QUASILINEAR STRUCTURE OF LUMINESCENCE SPECTRA OF TRIPHENYLENE IN FROZEN CRYSTALLINE SOLUTIONS*

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Fluorescence and slow fluorescence (phosphorescence) spectra of triphenylene in frozen crystalline n-alkanes (from n-pentane to n-undecane) and cyclohexane were examined at 77°K. In n-hexane and n-heptane solutions the spectra show typical quasilinear structure, whereby the narrowest and best resolved lines appear when using the latter solvent. There have been obtained both quasilinear absorption spectra within the range of the first singlet electronic transition of triphenylene molecule and the long wavelength absorption spectra arizing from the $T^* \leftarrow T$ absorption.

The influence of solvent on the structure and position of spectra was discussed. The vibrational analysis of quasilinear spectra was performed, and the frequencies of $0—0(S^* \dashrightarrow S$ and $T \rightarrow S)$ transitions as well as of several vibrations of triphenylene molecule in the ground state and first excited singlet state were determined. In the luminescence spectra of triphenylene, above all, the non-totally symmetric vibrations appear due to which the vibronic transitions become symmetry allowed.

Introduction

From among aromatic, condensed hydrocarbons triphenylene ($C_{18}H_{12}$ — *cp.* formula in Fig. 2) distinguishes itself by some interesting luminescence properties. The lifetime τ of molecules of this compound in metastable state is exceptionally long (15.9 sec.) [1] when examined solid EPA[1] solutions at 77°K, whereby the quantum yield of slow fluorescence[2] exceeds at these conditions, twelve times the fluorescence yield [2]. For this reason the intensity of slow fluorescence of solid triphenylene solutions is very strong while the fluorescence is rather weak.

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[1] Mixture of isopentane, ether and alcohol.

[2] Term "slow fluorescence" is used in present paper in agreement with the nomenclature given by Pringsheim [3], and denotes spontaneous radiative transition from the metastable level into the ground level of a molecule. This transition is described by many authors as "phosphorescence" or "β-phosphorescence".

Examination of photomagnetism [4] and electron paramagnetic resonance [5], [6] of triphenylene solid solutions shows, in keeping with general hypothesis of Lewis—Kasha and Terenin, that the metastable state of molecule of this compound is a triplet state. Many a time an opinion was expressed that the transition from the metastable state into the ground state is in triphenylene not only spin forbidden but also symmetry forbidden (*e.g.cp.* [7], [8]). This is also evident from the assignment of the triplet states given by Ham and Ruedenberg [9]. The results of theoretical calculations and experimental data concerning the absorption spectra of triphenylene solutions show that electronic transition between the ground state and the first excited singlet state is also forbidden [9], [10], [11], what is the general rule in catacondensed hydrocarbons. For this reason one should expect that in the fluorescence and slow fluorescence spectra of triphenylene non-totally symmetric vibrations of molecule will appear.

The fluorescence and slow-fluorescence spectra of triphenylene in frozen solutions were examined many a time whereby such solvents as ethanol or EPA were used [1], [8], [12]—[14]. Some results of above investigations considerably differ (up to few hundred cm^{-1}) between each other especially when the positions of initial bands (0—0) of both radiative transitions are involved, and do not permit to establish the vibrational structure of spectra with a reasonable accuracy.

The most accurate, as yet, data dealing with electronic emission spectra of aromatic hydrocarbons, as well as of some derivatives and other related compounds, can be obtained using the method described for the first time by Shpolskii and coworkers in 1952 [15]. The above method depends on examining the spectra of highly diluted solutions in adequately chosen *n*-alkanes[3] at liquid air or even lower temperatures. Such solutions possess the crystalline form in contrast to frozen glassified solutions obtained in such solvents like alcohol and EPA. By applying the above experimental conditions the spectra of substances being examined consist of so called quasilines of width equal to about 10 cm^{-1} or less. The individual quasilines, as shown in many works, correspond to molecule transitions from the excited electronic state (the lowest singlet or metastable state) to various vibrational levels of the ground state. The analysis of these spectra enables to determine the frequencies of vibrations active in given electronic transition. The absorption spectra of the discussed solid solutions also possess qualinear character, and frequently permit to identify the 0—0 transition due to the resonance agreement between the frequencies of initial absorption and fluorescence lines [16].

In the present work the investigations were undertaken on quasilinear spectra of triphenylene in various solvents. The quasilinear spectrum of slow fluorescence of triphenylene in frozen *n*-hexane was first obtained by Bowen and Brocklehurst [17]. The above authors have not determined, however, the 0—0 trasition frequency and have not given the complete vibrational analysis of the spectrum. During the elaboration of present results a note appeared [18] in which the quasilinear absorption and emission spectra of triphenylene, dissolved in *n*-hexane, are shortly described. The results presented below and their interpretation essentially differ at some points from those given in the already mentioned paper [18].

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[3] Sometimes branched isomers of alkanes or cyclohexane are used.

Experimental part

Frozen solutions of triphenylene of concentrations 10^{-4} to 10^{-3} moles per liter in normal alkanes from n-pentane to n-undecane and also in cyclohexane have been examined. All the solvents used were of the high purity and have not shown any luminescence under the action of ultraviolet light. During measurements the solutions were kept in closed flat quartz cells of the thickness 0.5 to 3 mm immersed in transparent Dewar flasks filled up with liquid nitrogen $(77.3\,^\circ\mathrm{K})$.[4]

The fluorescence spectra were taken by a quartz spectrograph ISP-28 (reciprocal dispersion 26 Å/mm at 3600 Å). The fluorescence was excited by a high-pressure xenon lamp (1000 W) the light of which was passed through a quartz monochromator (Bausch-Lomb) separating a broad band lying around 275 nm. The above light brings about the excitation of triphenylen molecules in the range of the second electronic transition $(^1L_a$—$^1A)$.[5] The molar absorptivity of triphenylene is in this range by an order larger than that in the first transition range $(^1L_b$—$^1A)$,[5] and therefore comparatively higher emission intensity is reached.[6] In spite of the above fact, because of rather low quantum yield of fluorescence, the exposure of spectra required in our experimental conditions 5 to 15 hrs at the slit width of spectrograph equal to 0.05 mm.

The absorption spectra were also photographed by means of a ISP-28 spectrograph in which as the light source a high-pressure xenon lamp was used. The beam of light focussed by a lens passed through the frozen solution contained in a thin cell placed in a Dewar flask just at the diaphragm of middle lens of illumination system consisting of three lenses.

The slow fluorescence spectra were excited by a highest-pressure mercury lamp (250 W) supplied with a filter transmitting 313 nm line mainly. The spectra were photographed by means of a glass spectrograph ISP-51 with a camera UF-84 $(F = 800$ mm, reciprocal dispersion 17.5 Å/mm at 5000 Å). The slow fluorescence of triphenylene in n-pentane was examined using the same spectrograph with a smaller camera $(F = 270$ mm, reciprocal dispersion 47 Å/mm at 5000 Å). The exposure time ranged from few minutes to one hour at the slit width 0.05 mm.

In addition to examined spectra Fe-arc spectrum was always photographed. The measurements of wavelengths were performed by means of a comparator IZA-2, photomeasuring micrometer ($Hilger$ $L78$) or a Zeiss spectrum projector. From the measured values the wave numbers reduced to vacuum were calculated [19]. The measurement errors, mainly resulting from the natural width and diffuse character of quasilines, reached in general 10 cm^{-1}, while for sufficiently narrow and sharp lines it did not exceed 5 cm^{-1}. For very weak and diffuse lines the error was somewhat larger (about 15 cm^{-1}). The above figures refer in the first place to the spectra obtained for solutions in n-heptane (cp. Table II and IV).

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[4] During examination of solutions in n-pentane liquid air was used.

[5] Transition symbols after Platt [10].

[6] As should be expected the spectral composition and structure of fluorescence spectra is the same when excitation in the first or second electronic transition range is performed and correspond still to ^1L_b→^1A transition.

Results and discussion

a) Solvent effect on the quasilinear structure of spectrum

Performed experiments have shown that n-heptane is the most suitable solvent permit-ting to obtain the best quasilinear spectra of triphenylene. In this solvent the quasilines are rather narrow and sharp creating satisfactory conditions of performing the vibrational analysis of spectra. The spectra of triphenylene solutions in n-hexane do not differ very much from those in n-heptane but in former case some lines are worse resolved. E.g. in the slow fluorescence spectrum one can distinguish only 67 lines while in n-heptane solution 80 lines are visible. The fluorescence spectrum in n-hexane is also more diffuse when compared with that in n-heptane. In n-pentane solutions the spectra are distinctly diffuse and partially loss the quasilinear character (Fig. 2, a). The change from n-heptane to n-alkane of longer chain makes also the structure of spectra less distinct. The spectra in n-octane maintain in prin ciple the quasilinear character (Fig. 2, b) but in n-nonane in place of previously strong lines narrow bands appear which in higher n-alkanes become still wider (Fig. 2, c). In cyclohexane the vibrational band structure practically disappears.
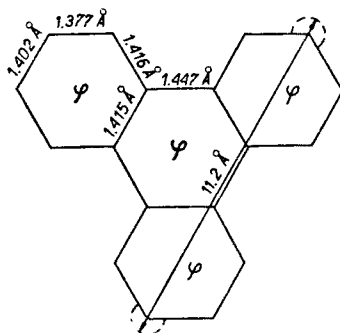

Fig. 1. Dimensions of triphenylene molecule. The mean lengths of bonds are given according to [21]

From the spectral examination of other hydrocarbons, when using the described method, it is known that quasilinear structure of spectra is above all influenced by the size ratio of the solute and solvent molecules [16]. As exemplified by several linearly condensed poly-acenes it has been found that the most distinct structure of spectrum is observed when the length of n-alkane molecule is possibly close to that of long axis of dissolved polyacene [20]. The above fact was explained by a simple model, based on various possible modes of incorpora-ting the dissolved molecules in the crystalline lattice of solvent [16].

In the case of triphenylene the effective length of the longest molecule axis is equal to about 11.2 Å (cp. Fig. 1). This value was calculated on the basis of the most recent X-ray data [21] and van der Waals radii of outer hydrogen atoms ($r_w = 1.0$ Å in aromatic com-pounds [22]).

The length of the molecule chain of n-heptane, calculated on the basis of Kitaigorodski data [23] and van der Waals radii of outer $-CH_3$ groups ($r_w = 2.0$ Å [23], [24]), is equal
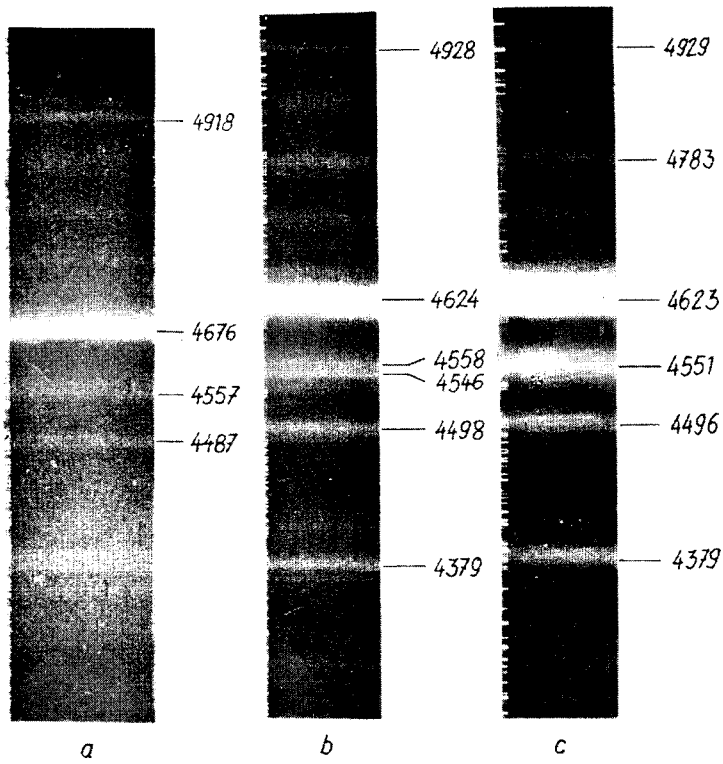
Fig. 2. a) Slow fluorescence spectrum of triphenylene in *n*-pentane at liquid air temperature, b) Slow fluorescence spectrum of triphenylene in *n*-octane at 77°K. c) Slow fluorescence spectrum of tripherylene in *n*-decane at 77°K (The numbers denote the wavelengths in Å units)
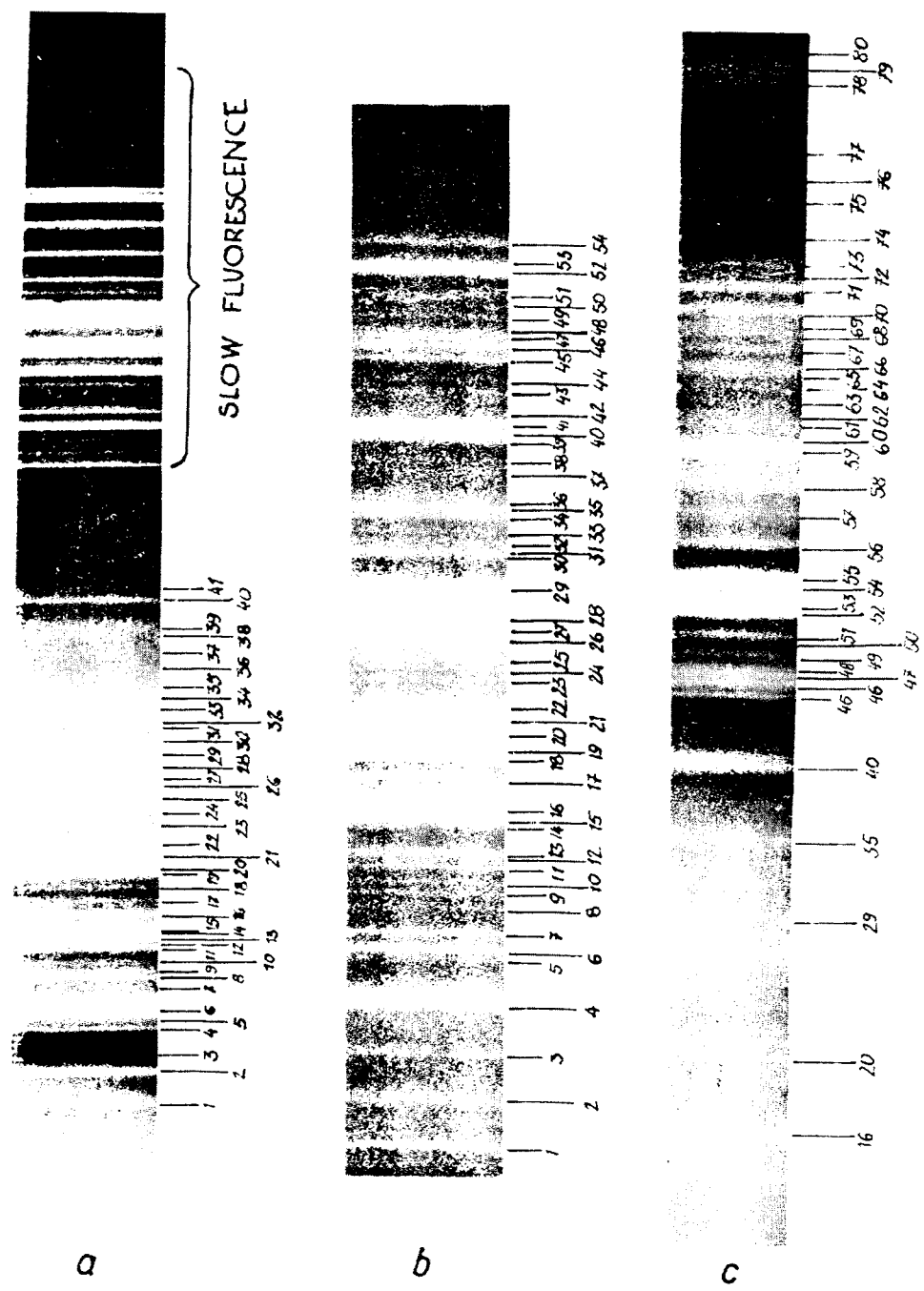
Fig. 3. a) Fluorescence spectrum of triphenylene in n-heptane at 77°K. (Numeration of quasilines according to Table II). b) Slow fluorescence spectrum of triphenylene in n-heptane at 77°K. Concentration 1×10^{-4} moles per liter. (Numeration of qualisines according to Table IV). c) Slow fluorescence spectrum of triphenylene in n-heptane at 77°K. Concentration 1×10^{-3} moles per liter. (Numeration of quasilines according to Table IV)

to about 11.6 Å[7]. On passing to the neighbouring n-alkanes (n-hexane or n-octane) the above value becomes smaller or larger by about 1.27 Å. Hence, it is evident that triphenylene gives the spectrum of the most distinct structure when the length of n-alkane molecule approaches the size of the longest axis of triphenylene. The above data indicate that also in our case the quasilinear spectrum results from a definite mode of incorporating the dissolved molecules in the solvent lattice, what in the case of the structure shown by triphenylene molecule is not so evident. From among the hypotheses put forward as yet, most probable seems to be that based on formation of some clathrate-like compounds [16] or grain boundary solutions in which the dissoved molecules are oriented in a definite way in respect to the limiting surfaces of microcrystalline blocks of the solvent [25], [26].

Most frequently the quasilinear spectra of given substance arise from the superposition of few spectra, differing somewhat between each other by 0—0 transition frequency. As result, to each vibronic transition few quasilines should be ascribed slightly differing in position and constituting so called "multiplet" [16]. According to the hypothesis put forward by Bowen and Brocklehurst [17] and experimentally confirmed in the coronene spectra [27], there should be accepted that the individual spectra shifted towards each other, arise from molecules differently situated in the solvent lattice and influenced by the crystalline fields showing some local deviations. In various n-alkanes the number of overlapping spectra, and hence the number of lines giving the "multiplet", is in general various for the same solute [16].

In the examined triphenylene spectra the multiplets do not appear in any of the solvent in which quasilinear character of spectrum is maintained. In this connection the rate with which frozen solutions are formed does not exert any influence on the structure of spectra (cp. [16]). In view of the last hypothesis this rather exceptional behaviour of triphenylene should indicate that the molecules of this hydrocarbon are incorporated in crystalline lattice of some n-alkanes in one way only.

b) Solvent shift of spectra

In spite of similar properties of various n-alkanes the examined emission spectra are slightly displaced in dependence on the solvent used. These changes are rather small and can be ascertained without any ambiguity only then when the structure of spectrum enables to determine with a reasonable accuracy the positions of quasilines corresponding to individual vibronic transitions. In Table I (second and third column) the mean shift of fluorescence and slow fluorescence spectra is given with reference to corresponding spectra in n-heptane.

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[7] The value calculated now (like the corresponding values for other n-alkanes) differs somewhat from that given by Shpolskii and coworkers (e. g. [16], [20]). Above authors have accepted as the chain length of n-alkane the values of the largest distances between (001) planes in crystal of given compound [23], [24]. However, n-alkanes from $C_5 H_{12}$ to $C_{10}H_{22}$ probably appear in a crystalline modification B in which the axes of chanis are not perpendicular to (001) plane and therefore the chain length is larger than the distance between appropriate planes [24]. Therefore the calculation mode accepted now seems to be more reasonable.

TABLE I

Solvent Shift of Spectra

(standard deviations given in paranthesis)

| Solvent | Mean value of $\varDelta\tilde{\nu}$ (cm^{-1}) | | $\tilde{\nu}$ of 0—0 transition (cm^{-1}) | |
	Fluorescence	Slow fluorescence	Fluorescence	Slow fluorescence
n-Pentane	—	+16 (8)	—	—
n-Hexane	+22 (2)	+6 (2)	29161	23270
n-Heptane	0	0	29137	23261
n-Octane	−16 (3)	−24 (2)	29118	—
n-Nonane	—	−22 (2)	—	—

In the fourth and fifth column of that the wave numbers of 0—0 transitions are given for those solvents in which the above values could be determined[8].

The described spectrum change undoubtedly represents typical polarization shifts connected with mutual dispersion interaction between non-polar molecules of solute and solvent. The theory of such a shift with reference to the absorption spectra was developed by Bayliss [28], Weigang [29] and other authors. The effects observed now are in agreement with this theory when the direction of observed changes is concerned (red shift with increasing chain length of n-alkane). Moreover, the values of the shift are similar to those measured in absorption spectra of some polycyclic hydrocarbons dissolved in n-alkanes [29]. A quantitative comparison of obtained results with relations given in cited papers is as yet not possible because of the lack of indispensable data concerning solid solvents at 77°K.

c) Fluorescence spectrum in n-heptane

The fluorescence spectrum of triphenylene in n-heptane at 77°K is shown in Fig. 3a. The numeration of quasilines corresponds to the consecutive numbers in Table II presenting the results of vibrational analysis of spectrum.

The spectrum begins with a comparatively weak line 29137 cm^{-1} (3431 Å) which according to absorption measurements constitutes a 0—0 line. Towards longer wavelengths the fluorescence extends up to the begin of visible spectrum. Above 4079 Å (last wavelength in Table II) there are still visible few extremely weak and highly diffuse lines belonging to fluorescence spectrum, which are not listed in the Table as sufficiently accurate estimation of their wavelengths was not possible.

In the fluorescence spectrum fourteen fundamental vibrations of molecule in the

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[8] Quasilines corresponding to 0—0 transitions in triphenylene spectrum are weak and not too sharp — see below.

ground electronic state were identified[9]. The remaining quasilines can be presented as the combinations of these fundamentals, whereby in the largest number of combinations only one or few quanta 1341 cm^{-1} participate (cp. Table II).

The intensity of obtained quasilines changes in a wide range because of various intensity of individual vibrations and their combinations. There have been not observed, however, in the fluorescence spectrum in n-heptane or n-hexane any additional broad and strong bands ascribed by other authors to $T^* \to T$ emission [18].

The comparison of vibration frequencies obtained from the analysis of quasilinear luminescence spectra with frequencies observed in Raman and IR spectra of the same substances, often makes possible the symmetry determination of vibrations participating in vibronic transitions (cp. [16]). The Raman spectrum of triphenylene have been not examined as yet. There are only known some not complete IR spectra of triphenylene solutions [30] and of crystalline powder of this compound in KBr wafer [31].

The molecule of triphenylene is usually reckoned in D_{3h} symmetry (cp. Fig. 1). There are known, however, some data suggesting that the molecule of this compound is not ideally planar because of some steric hindrances [11], [21], but the deviation from planarity is rather very small [21], [32]. It can be therefore assumed that the selection rules for electronic and vibronic transitions, to be obeyed in molecules belonging to D_{3h} point group, are not essentially changed.

TABLE II

Fluorescence spectrum of triphenylene in n-heptane at 77.3°K

No	λ (Å)	$\tilde{\nu}$(cm^{-1})	Intensity	$\Delta\tilde{\nu}$ ($\tilde{\nu}_{00} - \tilde{\nu}$)	Possible assignment	$\Delta\tilde{\nu}_{calc.} - \Delta\tilde{\nu}_{obs.}$	Remarks
1	3431.$_1$	29137	m—w	—	0—0	—	dif.
2	3461.$_6$	28880	s	257	0—257	—	
3	3480.$_7$	28722	vw	415	0—415	—	
4	3505.$_2$	28521	m—s	616	0—616	—	
5	3513.$_7$	28452	vw	685	0—685	—	
6	3524.$_2$	28367	vvs	770	0—770	—	
7	3547.$_7$	28180	vw	957	0—257—685	−15	
8	3559.$_4$	28085	m	1052	0—1052	—	
9	3566.$_2$	28033	w	1104	0—1104	—	The combination 0—415——685 cannot be excluded
					or 0—415—685	−4	
10	3576.$_7$	27950	w	1187	0—415—770	−2	

[9] Assignment of 1104 cm^{-1} frequency is uncertain — cp. Table II.

TABLE II (continued)

No	ν(Å)	$\tilde{\nu}$(cm^{-1})	Intensity	$\Delta\tilde{\nu}$ ($\tilde{\nu}_{00}-\tilde{\nu}$)	Possible assignment	$\Delta\tilde{\nu}_{\text{calc.}}-\Delta\tilde{\nu}_{\text{obs.}}$	Remarks
11	3591.$_3$	27838	m—s	1299	0—1299	—	
12	3596.$_6$	27796	vw	1341	0—1341	—	
13	3602.$_9$	27747	vw	1390	0—1390	—	
14	3608.$_0$	27709	m—s	1428	0—1428	—	
15	3613.$_4$	27667	m—w	1470	0—1470	—	
16	3631.$_2$	27532	m	1605	0—1605	—	
17	3646.$_2$	27418	m—w	1719	0—415—1299	−5	
18	3662.$_0$	27300	m—w	1837	0—415—1428	+6	
19	3677.$_4$	27185	m	1952	0—616—1341	+5	
20	3683.$_9$	27137	m	2000	0—616—1390	+6	
21	3699.$_7$	27021	vs	2116	0—770—1341	−5	
22	3715.$_6$	26906	s	2231	0—616—1605	−10	
					or 0—770—1470	+9	
23	3739.$_0$	26738	vvw	2399	0—1052—1341	−6	
24	3755.$_3$	26621	w	2516	0—415—770—1341	+10	
					or 0—1052—1470	+6	
25	3774.$_2$	26489	m—w	2648	0—1299—1341	−8	
					0—1052—1605	+9	dif.
26	3791.$_1$	26370	w	2767	0—1428—1341	+2	
27	3797.$_1$	26329	m	2808	0—1470—1341	+3	
28	3816.$_5$	26194	w	2943	0—1605—1341	+3	
29	3834.$_8$	26070	m	3067	0—3067	—	dif.
30	3851.$_1$	25960	w	3177	0—415—1428—1341	+7	
31	3869.$_2$	25838	w	3299	0—616—2×1341	−1	
32	3876.$_4$	25790	w	3347	0—616—1390—1341	0	
33	3892.$_7$	25682	m	3455	0—770—2×1341	−3	
34	3910.$_7$	25564	m	3573	0—616—1605—1341	−11	
					or 0—770—1470—1341	+8	see No 22
35	3928.$_8$	25445	w	3692	0—616—3067	−9	
36	3956.$_7$	25267	vvw	3870	0—415—770—2×1341	−3	
					or 0—1052—1470—1341	−7	see No 24
37	3977.$_9$	25132	vw	4005	0—1052—1605—1341	−7	dif.
38	4003.$_5$	24971	w	4166	0—1470—2×1341	−14	
					0—1104—3067	−5	dif.
39	4015.$_1$	24899	w—m	4238	0—1299—1341—1605(?)	+7	dif.
40	4058.$_8$	24631	m	4506	0—1428—3067	−11	
41	4079.$_3$	24508	w	4629	0—616—3×1341	+10	

Intensities: w — weak, m — medium, s — strong.

The lowest excited singlet electronic state of triphenylene molecule (^1L_b) has the symmetry A_2' [9]. From the character table of the point group D_{3h} (Table III, cp. e.g [33]) one can see, by calculating appropriate direct products, that electronic transition $A_2' \rightarrow A_1'$

is forbidden, except of superposition of vibrations of the type e' or a''_1 ($A'_2 \times e' = E'$ and $A'_2 \times a''_1 = A''_2$). In the IR spectrum of triphenylene the vibrations e' and a''_2 should be active. It is now evident that frequencies appearing simultaneously in fluorescence and

TABLE III

The D_{3h} Character Table

D_{3h}	E	$2C_3(z)$	$3C_2$	σ_h	$3\sigma_v$	$2S_3$	
A'_1	1	1	1	1	1	1	
A''_1	1	1	1	−1	−1	−1	
A'_2	1	1	−1	1	−1	1	R_z
A''_2	1	1	−1	−1	1	−1	T_z
E'	2	−1	0	2	0	−1	T_x, T_y
E''	2	−1	0	−2	0	1	R_x, R_y

IR spectra should be represented by vibrations of e' type. For low frequencies such a comparison is not possible as the IR spectra were not examined in the range below 650 cm^{-1} [30], [31]. In the examined IR range one can find the analogues of the following fundamental vibrations appearing in fluorescence spectrum: 770, 1052, (1104), 1299, 1428, 1605 and 3067 cm^{-1}. Some of these frequencies (1052, 1605 and 3067 cm^{-1}) are close to frequencies encountered in benzene spectra and representing there (for QD_{6h} point group) the vibrations of e_{1u} or e_{2g} type, corresponding to e' vibrations in the point group D_{3h} [33]. Analogically, one can assume that vibration of frequency 616 cm^{-1}, lying close to 606 (e_{2g}) vibration of C_6H_6 molecule, is also of e' type.

Strong vibration of frequency 257 cm^{-1} could belong to e' or a''_1 type, however, the former type is more probable as for a''_1 type the vibronic transition should be polarized perpendicularly to the molecule plane (cp. Table III). Examination of polarized fluorescence of triphenylene in frozen glasses [8], [13] does not show in this spectrum the existence of any strong components of polarization direction given above. It is more probable that 1470 cm^{-1} vibration of medium intensity can be of a''_1 type as one may ascertain that such a frequency is absent in the IR spectrum of triphenylene[10].

The vibration of frequency 1341 cm^{-1} shows very low intensity but gives either single or multiple combinations with the majority of other vibrations. It behaves itself in the same way in the slow fluorescence spectra (see below). In the IR spectrum it does not appear at all. It should be concluded that the above vibration is totally symmetric (a'_1). The appearance of a totally symmetric vibration of frequency about 1350 cm^{-1} in the slow fluorescence spectrum of triphenylene in frozen n-hexane was already observed by Bowen and Brocklehurst [17]. Very weak vibration of frequency 1390 cm^{-1} could be also considered as a totally symmetric one but such an assignment would bear in this case a hypothetical character only.

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[10] It appears, however, in IR spectrum a vibration of frequency about 1500 cm^{-1} [30], [31].

The lines corresponding to 0—0 transition as well as to vibronic transitions in which totally symmetric vibrations participate only (like 0—1341), are weak, as according to the previous discussion such transitions are here virtually forbidden. The appearance of these lines proves that in examined solutions the selection rules are to some extent not obeyed by triphenylene molecule, what may arise from the action of solvent or of crystalline field in frozen solution upon the dissolved molecules, or from thre mentioned earlier small deviation of triphenylene molecule shape from D_{3h} symmetry. A similar, partial relaxation of selection rules was observed in e.g. luminescence spectra of crystalline coronene [34] and benzene [35] solutions.

d) Slow fluorescence spectrum

Slow fluorescence spectrum of triphenylene in n-heptane at 77°K is shown in Fig. 3b and 3c. The results of vibrational analysis are presented in Table IV in which the numeration of lines corresponds to the numeration in enclosed reproductions.

The spectrum begins with transition $\tilde{\nu} = 23261$ cm^{-1} (4298 Å), and extends towards longer wavelengths up to the yellow part of visible spectrum. The intensity of the long-wavelength part of spectrum, above ~4950 Å, is considerably lower then that at the short wavelength side. When using the solutions of about 1×10^{-4} moles per liter, only few and mainly very weak quasilines were observed at the long wavelength side of spectrum (Fig. 3b). By increasing the concentration up to about 1×10^{-3} moles per liter a marked growth of intensity in the whole spectrum is observed facilitating the measurements in the long wavelength range, but obscuring those in the short wavelength range as simultaneously some broadening and related difussion of intensive quasilines takes place (Fig. 3c).

In the slow fluorescence spectrum twenty fundamental frequencies of triphenylene molecule in the ground state were identified[11]. The remaining quasilines represent double or tripple combinations of these frequencies whereby the latter are mainly observed in the long wavelength range of spectrum. Many combinations arise from the participation of 1344 cm^{-1} vibration the frequency of which is in perfect agreement, within the measurement accuracy, with the frequency 1341 cm^{-1} of the totally symmetric vibration identified in fluorescence spectrum.

For some of the vibronic transitions few possible assignments are given. The quasilines corresponding to such transitions are frequently somewhat diffuse (see Table IV). It seems to be possible that at lower temperatures (20 or 4°K) each of these lines will separate into few lying close to each other lines as it has been observed e.g. in quasilinear spectra of pyrene [36].

From among fundamental vibrations appearing in the slow fluorescence spectrum twelve have the same frequencies, within the experimental error, as the vibrations observed in the fluorescence spectrum (cp. Table V). The differences in the vibrational structure of both spectra seem to result, at least partially, from selection rules controlling the $T \rightarrow S$ transition resposible for the slow fluorescence.

In general the $T \rightarrow S$ transitions are possible due to the spin-orbit coupling between the

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[11] Assignment of 1106 frequency is uncertain — cp. Table IV.

TABLE IV

Slow fluorescence spectrum of triphenylene in n-heptane at 77.3°K

No	λ (Å)	$\tilde{\nu}$ (cm^{-1})	Intensity	$\Delta\tilde{\nu}$ ($\tilde{\nu}_{00}-\tilde{\nu}$)	Possible assignment	$\Delta\tilde{\nu}_{\text{calc.}} - \Delta\tilde{\nu}_{\text{obs.}}$	Remarks
1	$4297._8$	23261	m—w	—	0—0	—	
2	$4322._9$	23126	m—w	135	0—135	—	dif.
3	$4346._8$	22999	m—w	262	0—262	—	
4	$4374._3$	22855	s	406	0—406	—	
5	$4400._2$	22720	vw	541	0—135—406	0	
6	$4405._6$	22692	m—s	569	0—569	—	
7	$4415._6$	22641	m	620	0—620	—	
8	$4430._3$	22566	w	695	0—695	—	
9	$4439._6$	22518	w	743	0—743	—	
10	$4445._4$	22489	w	772	0—772	—	
11	$4455._4$	22439	w	822	0—2×406	+10	
12	$4460._9$	22411	vw	850	0—850 (?)	—	dif.
13	$4464._5$	22293	m	868	0—868	—	
14	$4480._1$	22315	vw	946	0—262—695	+11	
15	$4485._3$	22289	m	972	0—406—569	+3	
16	$4492._0$	22255	s	1006	0—1006	—	
17	$4512._4$	22155	m—w	1106	0—1106	—	
					or 0—406—695	−5	cp. Table II
18	$4525._0$	22093	m—s	1168	0—406—772	+10	
19	$4531._6$	22061	vw	1200	0—569—620	−11	
20	$4541._3$	22014	s	1247	0—1247	—	
21	$4552._4$	21960	s	1301	0—1301	—	
22	$4561._3$	21917	w	1344	0—1344	—	
23	$4580._3$	21826	w	1435	0—1435	—	
					0—135—1301	+1	dif.
					0—569—868	+2	
24	$4587._1$	21794	w	1467	0—1467	—	
25	$4594._2$	21760	m	1501	0—406—1106	+11	
					or 0—262—1247	+8	
26	$4612._0$	21676	s	1585	0—1585	—	
27	$4616._7$	21654	vs	1607	0—1607	—	
28	$4619._8$	21639	vs	1622	0—1622	—	
29	$4647._4$	21511	m—s	1750	0—406—1344	0	
30	$4672._5$	21396	m—w	1865	0—406—1467	+8	
31	$4677._5$	21373	vvw	1888	0—135—406—1344	−3	
					0—262—1622	−4	
32	$4682._7$	21349	vw	1912	0—569—1344	+1	
33	$4690._1$	21315	w	1946	0—695—1247	−4	
34	$4701._8$	21263	w—m	1998	0—743—1247	−8	
					0—695—1301	−2	
					0—406—1585	−7	
35	$4708._8$	21231	m—s	2030	0—406—1622	−2	
36	$4717._5$	21192	w	2069	0—772—1301	+4	
37	$4738._8$	21096	vw	2165	0—2×406—1344	−9	
					or 0—868—1301	+4	

TABLE IV (continued)

No	λ (Å)	$\tilde{\nu}$ (cm^{-1})	Intensity	$\Delta\tilde{\nu}$ $(\tilde{\nu}_{00}-\tilde{\nu})$	Possible assignment	$\Delta\tilde{\nu}_{calc.} - \Delta\tilde{\nu}_{obs.}$	Remarks
38	4747.$_6$	21057	vw	2204	0—868—1344	+8	
					0—620—1585	+1	
39	4765.$_2$	20979	vw	2282	0—406—772—1106	+2	
					or 0—262—406—1622	+8	
40	4772.$_0$	20950	m—s	2311	0—1006—1301	−4	
41	4780.$_0$	20914	m	2347	0—1006—1344	+3	
					0—743—1607	+3	
42	4791.$_3$	20865	vw	2396	0—772—1622	−2	
43	4807.$_4$	20796	w	2465	0—1006—1467	+8	
44	4817.$_7$	20751	w	2510	0—406—772—1344	+12	
45	4836.$_6$	20670	m	2591	0—1247—1344	0	
46	4848.$_6$	20618	m	2643	0—1301—1344	+2	
47	4858.$_3$	20577	m	2684	0—1247—1435	−2	
					0—1106—1585	+7	dif.
48	4863.$_6$	20555	w—m	2706	0—1247—1467	+8	
					0—1106—1607	+7	
49	4875.$_6$	20504	w	2757	0—1301—1467	+11	
50	4888.$_5$	20450	vw	2811	0—1467—1344	0	
51	4895.$_9$	20419	m	2842	0—1247—1585	−10	
52	4920.$_3$	20318	s	2943	0—1607—1344	+8	
53	4925.$_0$	20299	s	2962	0—1622—1344	+4	
54	4948.$_8$	20201	s	3060	0—3060	—	
55	4955.$_5$	20174	m	3085	0—406—2×1344	+9	
56	4989.$_9$	20035	w—m	3226	0—406—1467—1344	−9	
57	5024.$_9$	19895	w	3366	0—406—1622—1344	+6	dif.
58	5055.$_7$	19774	w	3487	0—406—1467—1622	+8	dif.
59	5095.$_1$	19621	m	3640	0—1006—1301—1344	+11	broad, dif.
					0—569—3060	−11	
60	5108.$_2$	19571	vw	3690	0—1006—2×1344	−4	
					0—743—1607—1344	−4	
61	5125.$_2$	19507	vw	3754	0—695—3060	+1	dif.
62	5139.$_2$	19452	vw	3809	0—743—3060	−6	dif.
					0—1006—1467—1344	+8	
63	5153.$_3$	19400	w	3861	0—406—772—2×1344	+5	dif.
64	5171.$_6$	19331	w	3930	0—1247—2×1344	+5	dif.
					0—868—3060	−2	
65	5185.$_1$	19281	w	3980	0—1301—2×1344	+9	
66	5194.$_6$	19245	w	4016	0—1247—1435—1344	+10	
67	5216.$_9$	19163	w	4098	0—1301—1467—1344	+14	
68	5238.$_3$	19085	w	4176	0—1247—1585—1344	0	dif.
69	5251.$_7$	19036	w	4225	0—406—1006—1344——1467 (?)	−2	dif.
70	5269.$_0$	18974	m—s	4287	0—1607—2×1344	+8	
71	5299.$_8$	18867	m—s	4394	0—3060—1344	+10	
72	5318.$_3$	18798	vw	4463	0—406—1247—1467——1344	+1	

TABLE IV (continued)

No	λ (Å)	$\tilde{\nu}$ (cm^{-1})	Intensity	$\dfrac{\Delta\tilde{\nu}}{(\tilde{\nu}_{00}-\tilde{\nu})}$	Possible assignment	$\Delta\tilde{\nu}_{calc.}-\Delta\tilde{\nu}_{obs.}$	Remarks
73	5332.$_2$	18749	w	4512	0—569—868—3060	−15	dif.
74	~5380.$_5$	~18580	w				very dif.
75	5425.$_2$	18427	m—w	4834	0—406—1467—1622——1344	+5	dif.
76	5462.$_6$	18301	vw	4960	0—569—3060—1344	+13	dif.
77	~5497.$_5$	~18185	vw				very dif.
78	5611.$_1$	17817	vw	5444	0—1301—1467—2×1344	+12	
79	5632.$_9$	17748	w	5513	0—1247—1585—2×1344	+7	dif.
80	5666.$_7$	17642	vw	5619	0—1607—3×1344	+20	

lowest triplet state T and some excited singlet state S' (cp.e.g. [37], [8])[12]. The components of the spin-orbit coupling operator belong to the same irreducible representations as rotations R_x, R_y, R_z. The coupling of T and S' states may take place under condition that the direct product of irreducible representations T, R_i and S' involves the totally symmetric representation (for triphenylene A_1') [8].

According to Ham and Ruedenberg [9], ^3L_a state of symmetry A_1' is the lowest triplet state of triphenylene molecule. As R_x and R_y belong to E'' representation while R_z to A_2' one (cp. Table III), it results from the above conditions that S' should possess the symmetry E'' or A_2' respectively. The transitions between E'' or A_2' states and singlet ground state A_1' are forbidden (cp. Table III) and therefore in realizing $T{\rightarrow}S$ transition it is necessary to consider the participation of non-totally symmetric vibrations, like e.g.in benzene (cp. [37]). As evident from the avove discussion, by considering the symmetry of these vibrations two possibilities should be taken into account:

1) $S' = E''$, then

a) coupling of a_1'' or a_2'' or e'' vibrations allows the transitions into the ground state polarized in the molecule plane, as T_x, T_y belong to representation E' — Table III — while $A_1'\times a_1''\times E'' = A_1'\times a_2''\times E'' = E'$ and $A_1'\times e''\times E'' = A_1'+A_2'+E'$.

b) coupling of vibrations e' allows the transitions polarized perpendicularly to the molecule plane as T_z belongs to representation A_2'', while $A_1'\times e'\times E'' = A_1''+A_2''+E''$.

2) $S' = A_2'$, then

a) coupling of vibrations e' allows the transition polarized in the molecule plane as $A_1'\times e'\times A_2' = E'$.

b) coupling of vibrations a_1'' allows the transitions polarized perpendicularly to the molecule plane as $A_1'\times a_1''\times A_2' = A_1''$.

The decision which of the above possibilities occurs requires above all the performance of polarization measurements for individual quasilines. Such investigations were not perfor-

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[12] Not only singlet states (π, π^*) but also (σ, π^*) ones should be here considered [8], [38], [39].

med as yet, as *n*-alkanes form during solidification a multicrystalline solid. However, it seems to be justified to draw some conclusions from the comparison of the quasilinear spectrum of slow fluorescence of triphenylene obtained now, with the band spectrum the polarization of which was examined by Dörr and Gropper [8]. The investigations of these authors have not permitted to ascertain without ambiguity the polarization of 0—0 band, but have shown that the polarization degree considerably varies within the spectrum and that the vibronic transitions corresponding to the strongest maxima of spectrum are polarized perpendicularly to the molecule plane. The localization of these maxima agrees very well with that of some most intensive quasilines of the spectrum obtained in the present work, showing differences below 50 cm^{-1}. For this reason it should be assumed that the lines corresponding to 0—406, 0—1247 and 0—1301, 0—1585, 0—1607 and 0—1622 as well as to 0—1607—1344 and 0—1622—1344 transitions (*cp.* Table IV) are polarized perpendicularly to the ring plane. Two of participating here vibrations (1301 and 1607 vm^{-1}) appear in fluorescence spectrum also (where the values of 1299 and 1605 cm^{-1} were found) and have been previously assigned to e' vibrations. The same symmetry type may be assigned to 1585 cm^{-1} vibration which has a distinct analogue of e_{2g} symmetry in the slow fluorescence spectrum of benzene [35]. The above comparison indicates that just vibronic transitions in which e' vibrations (and not a_1'') participate, are polarized perpendicularly to the molecule plane, and consequently the first coupling possibility discussed earlier should occur.

Accordingly, in the slow fluorescence spectrum other vibrations of the type a_1'', a_2'' and e'' should also appear. It is possible that a_1'' vibrations are represented by frequency 1467 cm^{-1} (1470 cm^{-1} in fluorescence spectrum — *cp.* part c)) while a_2'' vibrations are undoubtedly represented by 743 cm^{-1} frequency, which is known to be the strongest frequency in the IR spectrum of triphenylene [30], [31], and does not appear in fluorescence spectrum, where a_2'' vibrations should be forbidden. Additionally, in the slow fluorescence spectrum some other vibrations appear known from the fluorescence spectrum (partially discussed earlier — *cp.* Table IV and V) as well as some vibrations not observed in fluorescence spectrum and not discussed as yet (135, 569,868 cm^{-1}), the assignment of which is not possible at the present. It should be noted that low frequencies lying close to frequency 135 cm^{-1} found now, were often encountered in quasilinear spectra of other polycyclic hydrocarbons like coronene [40].

From the above considerations on the symmetry of vibrations which may participate in fluorescence and slow fluorescence spectrum, it results that the vibrations of e' type should appear in both spectra. According to the assignments proposed here some e' vibrations really appear in both the discussed spectra. There exist, however, some other e' vibrations which are observed either in the fluorescensce spectrum (1052 cm^{-1}) or in slow fluorescence spectrum (*e.g.* 1247 cm^{-1}) only. Similar phenomena are known in benzene spectra where both fluorescence transition ($^1B_{2u} \rightarrow A_{1g}$) and slow fluorescence transition ($^3B_{1u} \rightarrow A_{1g}$) become allowed, among others, as result of coupling of e_{2g} vibrations [37], [39]. From among four vibrations of this type, possible in benzene molecule, only two appear in the fluorescence spectrum (606 and 1178 cm^{-1}). In the slow fluorescence spectrum there have been observed: in frozen glasses — 1178 and 1585 cm^{-1} vibrations, and in crystalline solutions also 606 cm^{-1} vibration [35], [41]. In this manner not only the symmetry type

but also other properties of vibrations are most probably responsible for its activity in given electronic transition and in given medium. In triphenylene molecule consisting of 30 atoms the situation is by far more complicated than in benzene, wwhat is evident from this fact that in the former case the total number of doubly degenerated normal vibrations of e' type equals to 19 (*cp*. part f)).

e) Absorption spectrum

The absorption investigations undertaken in this work mainly aimed at identification 0—0 line of $^1L_b \rightleftharpoons ^1A$ transition. Like in fluorescence spectrum also in absorption spectrum the 0—0 line is weak and rather diffuse (Table II). The position of this corresponds, within the accuracy limits of measurements, to the first line of fluorescence spectrum. In the absorption spectrum of *n*-hexane solution the first line appears at 29161 cm^{-1} [13] (Table I). In the long wavelength part of the absorption system discussed, the quasilines have been identified corresponding to following frequencies (in cm^{-1}) of triphenylene molecule vibrations in ^1L_b state: 266 (medium-strong), 604 (medium), 754 (very strong), 932 (very weak), 1171 (weak), 1331 (medium) and 1419 (medium strong).

Additionally, in the absorption spectrum 4 narrow absorption bands were observed distinctly wider than quasilines. Their positions in *n*-hexane solutions are following: *I* — about 4326 Å (23110 cm^{-1}), II — about 4090 Å (24440 cm^{-1}), III — 3812 Å (26230 cm^{-1}), IV — 3618 Å (27630 cm^{-1}). Bands I and II are somewhat wider than III and IV. Similarly localized bands have been recently found in an analogical solution by Lochet and Nouchi [42]. The above bands should be assigned to the $T^* \leftarrow T$ absorption corresponding to absorption by molecules, which after excitation by the xenon lamp have reached a triplet state [18], [42]. In agreement with investigations of Porter and Windsor [43] one can assume that comparatively strong band I corresponds to the transition of an electron from the lowest triplet state into a higher one, while the weak band II results from transition into a higher vibrational level of the same excited triplet state. One can expect that the bands III and IV belong, also to one electronic transition, because the corresponding energy gap (1400 cm^{-1}) is similar to that observed for bands I and II.

f) Final remarks

In Table V the comparison is presented of fundamental vibration frequencies of triphenylene molecule determined from the analysis of fluorescence and slow fluorescence spectra. In addition to the data for solutions in *n*-heptane also those obtained for solutions in *n*-hexane are given, so far it was possible to take the frequency measurements with a satisfactory accuracy (*cp*. part a)). The differences between corresponding frequencies in fluorescence and slow fluorescence spectra as well as frequencies obtained in hexane and heptane solutions, lie within the limits of experimental error. The values resulting from analysis of *n*-hexane solution spectrum are mostly somewhat higher, but it seems to be questionable

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[13] In paper [18] the value of 29120 cm^{-1} was indirectly estimated by taking advantage of the mirror symmetry rule.

TABLE V

Fundamental vibration frequencies of the ground state active in the luminescence spectra of triphenylene molecule (cm^{-1})

(intensities given in paranthesis)*

From luminescence spectra in n-heptane		From luminescence spectra in n-hexane		Proposed assignment of symmetry type
Fluorescence	Slow fluorescence	Fluorescence	Slow fluorescence	
—	135(m—w)	—	140(w)	?
257(s)	262(m—w)	263(m)	270(w)	e'
415(vw)	406(s)		409(s)	e'
—	569(m—w)	—	572(m—s)	?
616(m—s)	620(m)	615(m—w)	624(w)	e' ?
685(vw)	695(w)		699(vw)	?
—	743(w)	—	745(vw)	a_2''
770(vvs)	772(w)	768(vvs)	777(vw)	e'
—	868(m)	—	870(m)	?
—	1006(s)	—	1008(s)	probably e'' or a_1''
1052(m)	—	1050(m)	—	e'
1104(w)**	1106(m—w)**		1110(m—w)**	e'
—	1247(s)	—	1251(s)	e'
1299(m—s)	1301(s)	1304(m)	1302(s)	e'
1341(vw)	1344(w)	1348 ?	1343(vw)	a_1'
1390(vw)	—		—	a_1' ?
1428(m—s)	1435(w)		1436(vw)	e'
1470(m—w)	1467(w)		1475(w)	a_1'' ?(or e')
—	1585(s)	—	1586(s)	e'
1605(m)	1607(vs)	1606(m)	1610(vs)	e'
—	1622(vs)	—	1622(vs)	e'
3067(m)	3060(s)	3071(m)	3062(m)	e'

* The intensities are exactly comparable between each other for the same spectrum only given in one column.

** *cp.* tables II and IV.

whether one may hence assume a solvent effect played upon the vibration frequency, as it was done in the case of *e.g.* phtalocyanines [26].

Some of the encoutered frequencies correspond to characteristic vibrations well known in benzene and polycyclic aromatic hydrocarbons composed of condensed benzene rings. Here belong, first of all, the vibrations of aromatic carbon skeleton, comprised in vicinity of 1600 cm^{-1}, affecting normally the appearance of few strong bands [30], [44] and revealed, among others, in quasilinear spectrum of slow fluorescence of benzene [35]. The frequency about 3065 cm^{-1} is characteristic for stretching C—H vibrations in aromatic hydrocarbons. Further, for a hydrocarbon of triphenylene structure out-of-plane vibrations lying in the range of 735—770 cm^{-1} are characteristic [45].

The vibrations appearing in the examined emission spectra of triphenylene constitute a small part only of all vibrations possible for this molecule. As one can easily calculate [33] the number of fundamental vibrations of each type for triphenylene molecule is following: a_1' — 10, a_1'' — 5, a_2' — 9, a_2'' — 4, e' — 19, e'' — 9. Also in quasilinear spectra of other polycyclic aromatic hydrocarbons much lower number of frequencies has been normally observed than one could expect from theoretical considerations [46].

Energy scheme of the lowest electronic levels of triphenylene molecule based on examination of quasilinear luminescence spectra, is shown in Fig. 4.

The comparison of quasilinear spectra of slow fluorescence of triphenylene and 1:4-diazatriphenylene (dibenzoquinoxaline) of the molecule symmetry C_{2v}, presents san additional
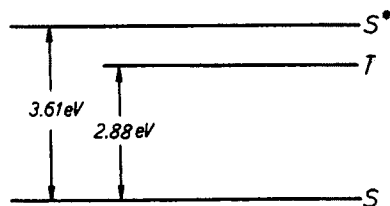
Fig. 4. Schematic presentation of the lowest electronic levels of triphenylene molecule

evidence speaking in favour of the concept that $T \rightarrow S$ transition in triphenylene bears a symmetry forbidden character, what has been earlier pointed out on the basis of band spectra of these compounds in EPA [8]. In recently obtained quasilinear spectrum of slow fluorescence of 1:4-diazatriphenylene it has been found that the intensity of 0—0 line (23055 cm^{-1} in frozen n-heptane) considerably exceeds that of all other lines [47].

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