RAMAN RESONANCE SCATTERING OF PYRIDINE ADSORBED ON SILVER

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It had been found in [1] that the Raman scattering (RS) cross section of pyridine adsorbed on silver for the line of 1005 cm^{-1} when excited with the wavelength $\lambda = 632.8$ nm is about 3000 times larger than that for the line of the same pyridine-ring vibration in solution. The suggestion had been made that this increase in scattering cross section possibly is due to Raman resonance scattering originating from the adsorbate–metal charge-transfer band. To check this suggestion one should try, of course, to detect an effect of λ on the RS cross section. Such an attempt is made in the present work, and the largest possible number of lines in the RS spectrum of adsorbed pyridine is studied as a function of electrode potential φ, too.

The equipment described in [1] was used to obtain the RS spectra. In addition to the LG-38 He–Ne laser ($\lambda = 632.8$ nm), we also used an LG-31 He–Cd laser ($\lambda = 441.6$ nm) having 10 mW nominal power. The frequencies of the RS lines were determined accurately to ± 3 cm^{-1} by comparison with the RS spectrum of liquid pyridine [2]. The electrode surface was treated as described in [3]. All potentials reported in the paper refer to the saturated silver–silver chloride electrode.

We were able to measure the intensities of the RS lines of adsorbed pyridine with the frequencies 617, 1005, 1035, 1215, and 1590 cm^{-1} as functions of φ while exciting them with the He–Ne and He–Cd laser (Fig. 1). The ratio between the scattering cross sections of adsorbed and liquid pyridine, which was determined as in [1], is 100 to 150 when RS is excited by the He–Cd laser. The clearest result of this drastic decrease in the scattering cross section of adsorbed pyridine with decreasing λ is found in the fact that with the He–Ne laser, RS spectra can be obtained even at smooth electrodes, while with the He–Cd laser this is not possible. Such a dependence of the RS signal on the wavelength of the exciting light is typical for Raman resonance scattering [4]. It is conspicuous to note that the same RS lines when excited with different lasers exhibit different φ-dependences due to adsorption (Fig. 1). For example, there is almost no change in the intensity of the line of 1035 cm^{-1} over the range $-0.3\ V \geq \varphi \geq -0.8\ V$ when it is excited with the He–Ne laser, but the intensity depends strongly on φ when the excitation is by He–Cd laser. It is remarkable, too, that the intensity ratios for the closely spaced lines of 1005 and 1035 cm^{-1} are different when they are excited with light of different λ. A change in the intensity ratios of RS lines with λ also is typical for resonance scattering [4].

The fact that there is a φ-dependence of the intensity ratios of RS lines implies that in addition to pyridine adsorption or desorption, there is also a change in the bonding of pyridine to the surface, which of course alters the resonance conditions. The changes observed in the spectra are not due to an effect of the double-layer field on the adsorbed molecules or to the oxidation or reduction of pyridine. The effect of the field on RS intensity, i.e., the inductive effect, must be practically free of inertia. Therefore, from the φ-dependences of the line intensities reported in Fig. 1 one must expect that a readily detectable RS signal which is independent of the modulation frequency will arise upon modulation even at rather low modulation amplitudes (e.g., 10 mV). But even at a modulation frequency of 20 Hz and amplitudes up to 100 mV, it was not possible to detect any RS spectra at steady φ values in the range of $-0.3\ V \geq \varphi \geq -0.8\ V$. This indicates that the RS signal is lacking an inertia-free component, or contains only a small one. The suggested possibility of pyridine oxidation or reduction is inconsistent with the known stability of pyridine as solvent over a wide range of φ, and also with the almost complete independence of the RS line frequencies on φ (which is in keeping with the stability) and the almost complete match of these frequencies with the vibration frequencies of pyridine in aqueous solution (Fig. 1). Thus, the changes in the RS spectrum most likely are the result of changes in the orientation of the pyridine molecules on the silver surface which occur as a function of φ. Pyridine is known [5–7] to be adsorbed on metals in an orientation where the plane of the ring either is parallel to the surface or is at a certain angle to it. Changes in orientation should substantially alter the wave-function

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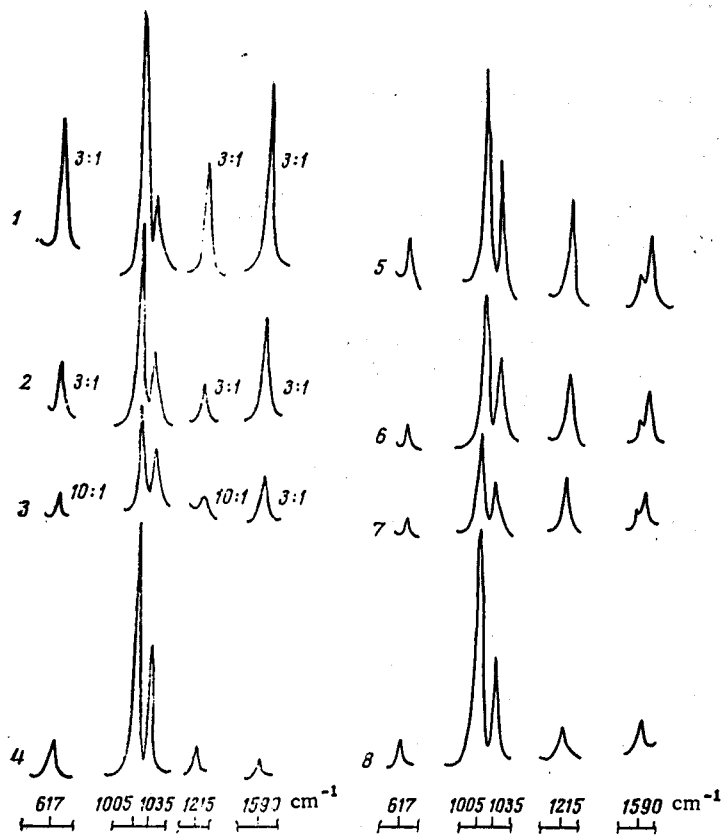

Fig. 1. The RS spectra of pyridine adsorbed on silver from 0.1 N Na_2SO_4 + 0.05 M C_5H_5N at $\varphi = -0.8$ V (1, 5), −0.6 V (2, 6), and −0.3 V (3, 7), and also the RS spectra of pyridine in 0.1 N Na_2SO_4 + 2 M C_5H_5N solution (4, 8). Excitation with light of $\lambda = 632.8$ nm (1-4) and $\lambda = 441.6$ nm (5-8).

overlap of metal and pyridine electrons, and hence there should be a strong change in the line intensities of Raman resonance scattering associated with the adsorbate−metal charge-transfer band.

When pyridine is adsorbed in several forms, then a procedure similar to that described in [8] can be used to define the number of these forms. We shall assume that two forms of adsorbed pyridine exist, with spectra $I_1(\nu)$ and $I_2(\nu)$, respectively, and that only the surface excesses $\Gamma_1(\varphi)$ and $\Gamma_2(\varphi)$ of these forms depend on φ. The resulting spectrum is of the form

$$I(\nu, \varphi) = \Gamma_1(\varphi) I_1(\nu) + \Gamma_2(\varphi) I_2(\nu). \quad (1)$$

The values of $I(\nu, \varphi)$ at any three potentials φ_1, φ_2, and φ_3 are connected via the linear relationship [8]:

$$\frac{I(\nu, \varphi_1)}{I(\nu, \varphi_3)} = \frac{I(\nu, \varphi_2)}{I(\nu, \varphi_3)} F_1(\varphi_1, \varphi_2, \varphi_3) + F_2(\varphi_1, \varphi_2, \varphi_3), \quad (2)$$

where F_1 and F_2 are constants which are independent of ν. A similar linear relationship links the values of $I(\nu, \varphi)$ at any three frequencies ν_1, ν_2, and ν_3; in this case, constants F_1 and F_2 depend on these frequencies but not on φ. One can see from Fig. 2 that the line intensities in the RS spectra indeed are linked by a linear relationship of the type of (2). Hence, two forms of adsorbed pyridine exist over the range of $-0.3\ \text{V} \geq \varphi \geq -0.8$ V on silver; the spectra of these two forms differ in the intensity ratios of the RS lines. Parameters F_1 and F_2 for the straight lines in Fig. 2 do not depend on ν; therefore, the straight lines obtained when analyzing spectra excited with He−Ne and He−Cd lasers ought to coincide (as observed), despite the fact that the spectra are different.

All lines in Fig. 1 increase in intensity as φ changes from −0.3 V to −0.8 V, although they do so to different degrees. This means that the wave-function overlap of metal and pyridine electrons becomes greater around the point of zero charge (p.z.c.) of silver [9]. One can suggest, therefore, that at this point the pyridine is oriented preferentially with the plane of the ring parallel to the surface. Then the interaction

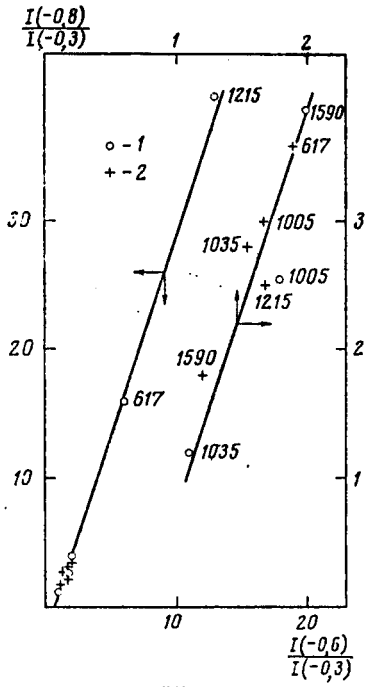

Fig. 2

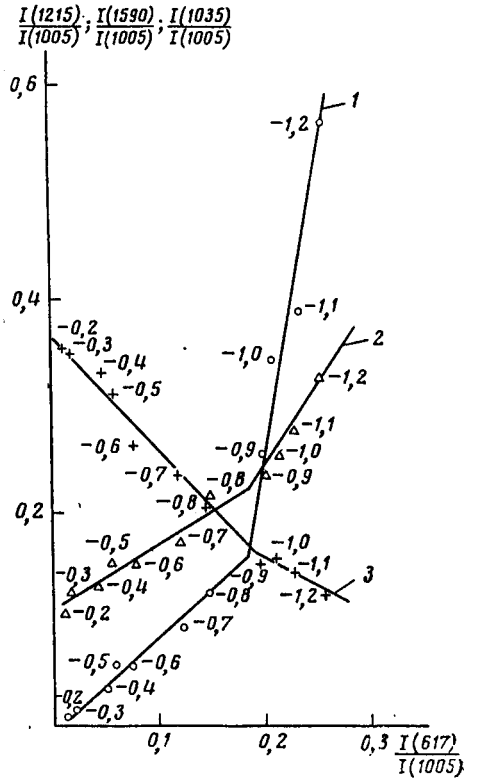

Fig. 3

Fig. 2. Linear relationships in the RS spectra at three values of φ when excitation is by light with $\lambda = 632.8$ nm (1) and $\lambda = 441.6$ nm (2). The numbers given in parentheses are the values of φ in volts; the numbers at the points indicate the frequencies in cm^{-1}.

Fig. 3. Linear relationships in the RS spectra over a wide range of φ at $\lambda = 632.8$ nm: 1) I(1215)/I(1005); 2) I(1590)/I(1005); 3) I(1035)/I(1005). The values stated in parentheses are line frequencies in cm^{-1}; the numbers at the points indicate the values of φ in volts.

of the π-electrons of pyridine with the metal is maximum. Spectrum 1 in Fig. 1 corresponds to this configuration. As one goes to more positive potentials, the double-layer field will orient the pyridine with the nitrogen atom toward the surface, and its RS spectrum comes close to spectrum 3 of Fig. 1. The changes in the intensity ratios occurring at $-0.8\ V \geq \varphi \geq -1.2$ V are substantially smaller than those occurring at $-0.3\ V \geq \varphi \geq -0.8$ V. An analysis of the RS spectra at three arbitrary frequencies (Fig. 3) shows that at φ from -0.2 V to -0.8 V, the points fall onto a single straight line; the RS spectrum evidently is formed here by two configurations of adsorbed pyridine: flat, and into space with the nitrogen atom pointing toward the electrode. The deviations from the straight line seen at $\varphi < -0.8$ V possibly are due to a further reorientation of the adsorbed pyridine at φ more negative than the p.z.c. of silver, with the nitrogen atom to the solution as found on mercury [6]. At these φ, the RS spectrum basically is formed by another pair of configurations: flat, and with the nitrogen atom toward the solution. It is characteristic that the breaks in the straight lines occur at φ close to the p.z.c. of silver, i.e., in the region where the flat orientation of the pyridine molecules is prevailing. It is natural, therefore, that the points in the plots of Fig. 3 which correspond to flat orientation in each case are part of both straight lines.

The intensity I_i of the i-th RS line, with frequency ν_i, is known [10] to be given by

$$I_i \sim \text{const}(\nu-\nu_i)^4 \left| \sum_e \left[\frac{f_e'}{\nu_e^2-\nu^2+i\nu\gamma_e} - \frac{2f_e\nu_e\nu_e'}{(\nu_e^2-\nu^2+i\nu\gamma_e)^2} \right] \right|^2, \quad (3)$$

where f_e is the oscillator strength of the absorption band for the electron transition 0→e (0 is the ground state, and e is the excited state); ν_e is the frequency in the maximum of the band; γ_e is the attenuation constant; ν_e' and f_e' are the derivatives of ν_e and f_e with respect to the normal vibrational coordinate of the

molecule; and ν is the excitation frequency. In the flat orientation of the molecules on the surface, the second term in (3) appears to provide the chief contribution to I_i, since in this case f_e' ought to be small. In fact, all frequencies that we could observe correspond to atomic vibrations in the plane of the pyridine ring [2]. In the flat disposition of the molecules on the metal surface, the ring vibrations have little effect on the wave-function overlap of the ring π-electrons and the metal electrons. But the oscillator strength is highest in this configuration. Both terms in (3) must be taken into account when the pyridine is oriented with the nitrogen atom to the metal surface; in this case the relative contribution of these terms is different for each line, since the f_e' and ν_e' are different (in this configuration, vibrations in the plane of the ring can influence f_e substantially, and for each type of vibration differently). In addition, the terms of (3) can have different signs for certain types of vibration. In particular, these terms can compensate each other for the lines of 617 and 1215 cm^{-1}, which exhibit a very strong decrease in intensity with increasing φ when they are excited with the He–Ne laser. But with the He–Cd laser, when $\nu_e^2-\nu^2$ increases, the ratio between the terms of (3) should become different, owing to the stronger dependence of the second term on ν, and the above compensation should become less important. Qualitatively similar considerations also are valid for the orientation of pyridine with the nitrogen atom toward the solution.

The Raman resonance scattering of adsorbed pyridine discovered in the present work gives rise to doubts concerning the models of pyridine adsorption suggested in [3], viz., via a layer of water molecules on the silver surface. Pyridine in aqueous solutions does not give Raman resonance scattering under our excitation conditions; it is not clear, therefore, how charge transfer can occur between pyridine and the metal in such a configuration.

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