

Substance	$\bar{\lambda}$, m μ	k	B_{ϕ}^q , %	B_{γ} , %		ρ , %	
				1	2	1	2
Tolane	380	1.14	50	0.60	0.59	1.2	1.2
Stilbene	394	1.10	50	0.61	0.61	1.2	1.2
Naphthalene	350	1.23	17	0.21	0.23	1.2	1.4
Terphenyl	395	1.12	30	0.30	0.34	1.0	1.1
Dibenzyl	373	1.25	44	0.39	0.40	0.9	0.9
KI - Tl**	417	1.02	76	1.7	0.71	2.2	0.9
NaI - Tl**	411	1.0	66	1.25	1.21	1.9	1.8
Naphthalene with anthracene . .	—	—	—	—	0.7 \pm 0.2	—	—

the fraction of reflected light, according to the measurements by Morgenshtern made on the same samples², is 10-16%. Alkali-halide crystals were excited with the 291 m μ line in the first absorption band of Tl.

As a result of the measurement for gamma excitation as well as for photoexcitation, magnitudes proportional to $\int E_{\lambda} f_{\lambda} d\lambda$ were obtained, where E_{λ} is the energy distribution in the luminescence spectrum, and f_{λ} is the spectral sensitivity of the photomultiplier. In order to convert to magnitudes, proportional to the real yields, i.e., $\int E_{\lambda} d\lambda$, we measured f_{λ} and E_{λ} for all substances. From these data the magnitudes of $\int E_{\lambda} d\lambda$ were determined in relative units. Previously we measured the absolute quantum yields of photoluminescence for naphthalene and stilbene³, and in reference 4 the absolute energy yield for gamma excitation of crystals of naphthalene with anthracene. This allowed us to give all magnitudes of yields in the absolute scale*.

In the above table $\bar{\lambda}$ — is the average wave length of the luminescence spectrum, K — relative sensitivity of the photomultiplier for the luminescence spectra, which is equal to $\int E_{\lambda} f_{\lambda} d\lambda / \int E_{\lambda} d\lambda$; B_{ϕ}^q , B_{γ} and ρ have the meaning given above. The magnitudes in columns 1 are from the measurements of the average intensity, those in columns 2 are from the scintillation measurements. For organic crystals ρ is the same with the precision $\pm 15\%$; this precision is within the limits of accuracy of the experimental measurements. The variation of ρ for the organic alkali-halide crystals cannot be explained by the fact that the latter have a greater probability for the photoeffect, and thus points out the different processes of excitation in these two types of crystals. The difference in the magnitudes of the yield in KI - Tl, as determined by the average intensity and by the scintillations methods, is explained by the phosphorescence of KI - Tl, which is not taken into account in the method of

scintillations.

We express our gratitude to L. M. Beliaev for submitting the crystals.

* The data obtained should be considered as the characteristics of the given samples, and not the substances, since it is possible that the samples contained small impurities which would influence the yield of luminescence.

** Crystals NaI and KI contained Tl in the concentration of the order of 10^{-3} gm/gm; this corresponds to a region where the intensity of gamma luminescence depends weakly on the concentration⁵.

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Influence of Intermolecular Forces in Solutions on the Intensity of Raman Lines

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EARLIER^{1,2} one of us observed anomalies in the thermal behavior of the intensities of the primary Raman series lines and explained these on the basis of the hypothesis of reciprocal deformation of

the potential function of the excited electron states due to the collision of the molecules and expressible directly by the factor $\partial \nu_e / \partial q$ in derived polarizability (ν_e - frequency of virtual transition, q - the normal coordinate). It logically follows from such an explanation that, corresponding to these observed anomalies, there be spectral differences with solutions at constant temperature. Since there are only fragmentary and unreliable data of the effect of the solvent on the intensity of Raman lines in the literature³⁻⁸, we made a systematic investigation of the pure substances carbon tetrachloride, benzene, hexane, chloroform, ethyl alcohol, acetone and of various 50% solutions of them. Spectra were recorded by photoelectric apparatus.⁹ Integrated intensities of lines were measured. Each spectrum was recorded in this manner several times (from 3 to 22). Spectral reproducibility was within 1-6.5%. Account was taken of the possible influence of the refraction of the fluid. Based on these researches, the following were determined:

1. Due to intermolecular forces, the intensities of lines in the spectra investigated clearly showed more or less substantial alteration for proportional concentrations. Increased intensities in solutions were found with only infrequent exceptions.

2. All lines of the spectra of non polar compounds in solutions in polar liquids as a rule were weakened. This is very clearly shown in the solu-

tion of CCl_4 and benzene in ethyl alcohol (Fig. 1) and acetone, where the decrease (for instance, the lines of CCl_4) amounted to 20-40%.

3. All lines of spectra of polar compounds in solutions on non polar substances are intensified. Thus, for example, in the spectrum of a solution of alcohol in CCl_4 the intensity of the lines 1047-1095 cm^{-1} increased more than 35% and the increase in intensity of other lines amounted on the average to about 20-25%.

4. In the case of an increase in intensities of lines of one component simultaneously there was, without exception, a decrease in intensity of the lines of the other component.

5. In certain non polar solutions and a few polar compounds for which additivity of the intensities might have been expected, lines of one component increased somewhat, but others were weakened (e.g. spectra of solutions of CCl_4 and chloroform in hexane). We are inclined to explain this on intricate spatial relations: The larger chlorine atoms of the molecules of CCl_4 and chloroform in a collision with hexane disturbs the reciprocal bonding interaction in such a close approach; which could easily occur to the hexane molecule in this mutual collision.

6. Elastic vibrations, as a rule, were more greatly modified by these intermolecular influences than valence vibrations. This rule is well illustrated by the data presented in Table I. The recordings of the spectra of solutions of acetone and ethyl alcohol in CCl_4 are exceptions where this difference between the elastic and valence vibrations does not appear. However, this result occurred in only this one instance.

Thus, in the behavior of intensities of lines in

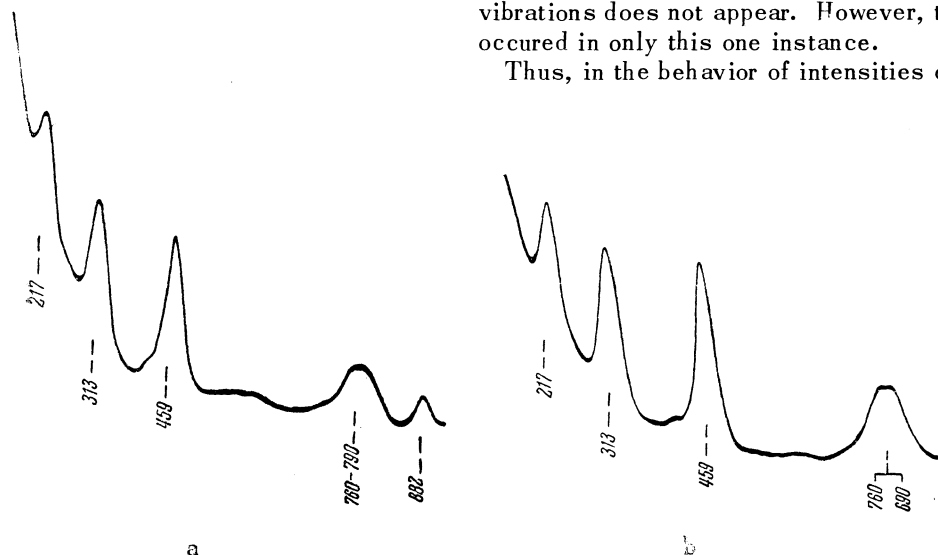


FIG. 1. Recordings of Raman Spectra
 a) Solution 50% CCl_4 in ethyl alcohol b) Solution 50% CCl_4 in Hexane

TABLE I

Variation in intensities of valence lines (v) and elastic oscillations (d) of the C-H coupling in certain solutions in comparison with pure substances.

Solution	frequency cm^{-1} type of vibration	$\frac{I_{\text{solution}} - I_{\text{pure substance}}}{I_{\text{pure substance}}} \%$
Hexane + CCl_4 Hexane lines	2852—2966, v	+ 8
	1440—1460, d	+13
Hexane + chloroform Hexane lines	2852—2966, v	+ 6.5
	1440—1460, d	+13.3
Hexane + chloroform Chloroform lines	3019, v	—16.7
	1216, d	—23.5
Benzene + chloroform benzene lines	3047—3065, v	— 5
	1176, d	—14.3
Benzene + CCl_4 benzene lines	3047—3065, v	0
	1176, d	+10.0

solution and in the temperature variation of the intensities of spectra of pure liquids, many common features are developed. In these and in other cases, due to the influences of the polarity of bonding on the intensity of lines varying in the same direction, differences appear in the behavior between elastic and valence vibrations, showing the influence of spatial conditions. Consequently, in the explanation of these variation effects due to mutual distortion of potential functions of excited electron states it is probably possible to assume an operating hypothesis and to examine both phenomena from a unified point of view.

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