

Vibrational excitation in gas-surface collisions

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Recent experimental observations and accompanying interpretation of Rettner, Fabre, Kimman, and Auerbach for vibrational excitation in NO molecules scattered from Ag(111) surfaces are discussed in terms of existing models for such events.

In a recent Letter, Rettner and co-workers¹ presented direct observations of enhanced vibrational excitation in a diatomic molecular beam scattered from a metal surface [specifically, NO/Ag(111)]. Their results displayed a surprisingly strong dependence on T_s , the surface temperature, and $\epsilon_{\text{vibe}} = \hbar\omega$, the NO vibrational quantum, which suggested to them a mechanism involving de-excitation of thermally excited Fermi-level electrons. Reflection on these observations led them to an expression for the population of $n=1$ scattered molecules,

$$\text{NO}(n=1) \sim \sigma \exp(-\epsilon_{\text{vibe}}/kT_s)(\epsilon_{\text{vibe}} - kT_s \ln 2), \quad (1)$$

where σ , defined as "the coupling," is a measure of the probability for vibrational excitation due to "scattering" with the surface electrons in some nonspecified way. Furthermore, they note that "vibrational excitation at surfaces, . . . has received relatively little attention. This is unfortunate since such excitations couple directly to dissociative reaction coordinates." The purpose of the present brief report is to demonstrate how the mechanism of "electron-transfer-assisted" vibrational excitation developed in an extensive series of papers² enables explicit estimation of the strength and the incident translational energy dependence of σ , the "coupling" term appearing in Eq. (1), in terms of the microscopic parameters characterizing the NO/Ag potential-energy surface, in a manner which is consistent with the reported data.

The fundamental ideas underlying our approach to the problem of thermal electron-hole pair excitation of molecular vibrations are illustrated in Fig. 1 for the case of two electronic states associated with the interacting molecule-surface system. The diatomic molecule, initially in electronic state A_2 and with normal kinetic energy ϵ_p , is directed upon the surface at temperature T_s with a high-energy tail of excited electrons given by the usual Fermi function. At the point of the curve crossing ($t=0$), electronic transfer involving excited surface electron-hole pairs with energy $\geq \epsilon_{\text{vibe}}$ occurs and subsequent translational motion inward to the classical turning point and back to the curve crossing (at $t=\tau_R$) takes place over the potential curve, here labeled A_2^- . At $t=\tau_R$, the electron is returned to the Fermi level, leaving the solid in a total-energy state ϵ_{vibe} less than at $t=0$ and the molecule in an

internally excited state. The essential feature required for vibrational excitation is solely the existence of *intramolecular potential curves* characterized by *equilibrium separations* displaced as a function of molecule-surface distance. Effects due to simple mechanical collisions are negligibly small.³ The intramolecular dynamics is particularly simple for the two-state system shown in Fig. 1. At time $t=0$, the *intramolecular wave packet* given by the A_2 vibrational ground-state wave function is prepared as a nonstationary state on the A_2^- curve, upon which it propagates until $t=\tau_R$ when it is returned to A_2 , most likely displaced from the A_2 equilibrium; thus A_2 emerges vibrationally excited.^{2(c),4} The degree of excitation depends upon the product $\tilde{\omega}\tau_R$, the lifetime of the intermediate state multiplied by the A_2^- vibrational frequency.

We have worked out in great detail the consequences of such a model in terms of both classical trajectories over multidimensional potential-energy surfaces^{2(b)} as well as analytic solutions for the intramolecular dynamics,^{2(c)} so now only the final results required to understand the observations of Rettner *et al.*¹ are quoted. The probability per collision for excitation of n vibrational quanta (in the harmonic approximation) is given by the Poisson distribution

$$P_n(\tau_R(\epsilon_p)) = \exp[-\beta(\tau_R)] [\beta(\tau_R)]^n / n! \quad (2)$$

characterized by the dynamic Poisson parameter

$$\beta(\tau_R) = 2[1 - \cos \tilde{\omega}\tau_R(\epsilon_p)] \beta_0, \quad (3a)$$

in which

$$\tau_R(\epsilon_p) = \frac{1}{\omega_z} [\pi + 2 \sin^{-1}(z_0/z_{am})], \quad (3b)$$

$$z_0 \simeq (2\epsilon_d / M\omega_z^2)^{1/2}, \quad (3c)$$

$$z_{am} \simeq [2(\epsilon_d + \epsilon_p) / M\omega_z^2]^{1/2}, \quad (3d)$$

where M = the total molecular mass, ω_z is the frequency associated with the A_2^- surface bond, and ϵ_d = the A_2^- well depth, as shown in Fig. 1. The ubiquitous "static Poisson parameter" for displaced harmonic oscillators is expressed as

$$\beta_0 = \Delta R_{eq}^2 \mu \omega / 2 \hbar, \quad (4)$$

where μ = the reduced mass and ΔR_{eq} is the change in intramolecular equilibria separation for the two electronic states in question. It must be emphasized that *any process* which inserts some electronic charge density into the bonding region of the A_2 will weaken the bond, thus resulting in bond extension. In the case of unit electron transfer a negative molecular ion is formed, which for NO/NO⁻ yields $\Delta R_{eq} \approx 0.11$ Å and $\beta_0 \approx 3$. For

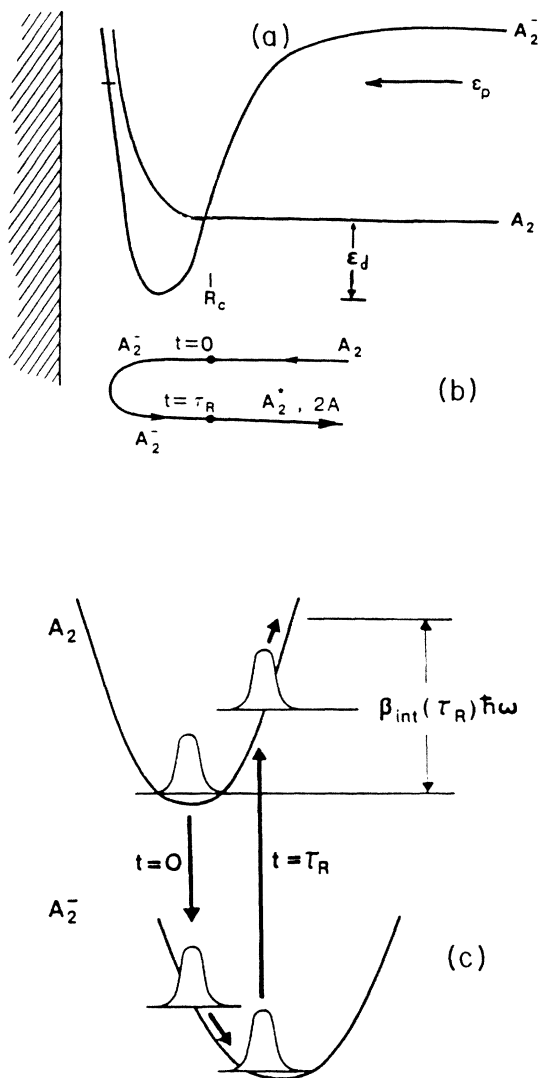


FIG. 1. (a) Diabatic potential-energy curves as a function of z , the normal distance from the surface of an incident A_2 molecule with center-of-mass kinetic energy ϵ_p . At the curve crossing ($z = R_c$) passage to the A_2^- negative molecular ion curve is possible. (b) Time line showing the state of the molecule at various times along its scattering trajectory. (c) Displaced intramolecular oscillator potentials as a function of the internal vibrational coordinate for A_2 and A_2^- . The evolution of the propagating wave packet, according to the electronic states dictated by the time line in the middle is depicted here.

molecule-surface systems in which electronegativity arguments are unfavorable towards charge transfer, on the basis of a broadened molecular electron-energy-level picture,⁵ a fractional charge transfer given by

$$\Delta n \approx \frac{1}{\pi} \cot^{-1}(\epsilon_\phi / \Delta) \quad (5)$$

can be expected, where $\epsilon_\phi \approx \phi - A - e^2/4z_0$ is the position of the electron affinity level of the molecule at separation z_0 with respect to the Fermi level, ϕ = the work function, A = the gas-phase molecular electron affinity, and Δ = the level width at z_0 . For NO on a $\phi = 4.5$ eV surface, with $\Delta = 1$ eV,⁶ $A = 0.024$ eV, and $\epsilon_\phi \approx 4.5 - 0.024 - 2.0 = 2.48$ eV, Eq. (5) implies that $\Delta n \approx 0.12$. Invoking the plausible scaling relation

$$\Delta R_{eq} \approx (d\Delta R_{eq}/d\Delta n |_{\Delta n=1}) \Delta n, \quad (6)$$

it is estimated that $\Delta R_{eq} \approx 0.01$ Å for NO/Ag and thus $\beta_0 \approx 0.03$, substantially reduced from the unit charge transfer value.

Turning now to the experimental observations, the main so-far-unexplained results are (i) the origins of the monotonic increase in the ratio $R \equiv \text{NO}(n=1)/\text{NO}(n=0)$ as a function of normal translational energy, rising from 0 at $\epsilon_p = 0^+$; and (ii) the basis for the magnitude of the effect as exemplified by the experimental fact that $R \approx 0.07$ at $\epsilon_p \approx 1.0$ eV. Equation (2) shows that $R = \beta(\tau_R(\epsilon_p))$, and this quantity is given by Eqs. (3a)–(3d). When $\epsilon_p = 0^+$, Eqs. (3c) and (3d) yield $z_0 = z_{am}$, so from Eq. (3b), $\tau_R(\epsilon_p = 0) = 2\pi/\omega_z$. Equation (3a) thus requires that $\bar{\omega}/\omega_z = \text{integer}$ when $\beta(\tau_R(\epsilon_p = 0)) = 0$ as observed. This is easily satisfied since $\hbar\omega \approx 0.25$ eV and it has been suggested^{2(b)} that $\hbar\omega_z \approx 0.2$ eV for the predominantly neutral C, N, and O diatomic molecules. For present purposes, setting the frequency ratio equal to unity is certainly reasonable.⁷ Thus the ratio of vibrationally excited to ground-state scattered molecules which follows from Eqs. (2) and (3) is

$$\beta(\epsilon_p) = 2\beta_0(\Delta n)(1 + \cos\{2 \sin^{-1}[\epsilon_d/(\epsilon_d + \epsilon_p)]\}),$$

which can be further reduced to

$$\beta(\epsilon_p) = 4\beta_0(\Delta n)y[(2+y)/(1+y)^2] \\ = \text{NO}(n=1)/\text{NO}(n=0), \quad (7)$$

with $y \equiv \epsilon_p/\epsilon_d$. The simple relation given by Eq. (7) is remarkably consistent with the qualitative features of the Rettner data. First, as with the data, the value of $\beta(\epsilon_p)$ rises monotonically with ϵ_p , initially linearly with slope $d\beta/d\epsilon_p = 8\beta_0(\Delta n)/\epsilon_d$ matching the data if, e.g., $\Delta n = 0.1$ and $\epsilon_d \approx 4$ eV or $\Delta n = 0.05$ and $\epsilon_d = 1$ eV and then saturates at the high-energy limit

$$\lim_{\epsilon_p/\epsilon_d \gg 1} \beta(\epsilon_p) = 4\beta_0(\Delta n). \quad (8)$$

Equation (8) sets the scale of the excitation probability for the fractional charge transfer mechanism. For instance, with NO parameters Eqs. (6) and (4) yield $\Delta R_{eq} \approx 0.11\Delta n$ Å and $\beta_0 \approx 3(\Delta n)^2$. Thus with $\Delta n \approx 0.1$, a value certainly compatible with Eq. (5), $\beta_{\text{max}} \approx 0.12$, providing an upper bound not in conflict with the experimental observations. The major goal of this brief report has thus

thus been attained, namely, the demonstration that the electron-transfer-assisted vibrational excitation model² provides explicit connections between microscopic NO/Ag system parameters and the coupling term in Eq. (1) which are not inconsistent with the relevant experimental observations reported by Rettner and co-workers.

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⁷While this particular choice of $\bar{\omega}/\omega_z$ in no way crucially affects the discussion presented here, it considerably simplifies the form of $R(\epsilon_p)$ by removing the nodal patterns [Ref. 2(b)] arising from resonances in A_2^- . These structures, while sharp for a limited range of phase-space trajectories, smear out immediately when any initial-state averaging is performed [Ref. 2(b)], resulting in smooth $R(\epsilon_p)$ distributions.