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Knocking on surfaces : interactions of hyperthermal particles with metal surfaces

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Chapter 3

The Interaction of Hyperthermal Argon Atoms with CO-covered Ru(0001): Scattering and Collision-Induced Desorption

Hyperthermal Ar atoms were scattered under grazing incidence ($\theta_i=60^\circ$) from a CO-saturated Ru(0001) surface held at 180 K. Collision-induced desorption of CO occurs, leading to ejection of fast CO (~ 1 eV). The angularly-resolved in-plane CO desorption distribution has a peak along the surface normal. This suggests that the CO desorption process involves lateral interaction with neighbouring molecules. The angular distribution of desorbing CO varies with the fractional coverage of the surface. As the total CO coverage decreases, the instantaneous desorption maximum shifts to larger outgoing angles. The scattered Ar has two components, one fast and one slow. The slow component is most evident when scattering from the fully-covered surface. The ratio and origin of the two components varies with the surface coverage of CO. The data indicates that the incident Ar cannot readily penetrate the saturated CO overlayer.

3.1 Introduction

The collision of energetic atoms or molecules with a surface can induce a variety of phenomena, including migration, desorption, absorption and dissociation. During gas-surface interactions in industrial catalytic processes (under high pressure and temperature conditions), such phenomena may play an important role [1, 2]. This motivates the study of collision-induced processes for a wide variety of systems. This paper is concerned primarily with one of those processes—collision-induced desorption (CID)—and its effect on the associated scattered particles.

CID can occur when energy sufficient to overcome the surface binding energy is transferred by an incident particle to an adsorbate in a direct collision. Due to inefficiencies in the energy transfer process, this typically requires the incident particles to have hyperthermal energies. The first experimental observation was reported by Beckerle *et al.* who scattered Ar beams from CH₄ physisorbed on Ni(111) [3, 4]. Subsequently a range of other adsorption systems such as NH₃-Pt(111) [5, 6], C₂H₄-Pt(111) [7, 8], NO-Pt(111) [9], O₂-Pt(111) [10, 11], O₂+CO-Pt(111) [12], O₂-Ag(001) [13, 14], N₂-Ni(001) [15-17], CO+H-Ni(001) [18], H₂O-Ru(0001) [2, 19], H₂O-Rh(111) [20] and Ar-Ru(0001) [21] have been studied. Based on hard cube analysis, the binding energies (E_B) of adsorbates can be determined from the threshold energy for CID [5-9].

The systems listed above involve atomic and/or small physi- or chemi-sorbed molecular adsorbates. CID has also been observed for large organic molecules [22-24]. Some CID processes have been investigated by specific theoretical modelling [25-30]. A combination of experimental and theoretical studies was undertaken for the N₂-Ru(0001) [31] and Xe-Pt(111) systems [32].

Various mechanisms have been proposed for collision-induced processes such as desorption, diffusion and absorption [1, 2, 33-35], and for dynamic displacement [36-39]. Collision-induced absorption refers to the uptake of adsorbates into the sub-surface region due to the impact of fast projectiles, such as energetic Ar atoms. Generally speaking the mechanisms can be separated into two classes: prompt processes, where the primary impact by the fast particle immediately causes the process observed, or secondary processes, where the primary impact transfers energy to the adsorbate-substrate system, which responds in a subsequent step by using this energy to produce an observable effect such as desorption. The two classes are not mutually exclusive. Tully and Kindt found that for collision-induced absorption the mass ratio determined which mechanism is dominant; projectiles and adsorbates of similar mass favouring a prompt process and a large mass-mismatch favouring a secondary process [35]. Velic and Lewis discussed collision-induced desorption in the near-equal mass case as part of a study involving species with a significant mass-mismatch [9]. They speculated that secondary collision processes could occur involving the incident particle and the recoiled adsorbate. When conditions are such that most of the projectile energy is transferred in a head-on collision to an adsorbate molecule, this molecule may be backscattered from the substrate and re-transfer some

energy back to the “stopped” projectile. Such processes might be discernable in the angle and energy distributions of the scattering projectile. Such an analysis of projectile scattering is performed in the present experimental study.

Recently we have studied scattering of hyperthermal Ar from a bare Ru(0001) surface at a high beam energy (~ 6 eV) [40, chapter 2]. The experimental results show that the interaction between Ar and the surface is dominated by the repulsive wall. The results were consistent with scattering from a corrugated static surface and the presence of structure scattering was confirmed. In this paper, we probe the dynamics of hyperthermal Ar atom scattering and CID of CO from a CO-covered Ru(0001) surface. The measurements are interpreted in the context of mechanisms mentioned above and with regard to influence of the incident atom-to-adsorbate mass ratio and the CO-coverage on the effectiveness of CID [9].

The adsorption of CO on Ru(0001) has been studied extensively. It is non-activated and non-dissociative [41-44]. The molecules attach to the surface via the C-end at all coverages [45-47]. They reside preferentially in the on-top position up to a coverage (θ_{CO}) of $1/3$ monolayers (ML) [48-51]. At this coverage a $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure is observed [52]. For $\theta_{\text{CO}} > 1/3$ ML, CO overlayers exhibit a complex behaviour. Depending on the surface temperature and coverage, various superstructures have been observed [41, 47, 49, 52-54]. At saturation ($\theta_{\text{CO}} \approx 2/3$ ML) a $(5\sqrt{3} \times 5\sqrt{3})R30^\circ$ structure persists [55, 56]. This is the starting structure of the overlayer used in the current study.

Scattering of CO from a CO-covered Ru(0001) surface was studied previously [43]. In that study it was found that the CO is scattered in a very wide angular distribution and that the energy transfer was consistent with collision of the incident CO with approximately two adsorbed CO molecules. Thus the picture was established of CO being reflected from a highly corrugated, but closed, CO overlayer. Neither exchange with the incident CO nor CID of adsorbed CO was observed in those measurements, which used a beam energy of 0.8 eV.

3.2 Experimental

The current experiments were carried out in a plasma beam scattering apparatus described previously [57-59]. It consisted of a cascaded arc plasma source mounted in a three-stage differentially-pumped beam line connected to a UHV scattering chamber with a base pressure of 2×10^{-10} mbar. This chamber contained the sample, supported on a three-axis goniometer [60], an ion sputter gun, a residual gas analyser and a differentially pumped rotatable quadrupole mass spectrometer (QMS). Ar (gas purity 99.999%) plasma was generated in the cascaded arc source [61, 62]. The plasma expanded into the first stage of the vacuum system from which particles passed a skimmer into the second stage of the beam line. This stage contained a 0.5% duty cycle chopper that was used to produce a pulsed beam, a beam flag to block the beam and a pair of deflection plates to eliminate charged particles. The third stage functioned as a buffer chamber.

For time-of-flight (TOF) experiments, the flight time of the Ar atoms was measured from the chopper in the second stage to the multiplier of the rotatable QMS in the scattering chamber. The incident energy, final energies as a function of scattering/desorption angles, and angular density distributions were all derived from TOF measurements. The incident Ar used had an average energy of ~ 6 eV with a full width at half maximum of ~ 5.8 eV. For Ar scattering, the TOF analysis and convolution over the spread of arrival times of the incident Ar beam was performed in the manner described in previous scattering studies [57, 63, 64]. Corrections for a trigger delay and the flight times of ions through the QMS have been applied to the raw data [59]. For CO desorption, the analysis was the same as has been employed in gas-surface reaction studies [65], where the incident and desorbed species are different.

The Ru sample was oriented to within 0.1° of the (0001) face. The surface was cleaned by repeated cycles of Ar^+ sputtering followed by annealing to 1500 K for several minutes and then annealing for several minutes at 1200 K in an O_2 atmosphere (1×10^{-8} mbar). The final cleaning step was Ar^+ sputtering followed by annealing to 1500 K for several minutes and 1530 K flashing. The surface cleanliness was checked by reference to the temperature programmed desorption (TPD) spectra of CO and $\text{H}_2(\text{D}_2)$ [66, 67]. The CO-covered surface was prepared by background dosing isotopic ^{13}CO gas (purity 99%) at a partial pressure of 1×10^{-8} mbar for 14 min. Prior to each new TOF measurement the surface was flashed and a new ^{13}CO overlayer was prepared. The Ar beam impinged on the surface at an incident angle of 60° with respect to the surface normal. During exposure the surface temperature (T_s) was held constant at 180 K.

3.3 Results and Discussion

The main observation is that exposing the CO-covered Ru(0001) surface to incident hyperthermal Ar atoms induce CO desorption with time-dependent angular and intensity distributions. The scattered Ar distributions also reflect the changing nature of the overlayer structure.

3.3.1 Collision induced desorption of CO by Ar

Figure 3.1(a) shows the in-plane angular distribution of desorbing CO intensity that was derived from TOF spectra measured at different outgoing (desorption) angles (defined with respect to the surface normal). Each data point represents the cumulative desorbed CO intensity arising from a total exposure equivalent to ~ 20 ML of Ar ($1 \text{ ML} = 1.58 \times 10^{15} \text{ atoms/cm}^2$). As can be seen, the largest desorption was measured along the surface normal at a desorption angle (θ_d) of 0° (the QMS angular acceptance is $\sim 1.6^\circ$ assuming a point source at the sample position). The corresponding average energy of the desorbing CO as a function of desorption angle is plotted in figure 3.1(b). In contrast to the CO intensity distribution, the energy

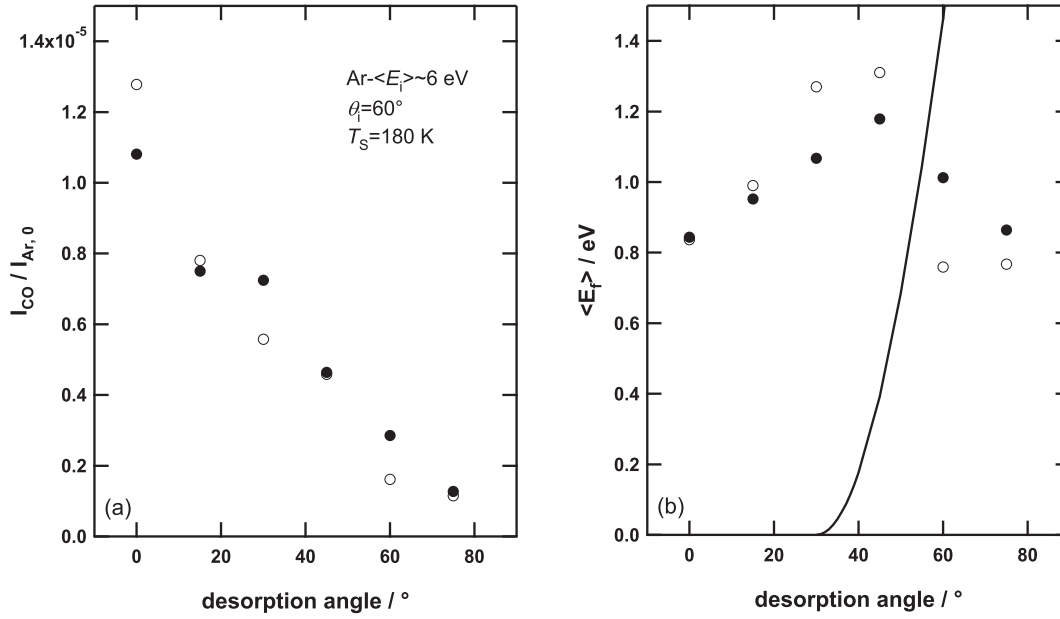


Figure 3. 1 (a) Integrated area of CO measured by TOF as a function of desorption angle for a total exposure to ~ 20 ML Ar. (b) Corresponding energy of the desorbing CO as a function of desorption angle. The line corresponds to a simple model of mass 29 being recoiled by mass 40. The open and filled circles correspond to the values determined from two independent set of measurements.

distribution has a maximum in the region $\theta_d = 30^\circ - 45^\circ$. The high desorption energies exclude the possibility of that thermally-induced desorption (a secondary process in which the Ar projectile locally heats the surface) is occurring. The line on figure 3.1(b) represents the model of direct elastic recoil of CO by an Ar atom. Clearly such a model also cannot account for the measured data.

In order to understand the desorption dynamics in detail, the time variation of the TOF spectra was monitored as shown in figure 3.2(a). This shows a time series of CO desorption TOF spectra measured at $\theta_d = 0^\circ$. Seven consecutive TOF spectra are collected. Each individual spectrum in the series corresponds to an exposure to ~ 2.8 ML, with the entire series corresponding to a cumulative exposure of ~ 20 ML Ar. CO desorption is not immediately evident upon exposure to the Ar beam, but it develops after a period of irradiation. Similar TOF series were acquired for several desorption angles ranging from 0° to 75° . Significant CO desorption is first detected at $\theta_d = 0^\circ$ and subsequently emerges at progressively larger θ_d as the total exposure time increases. The maximum of the instantaneous desorption intensity shifts to larger θ_d as a function of the exposure time.

In addition to the time-dependence of the angle of desorption, there is also a time-dependent CO desorption rate observed at any given θ_d . The behaviour is qualitatively similar at all measured θ_d . Once CO desorption commences, the desorption rate goes through a maximum and then gradually decreases below the level of detection once more. This trend is most clearly evident in the set of TOF spectra obtained at $\theta_d = 0^\circ$. At this geometry, significant CO desorption is first observed during the third TOF spectrum, which is collected after the sample has already been exposed to the

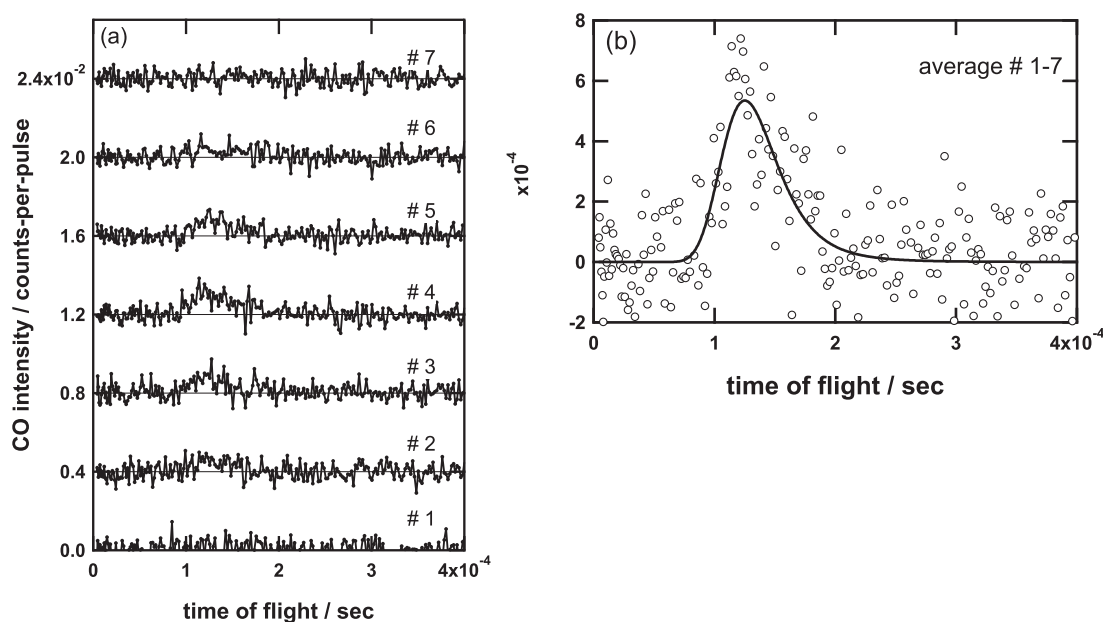


Figure 3. 2 (a) Time series of TOF spectra tracking CO desorption along $\theta_i=0^\circ$. The distributions are collected sequentially from the bottom to the top. They are plotted on the same scale, but are offset for clarify. The total exposure is ~ 20 ML of Ar; each individual distribution corresponds to an Ar exposure of ~ 2.8 ML. (b) The cumulative TOF spectra arising from the summation of the seven spectra shown in panel (a).

equivalent to ~ 5.6 ML (± 0.8 ML) of Ar. A relatively high CO desorption rate is observed for the third and fourth TOF spectra, which together constitute an additional ~ 5.6 ML Ar exposure. Subsequently the CO desorption along the surface normal decreases and is negligible during the seventh TOF spectrum in the sequence. Effective, all CO desorption along the surface normal occurs during an Ar exposure equivalent to ~ 11 ML out of a total exposure of ~ 20 ML. It is evident from the CO TOF spectra, that the rate of depletion is not constant in time, so the relationship between the total exposure and the fractional coverage is not linear. Figure 3.2(b) shows the cumulative TOF profile obtained from the sum of the seven spectra shown in figure 3.2(a). The deduced intensities and average energies plotted in figure 3.1(a) and (b) respectively have all been derived from such cumulative spectra. Given the relatively complex time and angular dependences of the desorption, it is difficult to extract an accurate value for the desorption cross section from the data.

Comparison of the integrated areas of CO measured by TPD from unexposed and post-exposure CO-covered surfaces reveals that about a quarter of the saturation coverage of CO is removed by the exposure to ~ 20 ML Ar. The area of the sample surface that is directly exposed to the incident beam is crudely estimated to be between 0.33 and 0.25 of the total surface area. In the not unlikely case of complete CO immobility, this would result in the beam footprint losing between three quarters and all of the originally adsorbed molecules. Conversely, an assumption of totally unrestricted CO mobility would imply a 0.5 ML CO coverage in the beam-spot at the end of the exposure. It is clear from the Ar scattering data (shown later) that the TOF spectra from the CO-dosed surface during the seventh (final) cycle are close, but not

identical, to those of the clean surface. It is very likely that the CO overlayer in the beam footprint will reorganise on the nano-scale in response to CID. The driving force for such local diffusion is mutual repulsion of closely-packed CO molecules. Such repulsion is strong above $\theta_{\text{CO}}=0.33$ ML [66]. Note that an experimental study by Deckert *et al.* found a diffusion barrier of about 0.48 eV for $\theta_{\text{CO}}=0.27$ ML and 0.27 eV for $\theta_{\text{CO}}=0.58$ ML [68], although a theoretical study has claimed almost barrier free motion [69]. It is much less likely that the beam footprint gets partially replenished by molecules from the unexposed areas of the surface during the course of the exposure. Ar impact obviously does not enhance diffusion outside the beam footprint, and we expect very limited diffusion of CO into the beam footprint.

In order to desorb, CO must gain sufficient energy from the Ar impact with the surface to overcome the surface binding energy. Given the relative masses involved (Ar=40 and $^{13}\text{CO}=29$ amu), energy transfer in an impulsive collision can be quite efficient and CID is not unexpected. Direct mechanical energy transfer between the Ar atoms in the beam and the chemisorbed CO molecules can be up to ~97% of the translational energy of the Ar atoms in the Baule (impulsive) limit [70]. However, this large energy transfer requires very small impact parameter collisions between Ar and CO, which are not very probable for a closed overlayer.

In a simple single binary collision between Ar ($M_{\text{Ar}}=40$) with $\theta_i=60^\circ$ and CO ($M_{\text{CO}}=29$) (i.e. disregarding the surface and all other CO molecules), CO cannot desorb along the surface normal. This is directly evident from a simple analysis of the kinematics of the collision. The smallest θ_f that could be attained in an Ar-CO collision is 30° , which corresponds to a recoil angle of 90° with respect to the original beam direction. Moreover, in such an idealised binary collision, the molecules that are “recoiled” by 90° gain no energy in the “collision”. The energy that can be gained by an elastically recoiled mass of 29 amu is represented by the model included on figure 3.1(b). Experimentally we observe CO desorption along the surface normal and at angles less than 30° , particularly from the (nearly) saturated surface. Furthermore, there is no correspondence between the prompt binary elastic recoil model and the measured desorption energies even for those angles where the model is applicable.

Clearly the CO desorption processes are more complex than prompt direct recoil of a single CO by an Ar atom. They must involve the underlying Ru lattice and/or lateral CO-CO repulsive interactions that arise from CO being pushed against neighbouring molecules before desorbing from the surface. Mutual CO-CO repulsion may change the motion of the recoiling molecules, directing them toward the surface normal. For high surface coverages this is the only direction along which molecules do not encounter hindrance from their neighbours. Redirection by neighbouring adsorbates was observed experimentally and theoretically for the Ar/Xe-Pt(111) system [32]. With increasing Xe coverage, the peak of the desorbing Xe angular distribution shifted to the surface normal. That neighbouring CO molecules must play a similar role in the current desorption process is evident from the time-dependent variation of the observed TOF spectra. Both the incident beam and the underlying Ru surface are

non-varying parameters in the scattering process. Only the instantaneous CO coverage varies over the course of the measurements.

It is known that at low θ_{CO} the E_{B} of CO is about 1.66 eV, and that between $\theta_{\text{CO}}=0.2$ and $1/3$ ML it increases to 1.81 eV. However for θ_{CO} beyond $1/3$ ML E_{B} drops to about 1.24 eV. At the saturation coverage, E_{B} decreases to about 1.14 eV due to the strongly repulsive CO-CO interactions [66]. Consequently, it is energetically easiest to remove a molecule from the surface with the highest θ_{CO} for a given applied impulse. However, at (near-)saturation coverage, mutual repulsion between adjacent CO molecules and the absence of small impact parameter collisions between Ar and CO due to shadowing of CO by CO results in the blocking of (off-normal) desorption paths. With time-dependent depletion of the CO, the overlayer becomes progressively more open and the off-normal desorption trajectories become more accessible. Concomitantly, desorption along the surface normal becomes less probable as the molecular density on the surface decreases (desorbing molecules are less confined by their neighbours). Prompt recoil is never seen.

Collision-induced displacement of CO can occur, since with an $\langle E_{\text{i}} \rangle$ of impinging Ar of 6 eV, the maximum translational energy of the CO parallel to the surface after the collision is estimated to be 4.4 eV (again assuming an optimum single elastic binary collision). For the saturation coverage, migration of CO is physically blocked by the neighbouring molecules. As has been demonstrated using molecular dynamics simulations, adsorbate-adsorbate collisions result in a significant reduction of migration distances [71]. Hence, any parallel motion induced by an Ar impact will only result in a temporary, localised compression of the overlayer structure, which might lead to desorption of either the directly impacted molecule or of one of the molecules it interacts with. As CO molecules are removed from the surface, displacement over increasingly longer distances becomes feasible. In view of results from experiments on transient mobility we expect the displacement to be limited to—at most—a nanometre. Simultaneously, the energy required to break the CO-surface bond increases. Ultimately, the dissipation of the lateral energy of the CO to the surface will set a limit on the total fraction of CO that can be removed as a result of collision-induced processes.

Previously, CID of N_2 from Ru(0001) by noble gases (Ar and Kr) has been reported [31]. Molecularly chemisorbed N_2 binds weakly, with its molecular axis perpendicular to the surface plane, which is similar to the adsorbed CO orientation. A rapid increase of desorption cross section was observed when θ_{i} was increased. This was interpreted in terms of a corrugated N_2 —Ru(0001) potential energy surface leading to coupling of both impulsive tilt and surface parallel motions, both of which are induced by the incident gas atoms, with motion normal to the surface. In the current system, this coupling with collision-induced tilt and parallel motions may also occur, since the $\theta_{\text{i}}=60^\circ$ experimental condition used leads to a rather glancing interaction. While lateral motion is restricted by neighbouring CO molecules at high coverage, tilt motion will reduce the CO binding energy. The importance of molecular orientation in determining the interaction dynamics is illustrated by, for example, the

behaviour of the NO-Pt(111) system [72]. A molecule oriented sideways is no longer bound to the surface.

As an intermediate conclusion we note that at high CO coverage CID is almost absent. The CO layer is too closely packed to allow sufficiently localised, small impact parameter energy transfer by the Ar projectile. When nevertheless the CO coverage decreases, localised energy transfer becomes possible and CO is driven off in a secondary process involving several CO-CO collisions. At even lower coverage, the primarily energized CO molecule can dissipate its lateral translational energy to the lattice before a collision with other CO molecules can lead to desorption.

3.3.2 Ar scattering from CO-covered surface

Turning our attention to the Ar scattering dynamics, the Ar TOF spectra also show a time dependency. As an example, series of Ar TOF spectra measured at $\theta_f=15^\circ$, 45° and 75° are shown in figure 3.3. Different behaviour is observed at the three outgoing angles. At $\theta_f=15^\circ$ no scattered Ar is initially observed. With increasing exposure a slow Ar peak emerges. The maximum scattered intensity is measured during TOF #5, after which the intensity decreases again. A bimodal distribution is clearly evident in the series measured at $\theta_f=45^\circ$. The distributions measured at this angle undergo dramatic changes during the course of the exposure. The initial measurements are dominated by a slow Ar component with a small fast component. Over the time-series the slow component broadens and diminishes. In the later TOF spectra, a fast Ar component grows to dominate the distribution. In contrast, for the measurements at $\theta_f=75^\circ$ the shape of the distribution is virtually constant over the time-series. The main change is a gradual reduction in the total scattered intensity measured as the exposure increases. The shapes of the distributions measured at this angle are similar to those we measured from the bare Ru surface. All time series illustrate that the structure of the surface “seen” by the Ar changes over the course of the exposure. The distributions measured at grazing outgoing angles are the least sensitive to the changing nature of the surface.

Figure 3.4(a) shows angular intensity distributions determined from the initial (#1) and final (#7) TOF spectra measured in the time series collected at different outgoing angles. The distribution for TOF #1 has more scattered intensity along the super-specular direction as compared to TOF #7, which has more intensity along the specular direction. The inset on figure 3.4(a) is an expanded view of the small outgoing angle region illustrating enhanced sub-specular Ar scattering measured during TOF #7. This confirms that the surface that produces the TOF #7 spectra is rougher than the CO-saturated surface (TOF #1).

Figure 3.4(b) shows the average energies of the fast and slow components as a function of θ_f derived from the cumulative TOF spectra. The spectra of scattered Ar for $\theta_f=30^\circ$ - 75° were fitted with a combination of two shifted Maxwell-Boltzmann distributions, which produced a good representation of the overall shape of the spectra (see figure 3.3). The spectra measured for $\theta_f<30^\circ$ were fitted with a single distribution

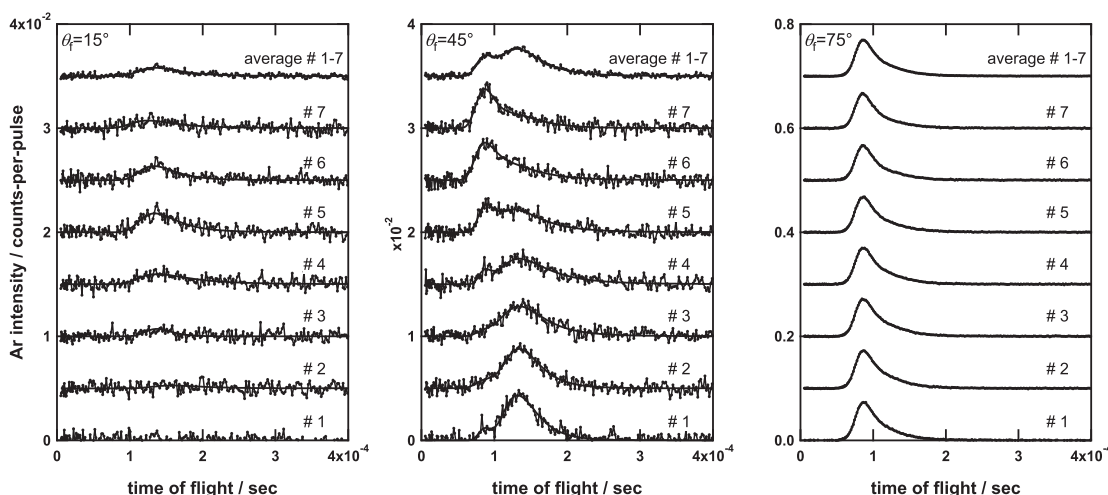


Figure 3. 3 Time series of TOF spectra tracking Ar scattering along $\theta_f=15^\circ$, 45° and 75° . The distributions are collected sequentially from the bottom to the top, with each individual distribution corresponding to an Ar exposure of ~ 2.8 ML. They are plotted on the same scale, but offset for clarity. The upper-most curve on each panel is the average distribution derived from the seven lower spectra. The lines through the data points are the net result of fitting with single ($\theta_f=15^\circ$) and double ($\theta_f=45^\circ$; 75°) shifted Maxwell-Boltzmann distributions.

because the signal level was too low to give a meaningful result from two-component fitting. The estimated average energy of the Ar scattered to these angles is consistent with that of the slow component.

Three binary collision models [73] are illustrated on figure 3.4(b), namely Ar (mass 40) scattering from Ru (mass 101), simultaneously from two ^{13}CO molecules (mass 58), and from a single ^{13}CO molecule (mass 29). Clearly, the fast component is consistent with scattering from a large effective surface mass. The example shown is for Ru, but any sufficiently heavy scattering centre (for example, collective scattering from a group of CO molecules) can produce comparable final energies. The energy of the slow component is effectively constant as a function of θ_f . It matches the single binary collision models for a single CO at $\theta_f=75^\circ$ and is in reasonable agreement with collective scattering from two CO molecules at small outgoing angles.

The inset on figure 3.4(b) shows the corresponding normalised angular intensities of the fast and slow components. For both components the bulk of the in-plane scattered particles emerge at large outgoing angles. This indicates that even the incident Ar atoms that lose the most energy (the slow component of the measured distributions) do not at all thermalise at the surface during the collision processes. Although the intensity of the two Ar components vary with the irradiation time as seen in figure 3.3, no major change in the average energy of the individual components is observed for the different TOF spectra within a series measured at any given θ_f . Of course, the average energy of the overall distribution changes during a time series due to the change in the relative contributions from the slow and fast components (the effect is most dramatic for $\theta_f=45^\circ$). These results suggest that, even though the overlayer structure changes during the collision process, the individual impact sites “seen” remain available and distinguishable.

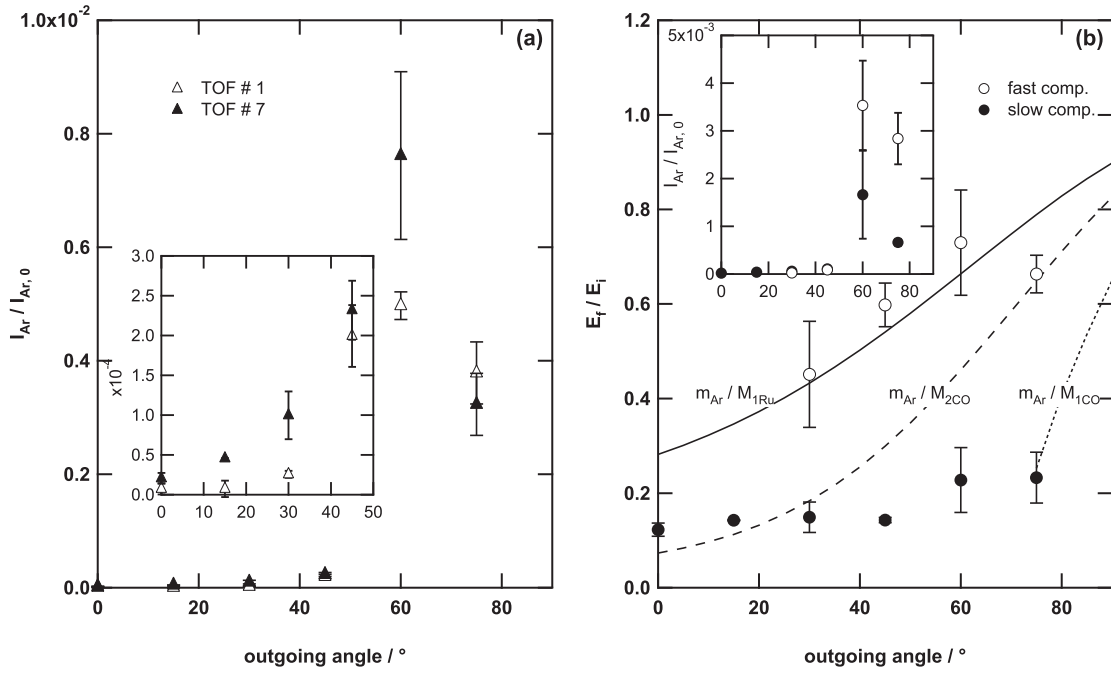


Figure 3. 4 (a) Normalised total integrated area of the TOF spectra as a function of θ_f for TOF series #1 and #7. The inset is an expanded view of the region for $\theta_f=0^\circ$ - 50° . (b) The average energies of the fast (open circles) and slow (filled circles) components as a function of θ_f derived from the cumulative Ar TOF spectra. Three elastic binary collision models are reproduced on the panel. From the top these are: Ar (mass 40) scattered by Ru (mass 101); $2 \times {}^{13}\text{CO}$ (mass 58); and ${}^{13}\text{CO}$ (mass 29). The inset shows the corresponding normalized intensities of the two components derived from the cumulative TOF spectra.

The varying bimodal Ar distributions of the current system can be correlated to the changes in the CO overlayer structure that are the result of CO desorption. The final Ar TOF spectra (#7) measured in the various series obtained from CO-covered Ru are qualitatively quite similar to the corresponding distributions measured from the clean surface. A direct comparison of the TOF spectra, as shown in figure 3.5, illustrates that the shapes of the distributions measured from the bare and “post”-exposure CO-covered surface at any given θ_f are virtually identical. However, they differ significantly in the absolute scattered intensity. Taking the intensity scattered from the bare surface as unity, the corresponding intensities measured during TOF #7 in the time sequence measurements at $\theta_f=30^\circ$, 60° and 75° were 2.7, 0.6 and 1.2 respectively. The partially-covered surface scatters fewer atoms along the specular direction and somewhat more to the super-specular outgoing angle. There is a dramatic increase in the relative number of sub-specularly scattered atoms. The shapes of distributions measured from these surfaces are noticeably different from those measured from the saturated surface.

The enhanced sub-specular scattering of Ar from the partially covered surface may be due to large impact parameter interactions of Ar with isolated CO molecules following back-scattering of the Ar atoms from specific sites on the Ru substrate. Such glancing collisions with CO will not significantly change the energy lost in the

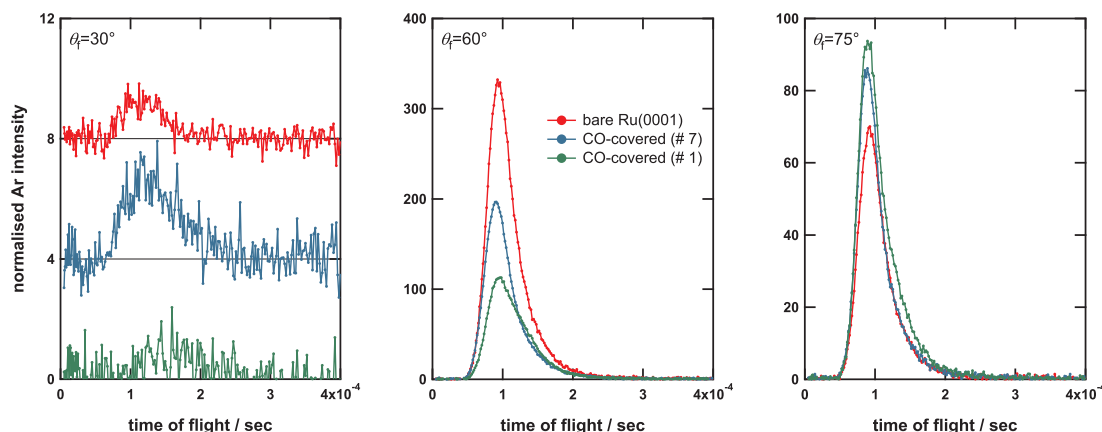


Figure 3. 5 Comparison between TOF spectra from bare (red), CO-depleted (blue) and CO-saturated (green) Ru(0001) surfaces for spectra measured at $\theta_i = 30^\circ$, 60° and 75° . The spectra at $\theta_i = 30^\circ$ have been offset for clarity. The spectra from the CO-saturated surface (TOF #1) were collected during Ar exposure of ~ 0 -3 ML; those from the CO-depleted surface (TOF #7) were collected during Ar exposure of ~ 17 -20 ML. All intensities have been normalised to the intensity of the corresponding direct beam.

overall collisions. An additional mechanism by which a low partial coverage of CO could influence the angular distribution of the scattered Ar is by introducing a focusing/defocusing effect on the incident atom trajectories. Since the CO molecules occupy a preferred site on the surface (atop), they are most likely to modify a defined subset of the Ar trajectories that can be produced by the (0001) atomic arrangement. The defocusing effect would involve blocking/dispersion of Ar trajectories that are traversing the on-top sites of the Ru surface. Concomitantly, the focusing effect would be due to atoms travelling along near-atop paths being preferentially redirected to an alternative scattering site.

The initial surface has the saturation coverage of CO, with the molecules packed as closely as is physically possible at 180 K. The delayed appearance of CO desorption suggests that it is relatively difficult for Ar to displace CO from this structure. As such, the incident Ar atoms primarily experience the corrugated potential energy surface generated by the oxygen atoms. However, with gradual removal of CO molecules (either from defect sites in the overlayer structure or by attrition as a result of a small but finite removal probability from the ideal adlayer) the overlayer is reconfigured to a more open structure (consistent with the ordering of a less-than-saturated CO overlayer). Mutual repulsion between the CO molecules should be sufficient to give rise to a continuous reordering of the overlayer structure in response to CID, at least in the high coverage regime. This should lead to both the higher CO removal rate (due to individual CO molecules being more exposed) and to the Ar experiencing a more corrugated and disordered surface (due to the increased inter-molecular spacing). The gradual emergence of scattered Ar signal at small θ_i as the exposure increases is consistent with an increased surface roughness. This signal subsequently disappears due to the removal of CO from the beam footprint.

On the (near-)saturated surface, CO molecules that attempt to laterally displace along the surface under the influence of an approaching Ar atoms are prevented from

doing so by their closely-packed nearest neighbours. Consequently, incident Ar encounters nearly-static CO molecules and may, depending on the impact parameters, be scattered to small outgoing angles. Note that a single CO molecule is not capable to scatter Ar to small outgoing angles (see the allowed final angles indicated for this mass ratio in figure 3.4(b)). In order for this to occur in a single collision the effective mass of CO must be increased by interaction with its neighbours. Such a process will be most effective provided the surface has lost sufficient CO to expose the individual molecules to direct Ar impact while still having significant nearest-neighbour interactions. In contrast, at sufficiently low θ_{CO} lateral displacement of CO becomes largely unhindered and the adsorbed molecules can more easily redistribute under the influence of approaching Ar atoms. In this case, as θ_{CO} decreases the effect of Ar on the CO shifts from one of desorption to one of displacement. As a consequence, the angular intensity distribution measured from the CO-covered surface may never fully converge to that obtained from the clean surface. The remaining CO continues to affect the Ar trajectories but is not desorbed in the process.

The average energies of the fast Ar component are compatible with the simple binary collision model of incident atoms from an isolated ruthenium atom (mass ratio of $m_{\text{Ar}}/M_{\text{Ru}}$: see figure 3.4(b)). For Ar scattering from the depleted CO surface, a significant contribution to the overall TOF distribution should indeed arise from direct scattering from the Ru substrate. Note however that the energy loss in scattering of Ar from clean Ru under the current conditions is far from simple (see ref. [40, chapter 2]). In contrast, the average energies of the slow component are significantly lower than the binary collision model for Ru and are essentially constant as a function of θ_{f} . The lack of observed CO desorption during TOF #1 of the time series strongly indicates that the Ar cannot penetrate the saturated overlayer. Hence both components observed for the TOF #1 spectrum must arise from CO-mediated interactions. As illustrated by the dotted line in figure 3.4(b), a single binary collision between Ar and CO cannot deflect Ar to small outgoing angles. Multiple collisions or single collisions with a large effective surface mass (e.g. collective scattering from more than a single CO molecule) are required to access $\theta_{\text{f}} < 70^\circ$. If multiple forward collisions are involved, then this would result in a flattening of the angular dependence of the final energy, which is qualitatively consistent with the slow component values in figure 3.4(b). Hence, considering the efficient energy transfer that is possible between Ar and ^{13}CO , it is possible to attribute the slow Ar component to such processes.

It is more difficult to explain the presence of the fast Ar component when scattering from the saturated surface. This is particularly the case for scattering to sub-specular outgoing angles, such as trace #1 at $\theta_{\text{f}} = 45^\circ$ in figure 3.3. It should be noted that the fast component that is evident in the early TOF spectra at $\theta_{\text{f}} = 45^\circ$ appears to be different from the fast component measured during the later TOF spectra. The intensity of the fast component drops from TOF #1 to TOF #3 before increasing strongly from TOF #4 onward. The extent of the decrease over the course of the first three spectra is somewhat masked by simultaneous broadening of the slow component. As mentioned above, the fast component in the later TOF distributions can be

attributed to scattering from Ru. The rapid growth of this component may be a proxy for the instantaneous fractional coverage of the surface. However, a CO-dominated process must be involved in producing the fast component at $\theta_f=45^\circ$ in the early stages. This component cannot be readily attributed to scattering from Ru since the angular distribution and time variation of the CO desorption are inconsistent with penetration of the saturated overlayer. In addition, CO CID would be anticipated to lead to a continuous increase in the intensity of any Ru-derived component rather than the initial decrease that is observed.

Previously, Xe and Kr collision-induced NO desorption from Pt(111) has been studied by Velic and Levis [9]. They speculated that, given the efficient energy transfer that can occur during collision of near-equal mass species, NO desorption might be suppressed by an additional (second) collision with an incident Ar atom. The Ar/ ^{13}CO mass ratio also allows for a very efficient energy exchange. Hence re-collision of CO with a “stopped” Ar atom might also suppress desorption while returning energy to the now recoiled Ar atom. It is conceivable that the fast component that is observed at $\theta_f=45^\circ$ during the early TOF spectra arises from a re-collision between the recoiled CO and the Ar. Such a double collision mechanism could have several consequences:

- Suppression of CO desorption (as proposed by Velic and Levis [9]).
- Broadening of the Ar angular distribution.
- Significant energy “retention” by the Ar.

These three points can all be recognised in the data, and thus can explain the fast component at $\theta_f=45^\circ$ from the saturated surface. However, it is difficult to estimate the probability for such a process as it requires a sequence of collisions, all with small impact parameter. In addition, our grazing incidence geometry coupled with the close-packed nature of the CO-saturated surface make the initial hard (small impact parameter) collisions, which are necessary in order to realise the double-collision process, difficult to envisage.

As an alternative, a fast Ar component can be scattered to sub-specular angles if it interact collectively with several CO molecules, thereby creating a scattering partner with a high effective mass. To reach $\theta_f=45^\circ$ while retaining the energy determined would require the involvement of at least three CO molecules. Note that the fast component observed during the early TOF spectra is quite well-defined. If this component does indeed arrive from scattering by a collective of CO molecules, it suggests that a very discrete and distinct scattering site is involved and that this site (and the associated scattered component) rapidly disappears once the CO coverage drops below the saturation level.

The same general picture emerges from the scattering data as was seen in the earlier CID data. Initially Ar is scattered exclusively from an ordered CO overlayer. However, progressive exposure results in CO desorption and in alteration of the Ar TOF distributions. The CO coverage depletion reduces the mutual shadowing effect of adjacent CO molecules. This increases the range of impact parameters between Ar and CO. As a consequence, the probability of a small impact parameter collision with

CO increases and CO desorption is enhanced. Once the concentration of CO in the beam spot has been substantially reduced, the measured Ar distributions arise primarily from scattering from the Ru substrate. Hence, the fast component that emerges rapidly in the later TOF spectra on figure 3.3(b) has a different origin than the small fast component that is present in the initial distributions. CID of the remaining CO molecules becomes difficult and they primarily act to modify the Ar trajectories (increasing diffuse scattering).

3.4 Conclusions

The interaction of hyperthermal Ar atoms with the CO-covered Ru(0001) surface was studied. Scattered Ar can lose a large fraction of its energy at that surface due to efficient energy transfer to the adsorbed molecules. Ar collision-induced desorption of CO was observed along the surface normal. This is a secondary process involving lateral interaction with neighbouring CO molecules. CID is not initially observed indicating that penetration of the saturated CO overlayer by the incident Ar is difficult. The initial Ar TOF distributions are dominated by scattering from CO. As the surface coverage gets gradually depleted, CID becomes more effective and the Ar ultimately removes the majority of the adsorbed CO. However, at low partial coverages the efficiency of CID again drops and the remaining CO molecules primarily act as a modifier of Ar trajectories while scattering from the Ru substrate is the dominant factor.

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