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## Abstract

## Full Text

## PHYSICS

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# LIGHT SCATTERING BY MOLECULES AND THE LIFETIME OF THE EXCITED STATE

*(Presented by Academician I. V. Obreimov on 25 XII 1962)*

Clarifying the relationships between the spectral composition of the incident light and the secondary radiation is of great importance for the development of ideas about the interaction of light with molecules. Under nonresonant conditions these relationships are comparatively simple, whereas near and under resonance conditions they are much more complex, especially if the lifetime of the level of electronic excitation of the molecule is not very short.

The practical possibilities for studying the dependence of the spectra of secondary radiation on the frequency of the incident light $\nu$ are limited by the insufficient choice of suitable light sources. Studying the dependence on $\tau$ (by this we denote the mean lifetime of those electron-nuclear excitation levels of the molecule which appear in the electronic absorption spectra and contribute to the matrix elements of the polarizability) is of primary importance; however, under experimental conditions it is not possible to vary only this one parameter and, moreover, to determine its actual value with sufficient accuracy. In this connection we note that the width of absorption bands can provide information rather about the lower limit of possible values of $\tau$. In liquids and solid solutions this width may depend, for example, on variations in the arrangement of surrounding molecules and the corresponding variations in the positions of the excitation levels of the molecules under study (more substantially at low temperatures and in solid solutions), and on irregular evolutions of the parameters of these levels*. In practice, $\tau$ can be varied by choosing a series of suitable chemical compounds, as well as the temperature, viscosity, and character of the medium.

In the present work we have studied the resonance spectra of combination scattering (c.s.) of diphenylpolyenes Ph—(CH = CH)$_n$—Ph, which have absorption bands with a clearly expressed vibrational structure. In this connection one may suppose that $\tau$ here is not as small as, for example, in $n$-nitroaniline, nitrodimethylanilinostilbene, and other compounds in which it was previously possible to observe resonance c.s. spectra ([1,2]).

Obtaining c.s. spectra (Raman spectra) of compounds with large $\tau$ makes it possible to determine how large, under these conditions, is the intensity of the c.s. lines of the fundamentals and overtones, and how it varies upon excitation

Fig. 1. Curves of the absorption spectra $\varepsilon$ and secondary emission $E$ of DFP and DFG in acetone solutions at 25°. The dotted curve gives, for DFP, the absorption spectrum at $-70°$ (left) and the region of fluorescence bands at $-196°$ (right); for the latter, data from (3) were used.

Figure 1: Fig. 1. Curves of the absorption spectra $\varepsilon$ and secondary emission $E$ of DFP and DFG in acetone solutions at 25°. The dotted curve gives, for DFP, the absorption spectrum at $-70°$ (left) and the region of fluorescence bands at $-196°$ (right); for the latter, data from (3) were used.

in different zones of the absorption band; what the line width is; and whether the sets of normal nuclear vibrations manifested in the absorption, scattering, and fluorescence spectra coincide.

The appearance (and observation) of intense resonance c.s. lines in diphenylpolyenes with a long chain is favored by the separation of the absorption region and the region of fluorescence bands by a considerable frequency interval, which increases as the polyene chain is lengthened. Apparently, the changes in the equilibrium values of some normal nuclear coordinates, $\Delta_n$, occurring as a result of the electronic transition are here sufficiently large.

* Both of these aspects lead to results of the same type with respect to the natural vibrations of the oscillator, but to quite different results for forced vibrations.

Fig. 1 (top) shows the absorption spectrum of diphenyldecapentaene (DFP), Ph $-(CH{=}CH)_5-$Ph, in acetone solution; on the ordinate axis is the molar (decimal) absorption coefficient $\varepsilon$. In the same plot, the solid curve qualitatively represents the distribution of energy in the secondary-emission spectrum of DFP in the frequency interval 24000-15000 $cm^{-1}$, which includes the Raman lines of the substance (the solvent lines—acetone—are not shown) and the fluorescence bands (at right). The vertical arrow marks the position of the exciting line of the mercury lamp (Hg $k$, $\nu = 24705$ $cm^{-1}$); the dashed arrow marks the position of the blue mercury line (Hg $e$, $\nu = 22938$ $cm^{-1}$), which was used in other experiments.

**Fig. 1.** Curves of the absorption spectra $\varepsilon$ and secondary emission $E$ of DFP and DFG in acetone solutions at 25°. The dotted curve gives, for DFP, the absorption spectrum at $-70°$ (left) and the region of fluorescence bands at $-196°$ (right); for the latter, data from ($^3$) were used.

In the same figure (bottom), analogous data are presented for diphenyldodecahexaene (DFG), Ph$-(CH{=}CH)_6-$Ph*.

DFP and DFG each have two very intense Raman lines ($\omega_1 =\sim 1140$ and $\omega_2 =\sim 1550$ $cm^{-1}$), which are readily observed at solution concentrations of $10^{-5}$-$10^{-7}$ mol/liter**. Table 1 gives the coefficients of the integrated intensity $I^{***}$ of these lines upon excitation of the spectrum by Hg $e$. These coefficients exceed in magnitude all those known for other compounds and, in particular, are 10–100 times greater than the maximum intensity of the lines of 4-nitro-4′-dimethylaminostilbene ($\sim 5 \cdot 10^6$ units ($^2$)).

Table 1 gives values of $K$, which show how many times greater the line intensity is upon excitation by Hg $k$ than upon excitation

* Both diphenylpolyenes were synthesized by A. Kh. Khomenko; the authors express their great gratitude to him. The melting point of the DFP preparation was 252°, and that of DFG 260°.

** Similar frequencies are also observed in the spectra of other polyene compounds not containing benzene rings; evidently, they pertain to vibrations of the polyene chain.

*** The unit is taken as 1/100 of the intensity of the 313 $\mathrm{cm}^{-1}$ line of $CCl_4$, calculated for an equimolar ratio of the substance and $CCl_4$. The internal standards in the intensity measurements were the 1225 and 1429 $\mathrm{cm}^{-1}$ lines of the solvent—acetone. Their intensity upon excitation by Hg $e$ is 8 and 15 units. The corrections for light absorption when using the indicated reference lines did not exceed 20% of the measured values. For the measurements a three-prism spectrograph with photoelectric recording of the spectrum was used.

from Hg $e$ (calculated for the same intensity of the exciting light). As is seen from Table 1 and the figure, the intensity of the Raman lines increases as the frequency of the incident light $\nu$ approaches the regions of individual maxima of the absorption band; moreover, the dependence $I(\nu)$ for the lines $\sim 1140$ and $\sim 1550$ is not the same. For more detailed comparisons of $I$ and $\varepsilon$, it would be necessary to separate, from the real contour of the absorption band, each component of the vibrational structure individually, which is difficult to do.

**Table 1**

| Compound | Lines | $I$ | $K$ |
|---|---|---|---|
| DFP | 1145 | $28 \cdot 10^6$ | 2.7 |
| DFP | 1567 | $50 \cdot 10^6$ | 3.3 |
| DFG | 1142 | $35 \cdot 10^7$ | 0.65 |
| DFG | 1552 | $53 \cdot 10^7$ | 0.25 |

When the temperature of the solutions is lowered, the intensity of the Raman lines of DFP and DFG changes to a much greater degree than in nonresonance spectra (in some cases one of the lines is strengthened, while the other is weakened). Here the increase of $\tau$, the decrease of $\Delta_n$ (see the convergence of the absorption and fluorescence bands in Fig. 1), and especially the shift of the absorption bands are important; as a result the exciting line turns out to lie in an entirely different region of the component of the fine structure of the absorption band (see Fig. 1).

The vibrational frequencies $\omega$, with which the frequency of the electronic transition $\nu_e$ is combined, according to the data of ($^3$), amount in the first absorption band (3500-4500 Å), both for DFP and for DFG, to 1210 and 1560 cm$^{-1}$, while in the fluorescence spectra they are 1160 and 1550 cm$^{-1}$ (accuracy ±50 cm$^{-1}$).

**Table 2**

Overtone and combination-tone lines of DFG upon excitation of the spectrum by Hg *e* and Hg *k*

| Raman line frequency, cm$^{-1}$ (Hg *e*) | Raman line frequency, cm$^{-1}$ (Hg *k*) | Assignment | Intensity, million units* (Hg *e*) | Intensity, million units* (Hg *k*) |
|---:|---:|:---|---:|---:|
| 2282 | ~ 2290 | $2\omega_1$ | 50 | ** |
| 2690 | 2690 | $\omega_1 + \omega_2$ | 100 | 100 |
| 3100 | 3102 | $2\omega_2$ | ** | ** |
| 3425 | 3423 | $3\omega_1$ | 20 | 10 |
| 3821 | 3822 | $2\omega_1 + \omega_2$ | 30 | 60 |
| 4232 | 4228 | $\omega_1 + 2\omega_2$ | 30 | 100 |
| – | 4635 | $3\omega_2$ | – | 30 |
| – | 4951 | $3\omega_1 + \omega_2$ | – | 20 |
| – | 5359 | $2\omega_1 + 2\omega_2$ | – | 30 |
| – | 5769 | $\omega_1 + 3\omega_2$ | – | 20 |

* According to a rough estimate.
** No estimate is given (because of overlap of the lines).

The approximate coincidence of the frequencies $\omega$ observed in the Raman, absorption* and fluorescence spectra gives grounds for supposing that in all three types of spectra the same kinds of normal vibrations of the nuclei are manifested and, consequently, that in all three cases the changes in the equilibrium values of the normal nuclear coordinates upon electronic excitation, $\Delta_n$, are of primary importance. This confirms the assumption of the great importance, for the Raman effect, of the dependence of $\nu_e$ on the nuclear coordinates, $\nu_e(q)$, taken into account in the simplest version of the semiclassical theory ($^5$). At the same time, the specificity of the Raman lines—their small width—is clearly expressed in the spectra of DFP and DFG.

Especially interesting in the resonance Raman spectra of DFP and DFG is the unusually large relative intensity of overtones and combination tones (see Table 2 and Fig. 1), which made it possible to observe lines of the 2nd and higher orders (their intensity is at times close to, or even exceeds, the intensity of the fundamental tone). As the frequency $\nu$ approaches the absorption band, the intensity of these lines increases substantially faster than the intensity of the fundamental tones (thus, in DFG the intensity of the line $2 \cdot 1145$ cm$^{-1}$ increases by a factor of 40 on going from Hg *e* to Hg *k*). This also confirms the great importance, for the Raman effect of light, of the dependence $\nu_e(q)$.

* Interesting comparisons for **other compounds** are given in the article by Behringer and Brandmüller ($^4$).

A very revealing comparison is that of the dependence of $I'(\nu)$ for the Raman line $\sim 1550$ cm$^{-1}$ of $C_2H_5OOC—(CH{=}CH)_6—COOC_2H_5$, which has a structured absorption band (similar to the DPT band) with its principal maximum at 26000 cm$^{-1}$, and the line $\sim 1300$ cm$^{-1}$ of 4-nitrodimethylaniline, which has a continuous absorption band in the same spectral region. The ratio of the intensities for acetone solutions (calculated for equal intensity of the incident light) at $\nu$ equal to 18307, 22938, and 24705 cm$^{-1}$ is, for the first compound, $1:160:3000$, and for the second, as is known, $1:90:300$.

The high intensity of the overtones, as well as the very large value of the ratio of Raman-line intensities upon excitation in resonance and outside resonance, are undoubtedly connected here with comparatively large values of $\tau^*$ (at considerable values of $\Delta_n$); see ($^6$). At still larger $\tau$, one may expect a further increase in the intensity of the resonant Raman lines (while the characteristic features of light scattering are preserved—as long as the width of the absorption bands still considerably exceeds the width of the exciting-light line).

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* The probable value of $\tau$ here is of the order of $10^{-12}$–$10^{-11}$ sec. The lifetime of the electronic level according to fluorescence data, $\tau_0$, is naturally considerably greater—$10^{-10}$–$10^{-9}$ sec.

*Note: Figure translations are in progress. See original paper for figures.*

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