

**V. M. Agranovich.** *Contemporary problems of surface spectroscopy.* This report contains a brief characterization of the main steps of development at the Institute of Spectroscopy of new optical methods of spectroscopy of surfaces and very thin (down to monolayer) films, which have arisen during the last ten years and which are based on use of the following techniques: a) surface electromagnetic waves in the optical range (see the review in Ref. 1) and b) enhanced Raman scattering.

a) Experimental determination of the dispersion of surface electromagnetic waves turned out to be possible at the beginning of the 1970's, in particular as the result of the widespread introduction of the comparatively simple method of frustrated total internal reflection. In this connection at the same time it was noted at the Institute of Spectroscopy<sup>2,3</sup> that the presence of a transition layer (or of a very thin film of thickness much less than the wavelength of the surface electromagnetic wave) in some cases leads to a fundamental rearrangement of the dispersion law of the surface electromagnetic wave—a law which, if one does not take into account the transition layer, is determined only by the bulk values of the dielectric permittivity of the media in contact. The influence of the transition layer turned out to be especially strong under conditions in which one or more eigenfrequencies  $\Omega$  of its vibrations resonate with the surface electromagnetic wave. In this case gaps of width

$\Delta \sim \Omega \sqrt{d/\lambda}$  are formed in the spectrum of the surface electromagnetic wave. The existence of the square-root dependence of the gap width  $\Delta$  on the dimensionless parameter  $d/\lambda$  was decisive: in many interesting cases the value of  $\Delta$  turned out to be greater than, or of the order of, the homogeneous line width of the surface electromagnetic wave, observation of the splitting became possible, and it was accomplished both in the infrared region and in the visible and ultraviolet regions of the spectrum.<sup>4-6</sup> As an illustration we have shown in Fig. 1 the results of observation of a gap formed on deposition on a silver surface of a monolayer of dye. The data obtained, according to Ref. 6, permit one to determine the orientation of the molecules in the monolayer and the oscillator strength of the transition. A more detailed discussion of resonance and nonresonance effects of the transition layer can be found in Ref. 7.

It is clear that the resonance phenomenon discussed above is of a universal nature, and in a certain sense it is an analog of the well known longitudinal-transverse splitting of light waves of bulk crystal optics. In connection with the possibility of experimental observation of the dispersion of surface electromagnetic waves in the region of a resonance, we have carried out at the Institute of Spectroscopy additional, more detailed studies in this direction. Here as a result of the allowance for the spatial dispersion, additional surface electromagnetic waves were observed.<sup>8</sup> The presence

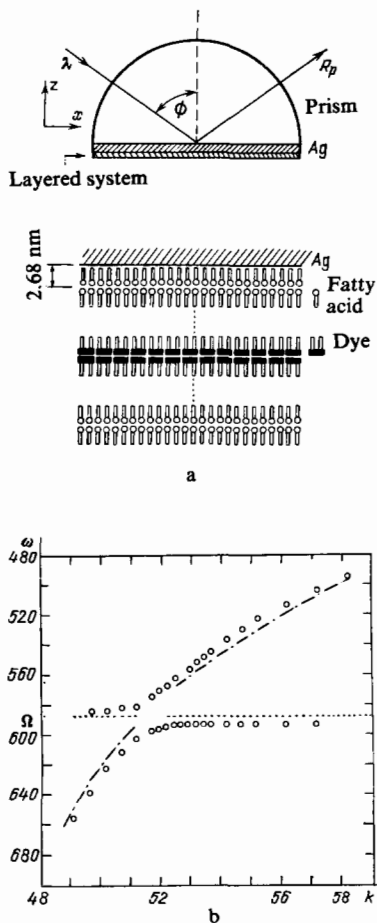


FIG. 1

of additional surface electromagnetic waves required generalization of the theory of diffraction of surface waves for the region of a resonance, which was carried out in a series of studies.<sup>9</sup> The theory developed in this work predicts a number of optical effects which may be of interest, especially for study of the spectra of thin films. For example, in study of the diffraction of a surface electromagnetic wave at an impedance step formed, for example, upon deposition on a metal of a thin dielectric, metallic, or semiconducting film, we observed an effect similar to the well known effect of residual rays: when a surface electromagnetic wave with a white spectrum falls onto the edge of the film, there are produced in the spectrum of the diffracted bulk radiation spectrally narrow peaks at the eigenfrequencies of the vibrations of the film. Since we cannot discuss the theoretical results in more detail here,<sup>9</sup> we shall only remark on the promise of development of the crystal optics of surface electromagnetic waves in the vicinity of a resonance with vibrations in the transition layer (film). Like bulk crystal optics in the region of exciton resonances, this field of research is also potentially rich. However, as has occurred in the case of bulk crystal optics, the development of research here is being held up mainly by technological difficulties in the preparation of the samples (surfaces) and the insufficiently rapid introduction into laboratory practice of various forms of spectrometers utilizing

the unique properties of surface electromagnetic waves (see for example Refs. 10 and 11). The requirements of science and technology and, in particular, the necessity of development of the technology of production of surfaces with specified optical (waveguide) and spectral properties, and also the need of development of the spectroscopy of physical and chemical adsorption, will apparently assist the initiation of new research.

b) For about the last five years the problems of enhanced (giant) Raman scattering of molecules adsorbed on rough surfaces of a number of metals (Ag, Cu, Au, and certain others) have evoked great interest and are being widely discussed at various kinds of conferences and also in numerous articles and reviews (see in particular Refs. 12 and 13). It is now usually assumed that the enhancement of the Raman scattering process (surface-enhanced Raman scattering—SERS) is, crudely speaking, due to two factors—the effect of the local field (the electrodynamic or long-range enhancement mechanism) and chemical (short-range) mechanisms. The electrodynamic enhancement mechanism appears most distinctly on surfaces which, accidentally or in special preparation, have been roughened so that the local plasmons (see for example Ref. 14) are rather stable. Since the effects of the local field should appear in all linear and nonlinear optical processes occurring on the surface, in a number of cases the contribution of the electrodynamic enhancement mechanism can be evaluated also from independent experiments (see Ref. 15, where the generation of the second harmonic on reflection of light from a roughened silver surface has been studied). Estimates of the long-range mechanisms of enhancement of Raman scattering have stimulated the development of the electrodynamics of rough surfaces<sup>12</sup> and rough films.<sup>16</sup> In this field many interesting results have already been obtained, but a number of possibilities remained inadequately studied, such as those due to plasmon localization and phase transitions.

Recently we have considered the possibility of the existence on a rough surface also of nonlinear local resonances, which are analogs of nonlinear surface waves on a smooth surface. These nonlinear local resonances, in particular for frequency values  $\omega$  close to  $\omega_{||}$  [ $\epsilon(\omega_{||}) = 0$ ], arise when one takes into account the dependence of the permittivity on the intensity of the electromagnetic wave,  $\epsilon(\omega) = \epsilon_0(\omega) + \alpha|\mathbf{E}|^2$ ; the frequencies of the nonlinear local resonances also depend on this intensity and even the region of their localization (a step or valley, etc.). The possibility of existence of nonlinear local resonances means that when the optical nonlinearity is taken into account, for example, the color of films or surfaces should change with increase of the intensity of the radiation hitting the surface, and that this change can, generally speaking, be modeled. It is clear that nonlinear local resonances should in general contribute also to the enhancement of Raman scattering on surfaces, harmonic generation on reflection, and so forth.

We note, however, that in spite of the abundance and diversity of still unsolved problems of the electrodynamics of rough surfaces and films, in study of SERS the interest has shifted to search for chemical enhancement mechanisms.<sup>13</sup> The existence of these mechanisms is now unquestioned (see

for example Ref. 14). Analysis of them is quite urgent, since it can be useful for study of the features of electron-electron and electron-phonon interactions in molecules chemisorbed on a metal surface.

At the Institute of Spectroscopy, even before the discovery of SERS, as the result of attempts to evaluate the influence of chemisorption on the temperature of superconductivity of thin metal films, theoretical studies were made of the effect of contact with a metal on the electronic and vibrational excitations of the molecules in physical adsorption<sup>17</sup> and chemical adsorption.<sup>18</sup> In particular, attention was devoted to the existence under these conditions of excitations corresponding both to the transfer of an electron from the metal to unfilled states of the molecule, and to the transfer of an electron from a molecule to the metal (see Ref. 19; here obviously we are considering so-called charge-transfer states). The existence of states of this type can lead to those features of SERS which correspond to resonance Raman scattering, and Otto<sup>13</sup> is inclined to this particular interpretation of the chemical nature of the enhancement. However, the question as a whole remains open since the spectrum of states of the metal in the bulk is broad, and for interpretation of the experiment in Ref. 13 it is necessary to postulate on the metal surface a rather sharp maximum of the density of surface states, which furthermore must be located near the Fermi level. In this connection interest is presented also by other chemical mechanisms of enhancement and particularly the mechanism proposed by Malshukov.<sup>20</sup> This mechanism, under conditions of SERS, permits one to relate the width of the lines of the scattering spectrum to that part of the intensity increase which is due to an adiabatic flow of charge from the molecule to the metal and back, which arises in the case of vibrations of the nuclei (details can be found in Ref. 21). It is very urgent to investigate both theoretically and experimentally the chemical nature of the enhancement and in particular the nature of the active spots<sup>13</sup> (see also Ref. 22). Only on the basis of such studies will it be possible, apparently, to answer the question of to what degree enhanced Raman scattering can be used also for study of heterogeneous catalysis and other questions of surface chemistry.

<sup>1</sup>Surface Polaritons/Eds. V. M. Agranovich and D. L. Mills, Amsterdam, North-Holland, 1982.

<sup>2</sup>V. M. Agranovich and T. A. Leskova, *Fiz. Tverd. Tela (Leningrad)* **16**, 1800 (1974) [*Sov. Phys. Solid State* **16**, 1172 (1975)]. V. M. Agranovich and A. G. Malshukov, *Optics Comm.* **11**, 169 (1974).

<sup>3</sup>V. M. Agranovich, *Usp. Fiz. Nauk* **115**, 199 (1975) [*Sov. Phys. Uspekhi* **18**, 99 (1975)].

<sup>4</sup>V. A. Yakovlev, V. G. Nazin, and G. N. Zhizhin, *Opt. Comm.* **15**, 293 (1975).

<sup>5</sup>T. Lopez-Rios, F. Abeles, and G. Vuys, *J. Phys. (Paris)* **39**, 645 (1978).

<sup>6</sup>I. Pockrand, A. Brillante, and D. Möbius, *J. Chem. Phys.* **77**, 6289 (1982).

<sup>7</sup>V. M. Agranovich, cited in Ref. 1, p. 187. F. Abeles and T. Lopez-Rios, cited in Ref. 1, p. 239. G. N. Zhizhin and V. A. Yakovlev, cited in Ref. 1, p. 275.

<sup>8</sup>V. M. Agranovich, *Zh. Eksp. Teor. Fiz.* **77**, 1124 (1979) [*Sov. Phys. JETP* **50**, 567 (1979)].

<sup>9</sup>V. M. Agranovich, V. E. Kravtsov, and T. A. Leskova, *Zh. Eksp. Teor. Fiz.* **81**, 1828 (1981) [*Sov. Phys. JETP* **54**, 968 (1982)]; *Sol. State Comm.* **40**, 687 (1981).

<sup>10</sup>Y. J. Chabal and A. J. Sievers, *Appl. Phys. Lett.* **32**, 90 (1978); *Phys. Rev. Lett.* **44**, 944 (1978).

<sup>11</sup>G. N. Zhizhin, M. A. Moskaleva, A. A. Sigarev, and V. A. Yakovlev, *Poverkhnost'. Fizika, khimiya, mekhanika (Surfaces. Physics, Chemistry, and Mechanics)*, No. 2, p. 44, 1983. G. N. Zhizhin, E. A. Vinogradov, M. A. Moskaleva, and V. A. Yakovlev, *Appl. Spectr. Rev.* **18**, 171 (1982/83).

<sup>12</sup>Surface-Enhanced Raman Scattering/Eds. R. K. Chang and T. E. Fur-tak, N. Y., Plenum Press, 1982.

<sup>13</sup>A. Otto, in: *Light Scattering in Solids*/Eds. M. Gardona and G. Guntherodt, Vol. IV, Berlin, Heidelberg, New York; Springer-Verlag, 1983.

<sup>14</sup>S. A. Lyon and J. M. Worlock, *Phys. Rev. Lett.* **51**, 593 (1983).

<sup>15</sup>C. K. Chen, A. R. B. de Castro, and Y. R. Shen, *Phys. Rev. Lett.* **46**, 145 (1981).

<sup>16</sup>V. M. Agranovich, V. E. Kravtsov, and T. A. Leskova, *Sol. State Comm.* **47**, 925 (1983).

<sup>17</sup>V. M. Agranovich, A. G. Mal'shchukov, and N. A. Mekhtiev, *Zh. Eksp. Teor. Fiz.* **63**, 2274 (1972) [*Sov. Phys. JETP* **36**, 1203 (1973)].

<sup>18</sup>A. G. Mal'shchukov, *Fiz. Tverd. Tela (Leningrad)* **16**, 2274 (1974) [*Sov. Phys. Solid State* **16**, 1484 (1975)].

<sup>19</sup>V. M. Agranovich, *Fiz. Tverd. Tela (Leningrad)* **14**, 3684 (1972) [*Sov. Phys. Solid State* **14**, 3085 (1983)].

<sup>20</sup>A. G. Malshukov, *Sol. State Comm.* **38**, 907 (1981).

<sup>21</sup>A. G. Malshukov, in: *Electrodynamics and Quantum Phenomena at Interfaces*/Ed. R. A. Dogonadze, N. Y., Plenum Press, 1984 (in press).

<sup>22</sup>A. V. Bobrov, A. N. Gass, O. I. Kapusta, and N. M. Omel'yanovskaya, *Pis'ma Zh. Eksp. Teor. Fiz.* **35**, 506 (1982) [*JETP Lett.* **35**, 626 (1982)]; *J. Phys. (Paris)* 1983 (in press).

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