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Non-Arrhenius surface temperature dependence in vibrational excitation of NO on Au(1 1 1): possible evidence for the importance of surface electronic states

Alec M. Wodtke^{a,*}, Yuhui Huang^{a,1}, Daniel J. Auerbach^b

^a Department of Chemistry and Biochemistry, University of California, Building 557, Room 1432, 4623C Physical Sciences North, Santa Barbara, CA 93106-9510, USA

^b IBM Research Division, Almaden Research Center, San Jose, CA 95120-6099, USA

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Abstract

We report the surface temperature dependence for $\Delta v = +1$ vibrational excitation of NO($v = 2$) due to collisions with Au(1 1 1) at two incidence energies. This is compared to previous measurements on Ag(1 1 1) and Cu(1 1 0). The standard model for electron hole pair mediated vibrational excitation predicts that all three metals will exhibit a nearly Arrhenius temperature dependence with the same effective activation energy. While scattering on Ag(1 1 1) and Cu(1 1 0) obey this prediction, our new results show that the temperature dependence is non-Arrhenius on Au(1 1 1). We suggest that the large spin–orbit interaction present for Au(1 1 1) surface states may be important for vibrational excitation.
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1. Introduction

We now possess a rudimentary understanding of the nature of vibrational energy transfer when a molecule collides with a metal surface. In particular, the central role played by electron–hole pair excitation and de-excitation [1–4] is now generally accepted and a remarkably simple model developed by Rettner, Fabre, Kimmman, Auerbach [3] and Newns [4] (hereafter referred to as RFKAN)

has produced quantitative agreement with existing data. During the collision, the vibrational motion of the incoming molecule may become coupled to the metallic electrons, which provide a high density of energy-accepting (unoccupied electronic) states in the case of vibrational deactivation and a source of energy donating excited electron–hole pairs in the case of vibrational excitation.

The RFKAN model of vibrational *excitation* in molecule–metal surface collisions uses a statistical mechanical approach to the calculation of the electron and hole energy distributions. From this, the probability to find excited electron–hole pairs at the correct energy separation to excite molecular vibrations can be easily calculated. Using a Fermi function with a realistic bulk density of

* Corresponding author. Fax: +1-805-893-4120.

E-mail address: wodtke@chem.ucsb.edu (A.M. Wodtke).

¹ Present address: Oplink Communications, 3469 North First Street, San Jose, CA 95134-1803.

states function, one obtains a nearly Arrhenius surface temperature dependence [3],

$$P_{\text{ex}} = k(E_{\text{in}}) \exp\left(-\frac{\Delta\omega}{k_{\text{b}}T_{\text{s}}}\right), \quad (1)$$

where P_{ex} is the excitation probability, $\Delta\omega$ is the vibrational excitation energy, k_{b} is the Boltzmann constant, T_{s} is the surface temperature and $k(E_{\text{in}})$ is a constant of T_{s} which increases approximately linearly with incidence energy, E_{in} . This behavior has been observed in experiments carried out for NO($v = 0 \rightarrow 1$) collisional excitation both on Silver [3,5] and Copper [6] single crystal surfaces.

In contrast according to RFKAN, vibrational *relaxation* exhibits no strong dependence on T_{s} as the energy distribution of unoccupied (energy accepting) electronic states in the metal is only weakly temperature dependent under most conditions. Likewise, this has been experimentally confirmed on several occasions. See for example [7].

The influence of incidence energy appears in Eq. (1) as a pre-exponential factor. Therefore, the influence of incidence energy is predicted to be independent of the effect of the surface temperature [4]. Results consistent with this picture have been experimentally observed on Silver and Copper [5,8]. Furthermore, the incidence energy dependence on Silver was reproduced quantitatively by the RFKAN model [4]. It is now believed that the coupling of molecular vibration to the metallic electron bath is controlled by access to a continuum of curve crossings between the lifetime broadened affinity level of the incoming molecule (that is the negatively charged molecule interacting with its image charge) and the repulsive wall of the neutral molecular adsorption well. For low vibrational states, these curve crossings represent an energetic barrier, implying that high incidence energy may enhance coupling between molecular vibration and metallic electrons.

In a striking confirmation of these predictions, it was possible to observe that the entrance channel barrier to vibration/electron coupling could be eliminated when the incoming molecules were prepared with high vibrational excitation ($v = 15$) [8]. Remarkably, the scattered distribution of vibrational states reflected the creation of

excited electron hole pairs with an average energy of 150 kJ/mol (2/3 of the vibrational energy of the incoming molecule). Furthermore, comparable experiments on an insulator revealed negligible vibrational energy transfer [8]. These results were interpreted as evidence of vibrational promotion of electron transfer from the metal to the molecule.

One of the most striking predictions of the RFKAN model is that the differences in vibrational energy transfer that appear from metal to metal only influence the pre-exponential contribution to the excitation probability. In other words, different metals may have different inherent coupling strength between molecular vibration and metallic electron motion, but the effective activation energy controlling the temperature dependence of vibrational excitation is independent of the metal.

This prediction is rooted in the assumptions that:

1. the bulk electronic structure of the metal provides excited electron–hole pairs, and
2. all excited electron–hole pairs of the correct energy are equally efficient in promoting vibrational excitation.

No attempt has been made (or indeed seemed necessary) to incorporate the detailed band structure peculiar to specific metal surfaces, despite the fact that high quality vibrational energy transfer data is now available on three different metals (NO on Ag, Cu, and with this work now on Au). Likewise, other aspects of the metallic electronic structure have been neglected. For example, neither surface electronic states nor the momentum associated with metallic electrons has been incorporated into our understanding of this phenomenon. It is interesting to note that electronic surface states may also exhibit spin orbit splitting, whose role in this type of energy transfer has never been considered.

In this Letter we will show first, that there are significant qualitative differences in the temperature dependencies of vibrational excitation between different metals. We will also show that these differences cannot be explained on the basis of the differences in the bulk electronic band structures. The results presented here suggest that the role played by electronic surface states in the

vibrational energy transfer at surfaces may have been underestimated.

2. Experimental

The experimental arrangement has been described previously in detail [7–9]. In these experiments NO($v = 2$, $J = 1.5$, $\Omega = 0.5$) in both e/f parity states was prepared by infrared overtone pumping of a supersonic beam of NO 15 cm upstream from the surface. For this, we generated 2.7 μm (3729 cm^{-1}) light (0.08 cm^{-1} linewidth, $\sim 6\text{ mJ/pulse}$, 5 ns pulse duration) by mixing 120 mJ/pulse of 761.8 nm light from a Nd:YAG pumped dye laser (operating on LDS-765) with the 1.064 μm fundamental of the Nd:YAG laser in a LiNbO₃ crystal. We estimate $\sim 2\%$ of the total population in the illuminated part of the molecular beam is pumped to the desired state.

The supersonic NO molecular beam was generated using a pulsed molecular beam source [10], collimated by passage through three differentially pumped stages, and impinging at normal incidence upon a Au(1 1 1) crystal mounted in an ultra-high-vacuum ($<10^{-9}$ Torr) chamber. Seeding NO in He and H₂ allowed us to vary the kinetic energy of the NO. The Au(1 1 1) surface was cleaned daily by sputtering with 2.8 kV Ar⁺ for 30 min and flash annealing to 1100 K. After 9-h of exposure to the NO beam, surface contamination was still below the detection limit of Auger electron spectroscopy (AES). Even so, we annealed the surface between each experimental run (approximate every 2 h).

We detected either the NO prepared state or scattered states with one-color, two-photon REMPI through the $A^2\Sigma^+ \leftarrow X^2\Pi_i\gamma$ -bands 1–2 cm from the Au(1 1 1) surface. Spectroscopic constants needed to assign the observed spectra were obtained from the following sources [11–13].

Signals from scattered NO($v = 3$), NO($v = 2$), and NO($v = 1$) are readily observed when NO($v = 2$) with a kinetic energy of 63 kJ/mol scattered from the Au(1 1 1) surface held at 480 K and some of this data has been previously reported [7]. When the pump laser was blocked, the REMPI signals arising from transitions in the A–X (0.2) and (0.3) band entirely disappeared.

3. Results and discussion

Fig. 1 shows the influence of surface temperature, T_s , on ' $\Delta v = +1$ ' vibrational excitation observed for two incidence energies (30 and 60 kJ/mol) when NO($v = 2$, $J = 0.5$, $\Omega = 0.5$) collides with a Au(1 1 1) surface. The solid circles indicate the measured data points. The solid and dashed lines indicate Arrhenius functions like Eq. (1) with effective activation energies indicated. Also shown are the T_s -dependent results for $\Delta v = +1$ vibrational excitation of NO($v = 0$) on Cu(1 1 0) [6] (shown as a dotted line)² and Ag(1 1 1) [3] (shown as dot-dashed lines).

Some but not all of the aspects of these results may be rationalized within the RFKAN model. One may first note that the excitation probability is significantly higher for the Au(1 1 1) experiments than for the other two metals at any chosen values of T_s and E_i , where data is available. This suggests that the vibrational coupling to electronic motion is higher for the experiments carried out on Gold. This may in part result from the fact that the Gold experiments employed NO($v = 2$), while the experiments on Ag and Cu investigated NO($v = 0$). It has been shown in other work, that vibrational excitation can enhance the coupling between molecular vibration and metallic electrons [8].

It is also worth noting that at low values of T_s , an Arrhenius behavior is observed in the present work and the effective activation energy is (within observed error) equal to the vibrational excitation energy ($\Delta\omega = 1820\text{ cm}^{-1}$) as expected from the RFKAN model. This suggests that despite the deviations from theoretical predictions reported here, some aspects of the RFKAN model need to be retained.

Above a certain temperature (indicated by arrows) deviations from the expected Arrhenius dependence on T_s are seen. Furthermore, the deviations from the RFKAN model are apparent over a wider (lower) temperature range at the higher incidence energy, indicating for the first

² Note that the incidence energy of the Cu(1 1 0) results was 50 kJ/mol. However, the incidence energy dependence observed in that work was small between 50 and 60 kJ/mol.

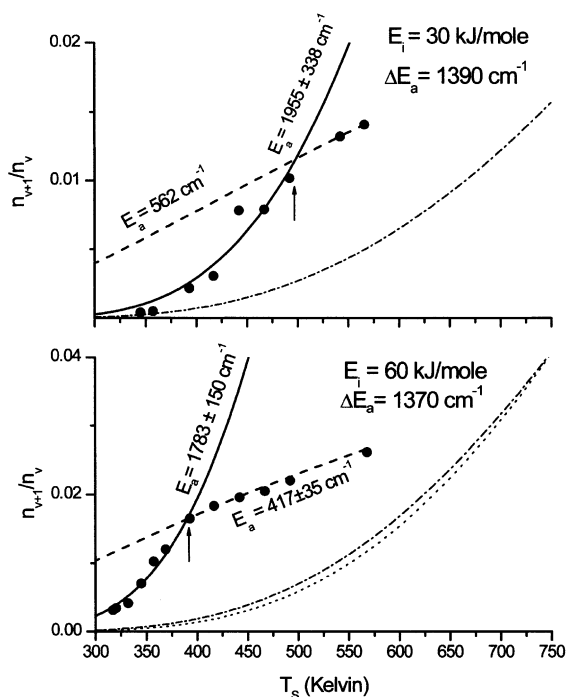


Fig. 1. Non-Arrhenius behavior for vibrational excitation of NO on Au(111). NO($v=2$) vibrational excitation to NO($v=3$) as a function of surface temperature, T_s (●) at two incidence energies. The solid line shows an Arrhenius function with $E_a \sim \Delta\omega$ as expected from the RFKAN model obtained by fitting the low temperature parts of each data set. The dashed lines are Arrhenius fits to the high temperature parts of the data. The dotted line represents the temperature dependence reported in [6] for Cu(110). The Dashed-dotted lines represent the temperature dependent data reported in [3] for Ag(111).

time an interaction between the surface temperature and incidence energy. This specific observation and more generally, the fact that vibrational excitation on Au(111) appears with a qualitatively different dependence on T_s than it does on Ag(111) or Cu(110) cannot be explained by our present models. These observations strongly suggest that we must consider the chemical and physical differences between the three metals in order to fully understand the nature of vibrational energy transfer at metal surfaces.

An obvious point of discussion concerns differences between the bulk band structures of the three metals. We have carried out calculations to investigate if this could be an important influence. Fig. 2 shows two energy functions, which are im-

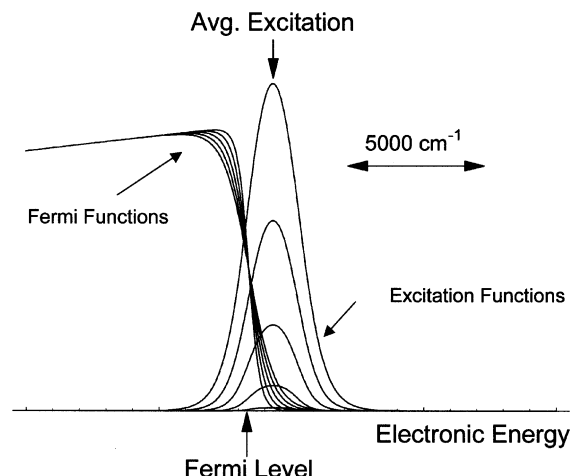


Fig. 2. The energy functions of relevance to the RFKAN model. The Fermi function for the electron distribution is shown for the temperatures $T_s = 300, 400, 500, 600$, and 700 K. Fermi functions become more rounded with higher temperature. The Fermi level is indicated. A particle in a box density of states function was used for these calculations. The excitation functions represent the energy of an excited electron with an excited hole 1800 cm^{-1} lower in energy. The excitation function grows with temperature. Shown are $T_s = 300, 400, 500, 600$, and 700 K. However, the center of the excitation function remains constants and the width remains less than 5000 cm^{-1} (shown as a double headed arrow) over this temperature range. The average excitation energy of the electrons important for vibrational up-pumping is nearly independent of temperature and has a value of $\sim 920 \text{ cm}^{-1}$.

portant for the RFKAN model. The step like functions are the product of the three dimensional particle in a box density of states function and the Fermi function.

$$\rho(E)F(E - E_F) = \frac{8\sqrt{2}\pi\sqrt{E}m_e^{3/2}}{(1 + \exp(E - E_F/k_b T_s))h^3}, \quad (2)$$

where, m_e is the mass of an electron, h is Planck's constant, E_F is the Fermi energy and as above, k_b is the Boltzmann constant and T_s is the surface temperature. These are shown for five temperatures within the range of these experiments: 300, 400, 500, 600, and 700 K.

Also shown are the excitation functions at these temperatures. The excitation function is defined as the probability to find an electron of energy E and a hole $\Delta\omega$ lower in energy. The excitation function can be expressed as in Eq. (3).

$$\begin{aligned}
P_{\text{ex}}(E; E_F, \Delta\omega, T_s) &= \left(64 \exp\left(-\frac{\Delta\omega}{2k_b T_s}\right) \pi^2 \sqrt{E} \sqrt{E - \Delta\omega} m_e^3 \right) \\
&\quad / \left(h^6 \left(\cosh\left(\frac{\Delta\omega}{2k_b T_s}\right) \right. \right. \\
&\quad \left. \left. + \cosh\left(\frac{\Delta\omega - 2E + 2E_F}{2k_b T_s}\right) \right) \right). \quad (3)
\end{aligned}$$

By integrating this function over E from $\Delta\omega$ to infinity, one obtains an approximately Arrhenius relation as in Eq. (1).

$$\begin{aligned}
64 \exp\left(-\frac{\Delta\omega}{2k_b T_s}\right) \pi^2 \\
\left(\int_{\Delta\omega}^{\infty} \frac{\sqrt{E} \sqrt{E - \Delta\omega}}{\cosh\left(\frac{\Delta\omega}{2k_b T_s}\right) + \cosh\left(\frac{\Delta\omega - 2E + 2E_F}{2k_b T_s}\right)} dE \right) m_e^3 / h^6.
\end{aligned}$$

Using values appropriate for NO on Au(111), we show the excitation function at the same five temperatures in Fig. 2. One can see that all of the important excited electrons that lead to vibrational up-pumping lie within 5000 cm^{-1} of the Fermi level. Now it is important to note that within 5000 cm^{-1} of the Fermi level, the bulk band structure of Ag, Cu, and Au are quite similar [14]. It appears therefore, that the differences in bulk electronic band structure are unable to account for the large deviations in the temperature dependence of vibrational excitation seen in this work.

In contrast to the bulk electronic states of the three metals, there are substantial differences between the electronic structures of the three metal surfaces. Angle resolved photo-emission studies have been used to characterize surface electronic states just below the Fermi energy on the (111) faces of all three noble metals [15]. The surface states on Ag(111) and Au(111) are nearly free electron states whose energy origins are 0.065 and 0.48 eV below the Fermi level, respectively. Surface states on Cu(110) have also been observed by inverse photo-emission but are more than 2 eV above the Fermi level [16]. Therefore, if surface electronic states play a role in vibrational exchange one could immediately understand why Cu(110) might behave differently than Au(111).

Another important difference between the three metal surfaces concerns the spin–orbit effect. For

bulk electronic states where metals possess a center of symmetry, no spin–orbit interactions are possible [17]. However, the absence of an inversion center at the crystalline surface permits surface electronic states with the same k_{\parallel} and opposite spins to exhibit different energies [17]. Spin–orbit splitting of the L-gap surface state on Au(111) has been observed [15,17,18] by angle resolved photo-emission spectroscopy [19]. Furthermore, theoretical study of Au(111) surfaces has confirmed the interpretations of the splitting as due to the spin–orbit effect [18,20].

Fig. 3 (left panel) shows the dispersion curves for the relevant surface states of Ag(111) (shown as a dashed curve) and Au(111) (shown as solid curves). These have been reproduced from the experimental data of [15]. The spin–orbit splitting of a metal surface state is dependent upon its parallel momentum k_{\parallel} and also its energy. Therefore it may be useful to consider the magnitude of the spin–orbit splitting for excited electrons in a Au(111) surface state at the average excitation energy predicted by the RFKAN model. This energy is found by examining the excitation functions of Fig. 2 and is only very weakly dependent upon surface temperature over this range. The average energy of the electrons inducing vibra-

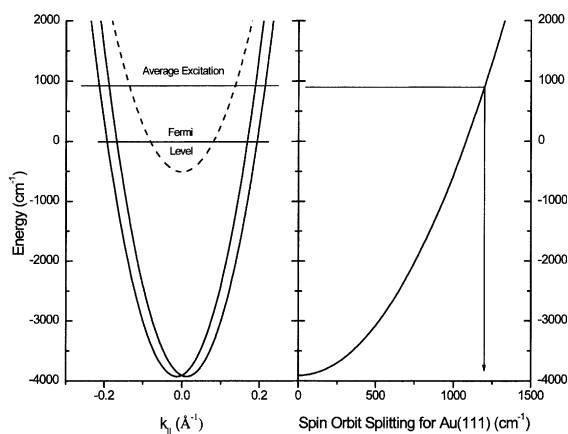


Fig. 3. Surface states of Au(111) (solid lines) and Ag(111) (dashed line). Reproduced from experimentally derived data from [16]. The surface states of the noble metals are split into two spin components, however this splitting is too small to have yet been observed in Ag(111). For Au(111) the splitting is proportional to k_{\parallel} and therefore proportional to the $\sqrt{\text{Energy}}$.

tional excitation in the RFGAN model at these temperatures is $\sim 920 \text{ cm}^{-1}$ ($\sim \Delta\omega/2$). This energy is also indicated in Fig. 3. At this level of electronic excitation the spin–orbit splitting (Fig. 3 right panel) is about 1200 cm^{-1} , of the same order of magnitude as molecular vibration. This is an indication one should proceed with caution when the spin–orbit quantum numbers of metallic electrons are treated adiabatically in vibration changing collisions of molecules at surfaces.

It should be noted that while coupling of spin–orbit excitation with molecular vibration in gas-phase bimolecular collisions has been known for over 20 years [21], this is the first preliminary evidence that such effects may be important in molecule surface scattering. Gas-phase collisions between $\text{Br}(^2\text{P}_{1/2})$ with $\text{H}_2(v)$ have been observed to produce $\text{H}_2(v+1)$ and ground state $\text{Br}(^2\text{P}_{3/2})$ [21]. This system has also been studied extensively theoretically [22,23] and more recently [24]. All of this work supports the idea that such processes can be important particularly when the spin–orbit excitation is in resonance with molecular vibrational states. It is reasonable to postulate that they may be of importance in molecule surface collisions as well.

In contrast, the spin–orbit splitting in $\text{Ag}(111)$ surface states is much smaller at the relevant levels of excitation. This is due to two factors. First as has been shown from theoretical work [20], the spin–orbit splitting of the surface state is related to the spin–orbit splitting of the isolated metal atoms as well as the surface potential gradients. Therefore the spin–orbit effect is much smaller on $\text{Ag}(111)$ surface states than is the case for $\text{Au}(111)$. Secondly, the origin of the $\text{Ag}(111)$ surface state is much closer to the Fermi level, so surface electrons excited about $\Delta\omega/2$ above the Fermi level have much lower values of k_{\parallel} and the spin–orbit splitting is reduced.

While there remains no proof that surface states explain the differences observed here for $\text{Au}(111)$ vs. $\text{Ag}(111)$ and $\text{Cu}(110)$, we believe it is the most likely area wherein these issues will eventually be resolved. Future theoretical work would be most informative as would scattering experiments on different faces of Au crystals, many of which have

no surface states and hence no spin–orbit effect close to the Fermi level.

Acknowledgements

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