Supporting Information:

Vibrational Relaxation of Highly Vibrationally Excited CO Scattered from Au(111): Evidence for CO^- Formation

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Introduction

We scatter highly vibrationally excited CO from a Au(111) surface. Prior to surface collision, the molecules are prepared in the single rovibrational state $X^1\Sigma^+(v'' = 17, J'' = 0)$ using the P^3D technique.[1] We use quantum state specific (1+1) $A^1\Pi(v', J') \leftarrow X^1\Sigma^+(v'', J'')$ REMPI detection in order to detect scattered molecules populating the vibrational levels $v'' = 14, 15, 16, 17$ after surface collision. In the following, we will derive the final vibrational state distribution of scattered CO from the measured REMPI spectra. The quantitative determination of final vibrational state distributions requires that the number of scattered molecules populating the detected vibrational levels equals the number of incident molecules prepared in the $X^1\Sigma^+(v'' = 17, J'' = 0)$ state. By analyzing REMPI spectra of the incoming beam as well, we show that this requirement is fulfilled.

Quantitative Analysis of REMPI Spectra

In P^3D, single quantum state preparation of CO in the $X^1\Sigma^+(v'' = 17, J'' = 0)$ state, also referred to as the dump sate, is achieved by stimulated emission ("dumping") from the perturbed $e^3\Sigma^-(v'' = 12, J'' = 1)$ level. However, populating other vibrational levels by means of fluorescence ("Franck-Condon pumping") cannot be avoided, leading to an undesired background in the REMPI spectra of surface scattered molecules. In order to subtract the Franck-Condon background, we recorded REMPI spectra for highly vibrationally excited CO prepared by dumping (dump laser on) and by Franck-Condon pumping (dump laser off).

The REMPI spectrum comprises different vibrational bands v'-v''. Analyzing each of these bands yields a number proportional to the population of the respective vibrational level v''. As an example, we demonstrate the analysis of the REMPI spectra using a single v'-v'' band.

The number proportional to the population of v'' is then given by

$$N_{\mathrm{s},\,v'\text{-}v''} \propto \left(\int \frac{S^{\mathrm{DUMP}}_{v'\text{-}v''}(\tilde{\nu})}{P_{\mathrm{REMPI}}(\tilde{\nu})} \mathrm{d}\tilde{\nu} - \beta_{\mathrm{FCP}} \cdot \int \frac{S^{\mathrm{FCP}}_{v'\text{-}v''}(\tilde{\nu})}{P_{\mathrm{REMPI}}(\tilde{\nu})} \mathrm{d}\tilde{\nu} \right) \cdot \gamma_{v'\text{-}v''} \cdot \langle v_{\mathrm{i}} \rangle \cdot \langle v_{\mathrm{s}} \rangle \cdot \Gamma(U) \cdot \Delta\Theta(\theta) \cdot \Delta\tau(t).$$

The subscript s refers to the scattered beam, v' denotes the v'-v'' band used for analysis. The REMPI signal S is a function of the wavenumber $\tilde{\nu}$ and has been measured for the dump laser turned on (DUMP) and for the dump laser blocked (FCP). We correct the REMPI signal by the online measured REMPI laser power $P_{\mathrm{REMPI}}(\tilde{\nu})$. Note that the REMPI signal scales linearly with $P_{\mathrm{REMPI}}(\tilde{\nu})$, indicating that the first step of the (1+1) REMPI process is saturated. The Franck-Condon background is subtracted from the signal after having integrated the spectra over the respective vibrational band. Note that the Franck-Condon background needs to be corrected by a depletion factor β_{FCP} since driving additional population in the $X^1\Sigma^+(v'' = 17, J'' = 0)$ state by dumping reduces Franck-Condon pumping into other states. In order to determine β_{FCP}, REMPI spectra of the vibrational bands are measured prior to surface collision with dump on and dump off. Density-to-flux conversion for laser preparation and detection of highly vibrationally excited CO is achieved by multiplication with the mean velocity of the incident $\langle v_{\mathrm{i}} \rangle$ and the scattered $\langle v_{\mathrm{s}} \rangle$ beam, respectively. $\Gamma(U)$ accounts for the voltage dependent gain of the multi-channel plate (MCP) detector. As the intensity of the REMPI signal depends on the angular and temporal spread of the scattered beam, we measure angular and temporal distributions as a function of scattering angle θ and time of flight t, respectively, and determine the distribution's full width at half maximum $\Delta\Theta(\theta)$ and $\Delta\tau(t)$. Finally, $N_{\mathrm{s},\,v'\text{-}v''}$ is yielded

by multiplication with a vibrational band specific detection efficiency $\gamma_{v'\text{-}v''}$. For experimentally determination of $\gamma_{v'\text{-}v''}$, we prepare highly vibrationally excited CO in the incident beam by means of Franck-Condon pumping and measure the corresponding REMPI spectra. The vibrational distribution in the incoming beam is proportional to Einstein *A* coefficients which we calculate using the programs RKR1 2.0 and LEVEL 8.0.[2, 3] Integration of the individual vibrational bands and division by the expected vibrational populations gives $\gamma_{v'\text{-}v''}$.

Determination of Final Vibrational State Distribution

As has been shown before, analyzing a certain *v*'-*v*'' band yields $N_{\mathrm{s},\, v'\text{-}v''}$ which is the population of *v*'' after scattering CO $X^1\Sigma^+$(*v*'' = 17, *J*'' = 0) from Au(111). If more than one vibrational band is available for the determination of the population of a certain *v*'', $N_{\mathrm{s},\, v''}$ is given by the mean value. Relative vibrational populations $R_{\mathrm{s},\, v''}$ are given by

$$R_{\mathrm{s},\, v''} = \frac{N_{\mathrm{s},\, v''}}{\sum_{v''=14}^{17} N_{\mathrm{s},\, v''}}$$

Number of Incident Molecules *versus* Number of Scattered Molecules

A quantitative analysis of the REMPI spectra is reasonable if the number of scattered molecules N_s leaving the surface in the detected vibrational states $14 \le v'' \le 17$ equals the number of molecules in the incident beam N_i. As a proof, we calculated the ratio $N_\mathrm{s}/N_\mathrm{i}$.

$$\frac{N_\mathrm{s}}{N_\mathrm{i}} = \frac{\sum_{v''=14}^{17} N_{\mathrm{s},\, v''}}{N_{\mathrm{i},\, v''}}$$

For the determination of N_i, REMPI spectra of the incoming beam are measured for both dump on and dump off. The analysis of these REMPI spectra follows the aforementioned analysis of REMPI spectra. For three different incident translational energies, 0.26 eV, 0.41 eV, and 0.57 eV, we calculate fractions of scattered molecules of 45%, 35%, and 107%, respectively. These values correspond to a lower limit because we omit corrections for angular distributions and time-of-flight distributions as the measurements were performed extremely close to the surface. The scatter of these values indicates the large error connected to this kind of estimation.

Furthermore, we probe low vibrational states (*v* = 1, *v* = 2) in the scattered beam using a (2+1) REMPI scheme *via* the B state. We cannot detect any population in these states, supporting the hypothesis that relaxation to low vibrational states does not occur.

Density Functional Theory (DFT) Calculations

The DFT calculations were performed with the FHI-aims code[4] using the spin-restricted GGA-RPBE functional and a tight basis set for CO. For NO the calculations were carried out using the same GGA functional with the spin-unrestricted approach and a light basis set. The Au(111) surface was modelled by a 4-layered (3×3) cell with a vacuum layer of 20 Å. A 4×4×1 mesh in the reciprocal space was used. The interaction energy of the CO (NO) molecule with the surface was calculated as a

function of center-of-mass distance from the surface for the bridge, *fcc* and *hcp* symmetry sites with the O-up molecular orientation. The surface plane is located at the center of the surface gold atoms. As an estimation for the position of the repulsive wall, we took the distance at which the interaction energy reaches the value of 0.5 eV (similar to the incidence energies used in the experiments) giving 1.9 Å for CO and 2.0 Å for NO. These values were taken to calculate the vertical electron binding energy for the closest approach to the surface (see Figure 4).

References

(1) Bartels, N.; Schäfer, T.; Hühnert, J.; Field, R. W.; Wodtke, A. M. Production of a Beam of Highly Vibrationally Excited CO Using Perturbations. *J. Chem. Phys.* **2012,** *136*, 214201.

(2) Le Roy, R. J. *RKR1 2.0, A Computer Program Implementing the First-Order RKR Method for Determining Diatomic Molecule Potential Energy Functions,* University of Waterloo, (CP657R), **2004**.

(3) Le Roy, R. J. *LEVEL 8.0, A Computer Program for Solving the Radial Schrödinger Equation for Bound and Quasibound Levels,* University of Waterloo, (CP-663), **2007**.

(4) Blum, V.; Gehrke, R.; Hanke, F.; Havu, P.; Havu, V.; Ren, X.; Reuter, K.; Scheffler, M. *Ab Initio* Molecular Simulations with Numeric Atom-Centered Orbitals. *Comput. Phys. Commun.* **2009**, *187*, 2175-2196.