

Combination Scattering and "Association of Molecules"

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Combination-Scattering and "Association of Molecules" (Preliminary note)

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The molecular association of polar liquids was studied by the combination-scattering (Raman-spectra) method. In the spectra of a water solution of acetic acid the lines corresponding to the wave number 623 cm^{-1} changed their relative intensity at a change of the concentration of solution. This wave number is therefore characteristic of acetic acid complex molecules. No associative lines were observed in the combination spectra of nitrobenzol solution in CCl_4 .

SOON after the discovery of the phenomenon of combination-scattering of light, attempts were made to connect certain facts observed in combination spectra with the molecular association of the substance (Meyer,¹ Ganesan and Venkateswaran,² Prinsheim and Schlivitch,³ Dadiou and Kohlrausch,⁴ and others). In fact, the combination spectra offer a suitable method for studying the phenomenon of association; when comparing the combination spectra of any substance taken in two different conditions and containing either single molecules or a considerable number of associated molecules, the following may be expected: (1) characteristic frequencies of a single molecule may be somewhat displaced because of the influences exercised on various parts of the molecule by the adjacent molecules; (2) There may be frequencies which are observed only in the presence of associated molecules, and disappear at the same time with

the latter. These frequencies may be considered the result of vibration of one part of the associated molecule relative to the other. The existence of such a pronounced frequency is possible, of course, only in cases when there are perfectly definite configurations of associated molecules with quite definite powers interacting between their parts. Otherwise, only diffuse bands may be expected to appear in the combination spectrum. The absence of clearly expressed association lines does not yet solve the question one way or another, but the appearance of such lines may be considered a reliable and suitable indication enabling one to judge of the nature of the new formations. The above-mentioned method of studying the association is convenient because it allows us to observe the effect which is completely connected with the existence of associated molecules and entirely independent of single ones.

The aim of the present work is to study the problem of the existence of associative frequencies characteristic of the substance. It is possible to distinguish the associative frequencies from the insufficiently deciphered combination spec-

¹ Meyer, *Phys. Zeits.* **30**, 170 (1929), **32**, 293 (1931).

² Ganesan and Venkateswaran, *Ind. J. Phys.* **4**, 195 (1929).

³ Prinsheim and Schlivitch, *Zeits. f. Physik* **60**, 582 (1930).

⁴ Dadiou and Kohlrausch, *Phys. Zeits.* **31**, 514 (1930).

trum of the majority of organic matter only by modification of the intensity of certain combination lines, as compared with the others, at a change of temperature or of the concentration of the given liquid in solution. In this work we confined ourselves to the modification of the concentration of the liquid in solution under investigation. As objects of study, nitrobenzol and acetic acid were used, both possessing considerable polar moments and giving noticeable association. CCl_4 was used as a solvent for nitrobenzol, and water for acetic acid. The installation was mounted according to Wood's scheme, with a vertical vessel and a lamp and a prism of total reflection. The Steinheil spectrograph with three prisms was used; we applied both the high and the low dispersion.

The thoroughly purified nitrobenzol, obtained from the Institute of Reagents (Moscow), was of a slightly yellow-green shade. The latter did not change even after it had been illuminated for several hours with a quartz mercury vapor lamp. A series of spectrograms was obtained with a molecular concentration of nitrobenzol from 100 percent to 5 percent. By changing the time of exposure of solutions of various concentration we succeed in equalizing the intensity of certain lines which served for comparison. In this particular case it was the line corresponding to $\Delta\nu = 1341 \text{ cm}^{-1}$ (oscillations of the group NO_2). No marked changes of relative intensity of separate lines could be observed. This may be explained either by the fact that in nitrobenzol the association does not form clearly defined complexes or by the low frequency of vibration of the forming complexes and the impossibility under the conditions of our experiment of separating the corresponding lines from the exciting line. It must be pointed out, however, that nitrobenzol has an absorbing power that drops suddenly in the part of the spectrum lying between $\lambda = 436\text{m}\mu$ and $\lambda = 491\text{m}\mu$, and the majority of the lines compared were in that region. The different absorption might obscure the sought for effect of relative variation of intensity of separate lines. Of much greater interest are the results obtained for acetic acid. In this case we succeeded in discovering a definite frequency which seemed to correspond to the oscillations of one part of the complex relative to the other. Glacial acetic

acid, also obtained from Institute of Reagents was studied at molecular concentrations of 100, 60, 40 and 20 percent. The spectrograms obtained lead to the conclusion that the lines corresponding to $\Delta\nu = 623 \text{ cm}^{-1}$, represented on our spectrograms as satellites of $\lambda = 436\text{m}\mu$ ($\Delta\nu = 22,938 - 22,315 = 623 \text{ cm}^{-1}$) and of the line $\lambda = 405\text{m}\mu$ ($\Delta\nu = 24,705 - 24,081 = 624 \text{ cm}^{-1}$), changed their intensity markedly as compared with the other lines used for comparison. For the latter the lines were taken which corresponded to the frequencies $\Delta\nu = 855$ and $\Delta\nu = 2938$. While they are well defined and intense in pure acetic acid the lines corresponding to the frequencies $= 623 \text{ cm}^{-1}$ weaken considerably at 40 percent concentration and the satellite of $\lambda = 405\text{m}\mu$ disappears completely at a 20 percent concentration, the satellite of the heavier line $\lambda = 436\text{m}\mu$ being hardly visible.

The results obtained by us for acetic acid are in agreement with the Bhagavantam's⁵ remark to the effect that the low frequencies in a combination spectrum of acetic acid disappear at high temperatures.

This gives us reason to believe that in acetic acid there takes place a formation of complex molecules of a quite definite configuration characterized by a definite energy of connection and a definite characteristic wave number $\Delta\nu = 623 \text{ cm}^{-1}$.

Indirectly, the associative nature of this wave number is confirmed by the fact, that, according to Coblentz's⁶ data, it is absent in the infrared spectrum of acetic acid; the associative frequency is not active and therefore must not appear in the absorption spectrum.

The results obtained for the associative frequency of complex molecules in connection with other data enable us to compute certain parameters, characterizing these molecules the nature of interacting powers, the distance between single molecules within a complex one, etc. The computation made for acetic acid gives quite admissible values.

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⁵ Bhagavantam, *Ind. J. Phys.* **5**, 48 (1930).

⁶ Cited: Ganesan, *Ind. J. Phys.* **4**, 216 (1929).