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Abstract

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PHYSICS

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ON THE SIMULTANEOUS OBSERVATION OF RAMAN SCATTERING OF LIGHT AND FLUORESCENCE

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The parameters of lines in spectra of Raman scattering (Raman spectra) are closely connected with the character of the levels of electronic excitation. As the frequency of the exciting light approaches an absorption band, the intensity of the Raman lines increases rapidly. Under conditions in which the frequency of the incident light falls within the region of the absorption band of the dissolved substance, in many cases Raman scattering is not observed, but a broad fluorescence band is present. Its presence indicates a considerable lifetime of the excited state.

In other cases, in the absence of fluorescence, it is possible to observe some of the Raman lines. Thus, in solutions of *p*-nitroaniline one can observe the line of the nitro group and several other lines. The absorption band of *p*-nitroaniline has a considerable half-width (about 5000 cm^{-1}) and reveals no fine structure either in solutions at low temperatures or in vapors. Apparently, the mean lifetime of the excited state (τ) is very small here ($< 10^{-11}$ sec).

The question arises whether fluorescence and Raman scattering can be separated in the region of an absorption band. If scattering is regarded as the result of two successive acts (absorption and emission), then one cannot imagine that these acts are separated by a considerable interval of time. If this were so, then in a polar liquid with strong intermolecular interaction (which leads to a displacement of the absorption band by several thousand cm^{-1}), the molecules scattering the light would have time, during their stay in the excited state, to change their position relative to neighboring solvent molecules and thereby to change the conditions of perturbation of the levels of electronic excitation. In such a case one could expect broadening of the emission lines up to several hundred reciprocal centimeters, which would practically lead to the nonobservability of the corresponding transition (to the disappearance of the Raman line).

Even if one assumes that τ is very small and amounts to about 10^{-13}–10^{-14} sec, it is still impossible to deny the possibility of some change in the orientation of the excited molecules, sufficient to broaden the emission line by several cm^{-1}. In reality, no noticeable broadening is observed.

The consideration of scattering as two successive acts leads to entirely different selection rules, according to which, in emission, the probabilities of transitions to higher vibrational sublevels of the ground electronic state may prove greater than the probabilities of transitions to the lower sublevels. Meanwhile, experimentally, overtones have so far not been observed in resonance Raman spectra. These spectra should differ from resonance fluorescence in their selection rules, by the absence of afterglow, and by a much smaller sensitivity to the influence of the medium.

For the further study of the relationships between light scattering and fluorescence, it is important to examine a large set of compounds with different types of electronic excitation levels.

In the present work we investigated the spectra of 4-nitro-4′-aminostilbene,

$$\mathrm{H_2N} - \between - \mathrm{CH : CH} - \between - \mathrm{NO_2},$$

and 4-nitro-4′-dimethylaminostilbene,

$$\mathrm{Me_2N} - \between - \mathrm{CH : CH} - \between - \mathrm{NO_2}.$$

Pure samples of these compounds were obtained by M. A. Geiderikh. Judging from the melting point and the absorption spectra, both substances had the trans form (see the data on the absorption spectra ($\frown$1)).

Table 1

4-nitro-4′-aminostilbene

Solvent	ν_{abs}, cm^{-1}	ν_{fl}, cm^{-1}	Quantum yield	τ, sec	ε_{4358}	$\omega_{\mathrm{NO_2}}$, cm^{-1}
Cyclohexane	26100	–	–	–	–	–
Benzene	25600	18000	0.6	–	17000	–
Chlorobenzene	24400	16400	0.5	–	22000	1340
Ethanol	24500	–	< 0.05	–	20000	1339
Pyridine	23500	–	< 0.05	–	22000	1338
Dioxane	24700	16800	0.5	–	18000	–

Nitroaminostilbene has a very intense absorption band in the region 4000–4500 Å (molar absorption coefficient at the maximum about 25000, oscillator strength ~ 0.4) and, when irradiated with light of frequencies in the region of this band, gives strong fluorescence. Nitrodimethylaminostilbene has similar spectra. The influence of solvents on the absorption and fluorescence spectra of these compounds was previously studied by Lippert (~2).

Table 1 gives the following data for 4-nitro-4′-aminostilbene: 1) the position of the maximum of the absorption band, ν_{abs}, in cm^{-1}; 2) the position of the maximum of the fluorescence band, ν_{fl}; 3) the fluorescence quantum yield, determined upon excitation of the spectrum by the mercury line 4358 Å (22938 cm^{-1}); 4) the mean lifetime of the excited state, τ, determined under the same excitation conditions; 5) the molar (decimal) absorption coefficient in the region 4358 Å, ε_{4358}; 6) the frequency of the symmetric valence vibration of the nitro group in the Raman spectrum (ω_{NO_2}).

Table 2 gives analogous data for 4-nitro-4′-dimethylaminostilbene. Here I_{NO_2} is the molar coefficient of the integral intensity of the nitro-group line in Raman scattering upon excitation of the spectrum by the mercury line 4358 Å (according to a rough approximate estimate, on a scale in which one one-hundredth of the intensity of the 313 cm^{-1} line of CCl_4 is taken as unity).

The data of Tables 1 and 2 show that solvents strongly affect the position of the absorption bands and have almost no effect on the vibrational frequencies (it should be noted that the frequencies of electronic transitions almost always prove to be far more sensitive to the influence of intermolecular interactions than the frequencies of vibrational transitions).

By varying the solvents, we thereby varied the magnitude of the difference between the frequency of the electronic transition, ν_{abs}, and the frequency of the incident light ν, as well as the magnitude of τ.

Figure 1 shows the absorption curve $\varepsilon = f(\nu)$ of 4-nitro-4′-dimethylaminostilbene dissolved in pyridine. Arrows mark the positions of the violet, blue, and green mercury lines used for excit—

Table 2

4-nitro-4′-dimethylamino-stilbene

Solvents	$\nu_{\text{abs.}}$, cm^{-1}	$\nu_{\text{fl.}}$, cm^{-1}	Quantum yield	τ, sec.	ε_{4358}	ω_{NO2}	I_{NO2}
Cyclohexane	24000	19800	0.3	$1.5 \cdot 10^{-9}$	21000	–	–
Benzene	23200	16900	0.7	$3.3 \cdot 10^{-9}$	27000	1340	5000000
Chlorobenzene	22500	15200	0.3	$2.2 \cdot 10^{-9}$	29000	1337	–
Ethanol	23400	13500	< 0.05	–	27000	1339	4000000
Pyridine	22300	–	< 0.05	–	27000	1335	–
Dioxane	23400	16200	0.4	–	28000	1340	–
Acetone	23200	14100	< 0.05	–	29000	1338	6000000

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Solvents	$\nu_{\text{abs.}}$, cm^{-1}	$\nu_{\text{fl.}}$, cm^{-1}	Quantum yield	τ, sec.	ε_{4358}	ω_{NO2}	I_{NO2}

the Raman spectrum, and by dotted arrows the position of the nitro-group line for all three cases (the differences in their length correspond qualitatively to differences in intensity). Here it was possible to observe Raman scattering under conditions in which the incident frequency exceeded the frequency of the maximum of the absorption band by 2000 cm^{-1}.

The search for possibilities of obtaining Raman spectra in the short-wavelength region of absorption bands creates the prerequisites for studying the frequency dependence of the intensity of Raman lines over the entire absorption region.

Fig. 1

In Fig. 2 the absorption curve of 4-nitro-4′-dimethylaminostilbene in benzene solution is presented (dotted line). The solid curve depicts qualitatively the distribution of energy in the emission spectrum at a substance concentration of the order of 0.001% in the frequency interval 16000–22000 cm^{-1}. The position of the exciting spectral blue mercury line (22938 cm^{-1}) is indicated by a vertical arrow. Crosses mark two Raman lines of benzene (1176 and $ 1600cm^{-1}$). The number 1340 indicates the vibrational frequency of the Raman line of the dissolved substance; its second line overlaps the benzene line $ 1600cm^{-1}.Inthelong−wavelengthpartofthespectrumthecurveformsabroad,intensebandwithamaximumintheregion16900cm{- 1}$; this is the fluorescence band.

Fig. 2

In methanol solution at a concentration of 0.002%, two Raman lines of the substance are readily observed, which in intensity exceed all the lines of the solvent; in this case the fluorescence band is very weak (barely noticeable).

The most important circumstance is the simultaneous observation of Raman scattering and fluorescence. In this connection, the question of whether the same is responsible for both phenomena is of particular interest⋯

of the same electronic excitation level or different levels, or different regions of one and the same level.

It should also be borne in mind that, under prolonged illumination of solutions of nitroaminostilbenes, not only photochemical decomposition of the substance[1] (which is accompanied by bleaching) is possible, but also isomerization of the trans form into the cis form. The absorption band of the cis form[2] is three times weaker than the band of the trans form. A priori, one could not exclude the possibility that the fluorescence band is caused by the trans form, while the Raman lines belong to the cis form, which is formed upon illumination. Against this speaks the possibility of observing these lines at small exposures, which do not cause a decrease in the absorption coefficient.

Determination of the quantum yield of fluorescence upon excitation by different frequencies shows that the observed contour of the absorption band in the region 4000–5000 Å corresponds to the electronic transition responsible for fluorescence. It was difficult to make precise measurements of the frequency dependence of the intensity of the Raman line because of the poor visibility of the lines in the violet region; however, approximate estimates (as well as the large intensity coefficients) indicate that the same electronic transition is also responsible for the appearance of the Raman lines.

It should therefore be assumed that, in the case investigated in this work, comparatively slowly proceeding fluorescence (including afterglow) and, independently of it, a rapidly proceeding scattering process (forced emission) are associated with a long-lived electronic level.

The frequency of the nitro group of the investigated nitrostilbene derivatives is lower than that of unsubstituted nitrostilbene (1343 cm^{-1} in benzene solution) by 3–5 cm^{-1}. This lowering should be attributed to the influence of the amino group, which is transmitted through the chain of conjugated π-bonds. In n-amino derivatives of nitrobenzene the influence of the amino group is expressed much more strongly (a decrease of ω_{NO2} by 12 cm^{-1}), and in nitroamine $H_2N \cdot NO_2$, the decrease in the frequency of the nitro group reaches 60 cm^{-1}. From these data one may conclude that, with lengthening of the chain of conjugated π-bonds situated between two groups of atoms, the mutual influence of these groups is weakened.

In this connection it should be noted that the sensitivity of the frequency of the nitro group to the influence of intermolecular interaction in nitroaminostilbene is also considerably lower than in n-nitroaniline, although the dipole moment of nitroaminostilbene is substantially higher. (The same may be said about the frequency of the maximum of the absorption band.) This is probably due, to a considerable extent, to the smaller value of the derivative of the dipole moment with respect to the corresponding nuclear coordinate, and is connected with the weakening of the influence of the amino group on the nitro group.

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Institute of Organic Chemistry named after N. D. Zelinsky

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[1] G. Lewis, T. Magel, D. Lipkin, J. Am. Chem. Soc., **62**, 2973 (1940).
[2] M. Calvin, H. Alter, J. Chem. Phys., **19**, 765 (1951).

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