

# Surface-enhanced Raman spectra of ethane adsorbed on silver

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Surface-enhanced Raman spectrum of ethane molecules adsorbed on cold-deposited silver films in an extremely high vacuum is detected for the first time. Three types of ethane adsorption are observed. The adsorbed ethane undergoes a photostimulated conversion to ethylene in the case of slight filling of the surface by the adsorbate and a catalytic conversion in the case of intense filling of the surface by the adsorbate.

It has been established elsewhere<sup>1</sup> that the most intense surface-enhanced Raman spectra are found in molecules which are chemically bound to a silver surface when the electrodynamic and "chemical" mechanisms are responsible for the surface enhancement. The surface-enhanced Raman spectra of molecules which are not expected to have a strong chemical bond with silver (saturated hydrocarbons) have so far not been found, although such attempts have been made.<sup>2</sup>

We have shown elsewhere<sup>3</sup> that the active surface of a cold-deposited ( $\sim 85$  K) silver film can be enhanced several fold by thermal activation (by heating the film to 180 K and then cooling it to  $\sim 85$  K). Using this procedure, we were able to record for the first time a surface-enhanced Raman spectrum of ethane on a silver surface (see Fig. 1). The experimental method is described in Ref. 4.

All the oscillations which are observed in the Raman spectrum of gaseous ethane<sup>5</sup> are also present in the surface-enhanced Raman spectrum, including the harmonic spectrum. Also present are the inactive  $\nu_6$ ,  $\nu_9$ , and  $\nu_{11}$  in the Raman spectrum and active  $\nu_6$ ,  $\nu_9$ , and  $\nu_{11}$  in the infrared spectrum and possibly  $\nu_4$ , which is inactive in both the infrared and Raman spectra.  $\nu_1$  and  $2\nu_{11}$  are the Fermi doublets.<sup>6,7</sup> All the observed frequencies are shifted toward the low-frequency region in comparison with the gaseous-state frequencies.

Several lines coincide in position and intensity with the surface-enhanced Raman spectrum of ethylene.<sup>3,4</sup> We accordingly note that a thorough study of the changes in the surface-enhanced Raman spectrum of ethane, produced as a result of increasing the exposure  $\dot{D}$ , has revealed the presence of at least three types of adsorption occurring sequentially. For lack of space, we will simply mention that three lines increase in

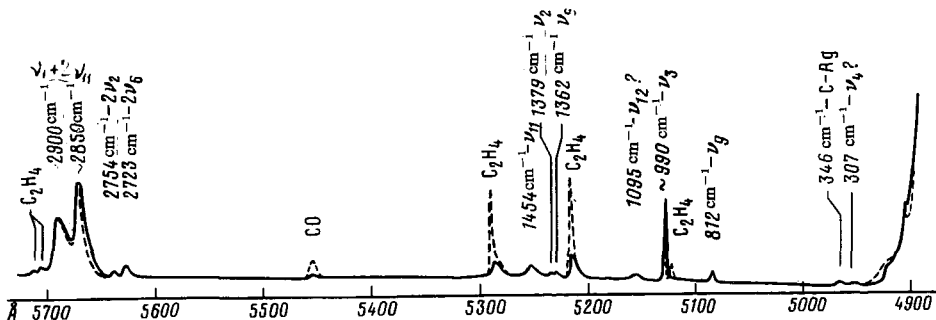
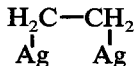


FIG. 1. Surface-enhanced Raman spectrum of ethane adsorbed on the cold-deposited silver film. The excitation is caused by the 488-nm line, the power is 100 mW, and the resolution is  $\sim 3 \text{ cm}^{-1}$ . The spectra were recorded after the exposure:  $D \sim 8L$  (solid curve) and  $D \sim 1500L$  (dashed curve).  $1L = 10^{-6}$  torr-s (without a correction for the relative sensitivity of the ionization gauge to ethane).

intensity sequentially in the frequency region corresponding to the stretching vibrations of the C-C bond: 1)  $990\text{-cm}^{-1}$  line appears at minimum  $D \sim 0.1L$ , increases to  $D \sim 1L$  and then its intensity  $I_1$  remains essentially constant. 2)  $983\text{-cm}^{-1}$  line appears at  $D \sim 0.3L$  when  $I_1 \sim 1/2 I_1 \text{ max}$ , increases to  $D \sim 1L$  and then falls off to  $D \sim 3600L$  (maximally studied exposures). 3)  $987\text{-cm}^{-1}$  line appears at  $D \sim 1L$ , increases to  $D \sim 10L$  and then remains essentially constant.

The same systematic features have been observed for lines corresponding to the vibrations of the C-H bonds ( $\sim 2900$  and  $\sim 2850 \text{ cm}^{-1}$ ).

The lines of the surface-enhanced Raman spectrum of ethylene increased in intensity (the increase corresponds to the narrow, high-frequency part of these lines) at the same time as the intensity of the  $983\text{-cm}^{-1}$  line of ethane decreased. This behavior leads us to assume that ethylene is produced from that form of adsorbed ethane which corresponds to the  $983\text{-cm}^{-1}$  line. It appears that the fragment of the molecule which is produced as a result of a catalytic dehydrogenation of ethane and which is di- $\sigma$ -bonded to the silver film surface is of this form,



The low-frequency "tail" of the ethylene lines appears when the degree of surface coverage is low. The intensity of the tail increases to  $D \sim 0.3\text{--}0.4L$  and then remains constant until the narrow, high-frequency part of the tail begins to increase. The conversion of ethane into ethylene is, however, photostimulated in this case. If we use a sample whose spectrum exhibits a tail of intensity  $I$  and redirect the laser beam to the part of the sample's surface which was previously not subjected to the beam bombardment, the intensity will increase from zero to  $I$  within 60 min.

The observed formation of a sharply asymmetric surface-enhanced Raman-scattering line of ethylene is evidence that the asymmetry is determined by the distribution of molecules among different adsorption sites, as was suggested by Pockrand,<sup>8</sup> but not by the Fano-interference of the vibration of an adsorbate with a background.<sup>9</sup>

The 359-cm<sup>-1</sup> line is related to the vibrations of the C-Ag bond of dehydrogenated ethane. Note that Ibach and Lehwald<sup>10</sup> observed analogous vibrations at 470 cm<sup>-1</sup> for a bond with platinum.

The 1092-cm<sup>-1</sup> line is related to the deformation vibrations of the CH<sub>3</sub> groups of ethane,  $\nu_{12}$ . An inordinately large frequency shift of this vibration raises doubt, however, as to whether such a relation is valid. The appearance of this line may indicate that surface groups -O-C<sub>2</sub>H<sub>5</sub> have been formed, as in Ref. 11, as a result of adsorption of methyl bromide on chromium molybdate, although under our conditions the number of oxygen-containing molecules on the film surface is negligible, as was confirmed by Auger spectroscopy.

In summary, we have shown that not only is it possible to observe the surface-enhanced Raman spectrum of saturated hydrocarbons but also to study the conversion of these hydrocarbons on the surface.

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