Higher-order surface-enhanced Raman scattering

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A rich Raman spectrum has been observed for perylene molecules adsorbed at a concentration of 10^{-7} M on the particles of a silver hydrosol. The spectrum contains the lines of the fundamental vibrations and also higher harmonics and sum frequencies of up to fourth order inclusively. The changes caused in the intensity distribution in the spectrum by changing the excitation frequency were studied.

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Surface-enhanced Raman scattering (or "giant Raman scattering," as it is called in the Russian-language literature), consists of an extreme increase (by a factor of up to 10^6) in the Raman cross section of substances absorbed on the surfaces of certain metals, particularly silver.[1] In one method for observing this effect, the adsorbent consists of the particles of a metal hydrosol.[2]

In the present experiments we synthesized and used a stable silver sol, free of side products, by reducing the oxide of silver with hydrogen in aqueous solution. The procedure for producing the sol and its optical properties are described in Ref. 3. Substances which are insoluble in water were introduced into the sol through a pyridine solution. The Raman scattering was excited by the beams from Ar^+ and He $+Cd^+$ lasers with wavelengths of 514.5, 496.5, 488.0, 476.5, and 441.6 nm in the usual geometry. The laser beams made an angle of about 90° with the observation direction. We used an DFS-24 spectrometer.

The Raman spectra of perylene were studied over the concentration range 10^{-6}–10^{-10} M. We detected seven lines corresponding to fundamental vibrations, along with 39 higher harmonics and sum frequencies of various orders. Some of the results are shown in Fig. 1.

The classification of all the observed lines surface-enhanced Raman scattering is based on the following pieces of evidence: 1) The scattering cross sections are very large, so that clear spectra can be found at unusually low perylene concentrations in the solution. 2) The observation of a broad range of higher harmonics and sum frequencies proves that this is a sharp-resonance process. Free perylene molecules, on the other hand, lose their ability to absorb light appreciably even in the green part of the spectrum. 3) There is essentially no luminescence (which would prevent the excitation of Raman scattering in liquid solutions of perylene not containing silver particles).[3] 4) The degree of depolarization of all the spectral lines is high; this is a distinctive property of surface-enhanced Raman scattering.[4]

Analyzing the complete spectra, we find that the harmonics and sum frequencies differ only slightly from those which would be generated by simply multiplying
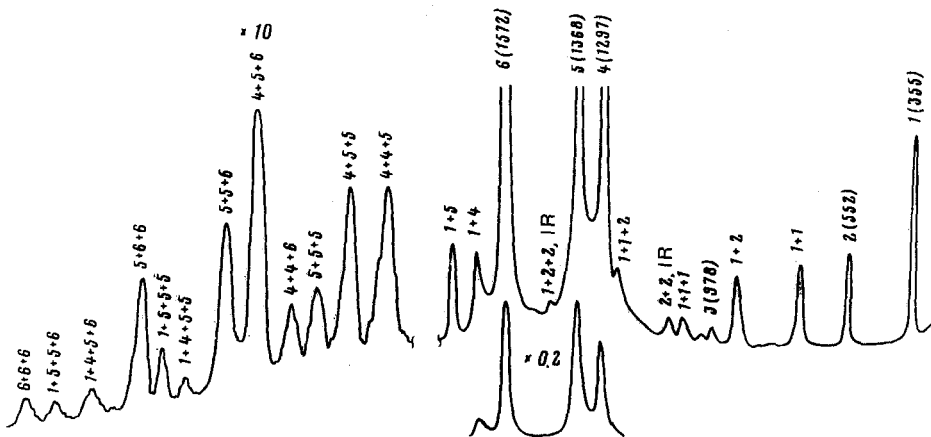
FIG. 1. Spectrum of surface-enhanced Raman scattering in the fundamental vibration region and part of the spectrum of third-order surface-enhanced Raman scattering of perylene $(C = 10^{-7} M)$ adsorbed on particles of a silver hydrosol. $\lambda_{exc} = 441.6$ nm; $P = 50$ mW; 6-cm^{-1} slits; $\tau = 2$ s. The lines are labeled with the interpretation of the harmonics and sum frequencies. The frequencies of the fundamental vibrations, in reciprocal centimeters, are given in parentheses.

or adding the frequencies of the constituent vibrations. The greatest discrepancy (about 30 cm^{-1}) is found in the case of the quaternary combination of vibrations $1 + 5 + 5 + 5$ (Fig. 1): $4459 \rightarrow 4428$ cm^{-1}. The tripled frequencies of the fundamental vibrations exceed the actual frequencies by 6–7 cm^{-1} in most cases. There are even smaller discrepancies between the calculated and observed frequencies of the second harmonics ($2594 \rightarrow 2588$ cm^{-1}, $2736 \rightarrow 2734$ cm^{-1}, $3144 \rightarrow 3139$ cm^{-1}, etc.) and of the binary combination frequencies ($355 + 1297 \rightarrow 1649$ cm^{-1}, $355 + 1368 \rightarrow 1721$ cm^{-1}, etc.). These results are evidence that the mechanical anharmonicity constants probably have ordinary values. In contrast, we would expect an increase in the mechanical anharmonicity for adsorbed molecules in a monolayer because of the asymmetry of the strength field, by analogy with surface atoms in crystals.[5] We do not, however, rule out the possibility that the molecules in the adsorbed state are simultaneously exhibiting anharmonicities of third and fourth orders, with the latter making a positive contribution to the frequency, so that there is a partial cancellation of each of the contributions.

Previous work[6] has shown that the adsorption of certain aromatic compounds on silver iodide activates several vibrations in the IR absorption spectrum which are forbidden by the selection rules for free molecules. In the surface-enhanced Raman spectrum of perylene we do not observe IR-active vibrations in the fundamental-frequency region. There are two lines in the spectrum (marked "IR" in Fig. 1) which we have identified as corresponding to sums of symmetry-u vibrations, which are active in the IR region.

The intensity of the higher-order scattering is determined by the joint effects of the mechanical and electro-optic anharmonicities. The electro-optic anharmonicity

stems from the higher-order terms in the series expansion of the polarizability in the small displacements of the nuclei.[7] Even a semiclassical analysis shows that the intensities of the harmonics and sum frequencies may be appreciably more sensitive than the intensity of the fundamental vibrations to the excitation frequency.[7] We obtained excitation profiles for both types of lines over the entire range of laser frequencies used in the present experiments. The reference point was a vibrational line of CH of the perylene itself; the intensity of this line satisfies $I \cong \omega^4$, as we established in preliminary measurements with an external standard. As the excitation wavelength is reduced (441.6 nm), the intensities of the harmonics and the sum frequencies do in fact increase more rapidly. Particularly striking is the behavior of the harmonics 2×1368 cm^{-1}: Its intensity increases by nearly an order of magnitude in comparison with the fundamental vibration in the working wavelength range.

Finally, we note that there is a systematic broadening of the higher-order scattering lines; this broadening is completely consistent with the interpretation of this paper.

We believe that studies of this type may prove useful for identifying the physical nature of surface-enhanced Raman scattering.

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