorbed CO [10], positions of the effective

reference planes for indirect vdW potentials [14], and we have also given

a report on the implications of some of these effects on the scattering

cross section for the collision He+Xe/Ag [11].

In this paper we present detailed ab initio calculations of the

scattering cross section within the renomalized distorted wave Born

approximation (RDWBA) for the system He+CO/Pt(111), by taking into account

the effects quoted above. We also make a comparison with the experimental

data and correlate the theoretical predictions with the trends observed

[6].

2. Potentials for atom-adsorbate collisions

The potentials which govern the He atoms motion near an adsorbate

covered surface are manifold. First of all, there is an attractive

He-surface dispersive or vdW interaction which falls off with the inverse

cube of the atom-surface separation z, and this is by far the most

important interaction occurring at long range in the problem [15,16]. In

addition to this, one also encounters a short range repulsive He-surface

interaction which is due to the closed shell (inert) electronic structure

of He atoms. Since the affinity level of He is above the vacuum level,

the atom will repel the electrons from its vicinity and hence any overlap

of the He electronic structure with an external, nonuniform electronic

density will give rise to repulsive potentials. Such overlap induced

He-surface potentials have been studied by several authors [17].

The interaction of an He atom with an adsorbate will comprise of

both direct potentials as occurring in the gas phase, and indirect surface

mediated potentials which arise due to the proximity of a third

polarizable body, i.e. the surface, whose presence modifies the simple,

two-body gas phase interactions. This is expected to be of particular

importance in the case of long range interactions and much less so in the

case of short range potentials.

The importance of indirect vdW interactions between two atoms

near a dielectric surface was first pointed out by McLachlan [18] who

demonstrated that they would exhibit the same long range behaviour as the

direct interaction. The present authors derived the expressions for

surface mediated vdW potentials acting between a spherical atom and an

anisotropic molecule adsorbed on a surface by using the Feynman

diagrammatic technique [9].

The surface mediated atom-adsorbate vdW potentials are

necessarily anisotropic. They fall off with the sixth inverse power of

the atom-adsorbate separation and their strength parameters depend on the

polarization properties of all three subsystems involved, i.e. the

adsorbate $\underline{a}$, the atom $\underline{b}$ and the metal surface $\underline{M}$. Thus, the total

atom-adsorbate interaction E_{vdW} will be given as a sum of the direct,

gas-phase-like term E_{vdW}^{dir}, the pure image interaction E_{vdW}^{im} and their

interference E_{vdW}^{int} [9]:

$$E_{vdW}(R,\theta) = E_{vdW}^{dir}(R,\theta) + E_{vdW}^{im}(R,\theta) + E_{vdW}^{int}(R,\theta). \tag{1}$$

Here R and θ are the distance between the centre of the adsorbate located at R_a and the scattered atom located at R_b, and the angle between $R=R_b-R_a$ and the normal to the surface z passing through the adsorbate axis, respectively (see Fig. 1). Each of the terms appearing on the right hand side (RHS) of (1) is proportional to a constant C which contains the information on the polarizabilities of the subsystems. The C's corresponding to E_{vdW}^{dir}, E_{vdW}^{int} and E_{vdW}^{im} will be denoted by C_{ab}, C_{abM} and C_{aMbM}, respectively. In terms of these quantities the three contributions to the total atom-adsorbate vdW potential are given by [9]:

$$E_{vdW}^{dir}(R,\theta) = -C_{ab}\frac{C_1}{R^6}\left[1 + \frac{1-\mu}{1+2\mu} P_2 (\cos \theta)\right],\qquad(2a)$$

where $C_1=(2+4\mu)$, $\mu=\alpha_x/\alpha_z$ is the ratio of transverse and longitudinal adsorbate molecular polarizabilities, and P_2 is the Legendre polynomial of the second order. In the present case of adsorbed CO one has $\mu=0.62$. The pure image term exhibits identical angular dependence as (2a) except the image coordinates $R*$ and $\theta*$ (see Fig. 1) enter in the expression:

$$E_{vdW}^{im}(R,\theta) = -C_{aMbM}\frac{C_1}{R*^6}\left[1 - \frac{1-\mu}{1+2\mu} P_2 (\cos \theta*)\right],\qquad(2b)$$

where $R*$ and $\theta*$ are related to R,θ by the cosine law [9]. Finally,

$$E_{vdW}^{int}(R,\theta)=2\frac{C_{abM}}{(RR*)^3}\left[(4-3\cos^2\theta-3\cos^2\theta*)-(1-\mu)(4-6\cos^2\theta-6\cos^2\theta*\right.$$
$$\left.+9\sin\theta\cos\theta\sin\theta*\cos\theta*+9\cos^2\theta\cos^2\theta*+1)\right].\qquad(2c)$$

In all these expressions we have arbitrarily chosen the origin of the z-axis to coincide with the positive jellium background edge. A more precise definition of the origin can be obtained by carefully studying the wavevector dependence of the surface dielectric response (see below and ref. 14). By knowing the geometrical position of the adsorbate with respect to the substrate and the polarizability $\alpha(\omega)$ of each subsystem, one can calculate $E_{vdW}(R,\theta)$ for any adsorption system. For a typical case of CO adsorption on Ni(001) for which the adsorption geometry is known [19] the angular dependence of the contributions to E_{vdW} is shown in Fig. 2.

The formulae for C_{ab}, C_{abM} and C_{aMbM} have been derived in [9]:

$$C_{ab} = \int_o^\infty \frac{du}{2\pi} \alpha_a(iu)\, \alpha_b(iu)\qquad(3a)$$

$$C_{abM} = \int_o^\infty \frac{du}{2\pi} \alpha_a(iu)\, \alpha_b(iu)\, R_o(iu)\qquad(3b)$$

$$C_{aMbM} = \int_o^\infty \frac{du}{2\pi} \alpha_a(iu)\, \alpha_b(iu)\, R^2_o(iu),\qquad(3c)$$

where $\alpha_a(\omega)$ and $\alpha_b(\omega)$ are the polarizabilities of the adsorbate $\underline{a}$ and the incoming atom $\underline{b}$, respectively (in the case of the anisotropic

adsorbate $\alpha_a = \alpha_z$), $R_0(\omega)$ is the long wavelength limit of the surface

response function $R_Q(\omega)$ [20], and $u = i\omega$ is the imaginary frequency. The

evaluation of (3) requires the knowledge of α_a and α_b, (which are

expressed through the oscillator strengths and excitation energies of the

adsorbed CO and He atoms, respectively), and the response function of the

substrate. Here we assume that the polarization properties of adsorbed CO

are well described by the pseudo oscillator strengths and excitation

energies characteristic of gaseous CO, although some caution is needed in

this case because adsorption may give rise to a change in the relative

positions of the CO valence levels with respect to those in the gas

phase. For free electron metals the surface response is dominated by the

surface plasmon excitation mode and in this case the C's can be evaluated

analytically (c.f. refs. 10 and 14). If, on the other hand, the surface

response comprises also the interband transitions, one may use the optical

absorption data to calculate the imaginary part of the substrate

dielectric function numerically and hence the surface response function

[20]. This was the procedure we pursued in the present work and for the

He+CO/Pt system we obtained:

$$C_{ab} = 1.43 \text{ eV } \text{Å}^6 \tag{4a}$$

$$C_{abM} = 0.841 \text{ eV } \text{Å}^6 \tag{4b}$$

$$C_{aMbM} = 0.586 \text{ eV } \text{Å}^6 \text{ ,} \tag{4c}$$

where we have used a 30-term oscillator strength expansion for the

polarizability of He and a 10-term expansion for the polarizability of CO

[14].

The nonlocal character of the surface and its chemical activity

may give rise to additional effects which would further contribute to

E_{vdW}. The surface mediated terms E_{vdW}^{int} and E_{vdW}^{im} will depend on the exact

position of the molecule $\underline{a}$ with respect to the surface $\underline{M}$, and hence on the

proper positioning of the reference plane for the vdW interaction.

Expressions for the distances z^{int} and z^{im} of the reference plane

positions for E_{vdW}^{int} and E_{vdW}^{im} relative to the positive background edge have

been derived [14] and are found to depend on the frequency-dependent image

plane of the substrate, in addition to the oscillator strengths of the

subsystems. For the He + CO/Cu system, we have

$$z^{int} = 0.262 \text{ Å} \tag{5a}$$

$$z^{im} = 0.333 \text{ Å} \text{ .} \tag{5b}$$

We are going to assume the same values of z^{int} and z^{im} for the He +

CO/Pt system.

Another peculiarity which one may encounter in estimating the

strength of E_{vdW} is connected with a possible chemical bond formation

between the substrate valence band and the adsorbed CO valence molecular

orbitals. The CO 5σ molecular orbital may acquire partial metal

(substrate) character and thereby donate some of its electronic charge

into the metal states. Simultaneously, some of the metal charge may be

backdonated into the formerly unoccupied CO $2\pi^*$ derived molecular orbital

which may become a bonding one with respect to the metal-CO interaction.
The amount of the electronic charge transferred into the $2\pi^*$ derived state
will depend on the position of the latter with respect to the Fermi level
of the substrate. Since an increase of the charge localized on the
adsorbate would also contribute to the enhancement of the adsorbate
dynamic polarizability, the backdonation may affect the strengths of the
atom-adsorbate vdW potentials. This effect has been discussed in detail
in refs. 10 and 21 where it was shown that the backdonation may give rise
to an enh..acement of C_{ab}, C_{abM} and C_{aMbM} of the order 13, 20 and
26%, respectively [21].

Another effect connected with the electronic charge transfer to
the adsorbate and its spatial distribution over the localized $2\pi^*$ derived
states may be the occurrance of an extra repulsion between this charge and
the He atoms colliding with the adsorbate. This may enhance the repulsive
He-adsorbed CO interaction (arising from the orthogonalization of the He
and CO electronic wavefunctions), which is commonly modelled by the $1/R^{12}$
component of the Lennard-Jones potential. In general, the repulsive He-CO
interaction is also asymmetric and can well be represented by a Legendre
polynominal expansion of the term containing the powers of R^{-12} [22].
This gives the short range component of the so called asymmetric
Lennard-Jones(ALJ) potential which reads:

$$V_{sr}^{ALJ}(R,\theta) = \varepsilon \sum_{\lambda=0}^{2} v_\lambda P_\lambda (\cos\theta)(r_m/R)^{12}, \tag{6}$$

where ε and r_m are the constants typical of the Lennard-Jones potential
obtained from virial data, $v_0 = 1$ and v_1 and v_2 have to be estimated from

some geometric considerations or ab initio calculations. Usually, both
are only a small fraction of v_o.

Another possibility to account for the repulsive He-CO potential
is to resort to the so called "loaded sphere" (LS) model which assumes
spherical interaction centered at some "loading" distance away from the
molecular centre of mass [22]. In that case one is left with a single
parameter which can be fitted to the experimental data. In the following
we shall use this model for the repulsive He-adsorbed CO potential.
Gordon [23a] and Gordon and McGinnis [23b] have shown that the expression
for the total He-CO gas phase potential in the LS model is given by:

$$V_{LS}(R,\theta)/\varepsilon = \{1.628 \times 10^5 \exp[-12(R/r_m)] - 2(r_m/R)^6\}$$

$$+ \{1.139 \times 10^5 \exp[-12(R/r_m)] - 0.6(r_m/R)^7\}P_1(\cos\theta)$$

$$+ \{1.139 \times 10^5 \exp[-12(R/r_m)] - 0.4(r_m/R)^6\}P_2(\cos\theta), \tag{7}$$

from which the repulsive part can be readily extracted. Here $r_m = 6.61$
a_B (a_B = Bohr radius) and $\varepsilon = 1.08 \times 10^{-4}$ a.u. (23.6 cm^{-1}). The
short range repulsion described by an exponential is generally regarded as
more realistic than an inverse power appearing in the ALJ short range
potential.

3. Collision dynamics and calculation of scattering cross section

The knowledge of the He-adsorbed CO potentials enables one to
carry out the calculation of the scattering cross sections for various

incident energies and angles using the formalism of close coupled
equations [24]. The application of this formalism to the present problem
was described in [9] and here we only recall it briefly.

In developing the theory of He scattering from adsorbed CO one
may greatly simplify the calculations on noticing that at low He incident
thermal energies considered, the turning points of the atoms moving in the
surface potential would be close to the centre of the adsorbed CO
molecules [6]. This allows one to make an approximation in which the
actual He-surface potential is replaced by a hard wall at the centre of
the adsorbate [7-9], and the attractive component of the potential is
accounted for by making use of the so called Beeby's correction for the
perpendicular to the surface velocity of the incoming particle [7]. Hence
the effective angle θ_r at which the He atoms will strike the surface or
the adsorbate will be given by:

$$\sin \theta_r = \frac{v_i}{v_r} \sin \theta_i , \qquad (8a)$$

where θ_i is the incoming angle measured far from the surface and v_i
and v_r are the incoming velocity far from the surface and the effective
"refracted" velocity near the adsorbate, respectively. v_r is obtained
from the equation expressing the conservation of energy:

$$v_r = (2(E+W)/m)^{1/2} , \qquad (8b)$$

where m is the mass of the scattered particle and W is the effective
surface potential well depth.

Using these premises Jónsson et al. [7] showed that for a
spherically symmetric interaction between a single adsorbate and a gas
phase atom the total scattering cross section is given by:

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$$\sigma_A^0 = \sigma - \frac{4\pi}{k} \text{Im } f(k + k_s) , \qquad (9)$$

where

$$\sigma = \int |f(k - k')|^2 d^2\hat{k}' \qquad (10)$$

and k and k' stand for wavevectors of the incoming and specularly
reflected particles, respectively, and $f(k + k')$ is the scattering ampli-
tude for the effective He-adsorbate potential in the absence of the hard
wall (the usual gas phase total scattering amplitude). However, since the
potential between the He atom and the adsorbate is necessarily anisotropic
(c.f. Sec. 2), σ_A cannot be expressed solely in terms of the phase
shifts η_ℓ characteristic of the collisions governed by the isotropic
potentials. The approximation of isotropic potentials was used by Jónsson
et al. [7] to fit the experimental data. Here we want to carry out a
parameter-free calculation. If the anisotropy is weak, we can treat the
isotropic part of the potential exactly and the anisotropic part as a
perturbation within the distorted wave Born approximation (DWBA). This
would yield:

$$\sigma_A = \sigma_A^0 - \left(\frac{4\pi}{k}\right)^2 \text{Im} \sum_{\ell m} \sum_{\ell'm'} i^{\ell-\ell'} Y_{\ell m}^*(\hat{k}) [Y_{\ell'm'}(\hat{k}) - Y_{\ell'm'}(\hat{k}_s)] e^{i(\eta_\ell + \eta_{\ell'})} P_{\ell'm'\ell m} , \qquad (11)$$

where

$$\sigma_A^0 = \frac{4\pi}{k^2} \sum_\ell (2\ell + 1) \sin^2 \eta_\ell [1 - P_\ell(\cos(\pi - 2\theta_i))] , \qquad (12)$$

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is the contribution from the isotropic part of the potential derived
earlier [7], and $P_{\ell'm',\ell m}$ is the matrix element of the anisotropy
defined by eq. (4.18) of ref. 9. σ_A will depend only weakly on the
angle of incidence θ_i, and is related to the apparent, measured cross
section $\int$ found experimentally by

$$\int = \sigma_A/\cos \theta_r \quad , \tag{13}$$

where the factor $1/\cos \theta_r$ accounts for the increased number of
adsorbates within the area covered by the beam width (c.f. Fig. 1 of ref.
7).

However, one of the problems usually encountered in the use of
the DWBA is that it fails to satisfy the conservation of the flux, and
this could become a serious problem when the anisotropic potential is no
longer weak as in the case of the He + CO/Pt system. For the case of
atom-linear molecule scattering, the S-matrix elements should satisfy the
unitarity condition

$$\sum_{j'\ell'} \left| S^J_{j'\ell',j\ell} \right|^2 = 1 \tag{14}$$

from which follows

$$P(j,\ell) \equiv \sum_{j'\ell'J} \left[(2J+1)/(2j+1)(2\ell+1) \right] \left| S^J_{j'\ell',j\ell} \right|^2 = 1 \quad , \tag{15}$$

where j, ℓ and J are the rotational, orbital and total angular moments,
respectively. As the conditions (14) and (15) are violated within the
DWBA, one may introduce a renormalization of the DWBA expression for
$S^J_{j'\ell',j\ell}$ by dividing it by the quantity $\sqrt{P(j\ell)}$ [25]. This renormalized

distorted wave Born approximation (RDWBA) procedure has been employed to
calculate the gas phase CO-He inelastic total cross sections and compared
with the "exact" results of Green and Thaddeus [22]. It can be seen from
Table I that while the DWBA results overestimate the cross sections
significantly, the RDWBA scheme represents a drastic improvement and can
be expected to give reasonably accurate results for the present
He-adsorbate problem. The RDWBA expression for the S-matrix element in
the atom-adsorbate collision problem can be written as

$$S^{RDWBA}_{\ell'm',\ell m} = [\delta_{\ell\ell'} e^{2i\eta_\ell} - 2i \frac{e^{i(\eta_\ell+\eta_{\ell'})}}{k} P_{\ell'm',\ell m}]\delta_{mm'}/C_{\ell m} \quad , \tag{16}$$

where

$$C_{\ell m} = P^{1/2}_{\ell m} \tag{17}$$

and

$$P_{\ell m} \equiv \sum_{\ell'} \left| S^{DWBA}_{\ell'm,\ell m} \right|^2 = 1 + \sum_{\ell'} (2 P_{\ell'm,\ell m}/k)^2 \quad . \tag{18}$$

The final expression for the atom-adsorbate scattering cross section in
the RDWBA, which satisfies the conservation of the flux, now reads:

$$\sigma_A = \frac{8\pi^2}{k^2} \sum_{\ell m} [\bar{P}_\ell^m(x)]^2 [1 - (-1)^{\ell+m}] [1 - C_{\ell m} \cos 2 \eta_\ell] -$$

$$(\frac{4\pi}{k})^2 \sum_{\ell\ell'm} \bar{P}_\ell^m(x) \bar{P}_{\ell'}^m(x)(-1)^\ell C_{\ell m}[(-1)^\ell - (-1)^m] \frac{P_{\ell'm,\ell m}}{k} \sin[\eta_\ell + \eta_{\ell'} + (\ell+\ell')\frac{\pi}{2}], \tag{19}$$

where $x = \cos \theta_i$ and the $\bar{P}_\ell^m$'s are the normalized associated Legendre poly-
nomials. Note here that in the renormalization procedure carried out the
former "isotropic" part of the total scattering cross section (i.e. the
first sum on the RHS of eq. (19), which reduces to the expression for σ_A
if $C_{\ell m} = 1$), has also been renormalized by $C_{\ell m}$. Hence, a strict
division of the contributions to σ_A into isotropic and anisotropic parts
has here lost its meaning because $C_{\ell m}$ contain also the contributions
from the anisotropic part of the total scattering potential (c.f. eq.
(18)).

4. Results and discussion

As the main goal of the present work has been to confirm the
assertion of Poelsema et al. [1,6] that the scattering cross section Σ for
the He+CO/Pt(111) collision event is largely determined by the long range
He-adsorbate vdW potentials, we have carried out the calculations of Σ
within a strictly microscopic model and compared the values obtained with
the TEAS experiments without any adjustable parameters to fit the data.
The input quantities of our calculations consist of the gas phase
He-CO potential V_{LS} (eq. (7)) plus E_{vdW}^{im} and E_{vdW}^{int} given by eqs. (2b) and
(2c) (the effect of E_{vdW}^{dir} is already included in V_{LS}), the adsorption
geometry revealed by LEED experiments [19] and the parameter W in eq.
(8b) chosen by Poelsema et al. [1,6] to be 0.3 meV. The centre of mass of
the CO molecule is taken to be 1.52 Å away from the positive background
edge, in accordance with the adsorption geometry. In contrast to ref. [7]

where fitting was used to recover an appropriate atom-adsorbate pseudo-
potential, the only way of improving our results would be a refinement of
the input geometry and the physical and chemical role played by the
surface (which also implies the use of the exact He-surface wavefunctions
[12,13]), and performing a convergent close-coupling calculation of the
S-matrix instead of using the RDWBA. The effect of the adsorbate-
substrate chemisorptive bond on the adsorbate polarizability, and thereby
all the vdW potentials involved, will be considered in later publications
[21,27]. Thus, in the present calculation of Σ the input quantities were
the potentials described in Sec. 2 and refs. 9, 22 and 23, and we employ
the RDWBA as outlined in Sec. 3.

The experimental angle of incidence θ_i of He beams, measured
with respect to the surface normal, was varied between 30° and 80°, and
$\theta_i = 40°$ was used as a reference angle [16]. The incident velocities
v_i were ranging from 500 to 3000 m/s. To keep to this set of data we
have plotted in Fig. 3 the behaviour of $\Sigma(v_i, \theta_i = 40°)$ as function of
v_i, with and without Beeby's correction of eq. (8). If we expect that Σ
would be dominated by the long range He-adsorbate potentials, the
modification of He wavefunctions by the scattering event should already
occur at large distances where the "refraction" effect described by the
Beeby correction is minimum. Following this argument we have substituted
the initial values of v_i and θ_i in expressions (11) and (18) for σ_A.
On the other hand, since the reflection of the He atoms from the surface
takes place in the region where the short range potentials are dominant
and attractive potentials large, we have substituted the "refracted" angle
θ_r obtained from Beeby's correction (8a) into eq. (13) to derive Σ from

σ_A. This, to some extent arbitrary, use of Beeby's correction could only be avoided by employing the exact He-surface wavefunctions (cf. the comment in the preceding paragraph and refs. 12 and 13), but that would lead us beyond the scope of the present treatment based on eqs. (9), (11) and (19).

The computed behaviour of $\sum(v_i, \theta_i = 40°)$ follows qualitatively a general pattern of weak glory oscillations of the gas phase scattering cross section observed in He + CO collisions [4]. In order to facilitate the comparison between our RDWBA results for $\sum$ and the experimental data, we plotted these together in Fig. 4 for $\theta_i = 40°$. It is seen that the theoretical values lie slightly below the experimental one for all $v_i > 2000$ m/s which may indicate that the loaded sphere repulsive potential (7) is a little too soft at these higher incident velocities, i.e. at higher collision energies. On the other hand, the calculated $\sum$ exceeds slightly the measured one in the interval 500 m/s < v_i < 2000 m/s, and the curves coincide again at $v_i = 500$ m/s. The overall qauntitative agreement between the theoretical and observed $\sum$, particularly in the limit of low incoming velocities (energies), points clearly to the conclusion that both components of He-adsorbate vdW potential, the direct one encountered in gas phase scattering (2a), and those originating from the dynamical polarizability of the substrate surface (2b and 2c) and occurring in surface collisions only, play important roles in the scattering event. Thus, by taking into account only the gas phase component of the He-CO potential one obtains the values of $\sum$ which are too small to agree with experiments [7].

The apparent He-adsorbate cross section $\sum = \sum(v_i, \theta_i)$ as a function of the angle of incidence is plotted in Fig. 5 for various incoming velocities. The increase of $\sum$ with θ_i is almost entirely accounted for by the $\cos \theta_r$ factor appearing in eq. (13), for all $\theta_i < 70°$. This becomes evident from the comparison of the calculated and measured values of $\sum$ for $v_i = 2760$ m/s given in Fig. 6. Only at $\theta_i > 70°$ the calculated values become too large, demonstrating the inadequacy of the shadowing correction (13) close to the grazing incidence. Strictly speaking, eq. (13) could only be applied to the collisions governed by the short range potentials and the discrepancy at the grazing incidence may, therefore, be expected.

The fact that at higher energies, σ_A is nearly constant in the interval $0 < \theta_i < 70°$ signifies that the asymmetry of the vdW potentials (2a), (2b) and (2c) averages out in the evaluation of σ_A in eq. (19). Because of the long range character of these potentials, the relevant matrix elements which determine σ_A comprise the contributions from over a large region of space in which the cancellation of the effect of asymmetry may occur. However, all three vdW potentials (eqs. (1) and (2)) contribute to the magnitude of σ_A. As has already been mentioned, the scattering cross section $\sum$ calculated only with the gas phase atom-adsorbate component of the vdW potential would be too small to agree with experiments (c.f. Fig. 2 of ref. 7). Thus, the former assertion that an "increased polarizability" of the CO adsorption complex with respect to the gas phase CO by almost a factor of two [6,7] would be responsible for an enhancement of the He-adsorbed CO scattering cross section has here been substantiated within a strictly quantum mechanical calculation and an

essentially parameter free model. The role of the phenomenological

"increased polarizability" has here been taken up by the existenc of the

substrate induced atom-adsorbate vdW potentials (2b) and (2c). This

emphasizes their importance in the total long range interaction and

enables us to formulate the main conclusion of the present paper: In TEAS

from surfaces covered with adsorbates the surface itself plays a far more

active role than being a mere reflecting wall or a mirror for the incoming

beam atoms. Due to its dielectric properties, the surface also modifies

the atom-adsorbate interactions and, in particular, the long range ones

which, in turn, affect the atom-adsorbate scattering cross section. More-

over, if the chemical activity of the surface gives rise to the formation

of a chemical bond btween the adsorbate and the substrate, then all the

atom-adsorbate vdW interactions will also be modified by the existence of

the chemisorption bond [10]. This latter aspect of the enhancement of the

vdW potentials and its effect on TEAS cross section will be studied

elsewhere [21,27].

Acknowledgments

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Table 1

Comparison of gas phase inelastic cross section for He-Co collision
calculated within DWBA, RDWBA and by using the close-coupled (CC)
procedures

	$j' \leftarrow j$	$\sigma(j' \leftarrow j)$ (Å^2)		
		DWBA	RDWBA	CC[a]
$E = 60 \text{ cm}^{-1}$	$1 \leftarrow 0$	19.4	8.8	9.5
	$2 \leftarrow 0$	26.5	12.1	12.2
$E = 150 \text{ cm}^{-1}$	$1 \leftarrow 0$	31.9	9.6	6.2
	$2 \leftarrow 0$	36.1	11.3	10.5

[a]Ref. 22

Fig.1

Fig.2

Fig.3

He → CO Pt (111)

- Θi = 40°
□ Θi = 80°
+ Θi = 70°

transformed data:
△ 80° → 40°
✳ 70° → 40°

Fig.4

Fig.5

○ − 500 m/s
□ − 1000 m/s
▷ − 1743 m/s
◁ − 2500 m/s

He ——CO/Pt (111)

$v_{He} = 2760$ m/s

$\Sigma\left(\overset{\circ}{A}^2\right)$

Θ_i

Fig. 6