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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(111) 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(100), which could only be explained by non-adiabatic effects [12]. Direct vibrational excitation was observed in gas-surface collision for NO scattering from

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_2 associative desorption from and dissociative adsorption on Ru(0001). Recently, studies of vibrational relaxation of H_2 on copper have suggested that electronically non-adiabatic influences may be important [19]. Most theoretical simulations (which rely of 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$4–5 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 ($v = 0 \to 1$) of HCl from Au(111). The key observations of this work are:

1. The absolute vibrational excitation probability is dramatically smaller than that of $NO(v = 0 \to 1)$ 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_2 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 μs FWMH 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_2 were used to vary the kinetic energy of the HCl.

The Au(111) single crystal resides in an UHV chamber ($\sim$1.5 × 10^{-10} Torr) and is mounted on a liquid nitrogen cooled manipulator permitting XYZΘ motions. The surface was cleaned daily by sputtering with 3 kV Ar$^+$ 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 cm^{-1}) was frequency doubled in BBO to produce 4–6 mJ of tunable radiation near

238 nm or 247 nm. The laser beam was focused into the UHV chamber with a $f = 30$ cm lens. The ion time-of-flight collection system consists of a repeller and two cylindrical focusing lenses followed by a MCP detector. The incident and scattered molecules were detected at the same position (20 mm away from the surface) with different delay time. The rotational distributions were recorded by scanning the probe laser wavelength and angular distributions were measured by moving the probe laser along the plane perpendicular to the molecular beam.

3. Results and discussion

As a check, we measured rotationally inelastic scattering of HCl in its ground vibrational state from Au(1 1 1) including variations of the angular and rotational distributions with incidence energy and surface temperature and compared these measurements with the literature. We do not report any of these results here except to note that they are in good agreement with the previous work of Lykke and Kay [20]. This agreement provides validation of the reliability of the data measured with our new instrument.

Vibrationally inelastic scattering producing HCl($v = 1$) is the main focus of this work. The rotational state (wavelength resolved $2 + 1$ REMPI spectra) and state-selected angular distributions (laser position scans) were measured at surface temperature $T_s = 273$ K at four different translational incidence energies, $E_i = 1.37$ eV, 1.12 eV, 0.86 eV and 0.59 eV. Two examples of the rotationally resolved $2 + 1$ REMPI spectra are shown in Fig. 1. In both panels of the figure, the $E^1\Sigma^+(v' = 0) - X^1\Sigma^+(v'' = 1)$ $2 + 1$ REMPI spectrum (band head found at a two-photon energy of 80,893 cm^{-1}) is displayed for an incident molecular beam containing 1% HCl in H_2 ($E_i = 1.37$ eV). The three spectral lines at a two-photon energy of $\sim$80,598 cm^{-1} result from S-branch of V $^1\Sigma^+(v' = 10) - X^1\Sigma^+(v'' = 1)$ band and are not used in the analysis. In Fig. 1(a) the timing between pulsed molecular beam and laser pulse is adjusted to observe the incoming molecules before colliding with the Au(1 1 1) surface. As testimony to the sensitivity of our instrument, the thermally populated HCl($v = 1$) can be clearly detected in the molecular beam even though thermal population ratio of HCl $v = 1$ to $v = 0$ at room temperature is only 9.8×10^{-7}. The small number of lines in the spectrum indicates the low rotational temperature ($T_R \sim 25 \pm 10$ K) of the incident molecular beam. We use this signal as an absolute calibration for excitation probabilities due to surface scattering as described below.

In Fig. 1(b) the same spectrum is recorded using a $\sim$20 μs longer delay between the pulsed nozzle and the probe laser pulse. The assigned Q-branch up to $J = 8$ lines are due to vibrational excitation after the HCl molecular beam collides with Au(1 1 1) surface. One can immediately see that the integrated intensity of the $v = 1$ assigned lines is substantially larger after scattering than before, indicating additional population in the $v = 1$ state has been produced
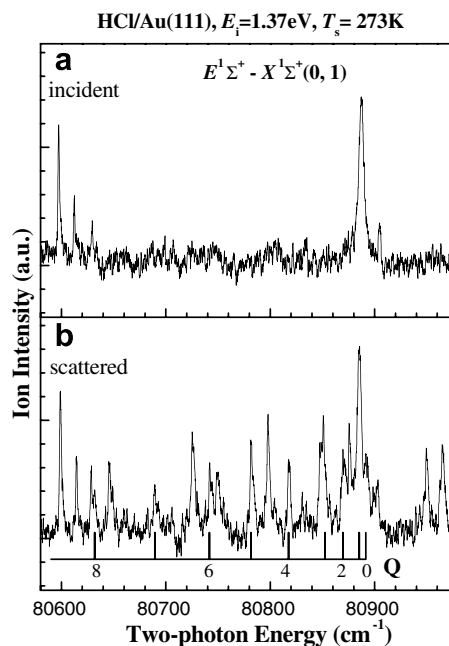

Fig. 1. $2 + 1$ REMPI spectra for (a) the incident HCl molecular beam and (b) HCl scattered from Au(1 1 1). (a) Thermally populated HCl($v = 1$) is observed in a molecular beam with 1% HCl seeded in H_2. Less than 10^{-6} of the beam is in the $v = 1$ state. The incident molecular beam is rotational cold. (b) Adjusting the timing between the short-pulsed molecular beam (<50 μs pulse duration) and the laser by only about 20 μs reveals the vibrationally inelastic scattering, indicated by the assigned Q-branch.

by the collisions with the surface. This increase in $v = 1$ signal in the raw data occurs despite the fact that the pulse of scattered molecules is spread over a wider angular range.

Angular distributions for scattered HCl($v = 1$, $J = 6$) at four incidence energies are shown in Fig. 2. Although not shown, the angular distributions for other J-states of $v = 1$ were not markedly different. Also shown for reference is the angular distribution of the incoming molecular beam. All the data have been fit with Gaussian distributions by a least squares algorithm, shown as solid lines in the figure. Note that the scattered molecules are deflected away from the direction of the molecular beam indicating the slightly ($3.2 \pm 0.3°$) off-normal incidence of the incoming molecular beam. For incidence energies above 0.59 eV, the scattering angular distributions are all peaked near the specular direction (shown in the figure) which is indicative of the direct-inelastic scattering. Note that the angular distribution obtained at $E_i = 0.59$ eV is much more sharply peaked than those obtained at higher incidence energies and has a maximum about 3° from the molecular beam, i.e. in the direction of the surface normal. We will shortly return to this observation after first presenting results necessary to understand its significance.

In Fig. 3, rotational distribution of scattered HCl($v = 1$) are shown as Boltzmann plots at four values of incidence translational energy. The rotational temperatures, T_R, reflecting the observed rotational state population distributions are presented in the inset. These rotational tempera-
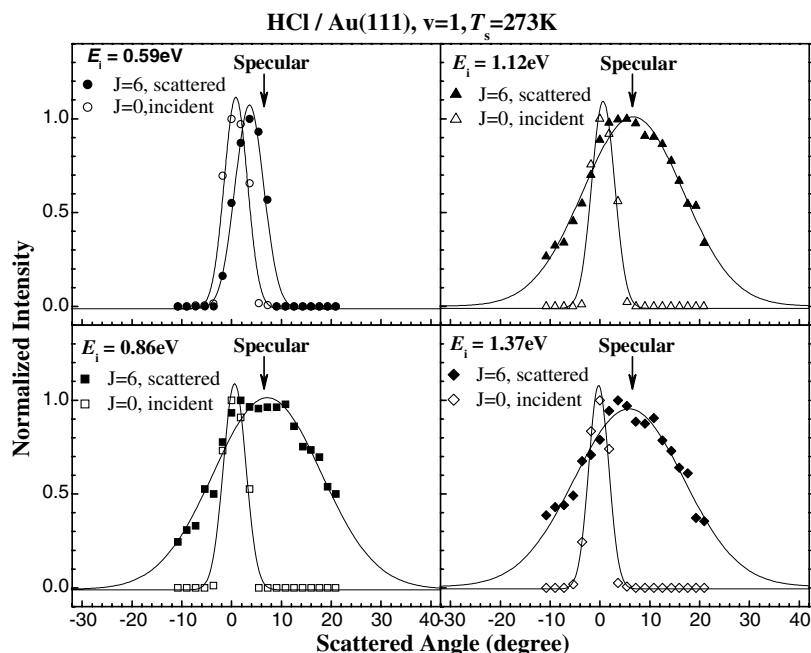
HCl / Au(111), v=1, T_s =273K

Fig. 2. Angular distributions for vibrationally inelastic scattering of HCl ($v = 0 \rightarrow 1$, $J = 6$) from Au(1 1 1) at four incidence energies. The points are the experimental data; while the solid lines are Gaussian fits to the data. Note that the scattering peaks at defection angle of 6–7°, due to the fact that the molecular beam is incident on the surface ∼3° off normal. The angular distribution at $E_i = 0.59$ eV appears at a smaller (∼3°) defection angle, indicating a preference for emerging near the surface normal.
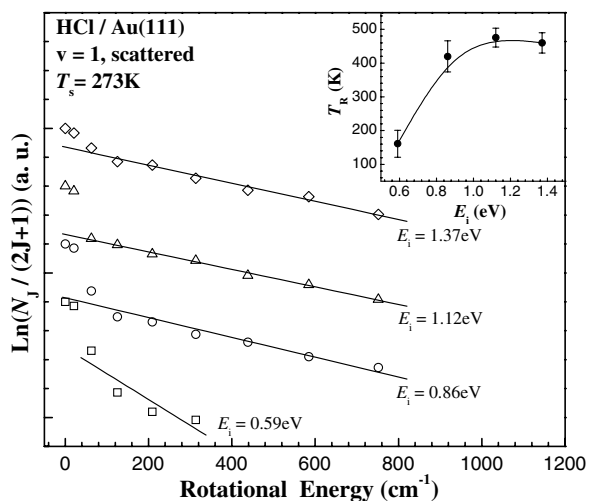

Fig. 3. Boltzmann plots for the scattered HCl($v = 1$) from Au(1 1 1) at surface temperature $T_s = 273$ K and incidence energies $E_i = 0.59$ eV, 0.86 eV, 1.12 eV and 1.37 eV. Inset: rotational temperature T_R derived from Boltzmann distribution fit. The rotational excitation is relatively insensitive to incidence energy of translation except near the threshold of vibrational excitation.

tures were derived from rotationally resolved signals, correcting for line-strength factors and fitted to Boltzmann distribution. Note the significant decrease in rotational temperature seen at the lowest incidence energy.

To obtain the absolute excitation probability, we compare the observed $v = 1$ signal resulting from scattering to the thermal population in the incident molecular beam. The observed relative signals must also be corrected for

the differences in angular, rotational and temporal distribution, as well as for laser power. The difference in the temporal distributions of the two signals was only minor. All of these measurements have been repeated several times.

The derived incidence energy dependence of the vibrational excitation probability of HCl($v = 0 \rightarrow 1$) is shown in Fig. 4. Several interesting things can be seen from this figure.

First, the vibrational excitation probability of HCl($v = 0 \rightarrow 1$) on Au(1 1 1) at low surface temperature
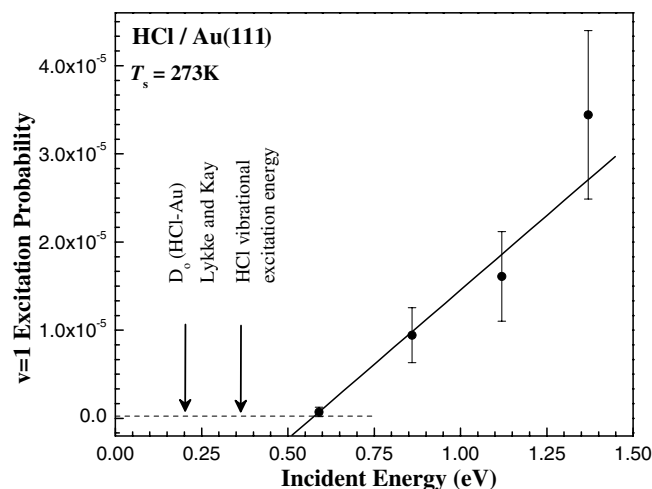

Fig. 4. Incidence energy dependence of vibrational excitation probability of HCl($v = 0 \rightarrow 1$) from Au(1 1 1) at 273 K surface temperature. The dash line at 2.5×10^{-7} is the thermal expectation value. Also shown is the orientation averaged binding energy of HCl to Au(1 1 1) derived by Lykke and Kay [20] and the HCl vibrational ($v = 0 \rightarrow 1$) excitation energy.

($T_s = 273$ K) is always less than about 5×10^{-5} (observed at the highest value of E_i) and the lowest excitation probability for HCl is 7.3×10^{-7}. Comparing to previously published results for NO($v = 0 \to 1$) on Ag(111) where the largest excitation probability for NO can reach $\sim 7 \times 10^{-2}$ [10,13], it is clear that the energy transfer is much less efficient in the present case, suggesting a different energy transfer mechanism.

Second, there is a marked threshold behavior at $E_i \sim 0.57$ eV. Such a threshold is consistent with a T–V energy transfer mechanism with accompanying phonon and rotational (and possibly electron hole pair) excitation. Note that the observed threshold (0.57 eV) is substantially higher than HCl($v = 0 \to 1$) vibrational excitation ($E_{vib} = 0.36$ eV). This higher threshold is expected for a T–V mechanism, because the available energy will be shared between vibrational excitation, phonon excitation, rotational excitation and center of mass motion of the recoiling HCl. An impulsive model balancing momentum between a single Au atom ($m = 197$) and a HCl molecule ($m = 36$) projectile, would dissipate $\varepsilon = 0.15 \times E_i$ into Au atom motion. Thus, if $E_i = 0.59$ eV then $\varepsilon = 0.09$ eV. This serves as a reasonable upper limit to the estimation of phonon excitation. Fig. 3 shows that the average rotational excitation kT_R is ~ 0.03 eV. Hence, it is reasonable that the threshold for vibrational excitation should exceed the HCl vibrational spacing by more than 0.1 eV as observed. We cannot rule out that some fraction of the incidence energy of translation (on the order of 0.1 eV or less) may also excite electron hole pairs in the metal.

We now return to the extraordinarily narrow angular distribution observed near threshold. We suggest two possible effects that might contribute to this narrowing of the angular distribution near threshold: one associated with surface thermal motion and the other with trapping. The width of the angular distributions of molecules scattered from low index planes of metal surfaces has a strong contribution from normal momentum transfer between the incident molecule and vibrational phase of moving surface atoms; collisions with surface atoms moving away from the surface result in deflection of the molecule towards the surface normal (supra-specular), while collisions with surface atoms moving into the surface, result in deflection towards the plane of the surface (sub-specular). Higher surface temperatures imply faster surface atom motion and thus a broadening of the angular distribution. Near threshold, however, the phase space of surface thermal motion which can contribute to HCl($v = 0 \to 1$) excitation is restricted. Thus the angular distribution will narrow and move towards the surface normal. This effect does not provide a complete explanation of the observed angular distributions. Note that the angular distribution is narrowed in both the positive and negative scattering angles. The clipping of the angular distribution at negative angles cannot result from the phase space restrictions associated with thermal surface atom motion.
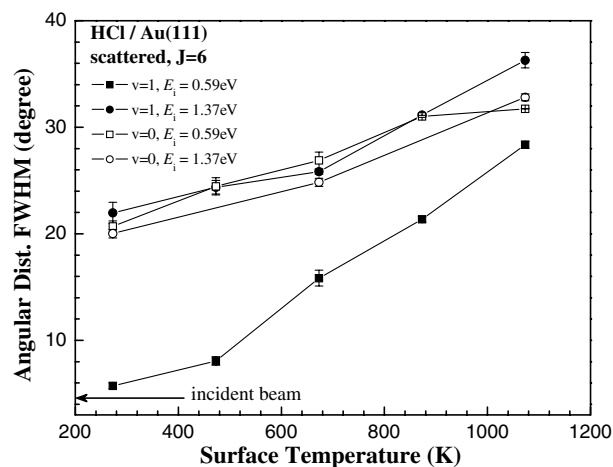

Fig. 5. Influence of surface temperature on the angular distribution for vibrationally inelastic scattering near threshold $E_i = 0.59$ eV. Comparison is made to the vibrationally inelastic scattering high above threshold and to vibrationally elastic processes at the same translational incidence energy. The symbols are the full widths at half maximum (FWHM) of Gauss fits to the observed angular distributions. Measurements are presented for $J = 6$.

Rather, we believe this dramatic narrowing of the angular distribution results from trapping of HCl($v = 1$) molecules produced near threshold. Consider for example those molecules that have undergone T–V excitation with phonon and rotational excitation and emerge from the surface with considerably lower recoil translational energy. Only those molecules that emerge near the surface normal, where nearly all of the molecule's remaining translational energy is useful for escape will remain un-trapped and be observed in this experiment. Conversely, those that emerge at large off-normal angles of recoil do not possess a large enough normal component of translation energy to escape the attractive forces of the surfaces.

To help confirm or disprove this view we also measured the effect of heating the surface on the angular distributions for this near threshold value of the incidence energy. The outcome can be seen in Fig. 5, where it is shown that a change in T_s of 673 K dramatically broadens angular distributions in the near threshold incidence energy scattering of $v = 0 \to 1$, while having a much weaker influence on the high above threshold $v = 0 \to 1$ scattering or the $v = 0 \to 0$ scattering. We believe this can be understood by the additional relative translational energy provided between Au atom and the HCl molecule with increasing surface temperature.

4. Conclusions

Molecular beam and quantum-state selective probe techniques have been used to study the energy transfer in the scattering of HCl molecules from gold surface. Direct vibrational excitation of HCl($v = 0 \to 1$) has been observed when H_2 seeded molecular beams are scattered from a Au(111) surface at low surface temperature ($T_s = 273$ K).

Absolute vibrational excitation probabilities of 10^{-6}–10^{-5} were obtained at four incidence energies, 1–2 orders of magnitude higher than the thermal equilibrium expectation value. The vibrational excitation is found to depend on incidence kinetic energy, E_i, exhibiting a threshold near $\sim E_i = 0.57$ eV. Angular distributions of the scattered HCl($v = 1$) are quasi-specular and collapse to a very narrow range near threshold values of E_i, suggesting a direct T–V mechanical energy transfer mechanism.

Acknowledgements

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