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STATE-TO-STATE INELASTIC AND REACTIVE
MOLECULAR BEAM SCATTERING FROM SURFACES

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ABSTRACT

Resonantly enhanced multiphoton ionization (REMPI) laser spectroscopic and molecular beam-surface scattering techniques are coupled to study inelastic and reactive gas-surface scattering with state-to-state specificity. Rotational, vibrational, translational and angular distributions have been measured for the inelastic scattering of HCl and N_2 from Au(111). In both cases the scattering is direct-inelastic in nature and exhibits interesting dynamical features such as rotational rainbow scattering. In an effort to elucidate the dynamics of chemical reactions occurring on surfaces we have extended our quantum-resolved scattering studies to include the reactive scattering of a beam of gas phase H-atoms from a chlorinated metal surface M-Cl. The nascent rotational and vibrational distributions of the HCl product are determined using REMPI. The thermochemistry for this reaction on Au indicates that the product formation proceeding through chemisorbed H-atoms is slightly endothermic while direct reaction of a gas phase H-atom with M-Cl is highly exothermic (ca. 50 kcal/mole). Details of the experimental techniques, results and implications regarding the scattering dynamics are discussed.

I. INTRODUCTION

There has been considerable interest in gas-surface scattering in recent years and a few reviews[1-3] outline some of the intense activity in the field. Additionally, the field of reactive scattering from well-characterized surfaces has shown promise and is reviewed in recent articles.[4,5] Most of the work in these areas has been done by detecting the scattered species without internal state resolution.[6] Time-of-flight detection of the products has allowed measurement of the translational energies involved. Other classical methods have been utilized to detect internal states of products (e.g. infrared absorption and emission, electron beam induced fluorescence, and chemiluminescence).[7-11] Theoretical studies[12,13] have indicated that there is much chemical information to be gained from knowledge of the internal state distributions (rovibrational) of the scattered particles.

The recent coupling of surface science, molecular beam and laser technologies has made possible the measurement of total energy disposal in gas-surface scattering (i.e. the quantification of translational, vibrational, rotational and electronic energies). Laser-induced fluorescence,[14-17] (1+1) resonantly enhanced multiphoton ionization (REMPI),[18-26] (2+1) REMPI,[27-32] and (2+2) REMPI[33-35] have all been employed in the study of state-resolved gas-surface scattering. In this paper, we report some recent results on the (2+1) REMPI detection of HCl and N_2 inelastically scattered from Au(111). Results are also presented for the internal state distributions of HCl produced during the reactive scattering from a chlorinated Au(111) surface.

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II. EXPERIMENTAL

The experimental apparatus utilized for quantum-resolved inelastic gas-surface scattering has been discussed in detail previously,[30] and thus, will only be outlined here. The experiment consists of scattering a pulsed supersonic molecular beam from a well-characterized single crystal surface and detecting the scattered molecules using (2+1) REMPI.[36-39] The molecular beam is prepared by expanding N_2 or HCl seeded in various rare gases through a pulsed nozzle. The gas issuing from the nozzle passes through three stages of differential pumping where it is collimated into a beam before impinging on the Au(111) target that is housed in an ultrahigh vacuum (UHV) chamber. The Au(111) surface is cleaned by Ar^+ sputtering and subsequently ordered by thermal annealing. The surface cleanlinesss is monitored with Auger Electron Spectroscopy (AES).

A schematic diagram of the experimental apparatus employed for reactive scattering is displayed in Fig. 1. In these experiments the two reactants that are utilized are gas phase H atoms and Cl atoms chemisorbed on Au(111). The H atoms are produced in a 2.45 GHz microwave discharge source and expanded into a quasi-effusive beam through an ~2mm diameter hole in a pyrex tube. Hydrogen pressure of ~1 torr in the discharge tube results in a beam that consists of >80% atomic hydrogen. The major portion of the gas flux issuing from the discharge source is exhausted by a 4" diffusion pump. The on-axis atomic flux enters a buffer chamber (pumped by a LN_2-baffled 6" diffusion pump) where it is collimated into a beam via an ~ 3mm orifice. The resultant beam enters a UHV scattering chamber that is pumped by a 1500 l/sec turbomolecular pump and a Ti sublimation pump. The H-atom beam impinges on the crystal target 12cm downstream from the discharge source with a flux of ~20 monolayers/second. The M-Cl reactant is prepared by dissociatively adsorbing gaseous Cl_2 onto Au(111) through a secondary effusive source projected at the target. The directionality of this source coupled with the large dissociation probability (near unity) enable a large surface concentration of Cl to be attained while still maintaining a small background of Cl_2 in the UHV chamber. The H atom beam is modulated at 20 Hz with an electromechanical shutter having an open time of 2 msec. This short pulse readily enables reaction products formed on the target to be distinguished from HCl formed on the walls of the UHV chamber. The Au(111) crystal is mounted on a manipulator permitting x,y,z,θ motion and is liquid-nitrogen cooled and resistively heated. The UHV reaction chamber also contains an Ar^+ sputter gun for cleaning and an AES and LEED spectrometers for monitoring surface cleanliness and order, respectively
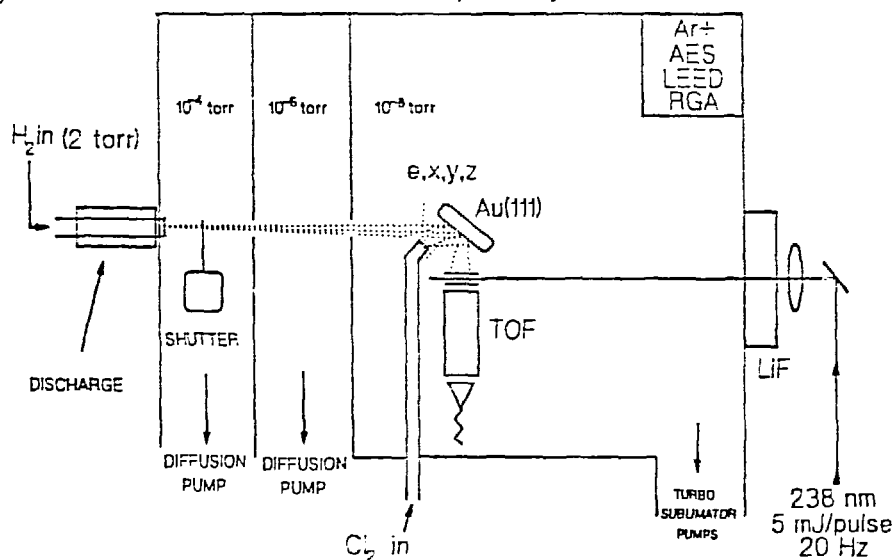

Figure 1. Schematic diagram of the reactive scattering apparatus.

Rovibrational distributions of the reactively scattered HCl product are determined using (2+1)REMPI. The ionizing radiation is generated using a Nd:YAG pumped dye laser whose output is frequency doubled and subsequently mixed with the residual fundamental of the YAG laser to produce pulsed, tunable UV light at ~235 nm (20 Hz,10 nsec, 5mJ/pulse).   This laser beam is focused by a 35 cm lens to a waist located between the plates of a time-of-flight mass spectrometer (TOF). The photogenerated HCl$^+$ ions are detected using a charge-sensitive gated integrator. The Q-branch-dominated (2+1) REMPI detection scheme gives essentially a direct map of the rotational population of the product HCl molecules[32].

III. RESULTS

A. Rotationally Inelastic Scattering of HCl From Au(111)

The utility of REMPI as a tool for detecting state-resolved gas-surface scattering is displayed in Fig. 2. The top part of the figure is a spectrum of 300K HCl gas taken at a total pressure of 10^{-8} torr. A cursory examination reveals that the relative intensities of the transitions have the envelope of a rotational Boltzmann distribution. This is due to the dominance of the "zeroth rank tensor"[36] in the (2+1) MPI of this $^1\Sigma <-- ^1\Sigma$ transition and makes the analysis of the data particularly simple.[32] This can be exploited in the analysis of the populations in the molecular beam (middle part of Fig. 2) and the scattered distribution (bottom part of figure). The incident molecular beam composed of ~ 85% J=0 is scattered into several rotational states after impacting the Au(111) surface. A cursory examination of the three panels in this figure points out that HCl scatters from Au(111) in a direct manner (doesn't leave the surface rotationally equilibrated) and in an inelastic manner (many rotational states are populated in the scattering event).

A rotational Boltzmann plot is presented in Fig. 3 for three different normal kinetic energies of HCl impacting the surface (normal kinetic energy is the energy associated with motion perpendicular to the surface, $E_n = E_i\cos^2\theta$). As clearly displayed in the figure, the scattered HCl rotational distribution depends on E_n. The departure of these plots from linearity is indicative of rotational "rainbow" scattering[40-42] and further indicates that the scattering is direct. Both the beam kinetic energy and surface temperature are found to be equally important in determining the rotational excitation probability. In fact, the mean scattered rotational energy (E_{rot}) can be globally fit to the simple bilinear relationship[17,32,43]:

$$<E_{rot}> = a(E_n + E_w) + b(2kT_s) \qquad 1)$$

where a is the efficacy for transfer of translational energy (of the incoming molecule) to rotational energy (a=.08), b is the efficacy for transfer of energy associated with the vibrational motion of the surface atoms to HCl rotational (b=.08), and E_w is the depth of the orientation-averaged attractive well (E_w=5kcal/mole) through which HCl is accelerated as it approaches the surface held at a temperature T_s.

We also find that the HCl scatters from the surface quasi-specularly[44] with very little (<20%) of the initial kinetic energy deposited into the surface phonons. These results were acquired by utilizing the angular rotation of the sample and the chopper wheel/laser delay aspects of the apparatus, respectively. The details of these measurements are discussed elsewhere .[32]
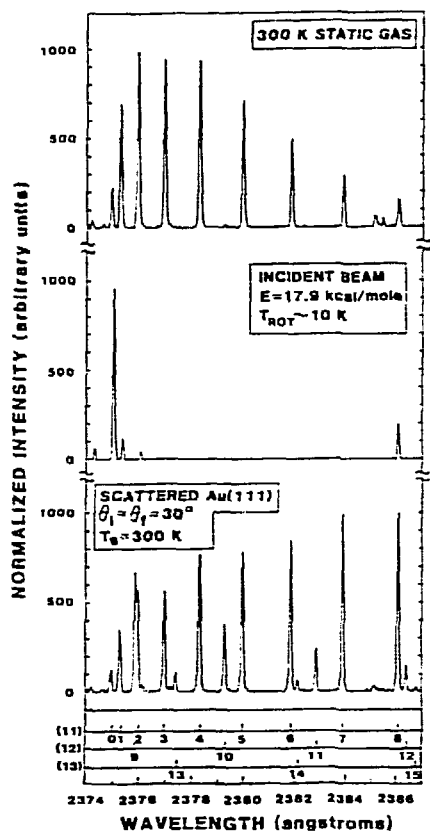
Figure 2. (2+1) REMPI spectra of HCl for a static gas(top), the incident molecular beam(middle) and for HCl scattered from Au(111) (bottom).
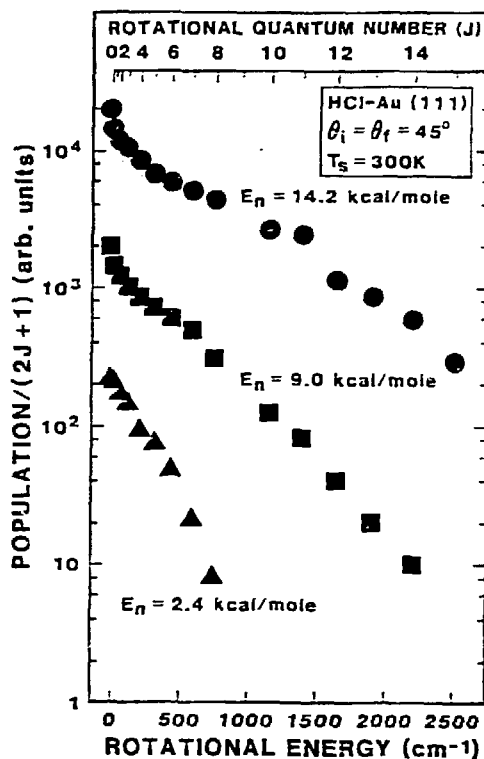

Figure 3. Rotational Boltzmann plot for HCl scattered from Au(111) for three different normal kinetic energies.

B. Rotationally Inelastic Scattering of N_2 From Au(111)

The development of a new, high sensitivity (2+1) REMPI scheme for N_2 has allowed the detection of N_2 at the 10^6 molecules/cm^3 level and has permitted state-resolved spectroscopy on molecules scattered from surfaces to be performed in a routine fashion.[31,45] The transition involved is a''$^1\Sigma_g^+$–X$^1\Sigma_g^+$ with the 2 photon a'' resonant state (the first Rydberg state with singlet character) ~ 3 eV below the ionization threshold, so that a third photon can easily ionize the N_2 species. BBO (β-BaB$_2$O$_4$) crystals make the wavelength range of 200nm-250nm easily accessible to any lab with a pulsed dye laser.[46] In fact, the same tripled dye allows the sensitive detection of N_2, H_2, D_2, HD, and NO and probably many other molecules as well.[47]

Figure 4 displays a (2+1) REMPI spectrum of 300K N_2 taken at a pressure of ~10^{-8} torr. The spectral resolution is limited by the bandwidth of the dye laser (~0.1cm^{-1}). Comparisons of spectra taken at 300K and 1100 K with computer simulations reveal that the line strengths for this Q-branch (ΔJ=0) are rotational state independent to first order. Thus, the observed spectrum is simply a map of the relative rotational population. Additionally, the use of linearly polarized light obviates the need for a complicated polarization analysis to extract the rotational population

distribution. This insensitivity to the angular momentum polarization has both advantages and disadvantages with regard to gas-surface scattering. On the plus side, a state-resolved spectrum can be obtained, documented, and analyzed for the rotational and vibrational populations in a time-efficient and straightforward fashion. Thus, this (2+1) REMPI scheme is ideally suited for cursory exploratory studies of potentially dynamically interesting systems. On the other hand, the (2+1)REMPI scheme masks any interesting dynamical effects that lead to angular momentum alignment and orientation produced in the scattering process. In a series of elegant papers, Zare and coworkers[33-35] have utilized (2+2) REMPI detection of N_2 via the $a^1\Pi_g - X^1\Sigma_g^+$ transition[48] to study such angular momentum polarization effects for the N_2/Ag(111) system.   A coupling of these two multiphoton techniques should enable the dynamicist to focus on interesting systems by first screening all systems with the (2+1) REMPI method, and then concentrating on a particular feature with the (2+2) procedure. With currently available lasers, the (2+1) scheme is roughly 100-fold more sensitive than the (2+2) scheme.
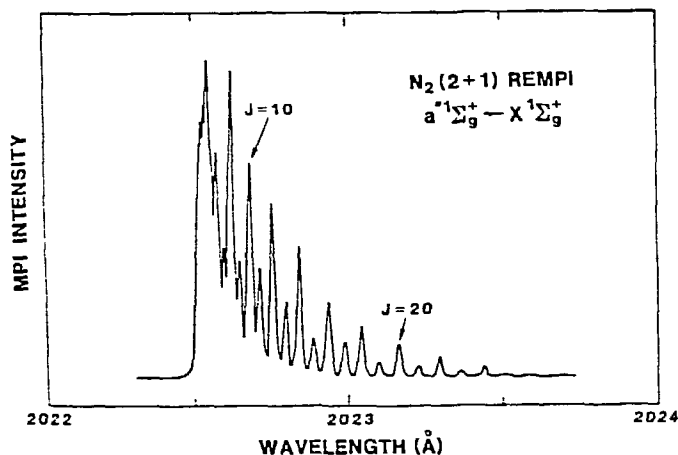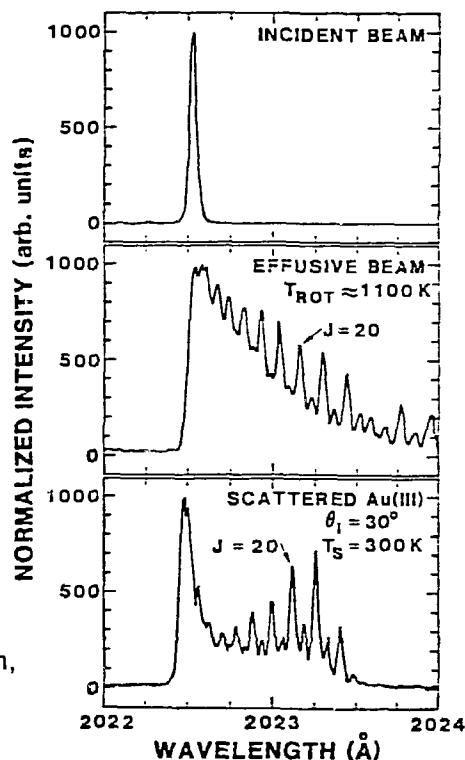

Figure 4. (2+1) REMPI spectrum of N_2.

Figure 5. N_2 spectra of the incident beam, effusive beam and scattered from a Au(111) surface.

Figure 5 displays some of the exciting results obtained by state-resolved detection of N_2 scattered from a Au(111) surface. The upper trace shows a (2+1) REMPI spectrum of the incident molecular beam. In this spectrum, the rotational temperature is below 10K and only levels J=0,1 have appreciable population. The center trace of Fig. 5 displays a (2+1) REMPI spectrum for an 1100K effusive beam. Rotational levels with J>30 are readily detectable and the rotational envelope is clearly characteristic of a Boltzmann distribution. The intensity alternation between even and odd J values arises from nuclear spin statistical effects.[49]   The lower trace displays a representative spectrum for N_2 scattered from Au(111). A comparison of the upper and lower traces clearly indicates that the scattering is highly inelastic; clearly many rotational levels are populated by the scattering process. A cursory visual comparison between the middle and bottom spectra indicate that the scattered distribution is markedly non-Boltzmann as evidenced by the pronounced bimodality of

the rotational envelope. The local maximum at J=22 is an unambiguous dynamical signature of rotational rainbow scattering.[40,42,50]

We have utilized the (2+1) REMPI scheme to study the inelastic scattering of N_2 from Pd(111) and Au(111). In this proceedings, we summarize some of the more interesting findings. Detection of inelastically scattered N_2 at different final scattering angles results in drastically different internal energy distributions. Molecules scattered into superspecular final angles (i.e. exiting closer to the surface than specular) show large rotational energy transfer and pronounced rainbow features, while subspecular detection (i.e. closer to the surface normal than the specular) results in nearly rotationally elastic scattering. In the parlance of scattering theory, these measurements reflect features in the doubly-differential (quantum state and angle) rotationally-inelastic scattering cross section. The observed dependence of the scattered rotational distribution upon final angle indicates that the forces that give rise to rotational excitation act predominantly perpendicular to the surface plane. In other words, the linear momentum of the N_2 molecule parallel to the surface plane is nearly conserved. Thus, those molecules for which a translational-to-rotational (T-R) energy transfer occurs are scattered into larger final angles than those which scatter without a T-R transfer. Additional dynamical information can be obtained by examining the dependence of the rotationally resolved angular distributions upon incident beam translational energy, incident angle and surface temperature. A discussion of these dependences is beyond the scope of these proceedings and the interested reader is referred to the references.[31,51]

C. HCl PRODUCTION VIA H-ATOM REACTIVE SCATTERING FROM CHLORINATED Au(111)

In an effort to further understand the dynamical details of gas-surface interactions, we have extended our REMPI studies of HCl to include the state-specific detection of HCl formed from the reactive scattering of a gas-phase H atom from a chlorinated metal surface: Au(111):Cl. The motivation behind this study is an attempt to experimentally distinguish between two limiting mechanisms of reactive scattering from surfaces: Langmuir-Hinshelwood (LH) and Eley-Rideal (ER).[52] The LH mechanism is characterized by both reactants being equilibrated in their respective chemisorption potentials prior to the reactive encounter, whereas the ER mechanism assumes that one of the reactants enters the reactive coordinate directly from the gas phase. In principle, these two mechanisms should be readily distinguishable by the disposal of attendant exothermicity of the reaction. If the reactants are both equilibrated with the surface, the reaction enthalpy is calculable from the bond energies of the reactants and the product to the surface. In the case of chemisorbed H-atoms and Cl-atoms on Au(111), the reaction to form gas-phase HCl is nearly thermoneutral. In contrast, the enthalpy calculated for a reaction of a gas phase H-atom with a chemisorbed Cl-atom is ~ 50 kcal/mole exothermic. This is enough energy to produce vibrationally excited HCl with up to 6 quanta in vibration. Thus, (2+1) REMPI measurements that probe the nascent internal state distributions of the HCl product should be useful in unraveling the reaction mechanism.

Figure 6 displays rotationally-resolved (2+1) REMPI spectra for the HCl product formed in the ground vibrational state (v=0) for two different surface temperatures, 700K (top) and 200K (bottom). Recall from the discussion in Section IIA that the intensities of the rotational transitions are a direct map of the relative rotational populations. As clearly evident from Fig. 6 the HCl (v=0) formed on the 700K surface has a greater degree of rotational excitation than that which is produced on the 200K surface. Additionally, a few transitions that were not observed in the direct inelastic scattering (cf. IIA above) of HCl from Au(111) are detected. These transitions correspond to the (2+1) REMPI of gaseous Cl atoms[53] in both the ground and spin-orbit excited (~880cm^{-1}) electronic states. Neither the absolute nor relative intensities of these two Cl atom transitions varied appreciably with Au(111) surface temperature.
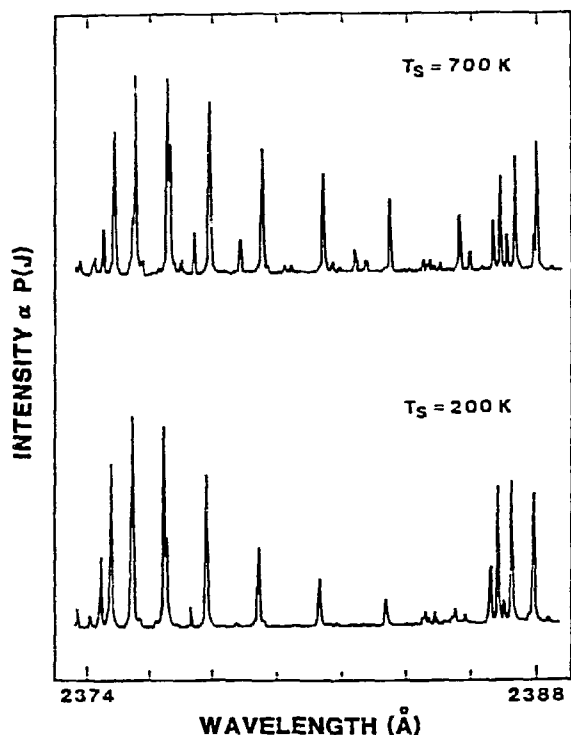
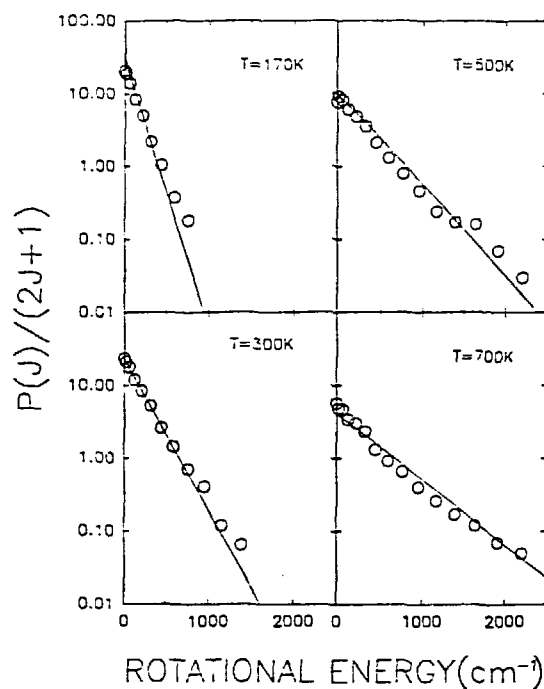**Figure 6.** HCl (v=0) formed from reactive scattering on Au(111).

Figure 7. Rotational Boltzmann plot for HCl (v=0) for four different surface temperatures.

Figure 7 displays a rotational Boltzmann plot for the HCl (v=0) produced at four different surface temperatures. Straight lines corresponding to rotational distributions thermally accomodated with the surface are shown for each plot. Clearly, the HCl (v=0) formed in the reaction is thermally equilibrated with the surface. The HCl (v=0) product yield (integrated over rotational levels) varies less than a factor of two over the surface temperature range 200K to 700K.

The (2+1) REMPI scheme for HCl is also capable of detecting HCl produced in its first vibrationally excited level (v=1). A representative spectrum of HCl formed in v=1 is shown in Fig. 8. In stark contrast to HCl (v=0) produced in the reaction, the HCl (v=1) has a rotational distribution that is independent of surface temperature over the range 200K to 700K, and is nearly Boltzmann with a rotational temperature of 300±50K. The drastically different nature of the v=0 and v=1 HCl formed in the reaction is further demonstrated by the fact that the rotationally integrated HCl (v=1) production is strongly dependent upon surface temperature while, as previously mentioned, the HCl (v=0) production rate is largely temperature independent. Figure 9 displays an Arrhenius plot for the rotationally integrated HCl (v=1) rate (i.e. relative signal) for the surface temperatures in the range 200K to 700K. The data display Arrhenius behavior for temperatures up to ~500K. Above 500K the production rate begins to roll over. This roll-over is due to the fact that the Cl coverage on the Au(111) surface is being depleted by thermal desorption into the gas phase. Analysis of the data below 500K yields an activation energy of 550±50 cm^{-1} (1.6 kcal/mole) for the production of v=1 HCl. This value is dramatically lower than the HCl (v=1) to HCl (v=0) energy gap of ~2900cm^{-1} that would be expected if the HCl (v=1) were produced in thermal equilibrium with the Au(111) surface.

The above results strongly suggest that the mechanism for forming HCl (v=1) is markedly different than the mechanism that leads to formation of HCl (v=0). The HCl (v=0) appears to thermally accommodate with the surface prior to desorption, consistent with a LH mechanism. The HCl (v=1) is in marked dis-equilibrium with the surface and thus may be produced via an ER-type channel. The temperature dependence of the reaction producing HCl (v=1) could originate from the thermal activation of a reactant on the surface. Possible sources of activation in the surface reactant are the ~500 cm^{-1} Cl-Cl stretch in a molecular aggregate[54] or a low-frequency metal-Cl stretch.[55] This suggests that HCl (v=1) may be formed from the direct reactive encounter of a gas-phase H atom with a vibrationally excited Cl atom bound to the surface. Further experiments are required to verify this hypothesis.
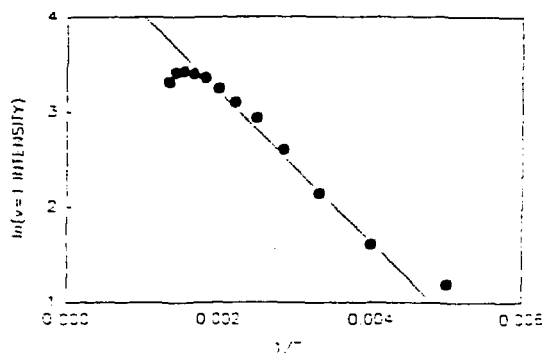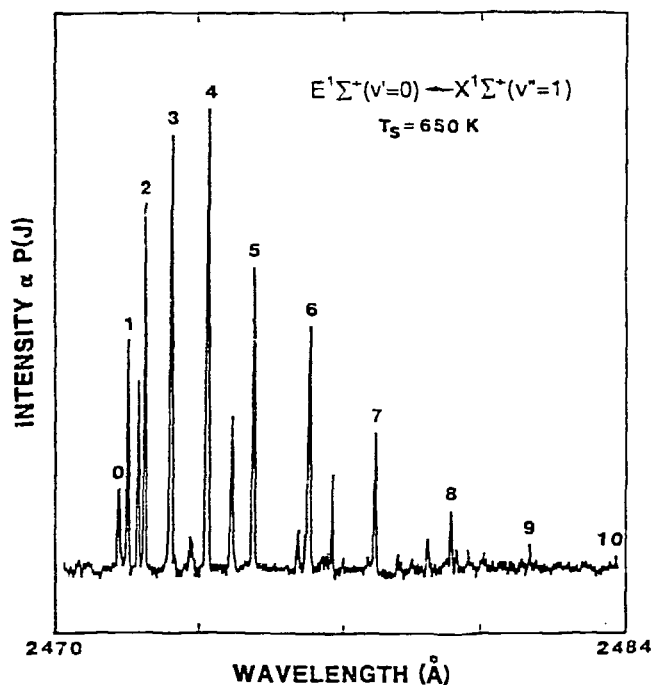

$E^1\Sigma^+(v'=0) \longleftarrow X^1\Sigma^+(v''=1)$

$T_S = 650\ K$

INTENSITY α P(J)

WAVELENGTH (Å)

2470   2484

Figure 9. Arrhenius plot for the formation of HCl (v=1).

Figure 8. HCl (v=1) produced on the Au(111) surface.

IV. SUMMARY

As demonstrated above, state-resolved REMPI detection of molecules inelastically and reactively scattered from surfaces is a powerful new experimental tool for elucidating the salient features of the potential energy hypersurface governing the gas-surface interaction. With the rapid development of non-linear optical methods for generating high intensity, tunable, pulsed vacuum ultraviolet laser radiation the outlook for state-resolved studies of a wide variety of inelastic and reactive collision processes is extremely promising. Of particular interest to us is the dissociative adsorption-associative desorption of hydrogen and its isotopes on surfaces. The detailed dynamics of this perhaps simplest of chemical reactions are presently not well understood.

V. ACKNOWLEDGMENTS

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