High-resolution infrared reflection absorption spectroscopy with a continuously tunable infrared laser: CO on Ru(001)

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A continuously tunable high resolution (0.2 cm^{-1}) infrared laser has been applied for the first time to infrared reflection absorption spectroscopy (IRAS) of submonolayer coverages of adsorbed molecules on a well-defined metal surface, i.e., single crystal Ru(001). The sensitivity, resolution, and continuous tunability of the laser are demonstrated with vibrational spectra of submonolayer CO adsorbed on Ru(001) $(\Theta = 0.65)$. The results indicate a smaller bandwidth of the CO stretch (5 cm^{-1}) than previously observed. With an increase in substrate temperature from 85 to 300 K, a small frequency red shift of 2.5 cm^{-1} is observed.

In recent years, vibrational spectroscopy has become a powerful tool for studies of the adsorption of molecules on well-defined surfaces.[1-4] Three useful techniques have emerged: electron-energy-loss spectroscopy (EELS), infrared reflection absorption spectroscopy (IRAS), and Raman spectroscopy. Although EELS is the most sensitive and widely used among these techniques, IRAS has considerable attraction because of its higher resolution and pressure independence. The high sensitivity of IRAS has been demonstrated in the spectral region above 1000 cm^{-1}. However, further expansion of the accessible spectral range depends critically on the availability of radiation sources with higher intensity than is currently obtainable from thermal emitters. At present, synchrotron radiation,[5] free-electron lasers,[6] and infrared lasers[7] are being investigated as potential tunable sources of infrared radiation in the 1000- to 10-cm^{-1} range: Synchrotron radiation holds promise as an intense broadband source with characteristics similar to thermal radiation in the spectral regime below 1000 cm^{-1} and could be useful in Fourier-transform infrared spectroscopy.[5] Infrared lasers offer the potential of powerful narrow-band radiation sources with extremely high resolution (0.20 to 0.01 cm^{-1}) and an intensity three to five orders of magnitude higher than thermal emitters. As such, infrared lasers would allow IRAS with much higher sample temperatures and with reduced interference from thermal background radiation. Additionally, pulsed laser sources would provide time resolution in the nano to picosecond range. In spite of these characteristics, infrared lasers have not been used for IRAS (Ref. 21) with the exception of photoacoustic spectroscopy in the 9—11-μm region (900—1100 cm^{-1}) accessible with CO_2 lasers.[8,9] The principal reason for this is the lack of broad tunability over wavelength ranges of interest for IRAS.

In this paper we report the first application to IRAS measurements of a newly developed wide-band tunable (10 000 to 900 cm^{-1}) high-resolution infrared laser. The sensitivity and resolution of the laser techniques are demonstrated with vibrational spectra of submonolayer

CO adsorbed on a Ru(001) surface. We also discuss possible ways to improve the sensitivity of measurement and the tuning range of the laser.

The experiments were performed in an UHV chamber $(10^{-11}\text{-Torr range})$ equipped to perform IRAS, LEED (low-energy electron diffraction), Auger electron spectroscopy, thermal desorption, work-function measurements, and EELS. Experimental procedures, preparation and cleaning of the ruthenium crystal (8 mm diameter), were similar to those described earlier in detail.[10,11] Infrared radiation was generated in a recently developed hydrogen Raman laser which will be described in detail elsewhere.[12] A frequency-doubled Quanta Ray DCR 201 Nd:YAG laser is used to pump a Lambda Physik dye laser and produces pulses of 7 nsec width over the tuning range of the dye. The dye radiation is directed into a multiple-pass hydrogen Raman cell (22 passes at 14 atm of H_2) and Raman converted third Stokes infrared radiation exits through a BaF_2 window. By tuning over the range of the dye, ~ 600 to 800 cm^{-1}, a corresponding range in the various Stokes orders in the infrared can be accessed. The full range of infrared is accessible by changing dyes. In the present configuration continuously tunable ir radiation between 10 000 and 900 cm^{-1} has been demonstrated.[12] The radiation consists of pulses of 7 nsec width and 1 mJ energy (at 2000 cm^{-1}), and 0.2 cm^{-1} bandwidth, linearly polarized and at a repetition rate of 10 Hz. The infrared radiation is passed through appropriate filters to remove lower-order Stokes radiation and is focused onto the Ru(001) sample at an angle of incidence of 80° from the surface normal. The polarization plane of the light is kept at 45° with respect to the plane of incidence. This gives approximately equal components of light polarized parallel and perpendicular to the plane of incidence. After reflection from the surface, the parallel and perpendicular components of the radiation are analyzed using a ZnSe prism, and are separately measured with a pair of pyroelectric detectors (Fig. 1). Since the surface dipole selection rule on metals allows only vibrational excitations with a dynamic dipole moment perpendicular to the sur-
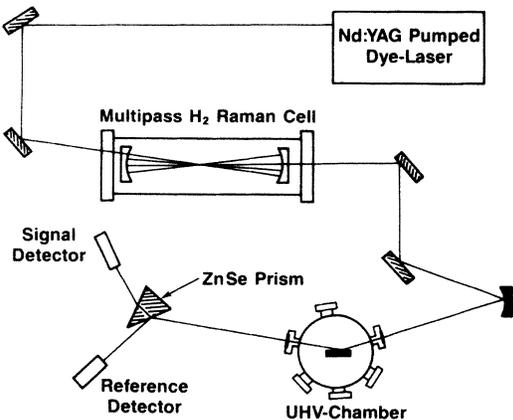
FIG. 1. Experimental arrangement.

FIG. 2. Scanned absorption spectra of CO/Ru(001) at 85 and 300 K for $\Theta = 0.65$ monolayer.

face,[4] only the p polarization is absorbed by the adsorbate. Thus one has a means to ratio the signal. This method of polarization modulation results in considerable reduction of signal fluctuations, which are caused by laser pulse-to-pulse instabilities as well as interference due to atmospheric background (mainly water absorption bands). This technique allows spectra to be collected at typical scan speeds of 0.1 cm^{-1} sec^{-1}, at signal-to-noise ratios of 200 to 500, with an inherent resolution of 0.2 cm^{-1}.

Experimental results are presented in Fig. 2, showing vibrational spectra of the C—O stretch region obtained for a layer of carbon monoxide adsorbed in molecular form at 85 K on a Ru(001) surface ($\Theta = 0.65$ monolayer). The spectra were taken after first raising the substrate temperature to 300 K and then recooling to 85 K. The C—O stretch frequencies of 2056.5 cm^{-1} and 2054 cm^{-1} are in good agreement with previous measurements.[13] A reduction in substrate temperature produces two distinct reversible changes of the spectra: both a small blue shift of 2.5 cm^{-1} in the C—O stretch frequency and a narrowing of the apparent linewidth from 7.5 to 5.5 cm^{-1}. These changes cannot be due to a reduction in adsorbate coverage (which could cause a frequency shift) because they are reversible with temperature and the integrated intensities are identical for both temperatures.

The linewidth of 5.5 cm^{-1} observed at 85 K is significantly smaller than previously measured,[14] and gives a new lower limit of 1.9 psec for the vibrational dephasing time of CO on Ru. There are a number of mechanisms that may be responsible for the observed temperature-dependent line shift and broadening, such as homogeneous dephasing[15-20] and inhomogeneous processes (e.g., order-disorder transitions[13]). Our signal-to-noise ratio (SNR) was not sufficient to distinguish between homogeneous and inhomogeneous broadening; thus, we are unable to definitively determine the mechanisms responsible for the observed line shapes. However, the asymmetry of the line shape suggests that the line width in Fig. 2 is still influenced by inhomogeneous broadening. Work in progress indicates that in the case of a well-ordered $\sqrt{3} \times \sqrt{3}$-R 30°-CO overlayer ($\Theta = 0.33$ monolayer), the line shape is symmetrical. Preliminary analysis of this data indicates that both the temperature-dependent line broadening and
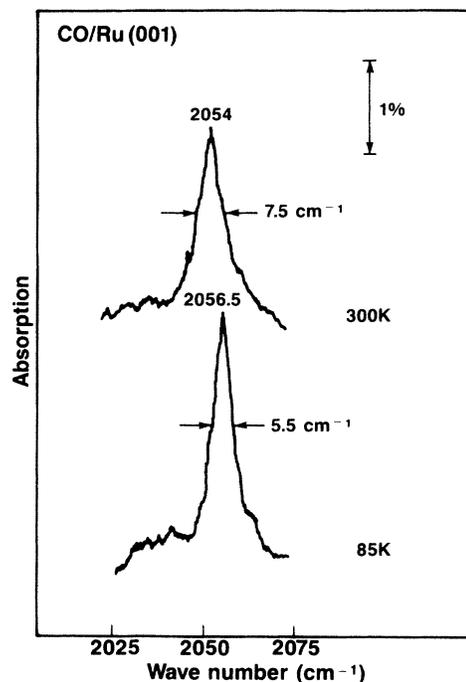
frequency shift can be fit to a vibrational dephasing model.[17,18] In this model, the C—O stretch is anharmonically coupled to a low-frequency external mode of the molecule (e.g., frustrated rotation), which is coupled to the phonon bath of the substrate. Confirmation of the fit would be of great importance in furthering our understanding of the energy exchange between the adsorbed molecule and the metal substrate and can be obtained through improved high-resolution measurements such as those afforded by the laser system.

In conclusion, we have demonstrated the application of tunable lasers to IRAS and have used the high resolution of this approach to obtain new data of line broadening and shifts. To fully realize the potential of this technique, it will be necessary to extend the tunability of the laser to the region below 900 cm^{-1} and to approach the fundamental sensitivity of the technique by increasing the laser amplitude stability. We are presently working towards both of those goals. This technique holds promise for a much better SNR than demonstrated in the present work, where laser pulse-to-pulse fluctuations of 30% determined the obtained SNR of 500 in a 100-pulse average. With greater laser stability and improved linearity in the detection and ratioing, an improvement of several orders of magnitude in the SNR is possible.

The present restriction of the ir laser to optical frequencies of greater than 900 cm^{-1} is due to a number of factors including the cutoff of the BaF$_2$ exit window on the Raman cell.[12] By replacing the BaF$_2$ window with one of KRS-5 and using more powerful pump radiation, it should be possible to obtain output down to the 300-cm^{-1} range. Improvements in laser stability and digitized selective data acquisition are being examined as a means of improving the signal-to-noise ratio of the data.

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