

# Direct translation-to-vibrational energy transfer of HCl on gold: Measurement of absolute vibrational excitation probabilities

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## Abstract

Vibrational excitation of HCl molecules ( $v = 0 \rightarrow 1$ ) has been observed when HCl molecular beams at energies of 0.59–1.37 eV are scattered from a Au(1 1 1) surface at low surface temperature ( $T_s = 273$  K). The incident and scattered HCl is probed state-selectively using 2 + 1 REMPI. The vibrational excitation probability depends strongly on incidence kinetic energy,  $E_i$ , exhibiting a threshold near  $\sim E_i = 0.57$  eV. We measured the absolute vibrational excitation probability which varies from  $10^{-6}$  to  $10^{-5}$  over this energy range, 1–2 orders of magnitude higher than the thermal equilibrium expectation value. The magnitude of the excitation probability, the near specular angular distributions of the scattered  $v = 1$  molecules and the dramatic narrowing of the angular distribution near threshold are all consistent with a direct translation to vibration (T–V) mechanical energy transfer mechanism.

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## 1. Introduction

The study of the dynamics of the energy transfer between gas molecules and solid surfaces provides fundamental information important to the understanding of interfacial chemistry [1–5]. While substantial work has been carried out to characterize the dynamical energy transfer pathways possible in molecule/surface interactions, there is still not a clear understanding of the role of molecular vibration in a molecule/surface collision. Vibrational energy transfer at metal surfaces is of potential importance to the understanding of sticking [6,7], it may be involved with vibrationally promoted surface reactions [7–9] and it may result in surface electronic excitation [10].

Vibrational energy transfer mechanisms can be characterized as “mechanical” (adiabatic) or “electronic” (non-

adiabatic). Mechanical energy transfer is dictated by the interatomic forces represented by the electronically adiabatic potential energy hypersurface. For molecular beams where the initial rotational excitation is negligible, the energy source of vibrational excitation may be the translational energy of the incident molecule, the surface atom motion, or both. For example,  $H_2$  produced in  $v = 1$  through collisions with a copper surface is thought to sample the stretching forces found near the dissociative adsorption transition state [7] allowing efficient conversion of translational to vibrational motion (T–V).

Electronically non-adiabatic mechanisms are characterized by dynamics where energy is directly transferred between the molecule and electrons in the metal. There are now a number of experimental observations that show the importance of electronically non-adiabatic behavior. Morin et al. [11] measured a picosecond vibrational lifetime for CO on Cu(1 0 0), which could only be explained by non-adiabatic effects [12]. Direct vibrational excitation was observed in gas-surface collision for NO scattering from

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Ag(111) [10,13]. This study showed that the vibrational excitation depended not only on incidence kinetic energy but also strongly on surface temperature and provided clear evidence that “hot” electron hole pairs in metals could excite molecular vibration. Later studies for NO on Cu(110) revealed similar results [14]. Observations of vibrational excitation and de-excitation of NO( $v=2$ ) on Au(111) [15], vibrationally promoted electron transfer [16] and vibrationally promoted electron emission [17] have all provided additional evidence for electronically non-adiabatic energy transfer. Diekhoner et al. [18] reported indirect evidence for strong non-adiabatic coupling for N<sub>2</sub> associative desorption from and dissociative adsorption on Ru(0001). Recently, studies of vibrational relaxation of H<sub>2</sub> on copper have suggested that electronically non-adiabatic influences may be important [19]. Most theoretical simulations (which rely on density functional theory) are still not capable of characterizing excited electrons in metals. Other approximate methods have been developed with some significant successes, but more work is needed [1].

Scattering experiments that probe vibrational energy transfer can also be divided into two categories by time scale, direct (specular) and indirect (trapping/desorption). Trapping mediated energy transfer leads to thermally accommodated surface adsorbates, which may desorb with their internal degrees of freedom still at or near thermal equilibrium with the surface. Direct scattering typically occurs on a picosecond time scale (or less) and is therefore much simpler to model theoretically. Furthermore, for direct scattering, molecular properties measured after the collision retain a “memory” of their initial conditions modified by the forces experienced during the collision. Obviously, the final properties of the scattered molecules need not be in thermal equilibrium with the surface and thus, at least potentially, observations of direct scattering events provide more detailed and specific information about the molecule/surface encounter.

Most of our knowledge of energy transfer in gas–solid collisions is based on the study of the limited number of model systems. Thus, generalizations are difficult. In order to extend our understanding of the molecular dynamics at the gas–surface interface, here we examine a new system, HCl on Au(111). While we say “new”, this system has been studied previously providing accurate observations for HCl *rotationally* inelastic scattering, where Lykke and Kay [20] carried out a complementary study of HCl( $v=0$ ) undergoing direct-inelastic scattering from Au(111). In addition to obtaining a detailed view of the rotationally inelastic scattering dynamics, this work led to the first quantitative estimate of the binding energy of HCl to Au(111) ( $\sim 4\text{--}5$  kcal/mol) a finding that is relevant to and consistent with the conclusions of this work to be presented below. Korolik et al. [21] observed the trapping-desorption and direct-inelastic scattering for HCl( $v=0$ ) from MgO(100) at two incidence energy regimes. No vibrationally inelastic channels were reported in either of these papers. In this proceeding, we report the first observation

of *vibrationally* inelastic scattering ( $v=0 \rightarrow 1$ ) of HCl from Au(111). The key observations of this work are:

1. The absolute vibrational excitation probability is dramatically smaller than that of NO( $v=0 \rightarrow 1$ ) excitation on Ag, Cu and Au, systems where electronically non-adiabatic mediated vibrational energy transfer is thought to dominate.
2. The vibrational excitation probability increases strongly with  $E_i$  with a clearly observable energy threshold at  $E_i \sim 0.57$  eV.
3. The angular distribution of vibrationally inelastically scattered molecules narrows dramatically as one approaches the threshold from above. To our knowledge such an effect has not been previously observed.

All of these observations strongly support a mechanical translation-to-vibration energy transfer mechanism.

## 2. Experiment

The measurements were performed on a new beam-surface scattering instrument. Here we give only a cursory description of this instrument deferring a detailed description to a future publication [22]. The instrument consists of a molecular beam source chamber, an ultrahigh vacuum (UHV) surface-science chamber separated by two differential pumping chambers. The pulsed jet-cooled HCl molecular beams are generated by expanding HCl seeded in H<sub>2</sub> at about 3 atm. stagnation pressure through a piezo-electrically actuated pulsed nozzle (1 mm diameter orifice, 10 Hz); by careful adjustment of the valve, beam pulses of  $<50 \mu\text{s}$  FWHM could be produced. The expanded HCl beam was skimmed by a 1.5 mm diameter skimmer and passed through first, second differentially pumped regions and a 2 mm diameter aperture into the UHV surface chamber to collide with a gold surface and then bounce back. The distance from nozzle to surface is only 180 mm. This short distance provides an intense molecular beam and the ability to resolve in time incoming and scattered (outgoing) signals. The mixtures with ratios of 1%, 2.5%, 5% and 10% HCl in H<sub>2</sub> were used to vary the kinetic energy of the HCl.

The Au(111) single crystal resides in an UHV chamber ( $\sim 1.5 \times 10^{-10}$  Torr) and is mounted on a liquid nitrogen cooled manipulator permitting XYZ $\theta$  motions. The surface was cleaned daily by sputtering with 3 kV Ar<sup>+</sup> for 15–20 min and then annealed to 780 K for 20 min every 2–3 h. Auger electron spectroscopy was used to check surface condition.

HCl( $v=0$  and 1) molecules were probed state-selectively by 2 + 1 resonance enhanced multi-photon ionization (REMPI) via the Q-branch of  $E^1\Sigma^+ - X^1\Sigma^+$  (0,0) band near 238 nm and (0,1) band near 247 nm. To obtain the required laser light, the output of a dye laser (Sirah, CSTR-LG-24, line-width  $0.07 \text{ cm}^{-1}$ ) was frequency doubled in BBO to produce 4–6 mJ of tunable radiation near

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