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# VERY LOW FREQUENCY SURFACE ENHANCED RAMAN SCATTERING

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We have observed Raman spectra of a very low frequency mode involving surface adsorbed molecules. Scattering from this mode appears to be sensitive to adsorbate orientation. With pyrazine as the adsorbate, the frequency shifts with electrochemical voltage, possibly because of changes in orientation of the molecule on the surface. With pyridine as the adsorbate, we find that the frequency of the peak in the scattered light intensity increases linearly with excitation frequency, suggesting that light is resonantly scattered from the surface adsorbed species.

The enormous increase of the Raman cross-section for molecules adsorbed on a metal surface has opened the way for the application of Raman scattering to a wide variety of problems in surface science and has stimulated attempts to determine the source of the unexpected enhancement [1]. Most studies of Surface Enhanced Raman Scattering (SERS) have been concerned with modes that are characteristic of the molecule itself, allowing the identification of the surface layer. These modes correspond to the high frequency peaks ($\Delta\nu \gtrsim 300\,\mathrm{cm}^{-1}$) in the SERS spectrum. In this paper we present some results on a very low frequency Raman mode that may be characteristic of the molecule bound to the surface. We tentatively attribute this mode to a libration involving the adsorbed molecule as a whole which is coupled to a continuum of silver surface modes.

Our experiments were performed in an electrochemical cell consisting of a polycrystalline silver working electrode, a platinum counter electrode, a saturated calomel reference electrode (SCE), and an electrolyte of 0.1M KCl and 0.05M pyridine in water. The Ag surface was prepared by mechanical polishing followed by a "mild" electrochemical roughening [1] consisting of a collection of $25\,\mathrm{mC/cm^2}$ at +0.2 V versus SCE followed by a replating of the silver surface at −0.6 V versus SCE. A backscattering optical arrangement was used, with ~30 mW incident laser radiation from a $\mathrm{Kr}^+$ or $\mathrm{Ar}^+$ laser. The scattered radiation was dispersed with a Spex triple monochromator equipped with holographic gratings using 20 $\mu$m entrance and exit slits for the double monochromator and a 70 $\mu$m slit for the third monochromator which was scanned in tandem. This gave a resolution of ~0.2 $\mathrm{cm}^{-1}$ and allowed us to come as close as 1.5 $\mathrm{cm}^{-1}$ from the exciting line.

The upper left of fig. 1 shows a spectrum for pyridine adsorbed on silver, and shows two very intense peaks which are separated by $\Delta\nu = \pm 8\ \mathrm{cm}^{-1}$ from the 5145 Å $\mathrm{Ar}^+$ laser line. This mode is ~20 times as intense as the 1008 $\mathrm{cm}^{-1}$ pyridine line. It is not seen when pyridine is not added to the electrolyte and has the same electrode-voltage dependence as the higher frequency pyridine modes [2]. The left hand side of fig. 1 shows the temperature dependence of the Raman scattering from the low-frequency mode. The sample was prepared electrochemically at room temperature and then forced flush against the cell window before being cooled [3]. Also shown in fig. 1 is the imaginary part of the susceptibility, $\chi''(\Delta\nu)$, obtained by dividing the Stokes and anti-Stokes data by $n(\Delta\nu)+1$ and $n(\Delta\nu)$ respec-

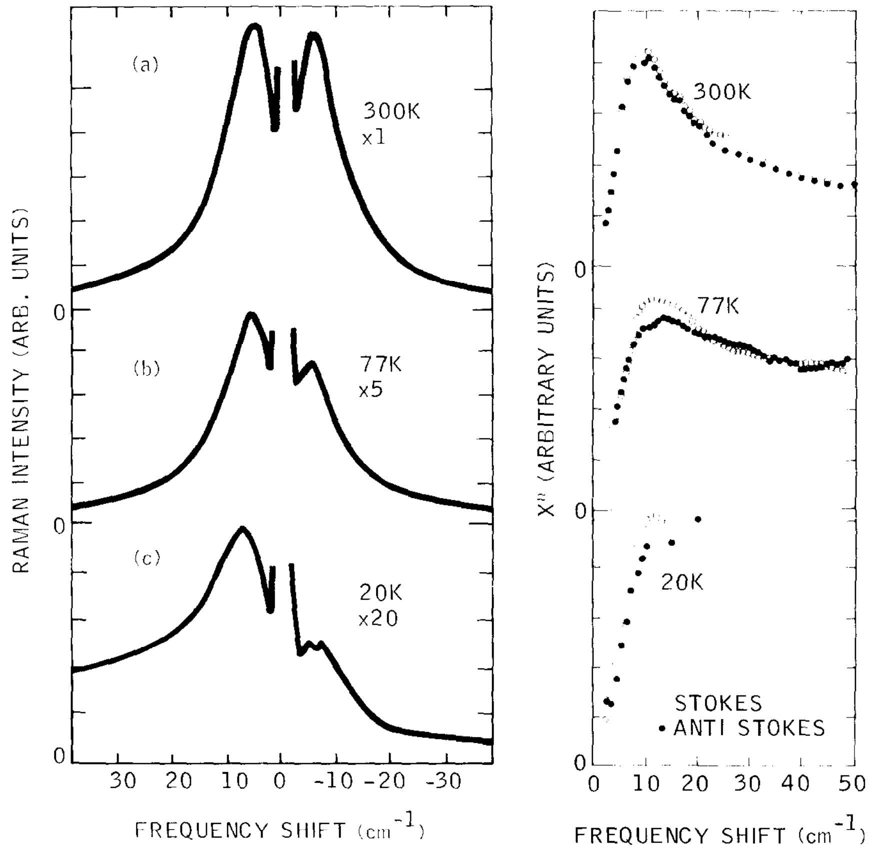

Fig. 1. Temperature dependence of low frequency RS from pyridine. The left side shows the RS data, while the right side shows the susceptibility.

tively, where $n(\Delta\nu)$ is the Bose–Einstein factor. The overlay of the Stokes and anti-Stokes portions of $\chi''(\Delta\nu)$ confirms that the peak is due to first order RS from a mode obeying Bose statistics, such as a vibration or rotation. At 2 K, the lowest temperature achieved in this investigation, $kT < h\Delta\nu$ and the anti-Stokes is negligible compared to the Stokes scattering as shown in fig. 2.

We expect the rotational degrees of freedom of the free molecule to be transformed into librations of the molecule as a whole when it is bonded to the surface. Depending on the coupling of the molecule to its solvation sheath and the bonding to the surface, such a librational motion may also involve some water molecules or silver atoms. For such a mode, there is no first order change of the distances of atoms directly bonded to the surface when the molecule "stands up" on the surface and so the libration frequency is expected to be low. Morawitz and Koehler [4] obtained rough agreement with the frequencies we observe by assuming the potential well for this mode is due to the interaction of the permanent dipole moment of the molecule with its image in the metal and that only the molecule itself is librating. Thus, we tentatively identify the mode as a libration involving the adsorbed molecule.

The low frequency Raman scattering has a number of unusual features. We see little change in the lineshape with temperature, even though some sharpening of the line might have been expected due to reduced dynamic broadening or anharmonic contributions. This suggests either that the line is inhomogeneously broadened or that the line width results from the coupling of the molecular librational mode to a continuum of phonon states in

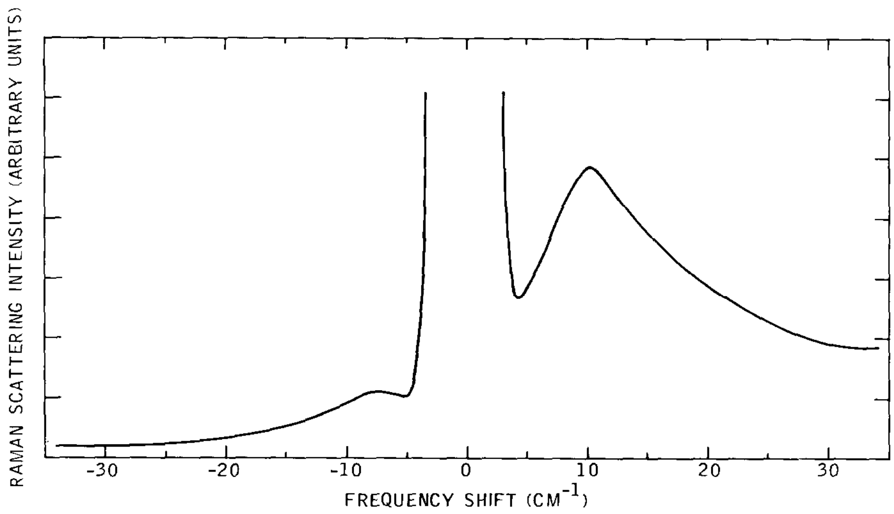

Fig. 2. Raman scattering from the low frequency mode of pyridine at 2 K.

the metal. The susceptibility of the resultant band of coupled modes would not be expected to have a strong temperature dependence. Further, we note that some of the high frequency modes (e.g., 216 $\mathrm{cm}^{-1}$) which also have a nearly Lorentzian lineshape also do not change significantly with temperature. Finally, we have found that the frequency of peak intensity of the low frequency RS for pyridine varies with the excitation frequency, increasing monotonically from $4.7 \pm 0.3\ \mathrm{cm}^{-1}$ when excited with 14,782 $\mathrm{cm}^{-1}$ radiation to $9.5 \pm 0.3\ \mathrm{cm}^{-1}$ with 20,983-$\mathrm{cm}^{-1}$ excitation. No shift is observed for scattering from the 1008 $\mathrm{cm}^{-1}$ mode. Although the shift is reminiscent of the scattering from a collective mode that has dispersion, we find no change in frequency as the component of the scattering vector along the surface is changed by varying the angle of incidence and collection [2]. A possible explanation for this anomalous shift is that the light may resonantly excite an electronic state of the molecule and adjacent silver atoms and that the coupling of this electronic state to vibrational modes involving the molecule and silver atoms may change with frequency. Thus, at different excitation frequencies, the light scattering may be sensitive to different portions of the band of librational modes and so the peak in scattered intensity would shift with frequency. We note that the change of the relative intensity of Raman peaks as the exciting frequency is tuned through a resonance is a characteristic feature of resonance Raman scattering [5]. Further investigations are in progress to ascertain the origin of this shift.

The peak of the low frequency Raman scattering from pyrazine on silver changes with electrode voltage, as shown in fig. 3 for excitation at 5145 Å. The frequency of the mode shifts with voltage, increasing from 7 $\mathrm{cm}^{-1}$ at −0.1 V (versus SCE) to 13 $\mathrm{cm}^{-1}$ at −0.4 V. At higher voltages, the frequency again decreases and at −0.7 V, the mode can no longer be resolved. The variation in frequency of the low frequency mode may result from voltage induced changes in the molecular orientation which would be expected to influence the librational frequency as well as the coupling of the excited electronic state to vibrational modes. Jeanmarie and Van Duyne [6] studied SERS from the higher frequency modes in pyrazine at −0.6 V and found very weak signals. They attributed the small enhancement of Raman scattering in this case to the molecule lying flat on the surface. Our results are consistent with this interpretation at −0.6 V and suggest further that at less negative voltages the molecule "stands up" and so has a low frequency librational mode and a large Raman cross-section. Thus it appears that the change in intensity and frequency of scattered light from the low frequency mode in pyrazine may both reflect changes in the molecular orientation. This change in orientation may be due to changes in coverage as the voltage is changed. The change in frequency may also be affected by a change in the adsorbate–adsorbate interaction if the coverage is voltage dependent, though this might not be expected to have a large effect on the intensity of the Raman scattering from the higher frequency modes. In experiments with

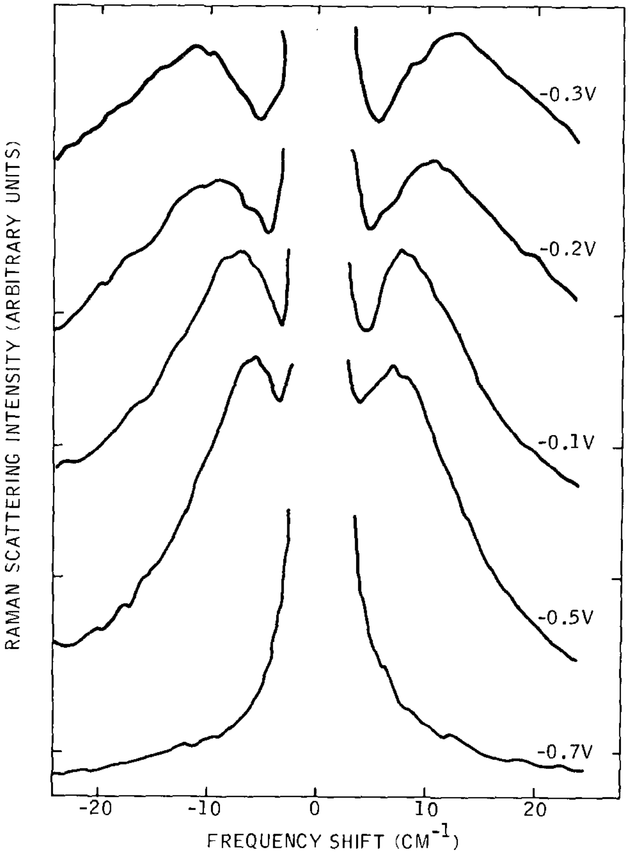

Fig. 3. Voltage dependence of the low frequency RS from pyrazine.

pyridine we find no such voltage shifts presumably because the pyridine adsorbate orientation does not change with voltage. Thus, as shown by the results, if the low frequency mode is indeed due to a libration of the molecule as a whole, it may be a useful probe of the adsorbate–surface and adsorbate–adsorbate interaction. However, a more complete understanding of its origin and its unusual behavior is required to fully interpret the effects of the environment on the mode.

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### *Note added in proof*

More recent experiments have suggested an alternate identification of the origin of the low frequency mode. Instead of a molecular libration, these experiments [7] suggest that the RS is from a mechanical vibration of the roughness features of a ~250 Å scale that constitute the metal electrode surface. When the electrolyte contains 0.1M KBr or KI, the presence of a specifically adsorbed organic molecule is not required to observe the low frequency mode. However, the increase in intensity which occurs with the addition of a specifically adsorbed organic molecules is necessary for the observation of the mode using KCl in the electrolyte. The frequency of the peak of the RS does not shift with the addition of an organic molecule and is independent of the specifically adsorbed organic molecule in most cases. The sole exception so far is the case of pyrazine, discussed above. These recent results suggest the mode is characteristic of the rough metal surface rather than the adsorbed molecule. We also observe a shift in the low frequency peak when the index of refraction of the surrounding medium is changed, suggesting that the intermediate electronic state involves a surface plasmon. The shift in the peak of the low frequency mode as the excitation frequency is changed can then be explained as being due to the variation in the characteristic mechanical vibration frequency as roughness features of different sizes and shapes are resonantly selected by the various exciting laser frequencies [7]. Further experiments are in progress to determine the source of the frequency shift with voltage observed when pyrazine is adsorbed on the electrode. Finally, we believe that RS from low frequency librations should also be observable when not obscured by other effects.