

## A Franck-Condon Factor Study for the Vibrational Relaxation of NO Molecules Colliding with a Metal Surface

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Recently, Wodtke and his coworkers<sup>1</sup> reported an experimental result showing a very efficient vibrational relaxation process, which is claimed to be a promoting reaction of electron transfer. They observed an efficient multi-quantum vibrational relaxation of NO ( $\nu = 15$ ) molecules colliding with a gold surface in essentially a single molecule-surface encounter. On the other hand, scattering studies of vibrational relaxation of small molecules on insulating surfaces (such as LiF)<sup>1,2</sup> have shown that there is essentially no vibrational relaxation even at all incident energies. Then, the vibrational relaxation of high efficiency should be possible only on non-insulating surface. It is generally believed that the vibrational quenching rates will be higher especially in the case of metal surfaces, where the possibility exists for coupling between the vibration of the molecule and electron-hole pairs in the metal. On the same line of reasoning, the authors of Ref. 1 suggested (without any calculation) an electron-jump model. On the other hand, there was an ab initio study of the electron affinity of NO.<sup>3</sup> Potential energy curves for NO and NO<sup>-</sup> were calculated at high levels, and the curves were fit with a modified Morse potential. The difference between NO curve and NO<sup>-</sup> curve is the electron affinity as a function of bond distance. At about the turning points of  $\nu = 15$  vibration of NO, the electron affinity shows extreme differences: NO is a strong electron acceptor when it is stretched, and NO<sup>-</sup> is an electron donor when it is compressed. This electron affinity difference originated by molecular vibrations can cause an electron transfer in the molecule-surface reactions. And then, the electron transfer should be reflected as a vibrational relaxation of NO molecules on the basis of energy conservation. Here we see a dynamic model in which the molecular electron affinity level crosses the surface Fermi level, thus allowing the electrons transfer back and forth between metal and molecules during the scattering process.

We note here that the electron transfer from gold metal to NO molecule brings a NO<sup>-</sup> anion. Then, the electron transfer between metal and molecule must be interpreted as a transition between NO and NO<sup>-</sup> potential energy surfaces. Of course, this transition results in a vibrational transition from  $\nu$  (vibrational state of NO) to  $\nu'$  (of NO<sup>-</sup>). The electron transfer at the molecule-metal interface involves the continuum of electronic states in the metal. Strictly speaking, this requires solving a many-electronic state problem for which only very approximate solutions exist up to now. Also, to

explain the electron transfer between molecule and surface we have to see how the interaction changes with time as a function of both bond distance and molecule-surface distance. This is rather an involved work, which we will pursue later. In the meantime, we present a Franck-Condon (FC) factor study, as a preliminary step, to explain the experimental results of the vibrational relaxation of NO molecules colliding with a gold surface.

The electron transfer between gold metal and NO molecule will bring a change in the nuclear wave functions of the molecule, following with a transition between two potential energy curves of NO and NO<sup>-</sup>. The transitions can be explained with the Golden Rule. As Gadzuk and Metiu<sup>4</sup> pointed out in their theory, the FC overlap between them will be one of the major factors determining the Golden Rule transition rate. Because, only those transitions of substantial FC overlap will contribute substantially to the rate. For the FC approximation, the readers are referred to eq. (III.14) of Ref. 4(b). The transition probability amplitude from the state  $|g\rangle \parallel gb \gg$  to  $|\lambda\rangle \parallel \lambda a \gg$  is given as

$$T_{\lambda a \leftarrow gb} \cong VO$$

where

$$V = \int dr \phi_{\lambda}^*(r, R) H_{el}(r, R) \phi_g(r, R)$$

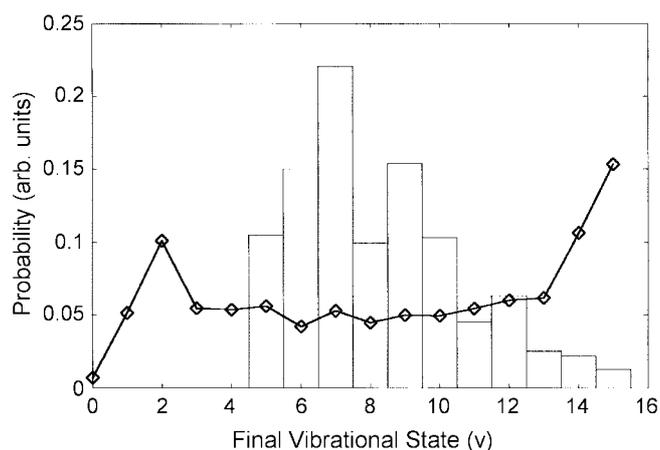
$$O = \int dR \tau_{\lambda a}^*(R) \eta_{gb}(R).$$

The first integral  $V$  is electronic coupling matrix element, and the second integral  $O$  is the FC overlap. The FC factors are merely the squares of the overlap integrals between the initial vibrational wave function and all the possible final vibrational wave functions. Within FC approximation, the coupling matrix (between a molecular electronic and a metal state) may be treated as an averaged quantity. We treat the coupling as a constant for simplicity in our model. So, the transition probability from the state  $|g\rangle \parallel gb \gg$  to  $|\lambda\rangle \parallel \lambda a \gg$  is given by the FC factors. However, to count in the surface effect, an orbital-band interaction study is desirable for this case.

To obtain the FC factors, we produced a nuclear wave function ( $\nu = 15$ ) of NO molecule, and then calculated the FC overlap with nuclear wave functions ( $\nu'$ ) of NO<sup>-</sup>. The magnitude of the FC factors here is believed to be directly proportional to the probability of the transition of an electron from metal to NO molecule, producing the NO<sup>-</sup> anion. And

then, we again calculated the FC factors between  $v'$  states of  $\text{NO}^-$  anion and  $v$  states of NO molecule. These FC factors reflect the probabilities of finding in which final vibrational state the NO molecule when the anion  $\text{NO}^-$  back transfers the electron to the metal. In other words, we calculated  $\Sigma_{v'} |\langle v_i = 15 | v' \rangle|^2 |\langle v' | v_f \rangle|^2$  for  $v_f = 0, 1, 2, \dots$ . This is the probability of finding the NO molecule in the final vibrational state ( $v_f$ ), and this is shown in Figure 1. Our prediction obtained through one cycle of transitions ( $v = 15$  of NO  $\rightarrow v'$  of  $\text{NO}^- \rightarrow$  final  $v$  of NO) is represented by line with diamond symbols. For comparison, we also plotted the experimental results of Ref. 1 as bar graph. Their measured vibrational distribution is derived from their experiments when NO ( $v = 15$ ) is scattered from the Au(111) surface at an incidence energy of only 5 kJ/mol. Detection of the electron transfer product was complicated by the fact that  $\text{NO}^-$  cannot escape the gold surface. It was therefore fruitless to look for the scattered anion directly. However, an adsorption study<sup>5</sup> of NO on Ag(111) has shown ~90% molecular desorption. They could not detect any clear sign of ionization or decomposition. Therefore, we expect that the portion lost by  $\text{NO}^-$  formation on the gold surface should not be larger than 10%.

Our FC result shows a high efficiency of relaxation. As we can see from Figure 1, after only one cycle of transitions the final vibrational state distribution is fairly even. This fast relaxation was possible only with an electron transfer model of two steps. First, the intermediate product  $\text{NO}^-$  has a substantially different diatomic potential and found in a range of different vibrational states ( $v'$ ). Second, by the time the electron jumps back to the metal surface, the molecular anion is at a different vibrational phase, which favors different vibrational states (final  $v$ ) of the NO molecule. So, the transitions from the neutral to ionic potential surface and the back transition to the neutral lead to very large changes in the NO vibrational states, resulting in a highly efficient route of vibrational relaxation. However, contrasting to the experimental results, one of the maximum probability peaks occurs at  $v = 2$ . In addition, the  $v = 15$  state still shows a substantial probability of returning to the initial state. Experimental result for  $v \geq 16$  distribution is not available. However, our result (not presented here) shows that those probabilities are clearly not negligible up to  $v = 20$ , then die away. These discrepancies can be explained by the different settings between experiment and our theoretical calculation. As mentioned before, the experiment was complicated by the fact that  $\text{NO}^-$  cannot escape the gold surface. Therefore, we cannot rule out the possibility of existing a fraction of the unseen NO adsorbed to the surface. In addition, our simple calculation was performed for only one cycle of transitions of the electron transfer process. In real experiment, the scattering time was about 0.1 ps, which is enough time for a couple of cyclic transitions of the electron transfer. However, if we consider the orientational effect of molecule to the surface, it is clear that not all the collisions will experience electronic transitions. Related with this, the NO molecule is



**Figure 1.** Probability distribution after one cycle of transitions between NO and  $\text{NO}^-$  potential curves. The bar graph is the experimental results of Ref. 1.

believed<sup>6</sup> to adsorb perpendicularly to the surface with the oxygen end away from the surface. Unfortunately, we do not know (at this stage) how many cyclic transitions really occur during molecule-surface collisions. However, we conjecture that the electronic transitions occur more than one time during a collision between molecule and metal. This part of the whole dynamics needs a separate study.

In summary, we presented a FC factor study, which is based on the Golden Rule. Our model based on the FC approximation reveals that a highly efficient multi-quantum vibrational relaxation is possible through an electron transfer between metal and vibrationally excited molecules. Basically this is the same conclusion as that found from the experimental results. An orbital-band interaction study is desirable for this case, and a further study is in progress to this direction.

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