

simple metals display very complex behavior when alloyed together. Care must obviously be taken to understand the electronic structure in detail before predictions for either the transport or glass-forming properties can be made in even a glass free of transition metals.

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## Scattering Cross Section of Low-Coverage CO on Pt(111) for Thermal He and H<sub>2</sub> Beams

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The scattering cross section of an adsorbed CO molecule is about 1 order of magnitude larger than expected from the van der Waals radius. The dependences on the He and H<sub>2</sub> incident velocities reveal glory structures similar to those in corresponding gas-phase experiments. Accordingly the long-standing puzzle of the extreme sensitivity of molecular beams to adsorbates is explained by inhomogeneities of the attractive potential.

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The diffraction of thermal atoms has become an increasingly important tool for investigation of the structures of clean and adsorbate-covered metal surfaces.<sup>1-4</sup> The diffraction patterns have been satisfactorily compared with calculations based on the assumption that the scattering is dominated by the repulsive potential. The various

models consider the repulsive potential to be a hard corrugated wall (HCW—see, e.g., Ref. 1 and references therein) or to have a shape permitting some penetration of the wave function into the metal.<sup>5</sup> Except for describing the selective adsorption phenomenon, the attractive potential played only the role of a correction accounting

for Debye-Waller and refraction effects.<sup>6,7</sup> Independent of their individual shapes, the attractive potentials used so far for metals have a common feature: They are only functions of  $z$ , the perpendicular component of the position vector, and do not depend on the parallel component  $R$ .

In this Letter we show evidence for the dominant role played by inhomogeneities of the attractive potential in the scattering of He and H<sub>2</sub> beams from metal surfaces covered with low adsorbate concentrations. This means that in contrast to former ideas, the attractive potential depends also on the parallel component of the position vector  $R$ . These inhomogeneities are due to the van der Waals attractive interaction between the beam particles and the sparsely adsorbed CO molecules. This interaction results in huge, gas-phase-like scattering cross sections, opening the way for the study of adsorbates in almost ideal dilution (~0.1%).

We will demonstrate our claim by investigating the scattering of neutral thermal particles from a Pt(111) surface at very low CO coverages ( $\theta_{\text{CO}} \leq 0.01$ ). The diffraction pattern of thermal particles from a clean close-packed (111) fcc metal surface is dominated by the specular peak,<sup>8,9</sup> indicating that such surfaces can be regarded as almost perfect mirrors. In our recent experiments on Pt(111) we obtained an "ideal" surface with a high reflectivity and with a specular beam shape identical to the incident beam within 0.02° (full width at half maximum 0.2°).<sup>10</sup> Only the intensity but not the shape of this peak is affected by the presence of adsorbates.<sup>10</sup> Additional diffraction peaks due to ordered CO structures were neither expected nor observed because of the very low coverages and the relatively high target temperature (400 K). Therefore we will use and discuss below only the height of the specular peak.

The total scattering collision cross section of an adsorbed CO molecule for an incident thermal He (H<sub>2</sub>) beam is determined straightforwardly by carrying out a simple adsorption experiment (see, for details, Poelsema<sup>11</sup>). The height  $I$  of the specular He (H<sub>2</sub>) peak is measured as a function of the CO exposure at constant target temperature and fixed pressure  $p_{\text{CO}}$ , as monitored with a quadrupole. As illustrated in Fig. 1, the peak height normalized to its value  $I_0$  for the clean surface decreases exponentially; the initial slope of this adsorption curve is given by

$$\left. \frac{dI/I_0}{dt} \right|_{t=0} = -\Sigma_{\text{CO}} \left. \frac{dn_{\text{CO}}}{dt} \right|_{t=0}, \quad (1)$$

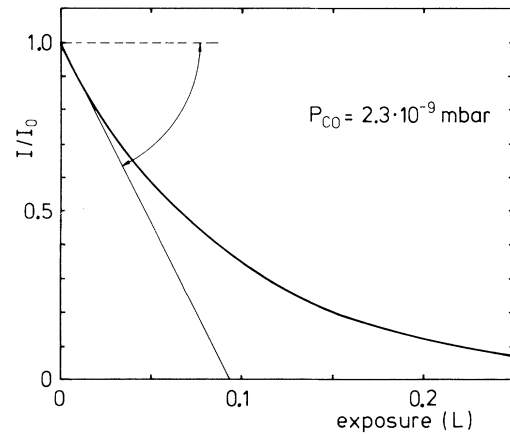


FIG. 1. Relative peak height of the specular He beam scattered from the Pt(111) surface vs CO exposure.  $E_{\text{He}} = 63$  meV and  $\theta_i = 40^\circ$ . (The noise level is about equal to the line thickness.)

where  $\Sigma_{\text{CO}}$  is the total collision cross section for a CO molecule, defined in analogy with gas-phase scattering,<sup>12</sup> and  $[dn_{\text{CO}}/dt]_{t=0}$  is the initial adsorption rate for CO given by

$$\left. \frac{dn_{\text{CO}}}{dt} \right|_{t=0} = \frac{p_{\text{CO}}}{(2\pi mkT)^{1/2}} s_0 \quad (2)$$

with  $p_{\text{CO}}(2\pi mkT)^{-1/2}$  the number of impinging CO molecules per unit surface area per unit time and  $s_0$  the initial sticking probability. From the adsorption curve in Fig. 1, measured with a 63-meV ( $v = 1740$  m/s) He beam, it follows that  $\Sigma_{\text{CO}}^{\text{He}} \cong 250s_0^{-1} \text{ \AA}^2$ , where  $s_0 = 0.84$ .<sup>13</sup> (The angular resolution of the apparatus leads to errors in the measured total cross section smaller than 5%–10%; see Pauly and Toennies<sup>14</sup> for a definition of the "limiting" angle.) The results presented here were obtained at an incident angle of  $\theta_i = 40^\circ$ , where the shadowinglike effects are already of minor importance.

The large  $\Sigma_{\text{CO}}^{\text{He}}$  is illustrative of the pronounced sensitivity of He scattering to the presence of adsorbates. The above-described experiment involves an accurate absolute pressure measurement. For this purpose quadrupole and ion gauge were calibrated *in situ* at  $10^{-6}$  mbar with a friction gauge which is currently used as an international pressure-transfer standard.<sup>15</sup> The simplicity and accuracy of the experiment and the fact that the  $\Sigma_{\text{CO}}$  values are about 1 order of magnitude larger than expected from the van der Waals radii seem to exclude a rigid-sphere description. On the other hand the  $\Sigma_{\text{CO}}$  values are rather similar to those obtained in gas-phase

scattering,<sup>16</sup> which is dominated by attractive dispersion forces.

In order to consider in more detail the similarity, the cross section  $\Sigma_{\text{CO}}$  was determined as a function of the velocity of the incident He and H<sub>2</sub>. The data taken at  $\theta_i = 40^\circ$  are shown in Fig. 2. The solid and dashed lines show helium (triangles) and hydrogen (inverted triangles) results, respectively. The range of incident velocities was covered by changing the nozzle temperature from 76 to 760 K and by employing beam-seeding techniques. The presence of the mixing gas Ar did not affect the situation at the surface as was checked by comparing results obtained with pure He (H<sub>2</sub>) and with HeAr (H<sub>2</sub>Ar) beams. We note that the target temperature was 400 K, i.e., sufficiently high to keep the hydrogen coverage negligibly small when probing beams containing hydrogen are used. This has been checked by measuring  $\Sigma_{\text{CO}}^{\text{He}}$  with both a mixed He/H<sub>2</sub> and a pure He beam. With equal He velocities in both beams the  $\Sigma_{\text{CO}}^{\text{He}}$  values are identical. The desorption rate for CO at the specified surface temperature is not negligible. However, this obviously does not affect the initial slope (at zero coverage) of the kinetic adsorption curves. This has been also confirmed by measurements with pure He beams at lower surface temperatures. For an additional check of the relative positions of the curves of

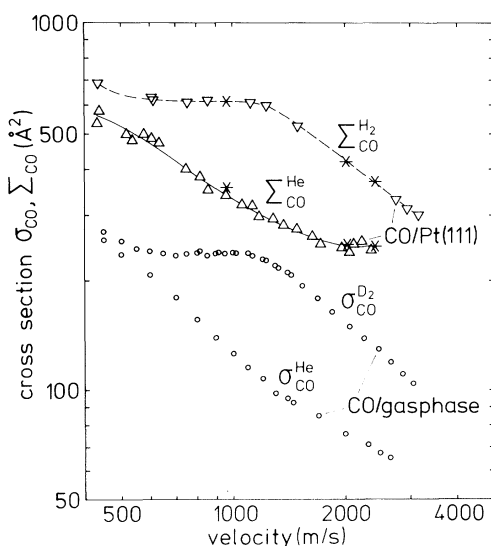


FIG. 2. Total scattering cross sections vs incident particle velocity.  $\Sigma_{\text{CO}}$  and  $\sigma_{\text{CO}}$  are the cross sections for CO adsorbed on Pt(111) (with  $\theta_i = 40^\circ$  and assuming  $s_0 = 1$ ) and for CO in the gas phase (Ref. 16), respectively. The superscript indicates the incident particle.

$\Sigma_{\text{CO}}^{\text{He}}$  and  $\Sigma_{\text{CO}}^{\text{H}_2}$  vs  $v$  along the  $v$  axis, we took advantage of the fact that in a mixed He/H<sub>2</sub> beam the velocities of He and H<sub>2</sub> are equal. Accordingly  $\Sigma_{\text{CO}}^{\text{He}}$  and  $\Sigma_{\text{CO}}^{\text{H}_2}$  were measured at the *same* velocity and under *identical* experimental conditions by only tuning the quadrupole mass spectrometer to He and to H<sub>2</sub>, respectively. The three pairs of data, obtained for  $v = 1000, 2010,$  and  $3180$  m/s ( $T_{\text{nozzle}} = 76, 300,$  and  $750$  K), are denoted with asterisks in Fig. 2. The points fall, within the experimental errors, on the two curves generated from the other data points.

For comparison the velocity dependencies of the total cross sections  $\sigma_{\text{CO}}^{\text{He}}$  and  $\sigma_{\text{CO}}^{\text{D}_2}$  for the scattering of He and D<sub>2</sub> by CO molecules in the *gas phase* are also plotted in Fig. 2. The gas-phase experiments were made by Butz *et al.* and have been analyzed in terms of glory oscillations superimposed on a Massey-Mohr cross section using a Lennard-Jones (12,6) potential.<sup>16</sup>

In Fig. 2 two features are apparent: The curves  $\sigma_{\text{CO}}^{\text{He}}(v)$  and  $\Sigma_{\text{CO}}^{\text{He}}(v)$  show definite similarities. This is even more pronounced for  $\sigma_{\text{CO}}^{\text{D}_2}(v)$  and  $\Sigma_{\text{CO}}^{\text{H}_2}(v)$ .<sup>17</sup> The similarity is illustrated well by the fact that the ratios  $\Sigma_{\text{CO}}^{\text{H}_2}/\Sigma_{\text{CO}}^{\text{He}}$  and  $\sigma_{\text{CO}}^{\text{D}_2}/\sigma_{\text{CO}}^{\text{He}}$  are more or less constant except at low velocities. This agreement is improved when the rough data in Fig. 2 are corrected for an attractive well in front of the Pt surface accounting for a change of the incident velocity.<sup>18</sup>

The obvious similarity between the shape of  $\Sigma_{\text{CO}}(v)$  and  $\sigma_{\text{CO}}(v)$  for both helium and hydrogen strongly suggests that the nature of the scattering process is the same whether the CO molecule is in the gas phase or adsorbed on the surface. This implies that, as in the gas phase, the total cross section for adsorbed CO is primarily determined by long-range attractive dispersion forces.

The systematic difference in absolute magnitude of  $\Sigma_{\text{CO}}$  and  $\sigma_{\text{CO}}$  is also obvious in Fig. 2, but not unexpected. Indeed, it is the electronic polarizability of the colliding molecules which determines the magnitude of the dispersion forces and thus ultimately the total cross section. It was recently shown<sup>19</sup> on the basis of ir data measured on CO/Ru(001)<sup>20</sup> that the electronic polarizability of the CO/Ru surface complex is about twice the polarizability of CO in the gas phase. The polarizability of the CO/Pt complex obtained by the same procedure from ir data measured on CO/Pt(111)<sup>21</sup> is even considerably larger. This seems to explain the differences in absolute magnitude in Fig. 2 (see, e.g., Ref. 12, p. 375).

We conclude from a straightforward experiment that the scattering of He atoms and H<sub>2</sub> molecules from the CO/Pt(111) surface at very low coverages is dominated by the *attractive* van der Waals interaction between the incident particles and the CO molecules located near the mirrorlike repulsive potential of the close-packed Pt(111) surface. The " $\gamma^{-6}$ " attractive potential around the adsorbed molecules creates local inhomogeneities in the otherwise flat attractive potential of the Pt(111) surface. This " $\gamma^{-6}$ " potential is, as in the gas-phase scattering, responsible for the very large scattering cross section, the overwhelming contribution being due to the dispersion interaction. The repulsive potential around the adsorbed molecules manifests itself mainly in the glory structure of the  $\Sigma_{\text{CO}}(v)$  curves. Likewise, the flat attractive potential of the Pt(111) surface plays a minor role: It induces changes in the effective incident angle<sup>18</sup> and velocity, which may become important at glancing angles and low velocities. Note that this explanation for the origin of the large  $\Sigma$  is at variance, for the CO/Pt case, with the hard-corrugated-wall model proposed recently by Ibanez *et al.*<sup>22</sup> (see also Ref. 18).

The possibility that localized van der Waals attractive potentials do more generally play a role in diffraction from clean and adsorbate-covered surfaces has to be considered. Indications for such an effect around step edges<sup>4</sup> and in He/graphite interactions<sup>23</sup> have been suggested recently. The influence of this phenomenon depends on the primary energy and on the angle of incidence.<sup>18</sup> Therefore indications for a soft repulsive wall (indeed a realistic physical feature), as inferred from energy and/or angular dependences of the obtained corrugation profile, may be partly confused with the present phenomenon. This might be the case even at higher coverages where its influence may be largely averaged out. Additional experimental and theoretical investigations are required in order to elucidate further the role of this phenomenon.

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