



Supporting Online Material for

Inverse Velocity Dependence of Vibrationally Promoted Electron Emission from a Metal Surface

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This PDF file includes:

SOM Text
References

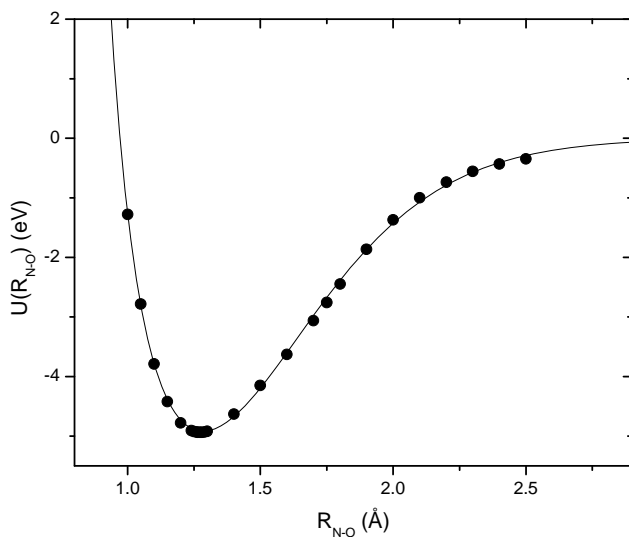
Supporting online material – Explanation of Fig. 3.

The long range interactions of NO with Cs/Au are modeled in the following way. First of all, a 2-D (r, z) coordinates system is defined, where,

r is the N-O inter-atomic distance measured in Å and

z is the distance of the surface to the CM of NO also measured in Å.

For the anion, a 2D potential (with energy units in eV) is constructed such that the r -dependence matches the NO^- inter-atomic potential obtained from *ab initio* electronic structure calculations. The plot below shows the quality of the fit to the *ab initio* points of Ref. S1.

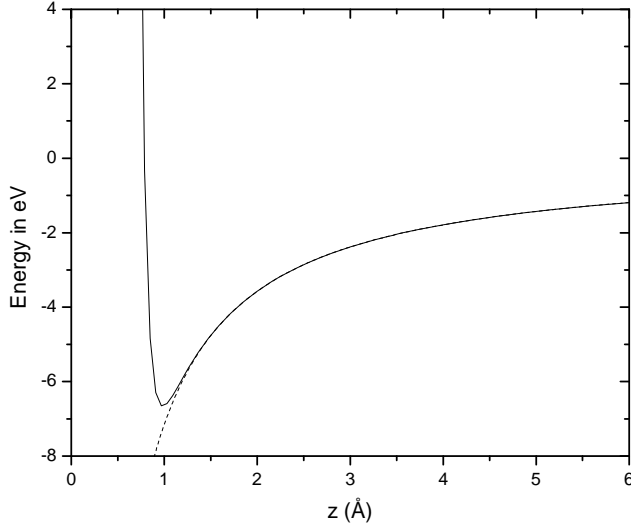


The solid line in the plot is the optimized fitting function. After shifting the origin of energy to the potential minimum, this becomes:

$$V_{\text{anion}}(r) = 4.917 - 41631.1 e^{-5.243r} (r - 0.971816)(1.03617 + r(r - 1.81663))$$

For the z-dependence of the anion potential an image potential with a repulsive wall is used.

$V_{anion}(z) = \frac{0.5}{z^{12}} - \frac{7.15109}{z}$. A plot of the z-dependence of the potential is shown below as a solid line.



Also shown is the $1/z$ part of the potential as a dashed line. One should note that the influence of the repulsive contribution to the potential is not important at $z > 2$ Å. The z and r dependent functions just described are combined as follows

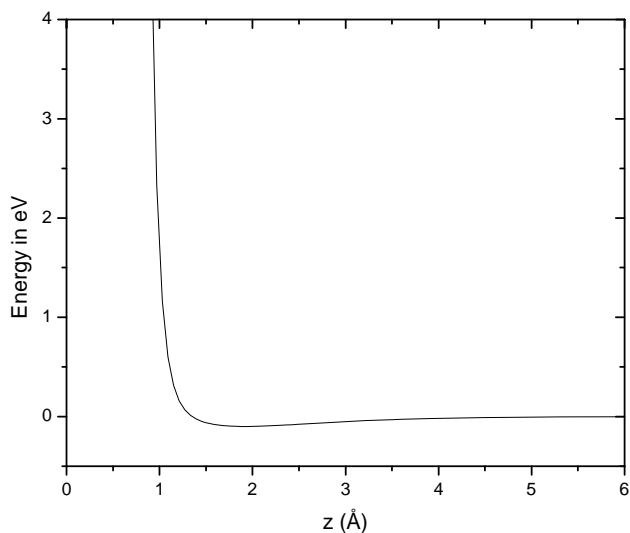
$$V_{anion}(r, z) = V_{anion}(r) + V_{anion}(z) = 4.917 - 41631.1 e^{-5.243r} (r - 0.971816)(1.03617 + r(r - 1.81663)) + \frac{0.5}{z^{12}} - \frac{7.15109}{z}$$

The Neutral NO potential is modeled in a similar 2-D fashion. Here the r -dependence is based on a Rydberg Function (somewhat more flexible than a Morse potential) and fitting constants determined by Huxley and Murrell in Ref. S2.

$$V_{NO}(r) = 6.614 - 15908.4 e^{-5.398r} (r - 0.895928)(0.749842 + r(r - 1.09722))$$

The z -dependence is modeled with a repulsive wall and a shallow minimum

$$V_{NO}(z) = \frac{1.5}{r^{12}} + e^{-1.5r} (3.19824 - 2.59317r)$$



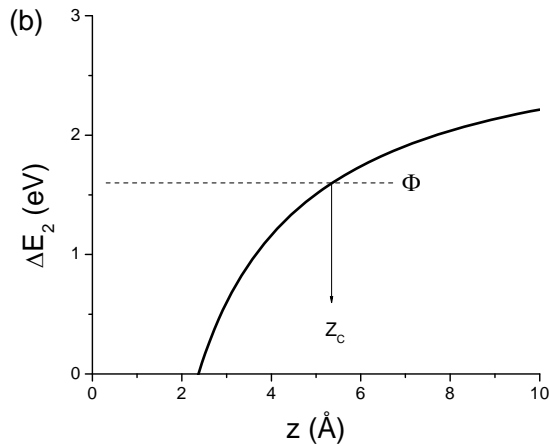
Likewise, the Neutral 2-D potential was constructed as for the anion.

$$V_{NO}(r, z) = V_{NO}(r) + V_{NO}(z) = 6.614 - 15908.4 e^{-5.398r} (r - 0.895928)(0.749842 + r(r - 1.09722)) + \frac{1.5}{z^{12}} + e^{-1.5z} (3.19824 - 2.59317 z)$$

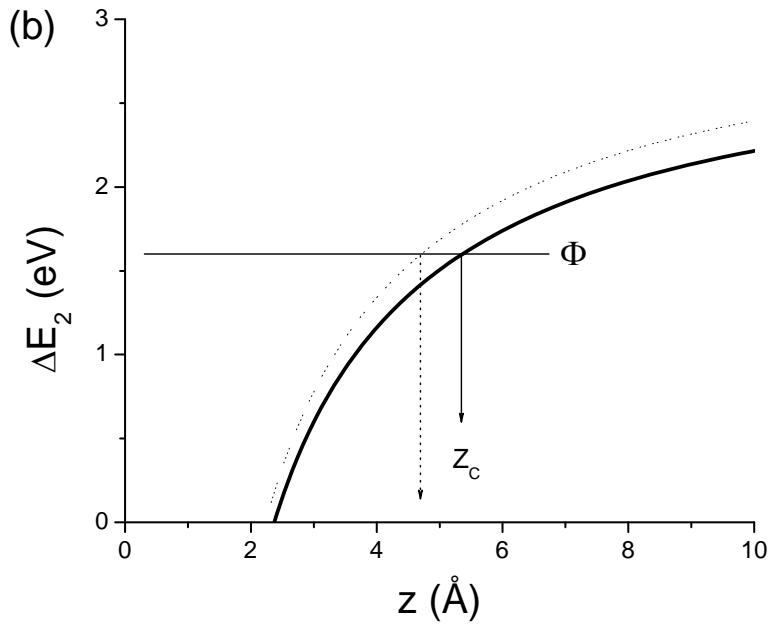
The two (anion vs. neutral) potentials are offset with respect to one another by the electron transfer energetics, Φ -EA. The anion potential has been adjusted upward by 0.24 eV to accurately reproduce the O-atom electron affinity at large values of r . This is due to the *ab initio* calculations' error in the dissociation energy of the anion. There is some ambiguity in this adjustment as the accuracy of the NO electron affinity is thereby impacted. However, making adjustments to this model to ensure accuracy of the EA of NO at the expense of the EA of O, does not significantly change the outcome.

Next, we show a cut through the 2D potentials at large values of z . This is shown as Figure 3a in the main text. We envision that at the outer turning point of vibration ($r_1 = 1.6\text{\AA}$) a vertical transition releases (wastes) a small ($\Delta E_1 \sim 0.4$ eV) amount of energy, promoting an electron from 0.4 eV below the Fermi Level to NO's LUMO. At the inner turning point of vibration (1.089\AA)

the energy release, ΔE_2 , depends on distance from the surface and drops below the surface work function at about $z=5\text{\AA}$. This result can be seen in the Figure below.



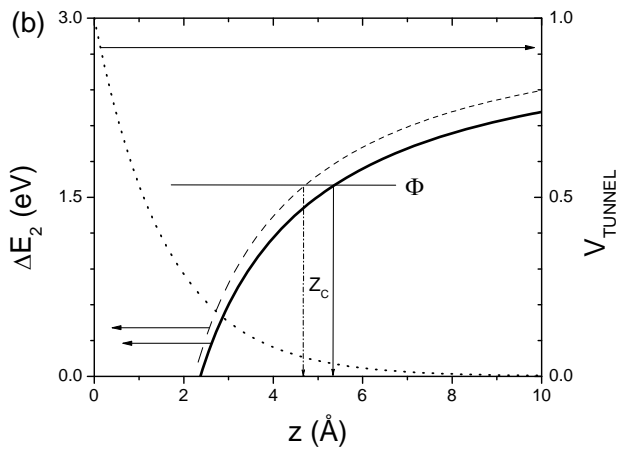
This is the basis for invoking a critical distance $z_c \sim 5\text{\AA}$. One might also imagine that the electron transfer at the outer turning point takes place adiabatically. This is the case described in the paper. Thus no energy is “wasted” in the initial electron transfer. In this case the energy available to eject the electron is somewhat larger and the approach to the surface can be somewhat closer before the image charge interaction prevents charge ejection. This is shown by the dotted line in the figure below. Thus there is an ‘*outer turning point adiabatic*’ (dotted lines in figure below) critical distance and an ‘*outer turning point nonadiabatic*’ (solid lines in figure below) critical distance. These differ however by little.



According to Shenvi et al. (S3) the tunneling coupling matrix element can be modeled by the function.

$$V(\varepsilon) \sim e^{-z \sqrt{\frac{2m_e(\Phi - \varepsilon)}{\hbar^2}}}$$

This shows that the tunneling coupling near the critical distance is significant. See Figure below (dotted line).



Here a work function of 1.6 eV was used and the energy of the Fermi level ($\epsilon=0$) was used.

REFERENCES

- S1. M. C. McCarthy, J. W. R. Allington, K. S. Griffith, *Chem. Phys. Lett.* **289**, 156 (1998).
- S2. P. Huxley, J. N. Murrell, *J. Chem. Soc. - Faraday Transactions II* **79**, 323 (1983).
- S3. N. Shenvi, S. Roy, P. Parandekar, J. Tully, *J. Chem. Phys.* **125**, 154703 (2006).