

Observation of "intramolecular" analog of surface-enhanced Raman scattering

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In a study of resonant Raman scattering by a molecule, which has two isolated chromophores, it has been observed that the scattering by the vibrations of one chromophore is intensified upon the excitation of Raman scattering in the absorption band of the other. The effect is interpreted in terms of an electromagnetic mechanism for surface-enhanced Raman scattering.

Previous research has established that a necessary condition for the intensification of Raman scattering in the electromagnetic mechanism for surface-enhanced (or "giant") Raman scattering is that the nonabsorbing molecule which is acting as scatterer be close to an oscillator having a large dipole moment, in whose absorption band the spectra are excited. In most cases the role of oscillator is played by local plasmons of ultradisperse metal formations, but the oscillator could also be of any other nature. Tobias¹ has shown that any interaction between a scatterer and an oscillator, which can be characterized by an operator of a very general type, can lead to an intensification of Raman scattering. Blok² carried out corresponding calculations for dipole-dipole interaction operator and suggested that it might be possible to observe an intensification of Raman scattering by vibrations of a molecule or part of a macromolecule associated with a probe molecule which has a large transition dipole moment.

In the present letter we are reporting experimental results which can be interpreted as the first observation of this type of intramolecular analog of surface-enhanced Raman scattering.

We studied the excitation spectra for the excitation of Raman scattering by molecules of a pyriline dye adsorbed (for a quenching of the luminescence) on silver particles in a hydrosol, in the interval 441.6–676.5 nm. A distinctive feature of this molecule (see the inset in Fig. 1) is the coexistence of two weakly interacting subsystems of energy terms, associated with π - π^* electronic transitions localized on different fragments (F1 and F2) of the molecule.^{3,4} Curve a in Fig. 1 shows the positions of the corresponding long-wavelength absorption bands in an aqueous solution of the dye (B1 and B2). The transition dipole moments are fairly large (the band absorptivities are $\sim 4 \times 10^4 \text{ cm}^{-1} \cdot \text{M}^{-1}$) and make an angle of 62–90° with each other. The moment corresponding to B2 lies in the plane of the figure, while the second moment makes an angle with this plane.⁴ There is an interaction between the subsystems, which leads to a radiationless transfer of energy from F2 to F1 (Ref. 3).

The Raman spectra were excited by the beams from Ar^{+2} , Kr^{+2} , He-Cd^+ , and He-Ne lasers; the second harmonic of a beam from a YAG laser; and the beam from a dye laser (rhodamine 6G) with a power of 30–50 mW. The spectra were detected at 90° by a DFS-24 spectral instrument. The test solution, consisting of a sol and a dye

(the absorption band shown by curve b in Fig. 1), was diluted to an optical density ~ 0.2 at 420 nm in order to reduce the effect of absorption on the results of the measurements. The excitation spectra were recorded in comparison with an external standard: Raman-scattering lines of acetone at 787 and 1707 cm^{-1} .

Figure 1d shows the Raman spectrum of the dye during excitation by light at 441.6 nm. The excitation spectra are plotted for all of the isolated and easily resolvable Raman-scattering lines. Figure 1c shows some typical excitation spectra. The following spectral features were found: 1. The excitation spectra of all lines contain a band whose maximum (585 nm) corresponds to the excitation profile of local plasmons in clusters of silver particles. 2. Two groups of Raman lines are observed. For the excitation spectra of these lines there is typically yet another maximum, which corresponds to either B1 or B2 (the lines at 922 and 1170 cm^{-1} in part c of Fig. 1). 3. Several lines

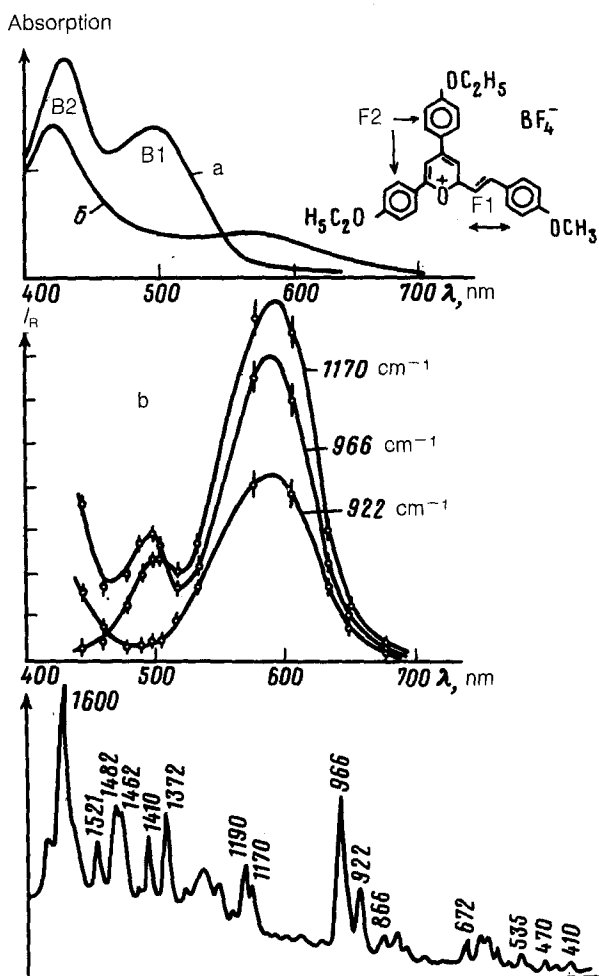


FIG. 1. a: Absorption spectrum of an aqueous dye solution. B1 and B2 correspond to transitions in F1 and F2. b: Absorption spectrum of a sol-plus-dye solution. c: Excitation spectra of Raman scattering lines with frequencies of 922, 966, and 1170 cm^{-1} . d: Surface-enhanced Raman scattering spectrum of a dye; excitation at 441.6 nm. The frequencies of the lines for which the excitation spectra are plotted are indicated. The inset shows the structural formula of the dye. Here F1 and F2 are fragments of the molecule.

(410, 470, 966, and 1602 cm^{-1}) have excitation spectra in which the two maxima, corresponding to B1 and B2, coexist.

The origin of the first two types of excitation spectra can be explained easily in terms of known models. The plasma nature of the maximum, common to all of the excitation spectra, is confirmed, in particular, by its redshift, which is accompanied by a simultaneous and corresponding shift of the long-wavelength knee of the absorption band of the sol-plus-dye solution upon the addition of a coagulant. The second type of excitation spectrum corresponds to the data of Refs. 3 and 4 on the electronic structure of this molecule. With regard to the third type of excitation spectrum, we should point out the following. At least one line, that at 966 cm^{-1} (a nonplanar deformation vibration of pyriline; No. 5 in Wilson's classification⁵), which can be attributed to a vibration which belongs to one fragment of the molecule (F2), is intensified in the absorption band of another fragment (F1). We believe that the effect which we mentioned at the beginning of this letter is responsible here. For three other lines with a corresponding type of excitation spectrum, we cannot in principle rule out the trivial interpretation of a random agreement or approximate agreement of vibration frequencies in different fragments, which would lead to a coalescence of the corresponding bands in the Raman scattering spectrum. The results of our comparative analysis of the spectra of the surface-enhanced Raman scattering of five pyriline dyes differing in the radicals in the 2, 4, 6 positions of the pyriline ring—including one which differed from that studied only in the presence of the CH_3 radical in position 6—confirm the identification of the 966- cm^{-1} line with fragment F2, but they do not provide an unambiguous answer to the question of what the other three lines belong to.

The absence of a corresponding maximum in the excitation spectra of the other Raman-scattering lines associated with F2 may be a consequence of insufficient accuracy in the determination of the excitation spectra and/or an unfavorable orientation of the vibration with respect to the transition dipole moment of B1 (Ref. 6). An estimate of the corresponding gain (under the assumption that the absorption bands have a Gaussian shape⁴ and under the assumption that the excitation spectra correspond completely to them) yields ~ 30 at the maximum of B1. We note in conclusion that suitable subjects for a further study of this effect might be certain asymmetric biscyanines and disazo dyes.⁷

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