observed for Pt-CO complexes.[16] The SEDOR data therefore are consistent with the viewpoint that the bonding of CO to the Pt surface is very much like the bonding in carbonyls. The bond is thought to involve the Pt 5*d* orbitals and the CO 5σ and $2\pi^*$ orbitals.[12,17]

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Resonantly Stimulated Desorption of Pyridine from Silver Surfaces by Polarized Infrared Laser Radiation

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Resonantly excited desorption of pyridine molecules adsorbed on silver surfaces at 95 K has been observed. The strong dependence of the laser-induced desorption on the laser wavelength and the polarization of the incident radiation clearly show that molecular vibrational activation plays a major role in the observed desorption phenomenon. The desorption yields per laser pulse are also determined from the thermal desorption spectra and the x-ray photoemission-spectroscopy intensity analyses.

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The subject of laser-stimulated desorption has recently attracted considerable theoretical as well as experimental attention.[1-5] In the experiment reported by Heidberg *et al.*,[4] it was shown that CH_3F molecules adsorbed on a NaCl surface could be desorbed by resonant vibrational excitation of the molecules with an infrared laser. A similar experiment by Chuang[5] also showed that CO_2 laser pulses could excite the asymmetric ring-mode vibration of pyridine molecules and induce the adsorbed species to desorb from the surface of a KCl crystal which is optically transparent in the CO_2 laser wavelength region. In this Letter, we report the first study of resonantly stimulated desorption of pyridine from metallic silver surfaces excited by polarized CO_2 laser radiation. It is well known that the extent of infrared absorption by a molecular monolayer adsorbed on a metal surface depends strongly on the angle of incidence and the state of polarization of the incident light.[6,7] At near-grazing angle of incidence, the absorption factor for infrared radiation polarized parallel (P) to the plane of incidence should be much greater than that for the radiation polarized perpendicular (S) to the plane of incidence. Therefore, it is expected that the P-polarized light should be more effective than the S-polarized light in vibrationally activated desorption. This expectation is confirmed in the present study.

The experimental apparatus consists of a pulsed CO_2 laser and a UHV chamber equipped with an ESCA/Auger spectrometer, an ion gun, a quadrupole mass spectrometer, and an rf induction heater.[8] The laser is line tunable between 9 and 11 μm and can provide 1.0-J pulse energy with about 100-nsec pulse duration. The unfocused laser beam can be attenuated with optical filters and is directed onto the sample at 75° from the surface normal. A half-wave plate outside the vacuum chamber is used to rotate the polarization of the laser light. For multiple-pulse operation, the laser pulse rate is fixed at 1 pulse per 3 sec. The mass spectrometer in the line-of-sight arrangement along the surface normal is located about 1.5 cm from the sample. The silver island film, prepared on a quartz substrate, has an average thickness of 120 Å. The grain size of the metal film ranges from several hundred to a thousand angstroms.[9] The sample (12×12 mm^2) held with a copper disc on a manipulator can be cleaned by brief Ar^+-ion bombardment and heated by the rf heater. Pyridine vapor is dosed through a small copper tube directly facing the Ag surface which is cooled to 95 K with liquid N_2. The amount of surface coverage is determined from the x-ray photoemission-spectroscopy (XPS) intensities of the adsorbate and the adsorbent as well as from the thermal desorption spectrum. Relative desorption yields per laser pulse are obtained by the mass spectrometer with a high-speed recorder.

The experiments involve mainly the laser excitation of the asymmetric ν_8 ring-mode vibration of pyridine molecules.[10] The vibrational spectrum of the adsorbed molecules on Ag surfaces as determined by surface-enhanced Raman scattering (SERS)[11,12] shows the band centered around 1032 cm^{-1} with a bandwidth of about 8 cm^{-1}. As a first step in the experiment, the CO_2 laser is tuned to 1033.5 cm^{-1}. When the laser with P polarization is incident at 75° onto the Ag surfaces with about two monolayers of pyridine, molecular desorption is readily detected by the mass spectrometer. The desorption yield per pulse strongly depends on the laser frequency. As shown in Fig. 1, major desorption occurs in the laser frequency region between 1025 and 1042 cm^{-1}. The full width at half maximum of the desorption spectrum is about 8 cm^{-1}, very similar to the vibrational spectrum obtained by SERS. For the adsorbed pyridine excited at 1033.5 cm^{-1}, the threshold for desorption is about 0.01 J/cm^2, i.e., ~ 0.1 MW/cm^2 or 5×10^{17} photons/cm^2. The desorption yield increases nonlinearly with the laser intensity (Fig. 2, curve a). When the laser is tuned off resonance from the pyridine vibrational bands, hardly any desorption is detected for laser intensity $I \lesssim 0.05$ J/cm^2 per pulse (Fig. 2, curve b). If the laser intensity at $\nu = 1085.8$ cm^{-1} is increased to 0.12 J/cm^2 or higher, substantial desorption occurs even though the laser photons are not directly absorbed by the pyridine overlayer. Clearly, if the laser intensity is too high, thermal heating due to the absorption of the laser light by the silver film and the underlying SiO_2 can cause sufficient temperature increase in the laser-irradiated area to thermally desorb pyridine molecules. This nonresonantly laser-induced desorption is the same as the earlier thermal desorption studies by other researchers using different lasers for different gas-metal systems.[13,14] At $\nu = 1033.5$ cm^{-1}, the observed desorption is due to both the resonant vibrational excitation of pyridine molecules and the substrate laser heating effect. The relative contribution of the substrate heating to the observed desorption is small at low laser intensity, but it increases

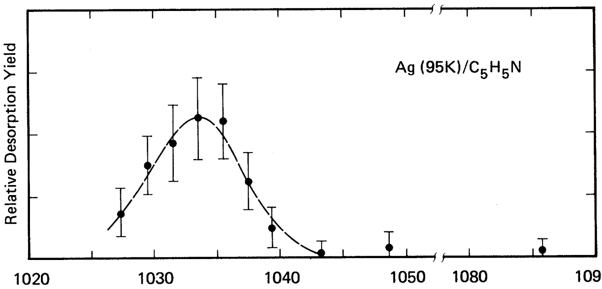

FIG. 1. CO_2 laser-stimulated pyridine desorption yield measured with a mass spectrometer as a function of the laser frequency. The laser is P polarized and incident at 75°. The laser intensity on the sample is 0.03 J/cm^2 per pulse. Each datum point is an average of the mass peak heights due to 10 laser pulses.

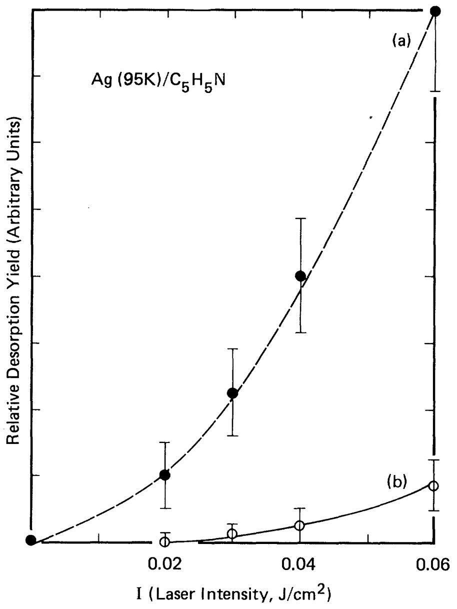

FIG. 2. The laser-stimulated desorption yield as a function of the laser intensity. The laser frequencies are fixed, respectively, at 1033.5 cm^{-1} (curve *a*) and 1085.8 cm^{-1} (curve *b*) both *P* polarized at 75° angle of incidence.

TABLE I. Observed desorption peak heights measured with the mass spectrometer at two different laser frequencies with either *P* or *S* polarization at 75° angle of incidence. About 2 monolayers of pyridine adsorbed on Ag island film at 95 K for each experiment. Every number is an average signal due to 10 laser pulses.

Laser polarization	$\nu = 1033.5$ cm^{-1}, $I = 0.04$ J/cm^2	$\nu = 1085.8$ cm^{-1}, $I = 0.12$ J/cm^2
P	8.0 ± 1.7	12.2 ± 2.8
S	1.2 ± 0.3	10.1 ± 2.3
P/S	6.7	1.2

rather rapidly with the laser intensity. For example, at $I = 0.03$ J/cm^2, the relative desorption yield between $\nu = 1033.5$ cm^{-1} (on resonance with pyridine ν_8 vibration) and $\nu = 1085.8$ cm^{-1} (off resonance) is 15:1 (Fig. 2). This ratio decreases to 9:1 at $I = 0.06$ J/cm^2 and to about 2:1 at $I = 0.12$ J/cm^2. At much higher laser intensity, it is expected that substrate heating by the laser pulse can become the dominant factor in determining the desorption behavior.

The observed effect of the polarization of the incident laser light on the desorption yield is summarized in Table I. Evidently, when the laser photons are in resonance with the pyridine vibration, the *P*-polarized photons can cause much more desorption than the *S*-polarized light. When the laser is tuned off resonance, the difference in the desorption yields between the two polarizations is very small. The slightly larger desorption yield by the *P*-polarized light at 1085.8 cm^{-1} is most likely due to the fact that the reflectivity of the *P*-polarized light on Ag surface is slightly smaller than that of *S*-polarized light at 75° incidence. Therefore, a greater amount of laser light is absorbed by the substrate when it is *P* polarized. Consequently, at a given laser intensity, the *P*-polarized photons can cause greater thermal desorption. The observed ratio of the desorption yields between the *P*- and *S*-polarized light at 1033.5 cm^{-1}, i.e., 6.7 in Table I, is not as large as the calculated ratio of the ir absorption factors between the two polarizations for an oscillating dipole adsorbed on a flat silver surface according to the formalism developed by Greenler.[6] This is not surprising because resonant ir absorption is only one of the many steps involved in the laser-stimulated desorption processes. Laser thermal heating of the silver and SiO_2 substrate obviously is also an important factor. Furthermore, the silver island film on the molecular scale has a less well-defined surface normal than an ideally flat surface. In any event, both the laser frequency dependence and the laser polarization dependence of the desorption yield clearly show that direct ir absorption by the adsorbed molecules resulting in molecular vibrational excitation plays a major role in the observed desorption phenomenon.

In order to understand better the desorption behavior, we have also performed ordinary thermal desorption studies on the pyridine-Ag system with an rf induction heater. Figure 3 shows the thermal desorption spectra of pyridine from Ag surfaces with and without irradiation by CO_2 laser pulses. The surface coverage for the experiment is about two molecular layers as estimated from the x-ray photoemission spectra of pyridine C(1*s*) and Ag(3*d*). From Fig. 3, curve *a*, it is clear that the physisorbed pyridine in the top monolayer adsorbed on the underlying chemisorbed layer can be readily desorbed around 140 K. In contrast, the chemisorbed pyridine in direct contact with the metal surface desorbs at a higher temperature ranging from 160 to 300 K with the broad peak at 195 K. When the Ag surface with two molecular layers is irradiated by 100 *P*-polarized laser pulses at 1033.5 cm^{-1} with 0.06 J/cm^2 intensity, we observe a substantial

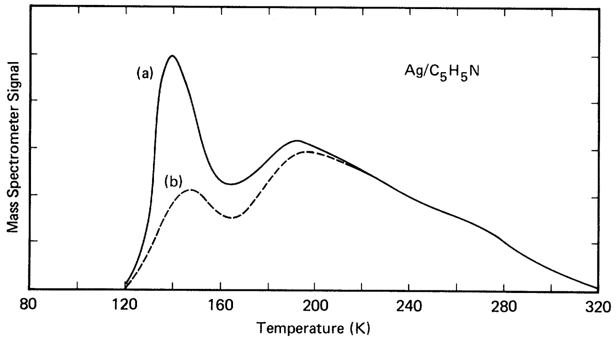

FIG. 3. Thermal desorption spectra of pyridine from Ag surfaces without (curve *a*) and with (curve *b*) the CO$_2$ laser irradiation. The surface coverage is about 2 monolayers in each case and the heating rate is 4 K/sec. For curve *b*, 100 laser pulses *P* polarized at 1033.5 cm^{-1} with $I = 0.06$ J/cm^2 are irradiated onto the sample surface at 75° incidence.

decrease in the C(1*s*) XPS intensity. Also the subsequent thermal desorption spectrum (Fig. 3, curve *b*) shows a sharp decrease in the intensity of the physisorbed peak, while the broad chemisorbed peak remains essentially unchanged. When an even larger number of laser pulses is irradiated on the sample, the physisorbed peak decreases further before the chemisorbed peak is also affected. It is therefore clear that the major effect of the laser excitation is to induce the more weakly bound molecules in the top layer to desorb. From the decrease of the physisorbed peak in the thermal desorption spectrum and the decrease of the XPS C(1*s*) intensity, we can estimate the actual desorption yield per laser pulse. Using the pyridine density[15] to be 3×10^{14} cm^2, we determine that about 1×10^{12} molecules are desorbed per pulse under the present experimental conditions with the laser $\nu = 1033.5$ cm^{-1}, $I = 0.06$ J/cm^2, *P* polarized and incident at 75° from the surface normal.

In summary, the phenomenon that we observed with the pyridine adsorbed on silver island films irradiated by CO$_2$ laser pulses can be described as resonantly stimulated desorption in which the laser light coincident with the pyridine ν_8 vibration is absorbed by the molecules causing some of the excited molecules to desorb. The desorption yield dependence on both the laser frequency and the polarization of the incident radiation clearly shows the major role played by the vibrational activation in the photon-stimulated desorption processes. The substrate heating effect is also important, particularly when the laser intensity is high. While the details, in particular the dynamics of molecular vibrational excitation resulting in the breaking of bonds between molecules and between molecules and metal surfaces, remain to be further elucidated, it appears certain that some degree of thermalization of the initially absorbed laser energy has occurred within the pyridine molecule, the pyridine layer, and the silver substrate. In laser-stimulated desorption, it is expected that when a particular vibrational mode is resonantly excited, intramolecular vibrational equilibration to other vibrational modes can occur rapidly. In this process, the vibrational modes involving the molecule-surface bonds are excited and weakened and consequently desorption can happen. On the other hand, the excitation energy can simultaneously be efficiently transferred via the surface potential to the surface phonons and create localized heating which can also cause the molecules to desorb. Obviously more experiments are needed to distinguish these two processes. In our experiment, the energies of the pyridine-pyridine bond (physisorbed state) and the pyridine-silver bond (chemisorbed state) are greater than a single CO$_2$ laser photon energy; it is therefore very likely that the observed desorption is due to multiple photon absorption and/or multiple excitation of pyridine molecules via ultrafast intermolecular energy transfer from the neighboring excited species. In this context, it is even possible that the desorbed molecules which are clearly from the top surface layer may not necessarily be the molecules that are originally excited by the laser photons. It should be further noted that resonantly laser-stimulated desorption is also observed for pyridine adsorbed on Ag(110) crystal surfaces. The desorption yields per laser pulse are, however, quite different because of the different thermal properties of the substrates. Detailed comparison of the two gas-solid systems will be discussed elsewhere.

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Dynamic Critical Neutron Scattering from a Two-Dimensional Ising System Rb_2CoF_4

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The dynamical behavior of the two-dimensional Ising-like antiferromagnet Rb_2CoF_4, which is expected to provide a real system within the $n = 1$, $d = 2$, universality class, has been investigated near $T_N = 102.96$ K with high-resolution inelastic neutron scattering. Measurement of the characteristic frequency of the longitudinal susceptibility fluctuations yields a dynamic critical exponent $z = 1.69 \pm 0.05$. This is close to the conventional theoretical value $z = \gamma = 1.75$.

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The theoretical value of the dynamic critical exponent, z, for the two-dimensional (2D) Ising system ($n = 1$, $d = 2$) has attracted considerable attention over the past few years. The results of various approaches to its calculation using two models, the time-dependent Ginzburg-Landau (TDGL) model, and the single spin-flip kinetic-Ising (KI) or Glauber model, have recently been reviewed by Mazenko and Valls.[1] In this Letter we report the results of the first direct measurement of the dynamic critical exponent for rubidium cobalt fluoride, Rb_2CoF_4, using high-resolution neutron inelastic scattering techniques. This compound exhibits static magnetic behavior[2,3] which follows very closely the prediction of Onsager's exact results for the 2D Ising antiferromagnet,[4] and its dynamical behavior is expected to fall within the $n = 1$, $d = 2$ dynamic universality class.

Rb_2CoF_4 has the K_2NiF_4 crystal structure, $I4/mmm$, in which the Co^{2+} ions, with effective spin $S = 0.5$, are arranged with separation of $a_0 = 4.12$ Å (at 110 K) in simple planar square arrays perpendicular to the fourfold c axis. The planes of spins are 6.80 Å apart (at 110 K) and are separated by two layers of RbF ions. The two-dimensional behavior of Rb_2CoF_4 arises both because the intraplanar exchange interaction between the spins is much stronger than the interplanar interaction, and because the interplanar interaction