Form of the tensor of spontaneous Raman scattering

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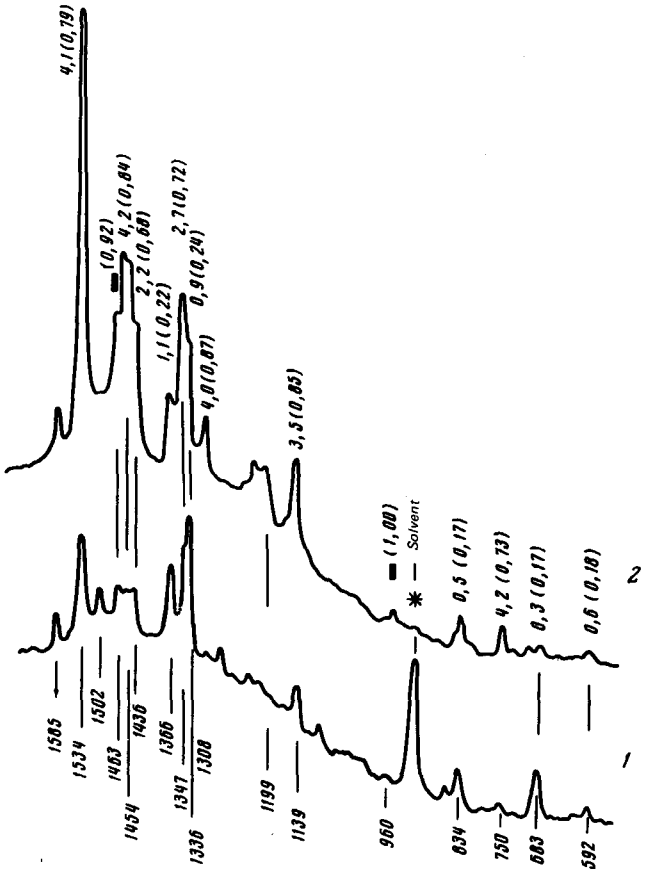
By measuring simultaneously the degree of depolarization and the inversion coefficients in spontaneous Raman scattering spectra, we show that the spontaneous Raman scattering tensor responsible for some of the oscillations is asymmetrical. The role of the resonance conditions for the excitation spectra and of the mixing of the electron and nuclear motions in this effect is explained. The possibilities offered by spontaneous Raman scattering in vibronic spectroscopy are demonstrated.

The spontaneous Raman scattering tensor produced on the vibrational levels of transparent media is usually assumed to be symmetric.[1] It is shown in [2], however, that this may not be the case in principle if the induced moment depends significantly on the nuclear coordinates, and the equilibrium internuclear distance q_0 varies little following electron excitation. The cause of the antisymmetrization of the spontaneous Raman scattering tensor may be the electronic degeneracy of the initial state and the accompanying dynamic Jahn-Teller effect in the nonlinear molecules.[3] Such cases, however, are encountered very infrequently. A major role can be played by the lifting of the Jahn-Teller electronic degeneracy of the upper level, and by the mixing



Polarization spectrum of the components P of Raman scattering of neutral Co-phthalocyanine molecules: 1 - component circularly polarized in the initial direction, 2 - in the opposite direction ($P = I_2/I_1$). The numbers (two- and three-digit) under the lower spectrum are the line frequencies in cm^{-1}. The numbers on top indicate the values of P, and those in the parentheses are the values of ρ of the lines. $\lambda_{exc} = 6328$ Å.

of different electronic states by vibrations that are not fully symmetric.[4,5] All these effects are particularly strongly manifest in resonant excitation of spectra[2,4,5] (see also [6]). Taking all the foregoing into account, we have chosen metal complexes of phthalocyanine for the experimental study of the problem. The absorption and luminescence spectra of these molecules differ by a small Stokes shifts, that indicates only an insignificant change of the value of q_0 following electronic excitation. On the other hand, the upper states of these molecules are certainly degenerate, and they are characterized by a mixing of the weak long-wave transition with the rather intense Soret band. Finally, they can be relatively easily investigated under resonance conditions.[7] The most suitable compound of this type turned out to be Co-phthalocyanine. In addition, we investigated its mono-anions, and also pure benzene, toluene, and nitrobenzene.

As is well known, the spontaneous Raman scattering tensor can in general be resolved into isotropic, anisotropic, and antisymmetric parts. Each of these parts has its own polarization characteristics in the spectra, namely the degree of depolarization ρ and the inversion coefficient P: $\rho_{isotr} = P_{isotr} = 0$, $\rho_{anis} = \frac{3}{4}$; $P_{anis} = 6$; $\rho_{ant} = \infty$; $P_{ant} = 0$.[6] This leads directly to the idea of the experiments for the complicated case when the oscillation in question is depolarized and is simultaneously allowed in the anisotropic and antisymmetric types of scattering. The idea is to measure simultaneously (and with high precision) the values of ρ and P. The partial asymmetry of the spontaneous Raman scattering tensor responsible for such vibrations can be inferred from the anomalously low values of P.

The spontaneous Raman spectra were excited by He + Ne, ionized-argon, He + Cd^+, and molecular-nitrogen lasers (wavelengths 6328, 4880, 4416, and 3371 Å, respectively). The spectral instruments were "Coderg," DFS-24, and SDL-1.[1)] The standard technique was used to measure P (see, e.g., [8]).

The obtained sharply-resonant spontaneous Raman scattering spectrum of the Co-phthalocyanine molecules, for the P components ($\lambda_{exc} = 6328$ Å), is shown in the figure. The figure gives also the values of P. A typical rms measurement error is ± 0.03. The results for the Co-phthalocyanine mono-anions are analogous. We see that certain line spectra have anomalously high (> 0.75) values of ρ. This in itself proves the asymmetry of the corresponding spontaneous Raman scattering tensor. For other lines, the value of ρ does not exceed 0.75. In these cases, however, the measured value of P turns out to be appreciably smaller (by a factor 2—2.5) than the value calculated from the formula $2\rho_{meas}/(1 - \rho_{meas})$, thus demonstrating convincingly the asymmetry of the spontaneous Raman scattering tensors in these vibrations.[6]

One of the features of the discussed results is that the spontaneous Raman scattering spectra show no lines with complete inversion of ρ (i.e., with $\rho \to \infty$). It is possible that this is a manifestation of the simultaneous activity of the investigated oscillations in both types of scattering. Since the quantity ρ is quite sensitive to changes in the form of the spontaneous Raman scattering tensor, we believe that such observations can turn out to be very useful in connection with the identification of the oscillations and with the determination of the true symmetry of the molecules, once a complete theory of the phenomenon is developed and the selection rules for the antisymmetrical type of scattering are concretely spelled out. Another distinguishing feature was observed when the polarization spectrum of the Co-phthalocyanine mono-anions was excited with radiation of wavelength 4416 Å. Under these conditions, the "anomalous" values of ρ become modified into values that do not exceed the range of the normal values. This fact itself emphasizes the connection between the "anomalies" of ρ and the resonant character of the spontaneous Raman scattering, in full agreement with the results of the authors of [9] and the conclusions of the theory.[5]

There are, however, no grounds for assuming that polarization "anomalies" of the character considered here cannot be observed when spontaneous Raman scattering spectra are excited in the region of transparency of a substance. We have demonstrated this with benzene, toluene, and nitrobenzene as examples. It is known that one of the vibrations of the benzene molecules, with symmetry type I_{2g} (606 cm^{-1}), mixes actively the electronic states B_{2u} and E_{1u}, and this is the reason

why the forbidden transition $A_{1g} - B_{2u}$ appears in the absorption spectrum.[10] It turns out that it is precisely this vibration in the spectrum of the spontaneous Raman scattering of benzene (and also its analogs in the two other substances) which exhibits distinctly the polarization anomalies at $\lambda_{exc} = 6328$ Å. For example, for benzene we have $\rho = 0.81 \pm 0.02$ and $P_{meas} = 5.6 \pm 0.2$.

According to the theory developed in [11] for spontaneous Raman scattering, the intensity of well-mixing vibrations should depend on the exciting-light frequency to a much greater degree than the intensity of the other oscillations. We were able to verify this with the aforementioned substances at the wavelengths 6328, 4416, and 3371 Å. The internal standards were the spontaneous Raman scattering lines 992, 786, and 852 cm^{-1}, respectively. On moving into the *UV* region of the spectrum, the intensity of the "anomalous" vibrations increases strongly (by an approximate factor of two). An even stronger increase is observed in the vibration of frequency ~1600 cm^{-1}, which pertains to the same symmetry type. It is interesting that its ability to mix the electronic states has no manifestation in electron-vibrational spectra.[10]

Thus, the entire set of the presented facts can be interpreted from one common point of view, which takes into account different cases of electron-vibrational interaction in complicated compounds. Being one of the methods of investigating problems of vibronic spectroscopy, Raman scattering of light can turn into a unique source of valuable information in this field.

[1)]The measurements with this instrument were made with the collaboration of A.I. Ryskin and E.G. Reut, to whom the authors are grateful.

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