Electron transfer mediates vibrational relaxation of CO in collisions with Ag(111)
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Roman J. V. Wagner, Bastian C. Krüger, G. Barratt Park, Mareike Wallrabe, Alec M. Wodtke and Tim Schäfer

We report experimental results on the state-to-state vibrational relaxation of CO(v = 17) in collisions with Ag(111) at incidence translational energies between 0.27 eV and 0.57 eV. These together with previous results provide a comprehensive set of data on two molecules (CO and NO)—one open and one closed shell—and two metals (Ag and Au). In all four cases, the incidence vibrational energy has been varied over several eV. We find a unifying relation between the probability of vibrational relaxation and the energetics of electron transfer from the metal to the molecule. This argues strongly that electronic friction based theories are not capable of explaining these data.

Introduction

Energy transfer from a solid metal’s electron–hole pairs (EHPs) to a molecule’s vibration was already evident when Rettner et al. showed that NO could become vibrationally excited in specular collisions with a hot Ag(111) surface even at low incidence translational energy yet, the mechanism for this type of Born–Oppenheimer approximation (BOA) failure in molecule–surface interactions remains a matter of debate. Since Rettner et al., vibrationally excited NO interacting with Au(111) has become a benchmark system for testing theoretical models beyond the Born–Oppenheimer approximation—these topics have been reviewed. There is evidence that electron transfer (ET) forming a transient negative ion is a crucial part of the mechanism of BOA failure. In this picture, electronic non-adiabaticity involves hops between a neutral and an anionic potential energy surface.

While these two theoretical models have similarities, they are derived using fundamentally different assumptions and describe physically different mechanisms. However, both theories fail to predict the correct amount of vibrational energy transferred to the surface and the incidence translational energy dependence of the vibrational relaxation probability. Since neither has succeeded in accounting for experimental observation, it is difficult to assess the validity of electronic friction versus surface hopping (ET). In this work, we show measurements that qualitatively distinguish between these two mechanisms without making quantitative comparisons to theory.

If electron transfer initiates BOA failure, the surface work function, \( \Phi \), and the molecule’s ability to bind an electron determine the energetics of the BOA failure. The work function and the molecule’s electron binding energy define the energy by which the molecule’s affinity level needs to be stabilized such that the anionic and the neutral diabats cross and the ET becomes energetically feasible. Scattering experiments in which the surface work function and the molecule’s electron binding energy are systematically varied allow the comparison of conditions that sample the ET curve crossing to those that do not. This requires a set of data for more than one molecule (variation of electron binding energy) and more than one surface (variation of work function).

Of course, the crossing is actually a seam in a high dimensional space and it depends strongly on the molecule’s distance from the surface and its vibrational coordinate. Hence, we choose molecules whose incidence vibrational and translational energy can be varied over as wide a range as possible.

NO is an ideal choice. Forming molecular beams of NO is a convenient way to control incidence translational energy. For controlling vibrational excitation, infrared overtone pumping and stimulated emission pumping (SEP) are both possible. Furthermore, background produced by competing spontaneous emission can be reduced.

CO is our second molecule. Forming CO molecular beams is straightforward as is overtone pumping. Unfortunately, for CO, SEP requires complex light sources in the vacuum UV making its implementation more difficult than for NO. Nevertheless, it is now possible to produce CO(v = 17) by the newly
developed PUMP-PUMP-PERTURB-DUMP (P3D)\textsuperscript{30} approach, which we will describe below.

To vary the work function of the solid we chose two similar metals, Ag(111) (\(\Phi = 4.7\) eV) and Au(111) (\(\Phi = 5.3\) eV). NO and CO interact weakly with both metals, the metals’ electronic structures are similar, and even their lattice constants are similar. For NO\((v)\), vibrational inelasticity has been studied on Au(111) and Ag(111)—the vibrational relaxation probability of highly vibrationally excited NO is significantly higher at Ag(111) (\(\Phi = 4.7\) eV) than at Au(111) (\(\Phi = 5.3\) eV).\textsuperscript{31} Furthermore, varying the thickness of atomically defined Ag thin films on Au(111) showed a clear correlation between vibrational relaxation probability and surface work function.\textsuperscript{32}

We have also employed P3D to study scattering of CO\((v = 17)\) from Au(111).\textsuperscript{33} The final vibrational state distribution indicates significantly less vibrational relaxation than is observed for NO scattered from Au(111). This observation is expected for an ET mediated process considering the reduced electron affinity of CO (\(E_A = -1.5\) eV) compared to NO (\(E_A = 0.03\) eV).

Table 1 displays previously investigated systems of highly vibrationally excited molecules scattered from metal surfaces. The molecule’s electron affinity and the metal’s work function exert a strong influence on the relaxation probability.

In this work, we complete a minimal data set needed to investigate the influence of electron affinity and work function by reporting experiments on the scattering of highly vibrationally excited CO\((v = 17)\) from Ag(111). As expected for an ET mediated interaction, we observe more efficient vibrational relaxation compared to scattering of CO\((v = 17)\) from Au(111). Combining all available data, we also find a unifying relation between the probability of vibrational relaxation and the energetics of electron transfer from the metal to the molecule.

### Experimental

Fig. 1 depicts the experimental apparatus used in this work. A pulsed supersonic expansion of CO is produced using a home-built nozzle. After passing through a differentially pumped chamber, the beam enters the scattering chamber mounted near 10\textsuperscript{−10} Torr. We tune the incidence translational energy of the molecular beam between 0.27 eV and 0.57 eV by seeding different amounts of CO in \(\text{H}_2\) carrier gas. We clean Ag(111) (MaTeK, 99.999% purity) by Ar-ion sputtering (LK Technologies, NGI 3000, 3 kV, 20 mA emission current, 12 \(\mu\)A surface current, 20 min) and subsequent annealing (870 K, 20 min). The cleanliness of the surface is probed by Auger electron spectroscopy (ESA-150, Staib Instruments). No chemical impurities can be found on the surface after 9 h exposure to the molecular beam. Scattering experiments using Ag(111) are performed at a surface temperature of 400 K; for experiments using a chlorinated silver surface, the temperature was 300 K. The chlorinated Ag(111) surface was prepared by leaking molecular chlorine into the chamber. The clean surface was exposed to a pressure of $5 \times 10^{-8}$ Torr Cl\(_2\) for 5 min. Following the procedure by Wu \textit{et al.}, the chlorine Auger signal was monitored in order to ensure that the dosed amount of chlorine leads to the desired increase of the work function by 1.5 eV.\textsuperscript{34}

Highly vibrationally excited CO is produced by the PUMP-PUMP-PERTURB-DUMP (P3D) method.\textsuperscript{30} First, a laser pulse (PUMP 1) transfers CO molecules from the ground state \(X\Sigma^+(v = 0)\) to the first electronically excited triplet state \(a^3\Pi(v = 0)\) using 1 mJ of 206.29 nm laser radiation generated by mixing the fourth harmonic of a Nd:YAG laser (Lab 170-10, Spectra Physics) with

<table>
<thead>
<tr>
<th>Work function: high ((\Phi = 5.3) eV)</th>
<th>Work function: low ((\Phi = 4.7) eV)</th>
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<tbody>
<tr>
<td>Electron affinity: high ((E_A = 0.03) eV)</td>
<td>NO((v = 11)/\text{Au}(111))\textsuperscript{12}</td>
</tr>
<tr>
<td>Medium vibrational relaxation</td>
<td>Strong vibrational relaxation</td>
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<tr>
<td>Electron affinity: low ((E_A = -1.5) eV)</td>
<td>CO((v = 17)/\text{Au}(111))\textsuperscript{13}</td>
</tr>
<tr>
<td>Weak vibrational relaxation</td>
<td>This work</td>
</tr>
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<td></td>
<td>Medium vibrational relaxation</td>
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the output of a home-built narrow-band injection seeded optical parametric oscillator (OPO), pumped by the second harmonic of the same Nd:YAG laser.\textsuperscript{35} In a second step (PUMP 2), we excite the $\epsilon^3 \Sigma^+ \left( v = 12 \right) \rightarrow \Delta^1 \Pi \left( v = 0 \right)$ transition using a 2.0 mJ pulse at 368.86 nm produced by the frequency doubled output of a dye laser (Spectra Physics PDL-2, Styril 8 (LDS 751) by Exciton), pumped by the second harmonic of a Nd:YAG laser (Continuum Powerlite 9010). A perturbation between $\epsilon^3 \Sigma^+ \left( v = 12, J = 1 \right)$ and $\Delta^1 \Pi \left( v = 8, J = 1 \right)$ (PERTURB) lends oscillator strength to the normally forbidden stimulated emission (DUMP) transitions to the $X^1 \Sigma^+ \left( v = 17 \right)$ level. For the DUMP step, we use the frequency doubled output of a dye laser (Sirah Precision Scan, Coumarin C480), pumped by the third harmonic of a Nd:YAG laser (Continuum Powerlite 9010) to generate 2.4 mJ per pulse at 234.16 nm.

We detect scattered CO molecules in $X^1 \Sigma^+ \left( 14 \leq v_i \leq 18 \right)$ using $\left( 1 + 1 \right) \Delta^1 \Pi \left( v', J' \right) \leftarrow X^1 \Sigma^+ \left( v, J \right)$ REMPI detection covering the wavelength range 228–245 nm with the frequency doubled output of a dye laser (Sirah Precision Scan, Coumarin C480), pumped by the third harmonic of a Nd:YAG laser (Spectra Physics Lab 230-10). Ions are detected on multi-channel plates (MCP, tectra, chevron configuration, 25 mm diameter). The signal is recorded at an oscilloscope (LeCroy, Waverunner LT344), which is connected to a personal computer (PC).

We record REMPI spectra both with the DUMP laser turned on and turned off. When the DUMP laser is turned off, CO molecules in $X^1 \Sigma^+ \left( 14 \leq v_i \leq 18 \right)$ are produced by spontaneous fluorescence and inelastic scattering. When the DUMP laser is turned on, differences in signals result directly from the enhanced population of $X^1 \Sigma^+ \left( v = 17, J = 0 \right)$. Thus the DUMP-off spectrum is a background that is subtracted in the data analysis.

Results

Fig. 2 shows REMPI spectra of scattered CO after CO($v = 17$) collides with Ag(111) and Au(111), in both cases at an incidence translational energy of 0.4 eV. Vibrational bands are well resolved and can easily be assigned. The difference in the band intensity when the DUMP laser is on versus off indicates population in final vibrational states due to incident CO($v = 17$). It is obvious that the relaxation probability of CO($v = 17$) is higher for collisions with Ag(111) than for collisions with Au(111). For Au, only bands probing the prepared state (8–17 and 7–17) increase in intensity with the DUMP laser turned on, whereas for Ag, every band in the spectrum increases.

Fig. 3 shows the effect of surface chlorination on the scattering of incident CO($v = 17$). Here, the work function is 6.2 eV and the vibrational relaxation probability is greatly reduced. We have used scattering from this surface as a convenient control—i.e. relaxation probability is close to zero—to derive absolute relaxation probabilities under other conditions by comparison of relative signal intensities. See ESI.\textsuperscript{†}

Fig. 4 shows angular distributions of state selected scattered molecules. The angular distributions are all narrow, indicating a direct scattering process. Furthermore, the final rotational energy of rotationally-inelastically scattered molecules and the final translational energy of rotationally- and vibrationally-elastically scattered molecules increase with incidence translational energy. These observations strongly suggest a direct scattering mechanism; a trapping-and-desorption mechanism is excluded for all presented results.
Using REMPI spectra and angular distributions like those mentioned above, we derive the vibrational state scattering distributions. See ESI† for detailed information about the analysis method. Fig. 5 displays the calculated distributions for incident CO($v = 17$) scattered from three surfaces: Au(111), Ag(111), and chlorinated Ag(111) at $E_i = 0.57$ eV. Whereas vibrational relaxation is close to absent on the chlorinated surface, it is stronger on Au(111) and strongest on Ag(111). For Au(111) and chlorinated Ag(111), all molecules scatter into $v = 14$. For Ag(111), about 60% of scattered CO molecules populate vibrational states below $v = 14$. Vibrational excitation is not observed in any case.

Fig. 6 displays the incidence translational energy dependence of the vibrational state scattering distributions for CO($v = 17$) scattered from Ag(111). The survival probability of the incident vibrational state decreases with increasing incidence translational energy.

Discussion

The strategy taken in this work is to aggregate data from multiple scattering systems for which the molecules’ electron binding energies and the solids’ work functions are varied. Fig. 7 provides an overview of different molecule–surface systems and different initial vibrational excitations. Here, relaxation probability is plotted versus incidence translational energy both at low and high incidence vibrational excitation. While the vibrational relaxation probability obviously depends on incidence translational energy, the ordering of the six data sets (from low to high probability) does not.

The relaxation probability is very sensitive to the initial vibrational excitation because the effective electron affinity depends on the vibrational state. This is due to the fact that the seam of crossing to the anionic potential energy surface is located at diatomic bond lengths greater than the corresponding neutral molecule’s equilibrium bond length. Therefore, we introduce the vertical electron binding energy, $E_v(r_{out})$, the energy difference between the neutral and anionic molecules at the outer classical turning point, $r_{out}$, of a specific vibrational state, $v$. The difference between this and the work...
function, $E_v(r_{out}) - \Phi$, describes the energy needed to transfer an electron from the metal to the molecule when the molecule is still far from the surface.

Fig. 8(a) shows this is a useful indicator of the likelihood of vibrational relaxation. Here, we plot vibrational relaxation probability versus $E_v(r_{out}) - \Phi$ for several scattering experiments. The graph includes different surfaces, different molecules, and different initial vibrational states. All these systems follow a common trend, showing an increase of the relaxation probability from 0 to 1 between $E_v(r_{out}) - \Phi = -5.25$ and $-3.5$ eV.

This trend reflects the distance of the molecule from the surface when ET occurs, as image charge interaction stabilizes the anion closer to the surface. Fig. 8(b) shows the image charge stabilization (ICS) as a function of distance from the surface. The ICS is computed by using eqn (1) of ref. 36. The onset of vibrational relaxation occurs for an $E_v(r_{out}) - \Phi \sim -5.25$ eV—ICS of this magnitude requires a close approach of 1.75 Å. When $E_v(r_{out}) - \Phi \sim -3.5$ eV, the required ICS is smaller, and the molecule need only approach to within 2.2 Å to reach the curve crossing for ET. Hence, the distance of the molecule’s closest approach appears to be in the region of 1.75 and 2.2 Å—these values agree well with DFT calculations for the repulsive wall which give 1.9 Å for CO/Au(111), 2.0 Å for NO/Au(111), 2.2 Å for CO/Ag(111), and 1.9 Å for NO/Ag(111). Here, we estimate the position of the repulsive wall by calculating the molecule–surface distance at which the interaction energy reaches a value of 0.5 eV.

Thus it is easy to understand why the curve of Fig. 8(a) appears as it does—ICS can easily compensate $E_v(r_{out}) - \Phi = -3.5$ eV at reasonably large distances from the surface. However, if $E_v(r_{out}) - \Phi \leq -5.25$ eV, the molecule cannot approach the surface closely enough to compensate this energy gap before encountering the repulsive part of the potential.

In the intermediate regime where $E_v(r_{out}) - \Phi$ is between $-3.5$ eV and $-5.25$ eV, the relaxation probability varies between 0 and 1.
Notice that in the intermediate case, we observe a strong dependence on $E_i$. See Fig. 7. For these systems, the relaxation probability critically depends on the closest approach of the molecule to the surface and the resultant ICS. Increased $E_i$ allows closer approach to the curve crossing, resulting in increased relaxation probability.

**Conclusions**

The aggregated results presented here show that the vibrational relaxation probability for CO and NO scattering from Au or Ag can be predicted knowing only the solid’s work function and the molecule’s vibrational state specific vertical electron binding energy. This strongly argues that electron transfer involving surface hopping governs the electronically non-adiabatic vibrational energy transfer in these systems.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**