

Observation of a Change of Vibrational Excitation Mechanism with Surface Temperature: HCl Collisions with Au(111)

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We have measured the vibrational excitation probability (P_v) of HCl incident on a Au(111) surface at kinetic energies (E_i) of 0.59 eV to 1.37 eV and surface temperatures (T_s) of 273 K to 1073 K. For all energies, the slope of the P_v as a function of T_s exhibits a sharp increase above $T_s \approx 800$ K. We show this change in slope and the threshold behavior of P_v to be consistent with a change in excitation mechanism from an electronically adiabatic mechanical mechanism to an electronically nonadiabatic mechanism involving excited electron-hole pairs.

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The study of energy transfer dynamics at gas-solid interfaces strives to reveal an atomistic picture of energy flow in molecular collisions with surfaces, which is essential to understanding processes such as sticking, diffusion, and reactivity. Both experiment and theory have probed many aspects of such interactions including translational, vibrational, and rotational energy transfer between gas-phase molecules and surface atoms [1–6]. Since the flow of energy into and out of chemical bonds is essential to bond rupture and formation, *vibrational* energy transfer takes a prominent place in this field [7–12]. For example, vibrationally inelastic scattering can be a sensitive probe of portions of the potential surface near the dissociation barrier [13]. Theoretical studies show that comparison of data on vibrational energy transfer and reactivity can even yield sensitive information on whether these two processes take place at different sites on the surface [13,14].

One of the most remarkable discoveries concerning vibrational energy transfer is the realization that molecular vibration may interact directly with electron-hole pair (EHP) excitations of the solid, destroying (creating) EHPs through vibrational excitation (relaxation) [15–23]. Such “electronically nonadiabatic” vibrational energy transfer is qualitatively different than “mechanical” (electronically adiabatic) energy transfer, which is dictated by the interatomic forces represented by a single potential energy hypersurface. In the adiabatic case, the energy reservoir for vibrational excitation must be the incidence energy of translation, E_i . This gives rise to a threshold in the dependence of vibrational excitation on E_i . In addition, the near harmonic nature of phonon motion and the low probability to couple multiple phonons to molecular vibration leads to a weak or absent dependence on T_s [12]. Electronically nonadiabatic mechanisms for vibrational excitation, in contrast, may exhibit little or no incidence energy threshold as well as a characteristic pseudo-Arrhenius T_s dependence resulting from the strong T_s -dependent variation of the Fermi function [11,17]. More recent evidence for the efficient coupling of intramolecular vibrational motion to

EHP excitations comes from the study of interactions of highly vibrationally excited molecules with metal surfaces. The observation of efficient *multiquantum* vibrational relaxation is hard to explain without invoking EHP excitation [24]. Taken together, these experiments provide strong indirect evidence for the role of EHP excitations. It has even been possible to provide direct evidence by the observation of efficient emission of electrons when NO ($v = 18$) molecules interact with a low work function surface [21].

Although existing evidence supporting the electronically nonadiabatic mechanism seems compelling, the role of thermally excited EHPs in vibrational excitation remains controversial. Holloway and co-workers [25,26] and Brenig and co-workers [27,28] have shown that it is possible to construct adiabatic models that reproduce the strong kinetic energy dependence and pseudo-Arrhenius T_s dependence seen in the vibrational excitation of NO. Furthermore, vibrational excitation showing a strong T_s dependence has so far only been seen for NO, making it difficult to assess the general importance of an EHP-V mechanism. Since both adiabatic and nonadiabatic mechanisms can contribute to vibrational excitation, it is desirable to find systems and circumstances where both mechanisms play a role and where a transition from an adiabatic to a nonadiabatic regime might be observed, thus providing a benchmark for theories of the relative importance of these two mechanisms.

In a previous paper, we reported the direct vibrational excitation of HCl in collisions with Au(111) at 273 K and presented evidence showing that a mechanical translational-to-vibrational energy transfer mechanism was at play [29]. Here, we extend the previous work to higher surface temperatures T_s (273–1073 K) and E_i (0.59–1.37 eV). As T_s is increased, we observe a sharp increase in the slope of the vibrational excitation probability as a function of T_s and a marked reduction in the previously reported translational energy threshold for vibrational excitation. We interpret these observations as a

transition from an adiabatic to a nonadiabatic vibrational excitation mechanism with increasing T_s and are able to quantitatively separate the two contributions to the energy transfer. These results provide an important benchmark as successful theories must treat adiabatic and nonadiabatic interactions on an equal footing.

The experiment has been described previously [29]. Jet-cooled molecular beams are generated by expanding HCl seeded in H_2 through a homemade piezoelectrically actuated pulsed valve. The expanded skimmed HCl beam passes through two differential pumping stages into the UHV surface chamber to collide with a gold surface. The short distance from nozzle to surface (180 mm) provides an intense molecular beam and the ability to time resolve incoming and scattered signals. The surface was cleaned daily by Ar^+ sputtering with subsequent anneals at 780 K. Auger electron spectroscopy was used to monitor the surface condition. HCl ($v = 1$) molecules were probed state selectively by 2 + 1 resonance enhanced multiphoton ionization (REMPI) via the Q branch of the $E^1\Sigma^+ - X^1\Sigma^+(0, 1)$ band using 4–6 mJ/pulse tunable light near 247 nm. The laser beam was focused with a 30 cm focal length lens. Laser generated ions were collected and guided by a repeller and two cylindrical focusing lenses to a microchannel plate detector. The incident and scattered molecules were detected 20 mm from the surface with different delay times (20–30 μs) between the probe laser and the pulsed molecular beam. The short duration of our pulsed molecular beam (<50 μs) provides some discrimination against “in beam background” even for these small delays. Rotational distributions were recorded by scanning laser wavelength, angular distributions were measured by translating the laser position along the line perpendicular to the molecular beam direction, and temporal profiles were obtained by recording the signal as a function of the delay between the laser with the nozzle.

Such data were obtained under 26 different conditions: six surface temperatures, $T_s = 273, 473, 673, 873, 973,$ and 1073 K, for four values of $E_i = 1.37, 1.12, 0.86,$ and 0.59 eV as well as a room temperature surface at $E_i = 1.37$ and 1.12 eV. The scattered molecules’ angular distributions all peak at the specular angle of 6.5° , due to the slightly ($3.3 \pm 0.3^\circ$) off-normal incidence of the incoming molecular beam. Angular distributions of scattered HCl($v = 1$) are all quasispecular and broaden gradually with increasing T_s due to surface atom thermal motion [30]. These observations are characteristic of direct “one bounce” interactions of HCl with the Au(111) surface.

To obtain absolute excitation probabilities [29], we compare the observed $v = 1$ signal resulting from scattering to the thermal population in the incident molecular beam. The observed relative signals were corrected for differences in angular, rotational, and temporal distribution, as well as for laser power. The derived T_s dependence of the vibrational excitation probability of HCl ($v = 0 \rightarrow 1$) in collisions with Au(111) is shown in Fig. 1. Previously published results for NO($v = 0 \rightarrow 1$) on Ag(111) [17]

are also shown. The solid or dashed straight lines are Arrhenius predicted calculations with effective activation energies equal to the vibrational excitation energy. There are several noteworthy observations. First, the vibrational excitation probabilities of HCl ($v = 0 \rightarrow 1$) on Au(111) over the T_s from 273 to 1073 K are in the range of 10^{-6} – 10^{-4} . In comparison to NO ($v = 0 \rightarrow 1$) on Ag(111) where the largest excitation probability for NO is as high as ~ 0.07 [11,17], it is clear that the energy transfer is much less efficient for HCl/Au compared to NO/Ag. Second, the vibrational excitation probabilities of HCl ($v = 0 \rightarrow 1$) on Au(111) exhibit two different regimes of T_s dependence. At low T_s (273 K to 873 K) the vibrational excitation is nearly independent of T_s . At higher values of T_s , the vibrational excitation probability P_v is strongly temperature dependent and follows an Arrhenius law

$$P_v = p(E_i)e^{E_a/kT_s} \quad (1)$$

with an effective activation energy E_a equal to the HCl($v = 0 - 1$) vibrational spacing, $E_{vib} = 0.36$ eV. It has been previously shown that the population of EHPs with energy exceeding E_{vib} is given by Eq. (1), assuming a metal whose density of states follows the Fermi function [17]. Thus, a pseudo-Arrhenius relation for vibrational excitation arises naturally for a mechanism involving the production of vibrational excitation via the deexcitation of thermal electron-hole pairs in the metal. We interpret the change in the degree of T_s dependence from a nearly T_s -independent region to an Arrhenius dependence as a sign of a transition between two fundamentally different energy transfer mechanisms. In a previous paper, the ob-

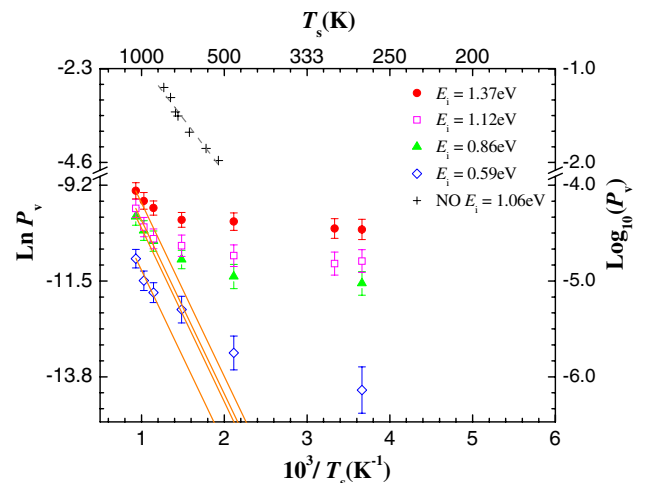


FIG. 1 (color online). T_s dependence of vibrational excitation probability of HCl ($v = 0 \rightarrow 1$) from Au(111) for 4 incidence energies. Comparison to NO data is also shown (from Ref. [17]). The Arrhenius-like dependencies with the expected E_a (slope) fixed at the HCl $v = 0 - 1$ energy spacing (0.36 eV) are shown as solid lines. The Arrhenius dependence expected for NO with E_a (slope) set by the vibrational spacing in NO (0.23 eV) is shown as a dashed line.

served incidence energy threshold at $E_i \sim 0.57$ eV as well as a collapsing angular distribution near threshold were taken as strong evidence for a mechanical energy transfer mechanism at $T_s = 273$ K [29]. In light of previous work [17,18], that the vibrational excitation probability follows the form of Eq. (1), we propose that this mechanism (EHP-V energy transfer) is operative for HCl/Au scattering in the high T_s limit of our data set. This line of reasoning allows us to separate the adiabatic and nonadiabatic contributions to P_v using a simple model,

$$P_v = P_v^{(1)}(E_i) + P_v^{(2)}(E_i, T_s) = p_1(E_i) + p_2(E_i)e^{-E_a/kT_s}. \quad (2)$$

Here, $p_1(E_i)$ is the adiabatic excitation probability assuming T_s independence [12]. The second term is the nonadiabatic excitation, where E_a was fixed at the HCl ($v = 0 - 1$) energy spacing (0.36 eV). The $p_2(E_i)$ factor reflects the inherent coupling of metal electrons to the scattering molecule's vibrational motion and depends only on E_i , following [17] and references therein. The results of using this model to fit the data from all 26 experiments are shown in Fig. 2. These fits allow us to extract values of $p_1(E_i)$ (adiabatic) and $p_2(E_i)$ (nonadiabatic) for all 26 experimental conditions. Note that we need make no assumption concerning the E_i dependence of $p_1(E_i)$ or $p_2(E_i)$; however, this analysis leads to the conclusion that both $p_1(E_i)$ and $p_2(E_i)$ are approximately linearly dependent on E_i . More specifically, $p_1(E_i)$ is linear with a threshold near $E_i = 0.57$ eV, similar to Fig. 4 of Ref. [29], while $p_2(E_i)$ is linear with no energy threshold (i.e., y intercept = 0).

Using these parameters we may calculate the relative contributions of adiabatic and nonadiabatic energy transfer $P_v^{(1)}(E_i)$ and $P_v^{(2)}(E_i, T_s)$ for 24 experiments at 6 surface

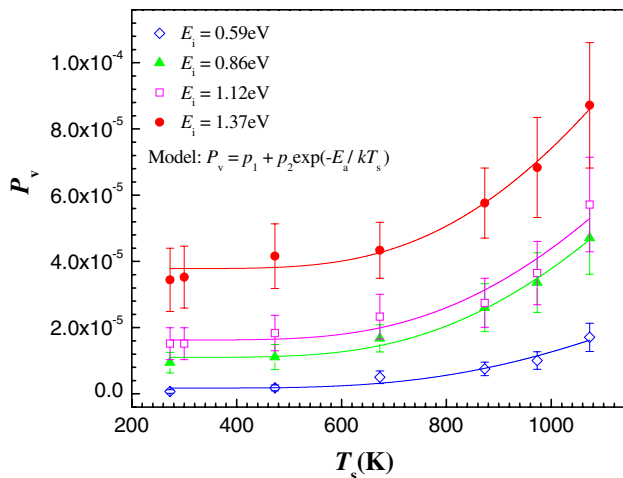


FIG. 2 (color online). Model simulation of $v = 0 \rightarrow 1$ vibrational excitation of HCl on Au(111). The symbols are the experimental measurements and the solid curves are the simulated results. Combined adiabatic and nonadiabatic mechanisms are used in the model.

temperatures ($T_s = 298$ K results have been left out for clarity) as shown in Fig. 3. The influence of E_i and T_s variation on the total P_v is shown in Fig. 3(a). Here the symbols are observation and the solid lines are the modeled values. The derived *adiabatic* and *nonadiabatic* contributions to the P_v are shown in Fig. 3(b) and 3(c), respectively. Thus, for a specific choice of T_s and E_i , the value of Fig. 3(a) is the sum of the values of Fig. 3(b) and 3(c). One can see that the adiabatic contribution, Fig. 3(b), depends monotonically on E_i and is independent of T_s within experimental error. There is a marked threshold ($E_i \sim 0.57 \pm 0.07$ eV) indicating conversion of E_i to molecular vibration, rotation, and surface excitation. As has been pointed out previously, the threshold is substantially higher than HCl ($v = 0 \rightarrow 1$) vibrational spacing ($E_{\text{vib}} = 0.36$ eV), reflecting the inevitable excitation of surface degrees of freedom when a high energy projectile encounters an Au surface [29]. Of particular note, the nonadiabatic component exhibits no incidence energy threshold and strong T_s dependence, whereas the adiabatic component exhibits a translational energy threshold and weak or absent T_s dependence. At low values of T_s , the nonadiabatic contribution is nearly absent; the excitation is dominated by an electronically adiabatic mechanism. With increasing T_s , the nonadiabatic excitation increases rapidly. It is in-

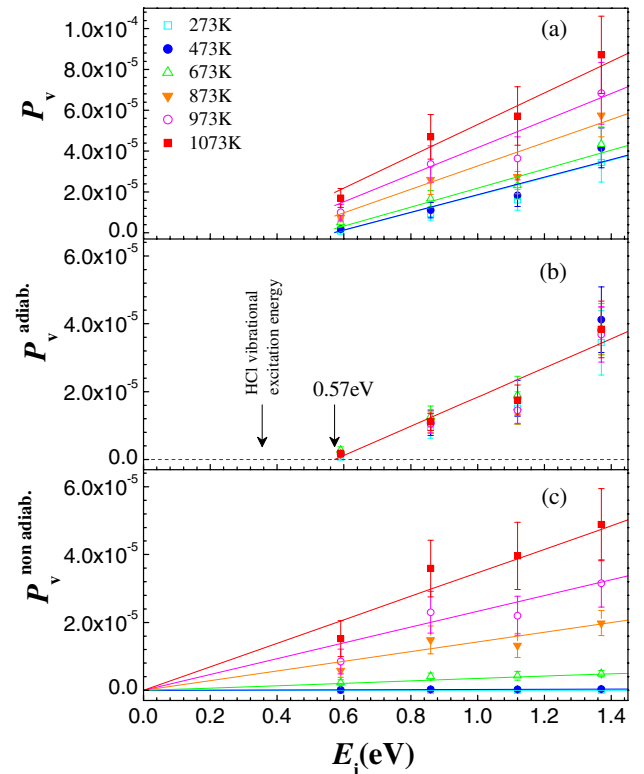


FIG. 3 (color online). E_i dependence of vibrational excitation probability of HCl ($v = 0 \rightarrow 1$) from Au(111) at 6 values of T_s . (a) Total vibrational excitation. (b) Adiabatic vibrational excitation. (c) Nonadiabatic vibrational excitation. The solid lines are the model calculations. $T_s = 298$ K data have been left out of the figure for clarity.

teresting to speculate that a high temperature regime may exist for many systems where molecule-surface interactions are dominated by electronically nonadiabatic influences. It is important to realize that in an EHP-V mechanism, the activation energy is expected to be independent of incidence energy and equal to the vibrational energy spacing (0.36 eV). While it is possible to obtain a pseudo-Arrhenius T_s dependence for a model phonon-to-vibration (adiabatic) energy transfer mechanism, the pseudo-Arrhenius activation energy in these models decreases [25,26] (in one model linearly [31]) with increasing E_i . Furthermore, activation energies predicted from theory for NO on Ag and H₂ on Cu for a phonon-mediated vibrational excitation mechanism are typically less than 0.1 eV and decrease with increasing E_i . In addition, phonon-mediated models have not been reported to exhibit as large a curvature in the Arrhenius plot as our data over the temperature range shown in Fig. 1 or a thresholdless incidence energy dependence as is seen in Fig. 3. Thus, it appears unlikely that the phonon-mediated mechanism could explain all of the observations of this work.

The ability to separate the nonadiabatic and adiabatic contributions to P_v allows us to quantitatively compare the nonadiabatic contribution for different molecule-surface systems. For example, comparison of $A_{\text{HCl/Au}}(E_i = 1.12 \text{ eV}) \sim 1.9 \times 10^{-3}$ with $A_{\text{NO/Ag}}(E_i = 1.06 \text{ eV}) \sim 1.8$ shows that electronically nonadiabatic effects are about 1000 times smaller for HCl/Au than NO/Ag. There is no apparent reason why systematic evaluations of nonadiabatic propensity cannot be generally measured in this way. While we have no predictive theory to explain these results, Newns [32] and others have postulated that the coupling between metal electrons and molecular vibration is strongly related to the energy of the affinity level near the point of closest approach. Relative to NO, the affinity level of HCl is energetically higher (electron affinity: 0.026 eV for NO and -0.5 eV for HCl). Thus, it can perhaps be qualitatively understood why HCl vibration would be less strongly coupled to the metal electrons compared to NO.

In conclusion, we report direct vibrational excitation of HCl ($v = 0 \rightarrow 1$) in the collisions with a Au(111) surface with a probability of the order of 10^{-4} – 10^{-6} , 2–3 orders of magnitude smaller than analogous vibrational excitation probability of NO on noble metals. We observe a transition from a regime with a nearly T_s independent excitation probability at low T_s to a regime with a strongly T_s dependent excitation probability at high T_s . The results are quantitatively consistent with a simple model involving a transition from an electronically adiabatic mechanism at low T_s to the onset of an electronically nonadiabatic mechanism at high T_s . We believe this is the first observation of a transition from electronically adiabatic to nonadiabatic behavior in a molecule-surface collision system and hope the results will provide a benchmark for theories of molecular interactions with surfaces.

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