Physics

1962

SovietRxiv

Abstract

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Physics

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On the Question of the Dependence of the Intensity of Raman Scattering Lines on the Frequency of the Exciting Light

(Presented by Academician A. N. Terenin, 3 IV 1962)

One of the main tasks of Raman-scattering spectroscopy consists in establishing detailed relationships between the intensity and polarization state of vibrational lines, on the one hand, and the characteristics of the electronic transitions responsible for the appearance of these lines, on the other. A partial solution of this problem—the determination of electronic transitions effective for scattering—is based on comparing the experimental and theoretical dependences of line intensity on the frequency of the exciting light. Such a comparison, however, is complicated by the fact that, when the well-known Kramers–Heisenberg dispersion formula is simplified (the semiclassical approximation), the influence of an electronic transition is in the general case conveyed by the sum of two terms with frequency factors $\nu_e^2/(\nu_e^2-\nu^2)^2$ and $(\nu_e^2+\nu^2)^2/(\nu_e^2-\nu^2)^4$, whereas with a rigorous account of the vibrational structure of the electronic levels it is conveyed by only one term with the frequency factor $\nu_e^2/(\nu_e^2-\nu^2)^2$ ([1,2]). (Here ν is the frequency of the exciting light, and ν_e is the frequency of the Franck-Condon electronic-vibrational transition.) The choice between these two methods of treatment—the approximate and the rigorous—is difficult. In any case, it is known that the latter method leads to results that contradict experimental data: to the same dependence of the intensity of the fundamental tone and the overtone on the frequency of the exciting light ([3,4]). It is natural to assume that the course of the intensity of vibrational lines for the usual objects of study—molecules possessing continuous, structureless electronic absorption spectra—will most likely correspond to the semiclassical approximation.

Another difficulty arises in connection with the need to include in the expression for line intensity one more factor, dependent on the frequency of the exciting light. According to the generally accepted quantum theory, in which radiation is treated classically and the correspondence principle is used, this factor is equal to $(\nu-\nu_{\text{vib}})^4$, where ν_{vib} is the frequency of the vibrational transition. A different result is obtained from a more rigorous solution of the problem on the basis of quantum electrodynamics: for the case in which one electronic transition is effective (the usual approximation), this factor proves to be equal to $((\nu-\nu_{\text{vib}})/\nu)^2$ ([5,6]).

Fig. 1

Figure 1: Fig. 1

A number of works ([7–10]) have been devoted to the experimental study of the question that interests us. In most of them, the frequency behavior of line intensity was obtained relative to an internal standard, which inevitably introduces some uncertainty into the interpretation of the results. The task of the present work was to measure the absolute frequency behavior of the intensity of various vibrations over as wide a range of excitation conditions as possible. The objects of study were complex aromatic compounds, in particular those containing functional groups in the para position of the benzene ring. Nitromethane served as the solvent. The concentrations of the solutions were chosen from the condition of commensurability of the intensities

the line under study and the comparison line (1376-1401 cm^{-1} of nitromethane). The spectra were excited by mercury lines 4047, 4358, 5461 Å and helium lines 4471, 5016, 5875 Å. In the latter case a special light source developed by L. A. Kir' yanova, V. M. Pivovarov, and S. A. Yakovlev was used. The spectra were recorded photoelectrically with a DFS-12 spectrometer.

Thus, the frequency dependence of the intensity of the lines in the selected substances relative to nitromethane was obtained. In order to take into account the possible influence of nitromethane, manifested in the dependence of the intensity of its own lines on the frequency of the exciting light, it was necessary to carry out absolute measurements in the spectrum of this substance. These required determination of the spectral sensitivity of the monochromator with the receiver and of the relative intensity of the exciting lines in the spectrum of the source. The errors in determining the intensity of the investigated lines, with allowance for the influence of the standard, amounted to about 15-20%.

In order to separate from the measured intensity value the contribution made by terms with resonance denominators, it was first necessary to establish according to which law, $(\nu-\nu_{\text{vib}})^4$ or $((\nu-\nu_{\text{vib}})/\nu)^2$, the intensity of Raman lines actually changes. An incorrect choice of the factor under consideration may lead to substantial errors in determining the position of the actual levels. As already indicated, we carried out measurements of the absolute frequency dependence of the line intensity in the spectrum of nitromethane (internal standard), as well as in the spectra of some other colorless liquids: carbon tetrachloride, chloroform, and benzene. Some of the data obtained are shown in Fig. 1.

Fig. 1. Absolute frequency dependence of the line intensity: a–459 cm^{-1} of carbon tetrachloride; b–992 cm^{-1} of benzene; v–1376-1401 cm^{-1} of nitromethane. 1–experimental curves;
2–$I \sim \left(\frac{\nu-\nu_{\text{vib}}}{\nu}\right)^2 \frac{(\nu_e^2-\nu^2)^2}{(\nu_e^2-\nu^2)^4}$;

3–$I \sim (\nu - \nu_{\text{vib}})^4 \dfrac{(\nu_e^2 + \nu^2)^2}{(\nu_e^2 - \nu^2)^4}$.

a–ν_e is the frequency of the edge of the absorption band, 43,400 cm^{-1}; b–ν_e is the frequency of the maximum of the absorption band, 40,000 cm^{-1}; v–ν_e is the frequency of the maximum of the absorption band, 43,400 cm^{-1}.

It is seen from the figure that in all the cases considered the observed dependence satisfies the law $((\nu - \nu_{\text{vib}})/\nu)^2$ rather well. Small deviations from it can readily be explained by a certain unaccounted contribution of other, less intense electronic bands, or by an inexact coincidence of the frequencies of the actual electron-vibrational transition and the maximum of the absorption band. The latter, as will be shown below, occurs for all the strongly conjugated molecules investigated in this work. The data relating to carbon tetrachloride deserve special attention. For this substance the values of the factor $(\nu - \nu_{\text{vib}})^4$ alone completely describe the experimental frequency dependence. This would seem to indicate a negligibly small role of the term with resonant

denominator, which, however, contradicts estimates based on a reasonable choice of the values of ν_e. Moreover, if the law $((\nu - \nu_{\text{vib}})/\nu)^2$ is accepted as valid, then the experimental data give a value of ν_e equal to 43 400 cm^{-1} (the boundary of continuous absorption), which also satisfies the results of other spectroscopic studies of this substance ([3],[4]). In this connection the correctness of the treatment of analogous measurements in work ([11]) is open to doubt.

Thus, the entire body of the data obtained and of the literature data ([5],[6]) apparently indicates the validity of the law $((\nu - \nu_{\text{vib}})/\nu)^2$, which is taken as the basis for the further discussion.

Let us now turn to the description and interpretation of data on the frequency dependence of the intensities of lines corresponding to different vibrations in conjugated molecules. These data are given in graphical form in Fig. 2. The position of the electronic-vibrational transition relevant for scattering was determined by selecting such a value of the frequency ν_e at which the theoretical frequency dependence best agrees with the experimental one. In doing so, within the framework of a semiclassical treatment only the second term in the expression for the intensity was taken into account, which is entirely legitimate near the bands of the molecules' own absorption.

Fig. 2. Absolute frequency behavior of the intensity of the line of the totally symmetric vibration of the nitro group (constructed by recalculating the relative behavior at points separated by equal frequency intervals) for solutions in nitromethane: 1 –nitrobenzene, 2 –*p*-nitrotoluene, 3 –*p*-nitrophenol, 4 –*p*-nitrophenetole, 5 –nitrostyrene, 6 –1,4-bis-(β-nitrovinyl)benzene, 7 –*p*-methoxynitrostyrene, 8 –*p*-nitroaniline. The arrows indicate the frequencies of the relevant transitions for the compounds listed, obtained by calculation from experimental data.

As a result of such semiempirical calculations it was established that, for all the vibrations considered, one and the same intense long-wavelength transition

Fig. 2. Absolute frequency course of the intensity of the line of the totally symmetric vibration of the nitro group (constructed by recalculating the relative course at points separated by equal frequency intervals) for solutions in nitromethane: 1 —nitrobenzene, 2 —paranitrotoluene, 3 —paranitrophenol, 4 —paranitrophenetole, 5 —nitrostyrene, 6 —1,4-bis-(β-nitrovinyl)-benzene, 7 — paramethoxynitrostyrene, 8 —paranitroaniline. The arrows indicate the frequencies of the relevant transitions for the listed compounds, obtained by calculation from experimental data

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is relevant. We were led to the same conclusion by the previously conducted study in work ([12]) of the polarization spectra of these and analogous substances. However, in practically none of the cases does the frequency ν_e coincide with the maximum of the absorption band; rather, it is shifted relative to it toward longer wavelengths. The exact values of these frequencies are given in Fig. 2. The error in their determination does not exceed ± 500 cm^{-1}.

In connection with the latter results, it was of interest to attempt measurements directly inside the absorption band of the molecules. Since there are no sources with a set of suitable lines, we varied the position of the absorption band of the substance relative to the selected exciting line (λ 4358 Å) by changing the composition of a two-component solvent. An accessible object for such a study proved to be *p*-nitrosodimethylaniline. The solvent used was a mixture of carbon tetrachloride—

of carbon tetrachloride with chloroform. Self-absorption was taken into account by means of empirical calibration curves.

Assuming that the shift of the absorption band achieved by the method described does not introduce significant additional effects and that it is therefore equivalent to variations of the exciting line, we constructed the frequency dependence of the intensity for the vibration of the nitro group at 1430 cm^{-1} (Fig. 3). At a certain frequency (23,900 cm^{-1}), shifted relative to the maximum of the absorption band toward the long-wavelength side, as in the indirect experiments described above, the intensity reaches a maximum. The latter is evidently associated with the influence of damping, which according to our estimate is about 1500 cm^{-1}.

Fig. 3. Absolute frequency dependence of the intensity of the line of the totally

Fig. 3

Figure 3: Fig. 3

symmetric vibration of the nitro group at 1430 cm^{-1} in *p*-nitrodimethylaniline. 1 –experimental curve; 2 $-I \sim \left(\frac{\nu - \nu_{vib}}{\nu}\right)^2 \frac{(\nu_e^2 + \nu^2)^2}{(\nu_e^2 - \nu^2)^4}$, where $\nu_e = 23\,900$ cm^{-1}; 3 –long-wavelength absorption band of *p*-nitrodimethylaniline in carbon tetrachloride.

An unambiguous physical interpretation of the fact that the actual electronic-vibrational transition does not coincide with the maximum of the absorption band corresponding to the Franck–Condon transition is so far difficult. Most likely, we are dealing here with a phenomenon analogous to anomalous dispersion. The possibility of interpreting this fact on the basis of the theoretical concepts developed in works ([2]) seems doubtful, since the absorption spectra of the molecules studied do not reveal vibrational structure.

Received
28 III 1962

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