Giant enhancement of line intensities in Raman scattering spectra of submonolayer ethylene films adsorbed on silver

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Raman scattering spectra of submonolayer ethylene films adsorbed on vapor-deposited silver films in a vacuum $\sim 10^{-10}$ Torr were obtained for the first time. The main increase in the Raman scattering cross section occurs in the first adsorbed monolayer and is estimated to be a factor of 10^4–10^6.

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The giant (by a factor of $\sim 10^5$) enhancement of the Raman scattering cross section was first observed while studying adsorption of different molecules (for example, pyridine, CN^- ion) on the surface of a silver electrode in an electrochemical cell.[1–3] It was subsequently observed with deposition of molecules on the surface of different metals in a vacuum.[4,5]

The study of adsorption of unsaturated hydrocarbons, for which a strong interaction with the electrons in the metal can be expected, is of special interest. The simplest unsaturated compound is ethylene. Ethylene spectra were investigated in Ref. 5 in a low ($\sim 10^{-7}$ Torr) vacuum. Raman scattering spectra of ethylene were studied previously under conditions of an ultrahigh vacuum on vapor-deposited silver films,[6] and on the surface of colloidal particles in an argon matrix.[7] However, in these experiments, a very thin layer of ethylene was deposited on the metal and lines belonging to the crystalline phase were also present in the Raman scattering spectra, together with the lines of the first adsorbed monolayer.

In the present work, we investigated the Raman scattering spectra of adsorbed ethylene with submonolayer coatings on vacuum deposited silver films in ultrahigh vacuum. We used the vacuum apparatus described in Ref. 8. The Raman scattering spectra were excited by the $\lambda = 4880$ Å line of an ILA-120 argon laser with a power ~ 200 mW and recorded by a DFS-24 spectrometer using the reflection method, for which windows were provided in the vacuum chamber for introducing the exciting beam and for collecting the scattered radiation. The films were deposited by evaporating silver from a Knudsen cell, made of molybdenum, onto a glass or copper substrate cooled to ~ 80 K; the vacuum during deposition was $(3–4)\times 10^{-10}$ Torr. After depositing the films, when the vacuum increased to 1×10^{-10} Torr (~ 100 s), ethylene was introduced into the chamber. The exposures varied from 0.03 to 20 L [1 L (Langmuir) $= 10^{-6}$ Torr s]. The spectra obtained are shown in Fig. 1.

The general features of these spectra correspond to those of the spectra published previously, but there are important differences. First, the lines of the crystalline phase are missing, which is a result of the very thin adsorbate layer on the silver surface. A simple calculation, based on the kinetic theory of gases, assuming that all ethylene molecules hitting the surface of the silver film are adsorbed, showed that a complete

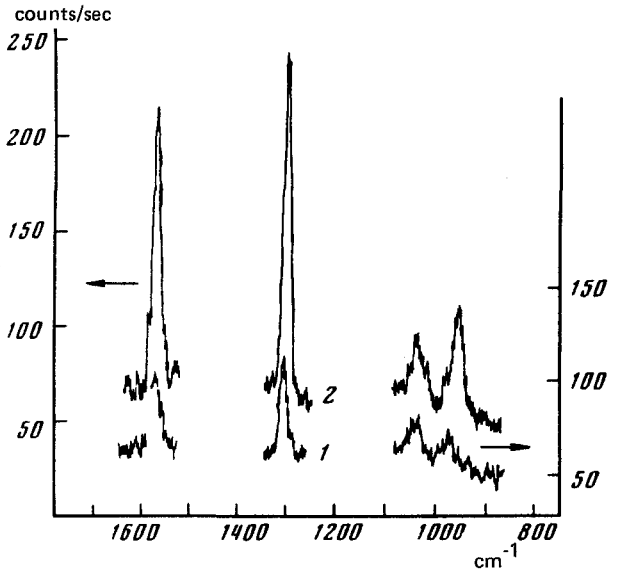

FIG. 1. The Raman scattering spectra of ethylene, adsorbed on silver, in the range 850–1650 cm^{-1} with the following exposures: 1) 0.03 L and 2) 0.25 L.

monolayer is formed with exposures of ~1 L. In addition, the greatest enhancement of the intensity occurs for the 1580 and 1320 cm^{-1} lines (see Fig. 1). These lines are already clearly evident with exposures ~0.03 L, which corresponds to a coating of ~0.03 monolayers (Fig. 1). For higher exposures, they become the dominant lines in the spectrum.

One of the important differences from the results in Ref. 5 is the fact that these lines are much narrower and their intensity is not less than an order of magnitude higher. The increase in intensity after exposures, corresponding approximately to a monolayer ethylene coating (1–2 L), is very insignificant (Fig. 2). This indicates the fact that the main increase in the Raman scattering cross section occurs in the first monolayer. In addition, the intensity of the lines is comparable to the intensity of the strongest lines in the Raman scattering spectrum of crystalline naphthalene. This allowed estimating the increase in the Raman scattering cross section as a factor of 10^4–

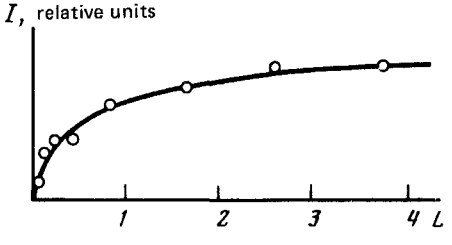

FIG. 2. The intensity of the 1580 cm^{-1} line as a function of exposure in an ethylene atmosphere.

10^6. Thus, the increase in the Raman scattering cross section accompanying the adsorption of molecules on silver films that were deposited in an ultrahigh vacuum is not smaller than the increase accompanying adsorption in electrochemical cells. Previously, this result was considered to be doubtful.[9]

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