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DOI

[10.1063/1.3545974](https://doi.org/10.1063/1.3545974)

Publication date

2011

Document Version

Final published version

Published in

Journal of Chemical Physics

[Link to publication](#)

Citation for published version (APA):

Ueta, H., Gleeson, M. A., & Kleyn, A. W. (2011). The interaction of hyperthermal argon atoms with CO-covered Ru(0001): Scattering and collision-induced desorption. *Journal of Chemical Physics*, 134(6), <http://dx.doi.org/10.1063/1.3545974>. <https://doi.org/10.1063/1.3545974>

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The interaction of hyperthermal argon atoms with CO-covered Ru(0001): Scattering and collision-induced desorption

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(Received 1 September 2010; accepted 4 January 2011; published online 10 February 2011)

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 involving the ejection of fast CO (~ 1 eV) occurs. The angularly resolved in-plane CO desorption distribution has a peak along the surface normal. However, the angular distribution varies with the fractional coverage of the surface. As the total CO coverage decreases, the instantaneous desorption maximum shifts to larger outgoing angles. The results are consistent with a CO desorption process that involves lateral interaction with neighboring molecules. Furthermore, the data indicate that the incident Ar cannot readily penetrate the saturated CO overlayer. Time-of-flight measurements of scattered Ar exhibit two components—fast and slow. The slow component is most evident when scattering from the fully covered surface. The ratio and origin of these components vary with the CO coverage. © 2011 American Institute of Physics. [doi:10.1063/1.3545974]

I. 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 transfer process, this typically requires the incident particles to have hyperthermal energies. The first experimental observation of CID was reported by Beckerle *et al.* who scattered Ar beams from CH₄ physisorbed on Ni(111).³ Subsequently a range of other adsorption systems such as NH₃-Pt(111),⁴ C₂H₄-Pt(111),⁵ NO-Pt(111),⁶ O₂-Pt(111),⁷ O₂+CO-Pt(111),⁸ O₂-Ag(001),⁹ N₂-Ni(001),¹⁰ CO+H-Ni(001),¹¹ H₂O-Ru(0001),^{2,12} H₂O-Rh(111),¹³ and Ar-Ru(0001)¹⁴ have been studied. Based on hard cube analysis, the binding energies (E_B) of adsorbates can be determined from the threshold energy for CID.⁴⁻⁶

The systems listed above involve atomic and/or small physisorbed or chemisorbed molecular adsorbates. CID has

also been observed for large organic molecules.¹⁵ Some CID processes have been investigated by specific theoretical modeling.¹⁶ Combined experimental and theoretical studies were undertaken for the N₂-Ru(0001)¹⁷ and Xe-Pt(111) systems.¹⁸

Various mechanisms have been proposed for collision-induced processes (desorption, diffusion, and absorption)^{1,2,19,20} and dynamic displacement.²¹ Generally speaking, the mechanisms proposed can be separated into two classes: prompt processes, where the primary impact by the fast particle immediately causes the observed effect, and 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 a measurable effect. The two classes are not mutually exclusive. For example, Kindt and Tully found that for collision-induced absorption (i.e., the uptake of adsorbates into the subsurface region due to the impact of fast projectiles) the mass ratio determined which mechanism is dominant; projectiles and adsorbates of similar mass favored a prompt process and a large mass-mismatch favored a secondary process.²⁰ Velic and Levis discussed collision-induced desorption in the near-equal mass case as part of a study involving species with a significant mass-mismatch.⁶ They speculated that secondary collision processes involving the incident particle and the recoiled adsorbate might occur in certain circumstances. When conditions are such that most of the projectile energy is transferred to an adsorbate molecule, this molecule may be backscattered from the substrate and retransfer some energy back to the “stopped” projectile. These 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

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(~ 6 eV).²² The experimental results show that the interaction between Ar and the surface is dominated by the repulsive wall. They 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 scattering of hyperthermal Ar and CID of CO from a CO-covered Ru(0001) surface. The measurements are interpreted in the context of the mechanisms mentioned above and with regard to influence of the CO coverage on the effectiveness of CID.⁶

The adsorption of CO on Ru(0001) has been studied extensively. It is nonactivated and nondissociative.^{23–25} The molecules attach to the surface via the C-end at all coverages.^{26,27} They reside preferentially in the on-top position up to a coverage (θ_{CO}) of $1/3$ monolayers (ML).^{28,29} At this coverage a $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure is observed.³⁰ For $\theta_{\text{CO}} > 1/3$ ML, CO overlayers exhibit a complex behavior. Depending on the surface temperature and coverage, various superstructures have been observed.^{23,27,29–31} At saturation ($\theta_{\text{CO}} \approx 2/3$ ML), a $(5\sqrt{3} \times 5\sqrt{3})R30^\circ$ structure persists.^{32,33} This is the starting structure of the overlayers used in the current study.

Scattering of CO from a CO-covered Ru(0001) surface was studied previously.²⁵ In that study it was found that 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 overlayer. Neither exchange with nor CID of the adsorbed CO was observed in those measurements, which utilized a beam energy of 0.8 eV.

II. EXPERIMENTAL

The current experiments were carried out in a plasma beam scattering apparatus described previously.^{34–36} 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,³⁷ an ion sputter gun, a residual gas analyzer, and a differentially pumped rotatable quadrupole mass spectrometer (QMS). Ar (gas purity 99.999%) plasma was generated in the cascaded arc source.³⁸ 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 QMS angular acceptance was $\sim 1.6^\circ$ assuming a point source at the sample position. 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, TOF analysis and convolution over the spread of arrival times of the incident Ar beam were performed in the manner described in previous scattering studies.^{34,39} Corrections for a trigger delay and the flight time of ions through the QMS have been applied to the raw data.³⁶ For CO desorption, the analysis was the same as has been employed in gas-surface reaction studies,⁴⁰ where the incident and desorbing 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 H_2 (D_2).^{41,42} 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. The Ar beam impinged on the surface at an incident angle (θ_i) of 60° with respect to the surface normal. The outgoing angle (θ_f) of scattered Ar and the desorption angle (θ_d) of CO were also defined with respect to the surface normal. The incident and outgoing/desorption angles are measured in the plane defined by the surface normal and the plasma source and QMS apertures. The surface temperature (T_s) was held constant at 180 K during the measurements.

The main potential contaminant in the scattering chamber was H_2 , with H_2O and ^{12}CO present at lower levels. Residual levels of ^{13}CO were also present as a result of the backfilling procedure. Checks on the level of surface contamination for the bare Ru surface showed <0.1 ML H coverage after ~ 35 min exposure and negligible levels of other contaminants.²² The current measurements all start from a ^{13}CO -saturated surface. This surface fully blocks H_2 adsorption.⁴³ In addition, H_2O does not stick to this surface at 180 K (Ref. 33) and further CO adsorption is impossible. Consequently, contamination of the surface by residual gas molecules only becomes possible once significant depletion of the CO overlayer has occurred and was not significant on the time scale of the individual TOF measurement shown in this paper (~ 1 h). Between each TOF measurement, the surface was flashed to 1530 K and a new ^{13}CO overlayer was prepared. This ensured that there was no cumulative buildup of strongly binding contaminants such as O atoms.

III. RESULTS AND DISCUSSION

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

A. Collision-induced desorption of CO by Ar

Figure 1(a) shows the in-plane angular distribution of desorbing CO intensity that was derived from TOF spec-

FIG. 1. (a) Integrated area of CO TOF spectra as a function of desorption angle for a total exposure to ~ 20 ML Ar. The intensities have been normalized to the intensity of the corresponding direct (Ar) beam. (b) Corresponding energy of the desorbing CO as a function of desorption angle. The line represents the elastic collision model of mass 29 being recoiled by mass 40.

tra measured at different desorption angles. Each data point represents the cumulative desorbed CO intensity arising from a total exposure equivalent to ~ 20 ML of Ar ($1 \text{ ML} = 1.58 \times 10^{15} \text{ atoms/cm}^2$). The largest desorption was measured along the surface normal ($\theta_d = 0^\circ$). The corresponding average energy of the desorbing CO as a function of θ_d is plotted in Fig. 1(b). In contrast to the CO intensity distribution, the energy distribution has a maximum in the region $\theta_d = 30\text{--}45^\circ$. The line in Fig. 1(b) represents the model of direct elastic recoil of CO by an Ar atom. Clearly, such a model 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 illustrated in Fig. 2(a). This shows a time series of CO TOF spectra measured at $\theta_d = 0^\circ$. Seven consecutive spectra were collected. Each individual spectrum in the series corresponds to an exposure of ~ 2.8 ML Ar, with the entire series corresponding to the cumulative exposure of ~ 20 ML. CO desorption is not immediately evident upon exposure to the Ar beam, but 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. This is illustrated in Fig. 2(b), which compares the integrated areas of the TOF spectra measured during #3 of the time series with those of the spectra measured during #7 as a function of θ_d . During TOF #3 the highest intensity is along the surface normal with only minor signal at off-normal desorption angles. In contrast, for TOF #7 significant desorption occurs along a broad range of off-normal angles with a maximum intensity measured at $\theta_d = 30^\circ$.

The high energy of the desorbing CO [Fig. 1(b)] excludes the possibility that its presence in the TOF spectra arises from local heating of the surface by the Ar projectile. A thermal process can also be ruled out on the basis of the change in the angular maximum of the desorbing distribution as a function of exposure. For a thermal process, the desorption maximum would remain along the surface normal irrespective of the fractional coverage of CO (although the angular spread might change). Note that thermal desorption is not entirely ruled out by our measurements, since any such particles would have low energy and, thus, could be hidden in the tail of the TOF spectra. However, it is clear that the signal we are monitoring is not thermally induced.

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 behavior was qualitatively similar at all θ_d studied. Once CO desorption commences, the desorption rate goes through a maximum and then gradually decreases 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 equivalent of ~ 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. Effectively, all CO desorption along the surface normal occurs during an Ar exposure equivalent to ~ 11 ML out of the total ~ 20 ML exposure.

Figure 2(c) shows a cumulative TOF profile derived from the seven spectra shown in Fig. 2(a). The deduced

FIG. 2. (a) Time series of TOF spectra tracking CO desorption along $\theta_d = 0^\circ$. The distributions are collected sequentially from the bottom to the top. They are plotted on the same scale, but are offset for clarity. The total exposure is ~ 20 ML of Ar. Each individual distribution corresponds to an Ar exposure of ~ 2.8 ML. (b) Plot of the integrated areas determined from raw TOF spectra at #3 and #7 in time series measured as a function of θ_d . (c) The cumulative TOF spectrum arising from the average of the seven spectra shown in panel (a). The line through the data points is the result of fitting with a single shifted Maxwell-Boltzmann distribution as described in the text.

intensities and average energies plotted in Figs. 1(a) and 1(b), respectively, have all been derived from such cumulative spectra. The TOF fitting procedure was only applied to the cumulative spectra primarily because of the very low signal-to-noise ratio. The individual TOF spectra in a series were not deemed of sufficient quality to justify a time-dependent determination of $\langle E_t \rangle$. Additionally, given the relatively complex time and angular dependences of the desorption, it is problematic to extract a value for the desorption cross section from the data. Since the TOF spectra illustrate that the rate of depletion is not constant in time, there is not a single cross section but rather a range of coverage-dependent cross sections.

Comparison of the integrated areas of CO measured by TPD from unexposed and postexposure CO-covered surfaces reveals that roughly one-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. Assuming complete CO immobility, this would result in the beam footprint losing between three-quarters and all of the originally adsorbed molecules. Conversely, under an assumption of totally unrestricted CO mobility there would be ~ 0.5 ML 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 surface during the seventh (final) cycle are similar, but not identical, to those of the clean surface. Hence, the beam footprint is not fully depleted of CO. It is

likely that the CO overlayer will reorganize on the nanoscale in response to CID. The driving force for such local diffusion is mutual repulsion of closely packed CO molecules. Such repulsion is strong above $\theta_{CO} = 0.33$ ML.⁴¹ Note that an experimental study by Deckert *et al.* found a diffusion barrier of about 0.48 eV for $\theta_{CO} = 0.27$ ML and 0.27 eV for $\theta_{CO} = 0.58$ ML,⁴⁴ although a theoretical study has claimed almost barrier-free motion.⁴⁵

In order to desorb, CO must gain sufficient energy from the Ar impact to overcome the surface binding energy. Given the relative masses involved (Ar = 40 amu and ^{13}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 $\sim 97\%$ of the translational energy of the Ar atoms in the Baule (impulsive) limit.⁴⁶ However, this large energy transfer requires a very small impact parameter collision between Ar and CO, which is not very probable for the closed overlayer. Of course, given the broad energy range of our beam, the particles in the high energy portion of the incident pulse may be able to induce CID even when the energy exchange in the collision is relatively inefficient. In spite of this, there is a delay in the onset of significant CO desorption, indicating that the saturated overlayer is relatively impervious to the incident beam.

The broad energy range makes it problematic to establish a CID threshold. However, an indication of likely threshold values can be obtained by comparison with other systems. For

example, in the case of Xe and Kr CID of NO from Pt(111) the threshold energies were reported as 2.55 and 2.05 eV, respectively, and those exhibited total energy scaling.⁶ Note that the E_B of NO on Pt(111) (1.08 eV)⁴⁷ is smaller than that of CO on Ru(0001).⁴¹

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_d that could be attained in such a collision is 30° , which corresponds to a recoil angle of 90° with respect to the original Ar direction. Moreover, in such an idealized binary collision, the molecules that are “recoiled” by 90° gain no energy in the “collision.” The theoretical energy that can be gained by an elastically recoiled mass of 29 amu is represented by the model included in Fig. 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 might be applicable. Note the simple collision models we discuss in this paper are only intended for conceptual purposes. A molecular dynamics simulation of the system would be required in order to obtain a precise and detailed picture of the energy partitioning.

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 neighboring 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 neighbors. Redirection by neighboring adsorbates was observed experimentally and theoretically for the Ar/Xe–Pt(111) system.¹⁸ With increasing coverage, the peak of the desorbing Xe angular distribution shifted to the surface normal. That neighboring 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 nonvarying 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.⁴¹ 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 by neighboring molecules result in the blocking of off-normal desorption paths. As θ_{CO} decreases, the overlayer becomes progressively more open and the off-normal desorption trajectories become

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 neighbors).

Collision-induced displacement of CO is feasible since, with an Ar (E_i) of 6 eV, the theoretical maximum translational energy of the CO parallel to the surface after the collision is ~ 4.4 eV (again assuming an optimum single elastic binary collision). Of course, under realistic collision conditions such a large energy transfer will never be realized. Conversely given the broad energy width of our incident beam, the extra energy that can be transferred by the highest energy Ar atoms will indirectly compensate for the losses induced by dissipation to the bulk.

For the saturation coverage, migration of CO is physically blocked by the neighboring molecules. As has been demonstrated using molecular dynamics simulations, adsorbate–adsorbate collisions result in a significant reduction of migration distances.⁴⁸ Hence, any parallel motion induced by an Ar impact will only result in a temporary, localized compression of the overlayer structure, which might induce desorption of either the directly impacted molecule or one of the molecules it interacts with. A recent detailed studies of collision-induced CO migration on Pt(997) shows that more than 80% of the energy transferred is imparted to the lateral translational motion of CO.⁴⁹ Hence, subsequent desorption induced by translationally excited CO is entirely feasible.

As molecules are removed from the surface, displacement over increasingly longer distances becomes possible. In view of results from experiments on transient mobility, we expect the displacement to be limited to, at most, 1 nm.⁵⁰ Simultaneously, the energy required to break the CO–surface bond increases. Ultimately, dissipation of the lateral energy of the CO to the surface may 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.¹⁷ Molecularly chemisorbed N_2 binds weakly with its molecular axis perpendicular to the surface plane, which is similar to the orientation of adsorbed CO. 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 $\theta_i = 60^\circ$ experimental condition leads to rather glancing interactions. While lateral motion is restricted by neighboring CO molecules at high coverage, tilt motion can still reduce the CO binding energy. The importance of molecular orientation in determining the interaction dynamics is illustrated by, for example, the behavior of the NO–Pt(111) system,⁵¹ where a molecule oriented sideways is no longer bound to the surface.

As an intermediate conclusion, we note that CID of CO is almost absent from the saturated surface. The layer is too closely packed to allow sufficiently localized, small impact parameter energy transfer by an Ar projectile. In addition, the

delayed appearance of CO desorption suggests that Ar does not readily penetrate the overlayer structure. Nevertheless, with gradual removal of CO molecules (either from defect sites in the overlayer or by attrition as a result of a small but finite removal probability from the ideal adlayer), localized energy transfer becomes possible and CO is driven off in a secondary process involving CO–CO collisions. At even lower coverage, the primary energized CO molecule can dissipate its lateral translational energy to the lattice before a collision with other CO molecules can lead to desorption.

B. Ar scattering from the CO-covered surface

Turning our attention to the 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 Fig. 3. Different behavior is observed at the three outgoing angles. At $\theta_f = 15^\circ$ no scattered Ar is initially observed. With increasing exposure a small 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 spectra 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 relatively 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 quite similar to those measured from the bare Ru surface (see later). All time series illustrate that the structure of the surface “seen” by Ar changes over the course of the exposure. However, the distributions measured

at grazing outgoing angles are the least sensitive to the changing nature of the surface.

Figure 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 superspecular ($|\theta_f| > |\theta_i|$) direction as compared to TOF #7, which has more intensity along the specular direction ($|\theta_f| = |\theta_i|$). The enhanced superspecular scattering observed for TOF #1 can be attributed to the “soft” nature of the CO-saturated surface. This surface is more likely to produce multiple scattering trajectories, where the Ar is gradually deflected in a series of interactions with individual CO molecules. Such processes tend to favor superspecular scattering. The inset in Fig. 4(a) is an expanded view of the small outgoing angle region illustrating enhanced sub-specular ($|\theta_f| < |\theta_i|$) Ar scattering measured during TOF #7. This indicates that the surface that produces the TOF #7 spectra is rougher than the CO-saturated surface (TOF #1).

Figure 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 Fig. 3). The spectra measured for $\theta_f < 30^\circ$ were fitted with a single distribution because the signal level was considered 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.

For indication purposes, three binary collision models⁵² are illustrated in Fig. 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

FIG. 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. The curves within individual panels are plotted on the same scale, but offset for clarity. The uppermost 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.

FIG. 4. (a) Normalized 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 $\theta_f = 0$ – 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 this panel. From the top these are: Ar (mass 40) scattered by Ru (mass 101); by $2 \times {}^{13}\text{CO}$ (mass 58); and by ${}^{13}\text{CO}$ (mass 29). The inset shows the corresponding normalized intensities of the two components derived from the cumulative TOF spectra.

is for Ru, but any sufficiently heavy scattering centre (for example, collective scattering from a group of CO molecules) could produce comparable final energies. The energy of the slow component is effectively constant as a function of θ_f suggesting a more complex, multiple collision process.

The inset in Fig. 4(b) shows the corresponding normalized angular intensities of the fast and slow components. For both components the bulk of the in-plane scattered particles emerges 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 thermalize at the surface during the collision process. Although the intensities of the Ar components vary with the irradiation time as evident in Fig. 3, no major change in the average energy of the individual components is observed for the various TOF spectra within a series measured at any given θ_f . Hence, the individual scattering processes that lead to the two-component distribution do not appear to be dramatically altered by the changing fractional coverage of the surface. Of course, the average energy of the overall distribution does change during the time series due to changes in the relative contribution from the different components (the effect is most dramatic for $\theta_f = 45^\circ$).

The varying bimodal Ar distributions of the current system can be correlated to the changes in the CO overlayer structure as a result of CID. The final Ar TOF spectra (#7) measured in the various series are qualitatively similar to the corresponding distributions measured from the clean Ru surface, as shown in Fig. 5. However, they differ significantly in absolute scattered intensity. Hence, the Ar data reveal that the beam spot has not been fully depleted of CO. The shapes of the distributions measured from these two surfaces are no-

ticeably different from those measured from the CO-saturated surface.

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° are 2.7, 0.6, and 1.2, respectively. The partially covered surface scatters fewer atoms along the specular direction and somewhat more to the superspecular outgoing angle. There is a dramatic increase in the relative number of subspecularly scattered atoms. The broader angular distribution and enhanced superspecular and subspecular scattering can be attributed to “roughening” arising from the continued presence of CO in the beam spot. In particular, the enhanced subspecular scattering of Ar from the partially covered surface may be due to large impact parameter interactions of Ar with isolated CO molecules following backscattering from the Ru substrate. Such glancing collisions with CO will not significantly change the energy lost in the overall process.

An additional mechanism by which a low partial coverage of CO could influence the angular distribution of the scattered Ar is via 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 alternative scattering sites.

On the saturated surface the incident Ar atoms primarily experience the corrugated potential energy surface generated

FIG. 5. Comparison of TOF spectra from bare (red), partially CO-covered (blue), and CO-saturated (green) Ru(0001) surfaces for spectra measured at $\theta_f = 30^\circ$, 60° , and 75° . The spectra at $\theta_f = 30^\circ$ 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 partially CO-covered surface (TOF #7) were collected during Ar exposure of ~ 17 –20 ML. The intensities have been adjusted on the basis of a normalized direct beam intensity.

by the oxygen atoms. With gradual removal of CO molecules and reconfiguration of the overlayer to a more open structure, Ar begins to experience a more corrugated and disordered surface. The emergence of scattered Ar signal at $\theta_f = 15^\circ$ as the exposure increases is consistent with increasing surface roughness. The subsequent disappearance of this signal indicates the overlayer transitions through a region of “maximum roughness” as a function of the CO coverage.

A single binary collision between Ar and CO cannot deflect Ar to small outgoing angles, as illustrated by the dotted line in Fig. 4(b). Multiple collisions or single collisions with a large effective surface mass (e.g., collective scattering from more than one CO molecule) are required to access $\theta_f < 70^\circ$. 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 Fig. 4(b). Hence, considering the efficient energy transfer that is possible between Ar and ^{13}CO , the slow Ar component can be attributed to such processes.

The average energies of the fast Ar component are compatible with the simple binary collision model of incident atoms from an isolated ruthenium atom [see Fig. 4(b)]. Indeed, for Ar scattering from the partially CO-covered surface, a significant contribution to the overall TOF distribution should be due to scattering from the substrate. Note, however, that the energy loss in scattering of Ar from clean Ru(0001) under the current conditions is far from simple (see Ref. 22). It is more difficult to explain the presence of the fast Ar component when scattering from the saturated surface. This is particularly true for the case of scattering to subspecular outgoing angles, such as trace #1 at $\theta_f = 45^\circ$ in Fig. 3. Since the CO data strongly suggest that Ar cannot easily penetrate the saturated layer, the fast component observed during the early TOF spectra must arise from a CO-mediated interaction.

It should be noted that the fast component that is evident at $\theta_f = 45^\circ$ in the early TOF spectra in Fig. 3 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. 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.

In a study of Xe and Kr collision-induced NO desorption from Pt(111), Velic and Levis 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 if incident Ar atoms were used.⁶ The recollision could transfer a significant fraction of the initial energy back to the Ar. The Ar/ ^{13}CO mass ratio also allows for efficient energy exchange. Hence, it is conceivable that the fast component that is observed at $\theta_f = 45^\circ$ during the early TOF spectra arises from a recollision between the recoiled CO and Ar, which would simultaneously act to suppress CO desorption. 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 makes the initial hard (small impact parameter) collisions necessary to realize a double-collision process, difficult to envisage.

Alternatively, a fast Ar component can be scattered to subspecular angles if it interacts 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. Scattering from a combined CO–Ru unit can also explain high energy subspecular scattering. Note that the fast component observed during the early TOF spectra is quite well defined. If this component does indeed arise from scattering by a collective mass (either several CO molecules or CO–Ru), it suggests that a very discrete and distinct scattering site is involved and that this site (and hence the associated

scattered signal) 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 alteration of the Ar TOF distributions. CO depletion reduces the mutual shadowing effect of adjacent molecules, increasing the range of accessible impact parameters between Ar and CO. As a consequence, the probability of a small impact parameter collision increases and CO desorption is enhanced. Once the concentration of CO in the beam spot has been substantially reduced, the measured Ar distributions begin to resemble scattering from the Ru substrate. Hence, the fast component that emerges in the later TOF spectra in Fig. 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). As a consequence, the Ar TOF distributions might never fully converge to those obtained from the clean surface.

IV. CONCLUSIONS

The interaction of hyperthermal Ar atoms with the ^{13}CO -covered Ru(0001) surface was studied. Ar collision-induced desorption of CO was observed along the surface normal. This is a secondary process involving lateral interaction with neighboring CO molecules. CID is not initially observed, indicating that penetration of the saturated overlayer by the incident Ar is difficult. The initial Ar TOF distributions are dominated by scattering from CO. Scattered Ar can lose a large fraction of its energy at the surface due to efficient energy transfer to the adsorbed CO. As the surface coverage gets gradually reduced, CID becomes more effective and Ar ultimately removes a significant fraction of the adsorbed CO. However, with even further reduction of the CO partial coverage the efficiency of CID again drops. Scattering from the Ru substrate becomes the dominant process, with the remaining molecules primarily acting as modifiers of Ar trajectories.

ACKNOWLEDGMENTS

This work is part of the research program of the “Stichting voor Fundamenteel Onderzoek der Materie (FOM)” and is supported financially by the “Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).” It is supported by the European Communities under the contract of Association between EURATOM and FOM and carried out within the framework of the European Fusion Programme. The views and opinions expressed herein do not necessarily reflect those of the European Commission. The authors are grateful to Dr. A. Fielicke and Dr. B. Redlich for the provision of isotopically labelled CO gas.

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