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# Observation of Charge-Transfer States for Pyridine Chemisorbed on Ag(111)

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The excited states of chemisorbed pyridine on Ag(111) have been determined with use of electron-energy-loss spectroscopy. In addition to weakly perturbed molecular states we observe new excitations above $\sim$1.4 eV, which we identify as metal-molecule charge-transfer excitations. These new electronic states provide an explanation for several features observed in surface-enhanced Raman scattering.

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Here we report the first measurements of the excited electronic states of a surface-enhanced Raman system, pyridine chemisorbed on Ag(111), using electron-energy-loss spectroscopy. We observe weakly perturbed states for chemisorbed pyridine as well as a new $\sim$1-eV broad onset excitation feature starting above $\sim$1.4 eV. The latter represents a new excitation of the metal-molecule system which we assign to charge-transfer excitations between the molecule and metal surface. Information regarding the changes in molecular excitations[1,2] as well as the possible occurrence of new electronic states for chemisorbed molecules[3,4] has been lacking and is needed to clarify and understand the origins of the chemically derived, localized components of surface-enhanced Raman scattering.[5,6] Our results demonstrate the occurrence of new electronic states which (a) will enhance the effective polarizability of chemisorbed pyridine, (b) can permit resonance Raman scattering, and (c) explain several features observed in surface-enhanced Raman scattering. We note that low-lying excitations (1.5–2.0 eV) for pyridine on Ag electrodes[7,8] and small particles in solution[9] have been observed by use of optical methods and have been proposed to arise from several different physical origins.[7-9]

These measurements were performed in a UHV system (base pressure $<1\times10^{-10}$ Torr) equipped with a hemispherical-deflector–based electron monochromator and energy analyzer described elsewhere.[10] This spectrometer has a fixed scattering angle of 90° and collects a well-defined ($\sim$0.2-mm-diam) collimated electron beam ($<1^\circ$) reflected from the sample. This sample which is cooled to 140 K can be rotated to observe both specular ($\theta_{\mathrm{in}}=\theta_{\mathrm{out}}$) and off-specular ($\theta_{\mathrm{in}}\neq\theta_{\mathrm{out}}$) scattering events in the plane of incidence. Beam energies up to 20 eV were used and our resolution was degraded to $\sim$20 meV (full width at half maximum of the specular beam) in order to more clearly observe the generally broad, low-intensity electronic excitations. Vibrational loss spectroscopy performed with this analyzer as well as uv-photoemission, low-energy electron-diffraction, and Auger studies done in an auxiliary system, were used to verify surface perfection and cleanliness as well as to characterize the adsorption of pyridine on Ag(111) as reported elsewhere.[10] Pyridine dosing was done via the ambient and an ion gauge correction factor of 5.8 was applied to all pressure readings.[6] Finally, we point out that our high-resolution, angle-resolved loss measurements at low energies reveal considerably more features than generally achieved (see, for example, Netzer, Bertel, and Matthew[11]).

Figure 1 shows the electron-energy-loss spectra for clean Ag(111) and after exposure to 1 L (1 L $=10^{-6}$ Torr sec) of pyridine. This corresponds to specular scattering conditions with an electron beam energy of 17 eV. For clean Ag(111) we observe plasmon losses at 3.9 and 8 eV.[12] Upon pyridine exposure the 3.9-eV plasmon peak shifts slightly to lower energies and new adsorbate-derived levels occur. In addition, a weak and broad feature is observed to start near ~1.4 eV. These same features are observed for incident beam energies between 4 and 20 eV. However, in going to smaller incident energies the relative cross sections of the lowest-lying excitations increase and a level at ~4 eV is clearly resolved above the tail of the surface-plasmon peak (see inset to Fig. 1). This as well as the higher-lying adsorbate-derived features corresponds well to the optical excitations[13] and electron-energy loss spectra[14] for gaseous pyridine as will be presented later.

The low-energy feature starting at ~1.4 eV is also observed more readily at lower beam energies and is shown in Fig. 2 for a 3.5–4-eV incident beam energy. Several checks were made to verify that this feature was real and not an artifact of our spectrometer. In particular, consecutive spectra of clean and adsorbed pyridine were run for a variety of beam energies and beam focusing conditions. Under similar conditions this excitation was observed for chemisorbed pyrazine but not for chemisorbed benzene.[15] In the case of chemisorbed pyrazine, the condensation of subsequent condensed layers (not possible for pyridine) attenuated this feature.[15]

In Table I we identify and summarize the energy-loss peaks for gas-phase electron impact scattering from pyridine, obtained for identical scattering conditions and beam energies,[14] as well as the energy-loss peaks observed here for the inclined-phase of chemisorbed pyridine (>0.6 L) shown in Fig. 1 and the flat-lying phase observed at lower coverages (<0.4 L).[10] In our data a few peaks overlap and must be deconvolved. For these peaks we have assumed a symmetric peak shape for this deconvolution and indicate their energies by a tilde. The precise energy for the $\tilde{X}^1A_1 \rightarrow {}^1B_2 + {}^1A_1$ excitation is also uncertain

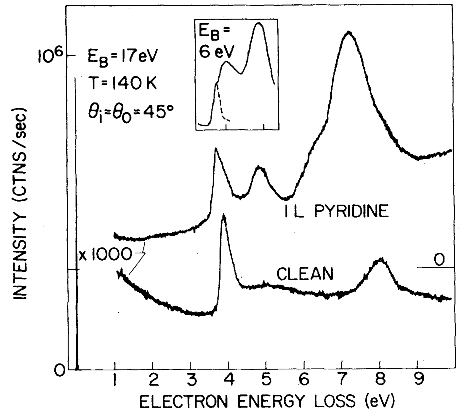

FIG. 1. Specular scattering electron-energy-loss spectra for clean Ag(111) and with chemisorbed pyridine on Ag(111) at $T \sim 140$ K (offset).

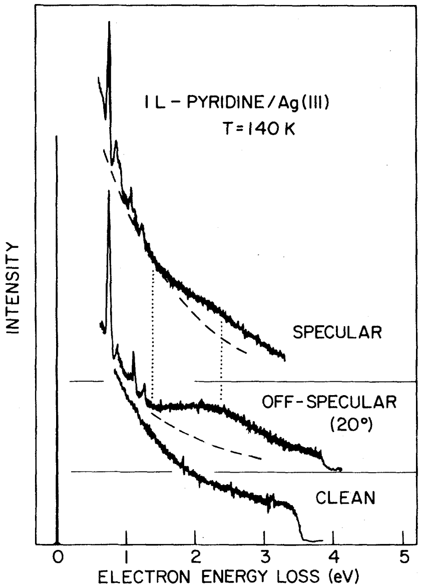

FIG. 2. Electron-energy-loss spectra for a 3.9 eV electron beam energy for chemisorbed pyridine on Ag(111) at $T \sim 140$ K. Both specular and off-specular ($\theta_{in}=55°$, $\theta_{out}=35°$) spectra are shown (offset) as well as a spectra for the clean surface. The dashed lines represent the smooth background expected from the clean surface.

TABLE I. Excitation energies and level widths (in parentheses) of gaseous and chemisorbed pyridine (in eV).

| Transition | Gaseous pyridine[a] | Chemisorbed pyridine Flat | Chemisorbed pyridine Inclined |
|---|---|---|---|
| $\tilde{X}^1A_1 \rightarrow {}^3A_1$ | 4.15(~0.55) | ~4.3(···) | ~4.1(~0.6) |
| $\rightarrow {}^1B_2$ | 4.95(0.55) | 4.95(0.75) | ~4.95(0.6) |
| $\rightarrow {}^1A_1$ | 6.4(0.51) | ~6.4(~0.85) | ~6.25(~0.85) |
| $\rightarrow {}^1B_2 + {}^1A_1$ | 7.15(0.45) | 7.3(1.0) | 7.25(1.1) |
| Ag/pyridine CT | ··· | ~1.9[b](~0.8)[b] | ~1.9[b](~0.6)[b] |

[a] Ref. 14.

[b] See text for an explanation of these values.

because of a change in its shape. The level widths at half maximum (after accounting for instrumental broadening) are also shown in parentheses.

The onset shape of the broad, low-energy feature is suggestive of excitations to or from some continuous set of states. Further support for this arises from considering the one-electron energy levels for pyridine[16] and the density of states for Ag.[17] Using the vacuum levels to align these electronic levels and including the saturation work function of chemisorbed pyridine on Ag, we find that the highest-lying occupied and lowest-lying unoccupied continuum states of silver (i.e., $E_F$) occur nearly midway between the highest-lying occupied and the lowest virtual orbital of pyridine. We thereby estimate that the smallest energies for charge-transfer (CT) excitations will be roughly half the lowest singlet-molecule excitation of 5 eV (Refs. 13 and 14), or ~2.5 eV.

In Table I, we have indicated the excitation energy and half width for the Ag/pyridine CT excitation assuming that a metal-to-molecule CT excitation dominates our spectra. Here we have deconvoluted the observed shape from a step-function initial state and find a final state having a peak shape similar to the $\tilde{X}^1A_1 \rightarrow {}^1B_2$ transition. This gives a peak position of 1.9 eV for the CT state in reasonable agreement with the aforementioned estimated value. Although this deconvolution is not unique due to the uncertainties in the actual CT states involved, a sharpening of the CT state for the inclined phase of pyridine is clearly observed.

Our observation of low-lying CT excitations is directly relevant to surface-enhanced Raman scattering (SERS) since these excitations will introduce new contributions to the polarizability tensor and can also lead to resonance Raman scattering. An enhanced polarizability for chemisorbed pyridine will occur as CT excitations will result in the modulation of the surface charge density in a fashion analogous to that proposed by Kirtley, Jha, and Tsang.[18] Their model requires low adsorbate-metal barrier heights which phenomenologically may reflect the presence of low-lying metal-molecule CT states. Since CT states will occur at the laser frequency, resonance Raman scattering can also occur whose magnitude will be determined by the level widths as well as the oscillator strengths and dipole matrix elements of these CT states. Clearly, quantitative calculations are needed to determine the magnitude of these additional matrix elements and their contributions to the Raman signal. Within a resonant Raman picture the narrower breadth of the CT excitation for inclined pyridine than for flat-lying pyridine would also explain the larger SERS signal observed when chemisorbed pyridine becomes inclined to the surface.[19] Our inability to obtain SERS for chemisorbed benzene on Ag(111) (Ref. 19) can also be related to its broader electronic levels and our inability to observe a similar CT excitation.[15]

We finally note that the occurrence of CT excitations involving the metallic states near $E_F$ and nearby states of pyridine and/or resonance Raman scattering is consistent with the selective enhancement of the symmetric ring-breathing mode observed on Ag(111).[6] Selective mode enhancements have also been observed in SERS from evaporated films,[20] electrochemical cells,[21] and tunnel junctions.[22] For resonance Raman scattering of free molecules the symmetry of the intermediate state permits coupling to certain molecular modes[23] and from electron impact studies of pyridine it is known that the lowest resonance excitation couples to the symmetric ring-breathing mode.[24] We further find from our self-consistent field, unrestricted Hartree-Fock molecular-orbital calculations[25] that the molecular vibrations modulate primarily the lowest-lying virtual orbitals ($2a_2$ and $3b_1$) and the highest-lying occupied orbitals ($1a_2$ and $2b_1$) with the symmetric ring-breathing mode yielding the largest modulation (approximately 3 times greater than the asymmetric ring-breathing mode). Such vibronic modulation of these levels can induce modulations in the surface charge density via the ground state or CT states. Since these strongly modulated levels are the molecular levels which we expect to be involved in the CT excitation, these excitations can strongly enhance the molecular polarizability. This CT state also provides a basis for the two-step mode proposed by Burstein.[4]

In summary, we have measured the excited electronic states of pyridine chemisorbed on Ag(111) and find weakly perturbed molecular states as well as evidence for charge-transfer excitations between metallic states near $E_F$ and the lowest-lying unoccupied or highest-lying occupied molecular states. These new metal-molecule states will permit mode-selective resonance Raman scattering on the flat surface and will contribute to the short-range component of the SERS enhancement mechanism.

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