

## Supplementary Materials

### Simulation of NO REMPI spectra

Simulated spectra are set up as follows: line positions of relevant transitions belonging to bands listed in Table I of the main text are calculated using Brown's Hamiltonian<sup>1</sup> and spectroscopic constants from Ref. 2, 3 (X state except for the  $\lambda$ -splitting constants) and Ref. 4 (A state and  $\lambda$ -splitting constants). It is assumed that the rovibronic line shapes are given by a Lorentzian function with fixed bandwidth determined by a preliminary analysis of the spectra. We correct for the Hönl-London factors and for the intermediate state  $M$ -distribution calculated according to the expressions given by Jacobs and Zare.<sup>5, 6</sup> Fit parameters are the population factors for each individual  $J$ -state, the branching ratio between the two spin-orbit states ( $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$ ) per vibrational state and the population factor for each vibrational band. Since we observe identical rotational state distributions for each pair of spin orbit states with given vibrational quanta, we reduce the number of fitting parameters accordingly. By minimizing the difference between model and experimental intensities optimal values for the population factors are obtained. These are proportional to the density of molecules scattered back in each quantum state given by  $J$ ,  $\Omega$  and  $v$ . This density related quantity is transformed into the flux equivalent by correcting for the final speed of the molecule. Figure A shows a comparison between experiment and simulation for the  $\gamma(1,8)$  band.

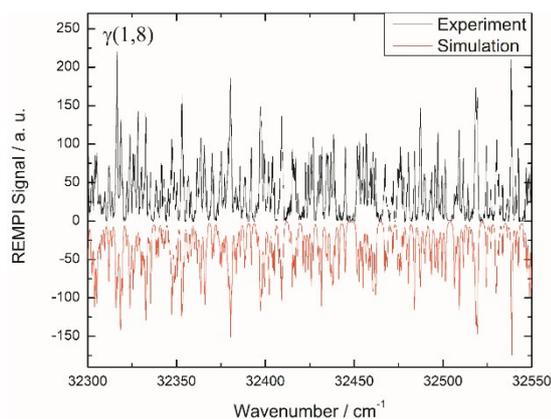


Figure A: Comparison between experiment and simulation. NO molecules in  $v_i = 11$  are scattered with  $E_i = 0.51$  eV from a Au(111). The backscattered molecules are detected using 1+1 REMPI spectroscopy via the A state of NO. The figure shows a part of the  $\gamma(1,8)$  band. The black line shows the experimental spectrum, the red line shows the simulation.

To derive rotational state distributions with using the same vertical scale, we can make use of the information on the

vibrational state distribution available from over 30 vibrational bands in the 1+1 REMPI spectra in the range of 245 nm to 315 nm. Since the spectra are partially heavily congested it is necessary to implement a model with fixed rotational state distributions. This procedure is described in detail in the Supplementary Material of reference 7. For the sake of completeness we show the relative population of each rotational state as derived from a combined analysis in Figure B.

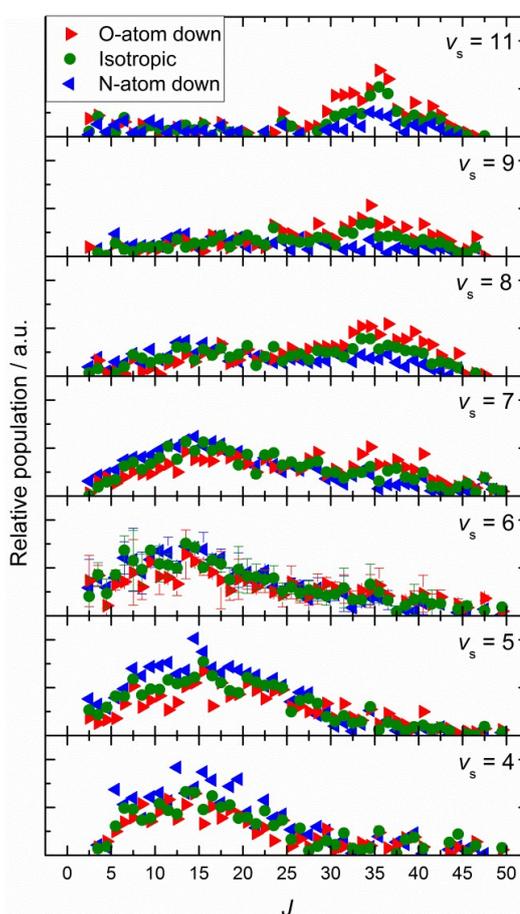


Figure B: Rotational state distributions for the same incidence conditions as in Fig. 1 of the main article. Here, we plot the distributions using the same vertical scale normalizing to the final vibrational state distribution deduced in a prior publication.<sup>7</sup> The relative population of the vibrational states is derived from a fit with fixed rotational state distributions to the complete 1+1 REMPI spectrum from 245 nm to 315 nm as described in reference 7.

### Notes and references

1. J. M. Brown, E. A. Colbourn, J. K. G. Watson and F. D. Wayne, *Journal of Molecular Spectroscopy*, 1979, **74**, 294-318.

2. A. M. Wodtke \*, J. C. Tully and D. J. Auerbach, *International Reviews in Physical Chemistry*, 2004, **23**, 513-539.
3. C. Amiot, *Journal of Molecular Spectroscopy*, 1982, **94**, 150-172.
4. J. Danielak, U. Domin, R. Ke, M. Rytel and M. Zachwieja, *Journal of Molecular Spectroscopy*, 1997, **181**, 394-402.
5. D. C. Jacobs, R. J. Madix and R. N. Zare, *J Chem Phys*, 1986, **85**, 5469-5479.
6. D. C. Jacobs and R. N. Zare, *J Chem Phys*, 1986, **85**, 5457-5468.
7. N. Bartels, B. C. Krüger, D. J. Auerbach, A. M. Wodtke and T. Schäfer, *Angewandte Chemie International Edition*, 2014, **53**, 13690–13694.