

Supplementary information:

**Electron transfer mediates vibrational relaxation of CO in collisions with Ag(111)**

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## Introduction

Vibrational state distributions are extracted from the resonance-enhanced multi-photon ionization (REMPI) spectra by a method similar to the one described previously for the vibrational relaxation of highly vibrationally excited CO on Au(111).<sup>[1]</sup> Small adjustments to the analysis are needed because of the increased vibrational relaxation on Ag(111). However, most of the derivation that is printed here has been lifted from the supporting information of Reference [1].

We scatter highly vibrationally excited CO from a Ag(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<sup>3</sup>D technique.<sup>[2]</sup> We use quantum state specific  $(1 + 1) A^1\Pi(v', J') \leftarrow X^1\Sigma^+(v'', J'')$  REMPI spectroscopy in order to detect final vibrational states,  $v_f$ , of the scattered molecules. The detection scheme allows us to detect the vibrational levels  $14 \leq v_f \leq 17$ . However, CO( $v = 17$ ) relaxes to vibrational levels below  $v = 14$  in collisions with Ag(111). In order to determine final vibrational state distributions, we also scatter highly vibrationally excited CO from a chlorinated Ag(111) surface, at which the vibrational relaxation is suppressed. Experiments with chlorinated silver serve as a reference, so that the total number of scattered molecules can be determined. With the help of this number, the fraction of molecules scattered into a certain vibrational state can be calculated for the scattering from clean Ag(111).

## Quantitative analysis of REMPI spectra

Incident CO is prepared in the single rovibrational state  $X^1\Sigma^+(v'' = 17, J'' = 0)$  by means of stimulated emission (also referred to as dumping) from the perturbed  $e^3\Sigma^-(v'' = 12, J'' = 1)$  state.<sup>[2]</sup> Unfortunately, fluorescence (also referred to as Franck-Condon pumping (FCP)) from the  $e^3\Sigma^-(v'' = 12, J'' = 1)$  state cannot be avoided and populates other vibrational states,  $14 \leq v \leq 18$ . This leads to an undesired background signal in the REMPI spectra of scattered molecules. In order to determine the magnitude of the Franck-Condon background signal, REMPI spectra of scattered CO are measured with both the dump laser turned on and the dump laser turned off.

The REMPI spectrum comprises different vibrational bands  $v'-v''$ . The integral of each band is a measure of 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

$$N_{s, v'-v''} \propto \left( \int \frac{S_{v'-v''}^{\text{dump on}}(\tilde{\nu})}{P_{\text{REMPI}}(\tilde{\nu})} d\tilde{\nu} - \beta_{\text{FCP}} \cdot \int \frac{S_{v'-v''}^{\text{dump off}}(\tilde{\nu})}{P_{\text{REMPI}}(\tilde{\nu})} d\tilde{\nu} \right) \cdot \gamma_{v'-v''}^{-1} \cdot \langle v_i \rangle \cdot \langle v_s \rangle \cdot \Gamma(U)^{-1} \cdot w_{\text{ang}} \cdot w_v.$$

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 with the dump laser turned on and with the dump laser blocked. We correct the REMPI signal for the online measured REMPI laser power  $P_{\text{REMPI}}(\tilde{\nu})$ . Note that the REMPI signal scales linearly with  $P_{\text{REMPI}}(\tilde{\nu})$ , indicating that the first step of the  $(1 + 1)$  REMPI process is saturated. The Franck-Condon background (dump off) is subtracted from the signal (dump on) after the spectrum has been integrated over the respective vibrational band. Note that the Franck-Condon background needs to be corrected by a depletion factor  $\beta_{\text{FCP}}$  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  $\beta_{\text{FCP}}$ , REMPI spectra of the vibrational bands are measured

prior to surface collision with dump on and dump off. Density-to-flux conversion for both laser preparation and laser detection of highly vibrationally excited CO is performed by multiplying the signal by the mean velocity of the incident ( $v_i$ ) and the scattered ( $v_s$ ) beam, respectively.  $\Gamma(U)$  is the voltage-dependent gain of the multi-channel plate (MCP) detector.<sup>1</sup> As the intensity of the REMPI signal depends on the angular and temporal spread of the scattered beam, we measure both angular and temporal distributions and determine the distribution's full width at half maximum  $w_{\text{ang}}$  and  $w_v$ , respectively. Finally,  $N_{s, v'-v''}$  is yielded by multiplication with a vibrational band specific detection efficiency  $\gamma_{v'-v''}$ .<sup>2</sup> For experimental determination of  $\gamma_{v'-v''}$ , 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.<sup>[3,4]</sup> Integration of the individual vibrational bands and division by the expected vibrational populations gives  $\gamma_{v'-v''}$ .

### Determination of final vibrational state distribution

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

$$R_{s, v''} = \frac{N_{s, v''}}{N_s},$$

where  $N_s$  is the total number of scattered molecules. Following the aforementioned procedure,  $N_s$  has been determined by analyzing REMPI spectra of CO( $v = 17$ ) scattered from chlorinated Ag(111). Here, all scattering products can be found in the detection range of the employed REMPI scheme. Thus,  $N_s = \sum_{v''=14}^{17} N_{s, v''}$ .

### References

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- [3] 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**.
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<sup>1</sup> Note that  $\Gamma(U)$  is reciprocally defined as in Reference [1].

<sup>2</sup> Note that  $\gamma_{v'-v''}$  is reciprocally defined as in Reference [1].