Raman scattering in systems with pronounced vibronic interaction

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By precision measurements it has been established that the multitude, as a rule, of weak lines in Raman scattering (RS) spectra of transparent substances have a degree of depolarization ρ which exceeds the limiting value (3/4) characteristic for the symmetric form of the scattering tensor, and in the majority of cases depressed (<6) values of the reversal coefficients *P*. These data provide evidence that, contrary to widely held notions, the RS tensors can be asymmetric. An investigation of the frequency dependence of the intensity of the lines has shown the relation between this effect and the mixing of electronic states by certain not fully symmetric oscillations. In experiments involving sharply resonant excitation of RS in a different class of compounds it was found that the intensity of a number of spectral lines and the very fact of their discovery depend on the absorption band in which excitation is produced. Spectra of ρ are obtained in which all the lines can be sharply divided into polarized, depolarized, and reversely polarized lines. The values of the quantities *P* for the latter two types of lines are anomalously low. The totality of these data indicates an asymmetry of the RS tensors, which, as previously, can be associated with mixing of electronic states and also with orbital degeneracy of the upper electron level. Using one compound as an example, an investigation has been made of the effect on the spectrum of ρ of the dynamic Jahn–Teller effect in unexcited molecules and of the interference of the probability amplitudes for dipole transitions responsible for the scattering. A general conclusion is drawn that simultaneous measurement of both polarization characteristics and of the intensity of the RS lines is a universal method for the study of vibronic interactions in complex molecules.

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THE STATE OF THE SUBJECT, THE STATEMENT OF THE PROBLEM AND METHODS FOR ITS SOLUTION

The symmetric form[1] is usually ascribed to the Raman scattering (RS) tensor for vibrational transitions in the absence of resonance. But the qualitative analysis of the dispersion formula carried out by Ovander[2] in the adiabatic approximation for a diatomic molecule shows that in principle this need not be so. The physical reason for the asymmetry of the RS tensor taken into account in [2] consists of the dependence of the induced angular momenta on the nuclear coordinates, which manifests itself particularly sharply (already in the zero-order approximation) when the equilibrium distance between the nuclei changes but little in the case of electronic excitation. In agreement with the semiclassical theory of RS the intensity of spectral lines in this latter case is particularly small, and its dependence on the frequency of the exciting light is relatively weakly expressed.[1] For this reason (and also from considerations involving general principles) a resonant excitation of spectra is desirable in order to observe the asymmetry of the RS tensors.[2,3]

New possibilities for asymmetry appear in complex molecules. In contrast to diatomic molecules they undergo many vibrations among which there are vibrations of an incompletely symmetric type which are frequently able to mix electronic states.[4] In such cases partial mixing of electronic and vibrational wave functions occurs as a result of which a simple adiabatic approximation can turn out to be no longer sufficient. Resonant excitation of spectra facilitates also in this case the demonstration of the asymmetry of the corresponding tensors.[5]

A very complex picture occurs in the case of orbital degeneracy of electronic states and of the Jahn-Teller effect accompanying it in nonlinear molecules. Of particular interest with respect to the effect on the RS spectra is the dynamic Jahn-Teller effect in the ground (initial) state. In such a situation the electronic and the vibrational wave functions are completely mixed and this excludes the justification for the adiabatic approach to the problem of scattering. In such cases for definite point groups the RS tensor indeed becomes antisymmetric.[6]

The intramolecular interactions considered above affect in a significant manner the selection rules for the dipole transitions, and at the same time not only the form of the scattering tensor, but also the distribution of intensity in RS spectra and its frequency dependence. For example, the process of mixing of electronic states in accordance with the vibronic theory of RS[7] leads to the result that as the frequency of the exciting light is increased the lines must be particularly sharply intensified in the RS spectra of those vibrations of incompletely symmetric type which activate in dipole spectra the "forbidden" components of allowed transitions, i.e., which remove the restriction imposed on the dipole transitions by the first order selection rules.

In the RS spectra of polyatomic molecules the distribution of intensity and its frequency dependence also are determined to a large degree by the specific characteristics of the intermediate electronic-vibrational state, even if we do not take into account the effect of mixing.[8] In particular, it is important whether the symmetry of a molecule is altered as a result of its excitation. If the symmetry is altered (i.e., lowered) certain incompletely symmetric oscillations are selectively intensified in the RS spectrum and, in analogy with the fully symmetric ones, acquire the ability of shifting equilibrium positions of nuclei. Purely formally this means that the incompletely symmetric (in terms of the group of the ground state) vibrations under consideration become fully symmetric in the group of the excited state.[8] The dipole transitions also be-have similarly: only those of them are allowed to which common symmetry elements correspond.[4] In accordance with semiclassical notions[1] the frequency dependence of the intensity of the RS spectral lines is significantly affected by whether the equilibrium position of the nuclei is shifted or not. For this reason in order to determine definitely on the basis of the intensity of the lines whether the vibration participates in mixing one must be certain that the symmetries of the normal and the excited molecules are identical. As regards the form of the scattering tensor, the relationship between the configurations under discussion determine in which approximation – the zero order or the first order – its asymmetry will become apparent.

The object of the present investigation consists of an experimental study of the influence of electronic-vibrational interactions, and first of all of mixing of electronic states, on the nature of the RS spectra. This influence, as has been noted, affects the form of the scattering tensors. It can be inferred from measurements of the degree of depolarization ρ and of the coefficient P for the reversal of spectral lines. By decomposing the RS tensor into an isotropic, an anisotropic and an antisymmetric part, the following values[3] can be ascribed to these quantities:

$$\rho_{\text{isotr}}=P_{\text{isotr}}=0;\quad \rho_{\text{anisotr}}={}^3/_4,\ P_{\text{anisotr}}=6;\ \rho_{\text{antisymm}}=\infty,\quad P_{\text{antisymm}}=0.$$

From the relations stated above it follows that one can draw conclusions concerning the partial asymmetry of the RS tensor responsible for such oscillations which are simultaneously allowed both in the anisotropic and the antisymmetric types of scattering for values of ρ not going outside the usual limits (3/4) by comparing the values of ρ and P measured in parallel with the required degree of accuracy, with the quantitative criterion being provided by the fact that the formula $P = 2\rho_{\text{meas}}/(1 - \rho_{\text{meas}})$ is satisfied.[3] Values of $\rho > 3/4$ already themselves indicate the asymmetry of the tensor. Precision measurements of the values of P are not reported in the literature. Neither have simultaneous quantitative investigations of both polarization characteristics been undertaken. In order to obtain additional information on the processes occurring we have also carried out measurements of the frequency dependence of the intensity of the spectral lines.

As objects transparent over the utilized part of the spectrum we have selected ordinary and deuterated benzenes, simplest aromatic substitutions – toluene, isomeric xylenes, mestylene, and also chloroform and bromoform. The RS spectra of all these substances have been reliably interpreted. In the literature information is also available on the vibronic interaction for some of them. This creates favorable prospects for the solution of the problem that has been posed. It has turned out to be convenient to trace the resonance effects of excitation on the example of the metallocomplexes of phthallocyanin (M-PC) and of their anions. The absorption and luminescence spectra of at least the neutral molecules of tetrapyrrole compounds differ by a small Stokes shift, and, consequently, by an insignificant change in the equilibrium internuclear distances accompanying electronic excitation. On the other hand, for these molecules the upper state is definitely known to be degenerate, and they are characterized by mixing of a weak long-wavelength transition with a very intense Soret band. Moreover, they are fairly easily excited under resonance conditions.[9,10] The most suitable compound from among a number of M-PC under consideration turns out to be cobalt-phthallocyanin (Co-PC) and its monoanions. Monoanions of highly symmetric molecules are unique objects with a degenerate ground electronic state. We have studied one of their representatives – the monoanions of coronene.

The RS spectra were excited by radiations from lasers based on a He + Ne mixture, on ionized argon, on He + Cd$^+$, and on molecular nitrogen with wave lengths of 632.8, 488.0, 514.5, 441.6 and 337.1 nm. Spectral instruments "Koderg", DFS-24 and a laboratory setup assembled on the basis of an MDR-3 monochromator were employed. The technique for the measurement of the magnitudes of ρ is the usual one. The magnitudes of P were measured utilizing one of the variants of the method – using "forward" observation.[11] The exciting beam was restricted by a diaphragm at the center of the entrance slit of the spectral instrument. After instrumental adjustment the polarization arrangements were checked using the RS spectrum of CCl_4. For its lines of 459, 313 and 217 cm^{-1} we obtained values of ρ which agree well with those obtained in [12] using laser excitation. The values of P corresponding to them satisfy the relation $2\rho/(1 - \rho)$. The method of obtaining molecular anions was described in [13]. The intensities of the lines were measured with respect to an internal standard – the 786 cm^{-1} line of acetone introduced into solution, or with respect to the line of completely symmetric vibration of the substance itself. The contours of the lines were gone over with a planimeter.

SPECTRA OF TRANSPARENT SUBSTANCES

For a convenient overview a part of the experimental material has been collected into a table. It can be seen that a number of lines in the spectra of each of the substances exhibits increased ("anomalous") values of ρ. In the majority of cases they correspond to lower values of P (as against those expected for depolarized lines). In complete agreement with the predictions of theory[2] as a rule the weakest lines of the spectrum turn out to be anomalous. This gives direct indications of the asymmetry of the tensors responsible for the vibrations. We begin a more detailed analysis starting with the simplest molecules of this series – molecules of ordinary and deuterated benzene.

It is well known that one of the three vibrations of the symmetry type e_{2g} in molecules of ordinary benzene (606 cm^{-1}) actively mixes the electronic states B_{2u} and E_{1u}, and this is associated with the appearance in the absorption spectrum of the forbidden transition $A_{1g} - B_{2u}$.[4] It is particularly this one and two other vibrations of the same symmetry (1176 and 1585-1605 cm^{-1}) that exhibit anomalous polarization characteristics.1)

Since in the case of electronic excitation the benzene molecules are definitely known to retain their symmetry, then the degenerate vibrations under consideration cannot correspond to a shift of equilibrium positions of the nuclei. From the point of view of the semiclassical theory[1] under such circumstances the intensity of these vibrations as a function of the frequency of the exciting light can not vary more strongly than that of the fully symmetric vibrations. But this contradicts experimental data on the behavior of a pair of weak lines 1585-1605 cm^{-1}: their relative intensity in the case of exci-

RS spectra of benzene and its derivatives

Frequency and symmetry of vibrations	ρ_{meas}	P_{meas}	Relative intensity of lines	
			632.8 nm	337.1 nm
Benzene, symmetry of the molecule D_{6h}				
606 (e_{2g})	0.82±0,02	5,6±0,2	0,1	0.064
992 (a_{1g})	0.05	—	1	1
1176 (e_{2g})	0.83±0.02	5.6±0.2	0.1	0.064
1585—1605 (e_{2g})	0,83±0.03	6.2±0,3	0.106	0.254
Deuterobenzene, D_{6h}				
580 (e_{2g})	0.81	—	0,08	0.013
662 (e_{1g})	0.83	—	0,08	0.057
868 (e_{2g})	0.83	—	0.2	0,044
945 (a_{1g})	0.06	—	1	1
1554 (e_{2g})	0.82	—	0.12	0,1
Toluene C_{2v}				
216 (b_2)	0.77±0.02	—	0,244	0.18
344 (b_1)	0.78±0.02	—	—	—
623 (b_1)	0.80±0.02	3.5±1.0	0.073	0.055
785 (a_1)	0.03	—	0.445	0.35
1004—1030 (a_1)	0.04	—	1	1
1208 (a_1)	0.04	—	0.15	0.274
1380 (a_1)	0,18	—	0.064	0,107
1585—1604 (b_1, a_1)	0.82±0.03	5.5±0.4	0.142	0,254
Paraxylene, C_{2h}*				
310 (b_g)	0.78±0.02	—	0.45	0.74
643 (a_g)	0.79±0.03 **	5,7±0,3	0.28	0.24
810—826 (b_g, a_g)	0.05	—	1.90	3 9
1313 (a_g)	0,87±0.04 **	5.4±0,5	0.07	0,09
1578 (a_g)	0.83±0.03 **	4.0±0,5	0.49	2,45
1614 (a_g)	0.71±0.03	3.5±0.2		
Orthoxylene C_{2v}*				
505 b_1)	0.78±0.01	4,9±0.5	0,33	0.49
578 (a_1)	0.18	—	0.58	0.66
733 (a_1)	0.04	—	1.4	3.24
984 (a_2)	0.04	—	0.21	0.42
1051 (a_1)	0.04	—	0.76	2.59
1222 (a_1)	0.05	—	0,61	2,93
1447 (b_1)	0.91±0.03	3.50±0.25	—	—
1583 (a_1)	0.68±0.02	3.5±0.2	0.42	2,95
1608 (b_1)	0.84±0,02	5.8±0.2		
Metaxylene, C_{2v}				
206 (b_2)	0.79±0.02	—	1.01	1,02
227 (a_2)	0.78±0.02	—		
280 (a_1)	0.84±0.04**	—	0.27	0.14
517 (b_1)	0.78±0.02	—	—	—
998 (a_1)	0.04	—	1.4	3.43
1173 (b_1)	0.90±0.01	—	—	—
1251—1266 (a_1, b_1)	0.04	—	0.46	1,61
1443 (b_2)	0.78±0.03	—	—	—
1592 (a_1)	0.76±0.02 **	4.4±0,4	0.41	2,57
1601 (b_1)	0.82±0.02	4,8±0,3		
Mesitylene, C_{3h}				
226 (e'')	0.78±0.01	5.7±0.2	1.26	1.65
274 (e')	0.79±0.02	5.7±0.3	0.45	0.62
514 (e')	0.80±0.02	6.0±0.1	—	—
574 (a_1)	0.05	—	1.72	1.65
882 (e'')	0.85±0,05	3.8±0.4	—	—
996 (a_1)	0.04	—	1,39	2,84
1038 (e'')		—	0.156	1.17
1164 (e')	0.82±0.02	5.6±0.3	—	—
1300 (a_1)	0.04	—	0.364	1.7
1422 (e')	0.83±0.03	—	—	—
1445 (e'')	0.78±0.02	—	—	—
1606 (e')	0.84±0.01	5.7±0.3	0.28	0.69

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*For these substances the measurement of the intensity was carried out in mixtures with acetone (1 : 1). The internal standard was the RS line for acetone of 786 cm^{-1}.

**The apparent inconsistency between the values of ρ and symmetry of vibrations is, possibly, associated with the high degree of their susceptibility to deformation.

tation of the RS spectra by radiation of 337.1 nm increases by a factor of approximately 2.5 (table).2)

One of the reasons for the observed phenomenon is probably related to the nature of the splitting of the vibration into two components. In the literature it is presumed that it is due to the Fermi resonance between vibrations of 992 + 606 cm^{-1} and ~ 1600 cm^{-1} (e_{2g}). Then the intensity of the components must depend on the frequency of the exciting light much more sharply than the lines of the fundamental vibration.[1] This enables us to explain, at any rate qualitatively, the characteristic behavior of lines of frequency of ~ 1600 cm^{-1}. A similar behavior is also exhibited by the lines of 760 – 790 cm^{-1} in the RS spectrum of CCl_4 which owe their origin to the Fermi resonance in accordance with the scheme 775 ~ 313 + 459.[15]

In order to verify the correctness of the considerations stated above we have investigated the RS spectrum of deuterated benzene in which there is no accidental coincidence of frequencies leading to a Fermi resonance. The results of these measurements are included in the table. One can note in particular that the intensity of the now single line of the degenerate vibration of frequency of ~ 1550 cm^{-1} varies as a function of the frequency of the exciting light in approximately the same manner as the line of a fully symmetric vibration at 945 cm^{-1}, i.e., noticeably more slowly than the intensity of the components of the splitting according to Fermi for an analogous vibration in molecules of ordinary benzene. Consequently, the assumption made above now finds its direct confirmation.

But the very fact itself of the same growth in intensity of the degenerate and the fully symmetric vibrations with the symmetry of the excited molecules being retained requires to be explained. The idea suggests itself of ascribing this effect to vibronic interaction. But the theory of Tang and Albrecht[7] is not directly applicable to the given case since this theory considers forbidden components in allowed electronic transitions, which are intensified as a result of borrowing energy from the more intense of the transitions undergoing mixing, while in benzenes the O-O transition to the B_{2u} state is forbidden by symmetry selection rules (D_{6h}). However, we do not exclude the possibility that a rigorous theoretical investigation of the case of a purely electronic transition forbidden by symmetry will lead to similar conclusions. Moreover, in the condensed phase of the substance the symmetry of the benzene molecules is undoubtedly distorted, as is indicated by the presence of the O-O band in the absorption spectrum of solid benzene,[4] and also by a relaxation of the alternative forbidden nature of transitions in vibrational spectra of liquid benzene.[1] Consequently, it is sensible to assume that for the condensed state of benzene the transition $B_{2u} \leftarrow A_{1g}$ is actually weakly allowed, as a result of which the vibronic theory of RS can be extended also to the given case in the form in which it was formulated in [7]. We also emphasize that the ability of the vibration of frequency of ~ 1600 cm^{-1} considered above (and also of the vibration of 1176 cm^{-1}) to mix electronic states does not manifest itself in spectra of electronic absorption or emission.[4] This means that a study of the polarization characteristics and of the intensity of RS lines can be a unique source of valuable information concerning this important physical phenomenon.

Turning to the derivatives of benzene we note first of all that they all have a lower symmetry than the benzene molecules themselves. Therefore transitions analogous to those considered above will no longer be strictly forbidden. In connection with this difficulties are removed in making the results of experiment agree with the vibronic theory of RS.[7]

The behavior of vibrations in the frequency region of ~ 1600 cm^{-1} again deserves a special discussion. In all the spectra of benzene derivatives with the exception of paraxylene conditions do not exist for the appearance of a Fermi resonance with a vibration of the quoted frequency. It is evident that the splitting of the corresponding line into two components in these cases is brought about by a lowering of the symmetry of the molecules. Nevertheless these lines are intensified when they are excited by ultraviolet radiation much more than the lines of fully symmetric vibrations of frequencies of ~1000 cm^{-1}. For example, in the case of orthoxylene the corresponding ratio amounts to 3.5. In our opinion this can be explained only within the framework of the vibronic theory of RS. The fact that the effect under consideration in benzene derivatives is sufficiently more pronounced than in benzene molecules is apparently due to the allowed nature of the O-O transition in benzene derivatives and to the shift of the edge of the long wavelength absorption to the visible region of the spectrum. Already in the case of toluene this shift compared to benzene amounts to the significant value of 900 cm^{-1}.[17]

Thus, an investigation of the methylated derivatives of benzene confirms the conclusion concerning the mixing of electronic states as a cause of the "anomalous" polarization characteristics and the frequency dependence of the intensity of lines in the region in the neighborhood of 1600 cm^{-1}. Apparently this phenomenon explains also the increased sensitivity of the vibrations referred to above to conjugation – a fact that is well known in the literature and utilized in structural molecular analysis.[18]

In electronic absorption spectra of some iodine and bromine substitutions of methane very weak bands were observed in the neighborhood of intense ones. According to theoretical considerations and on the basis of results obtained in the study of the effect on the spectra of solvents of different polarity the weak bands have been ascribed to $n - \sigma^*$-transitions.[19] In the paper by Kaya et al.[15] it was shown that some lines corresponding to incomplete symmetric vibrations in the RS spectra of molecules of this class differ by a considerably sharper frequency dependence of the intensity than the lines of fully symmetric vibrations. This was related to the mixing of $n - \sigma^*$- and $\sigma - \sigma^*$-transitions. A precision measurement of both polarization characteristics in the RS spectra of two representatives of such substances – chromoform and bromoform – became of interest.

These measurements have shown that some spectral lines are characterized by a distinct "anomaly" simultaneously of the magnitudes of ρ and P. This effect is particularly striking in the case of bromoform. For example, for its line of 1143 cm^{-1}(e) the degree of depolarization is $\rho = 0.80$, while $P = 5.1$. The accuracy of measurements is sufficiently good. A satisfactory correlation is observed between the behavior of polarization characteristics and the relative intensity of lines in the case of excitation of spectra by radiations of different frequencies. One should also note the existence of a lack of agreement between calculated and measured values of P for lines of frequency of ~3020 cm^{-1} for both substances: the latter are appreciably smaller (for example, in the case of chloroform we have: $P_{calc} = 0.50 \pm 0.01$, $P_{meas} = 0.42 \pm 0.01$). The totality of the facts enumerated above is capable of being interpreted from the point of view of the vibronic theory of RS and, in particular, shows that a certain contribution to the mixing of $n - \sigma^*$- and $\sigma - \sigma^*$-states can also be made by the fully symmetric valence vibrations of the C–H bonds.

THE RESONANT CASE. SYSTEMS WITH ORBITALLY NONDEGENERATE GROUND STATE

It was emphasized earlier that the study of the form of the RS tensor is fovored by resonance conditions of excitation of spectra. We illustrate this on the example of monoanions of Co-PC. Fig. 1 shows the general appearance of the spectrum of this compound. In brackets are shown values of the magnitudes of P. In carrying out actual measurements optimal conditions were chosen for each region of the spectrum (slit widths, amplification, time constant, rate of scanning of spectra and of motion of the paper chart strip of the potentiometer). This led to the improvement of resolution and to a reduction in the interference from background. When necessary the elementary contours were separated out from a complex band by the usual method.

The data obtained enable us to affirm the sharp division of all spectral lines into strongly polarized, depolarized and reversely polarized lines ($\rho > 3/4$). The lines of the second type (not to mention the last type) correspond to values of P smaller by approximately a factor of two compared to those calculated on the assumption that the RS tensors are symmetric. We have the same relations also in the case of the RS spectra of neutral molecules of Co-PC. This is evidence for the fact that the scattering tensors responsible for these lines, as well as for the lines with reversed polarization, are asymmetric. However, since not in a single case were lines observed with very strong reversal of $\rho(\rho \to \infty)$, one should assume that in the compounds that were studied no oscillations were excited of type a_{2g} which are active only in the antisymmetric type of

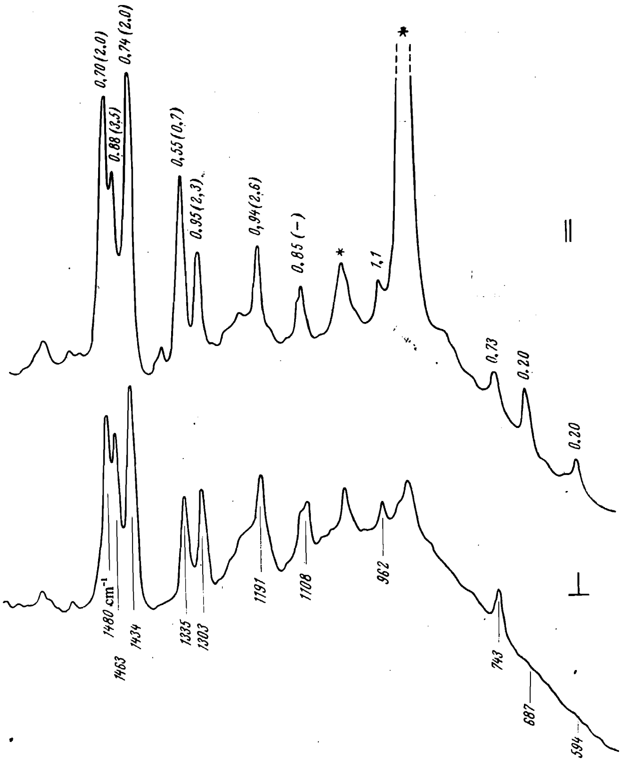

FIG. 1. The polarization spectrum of ρ of the Raman scattering of the monoanions of Co-PC. The numbers below the lower spectrum are the frequencies of the lines in cm^{-1}. Above are given the values of ρ and in brackets the values of P for the lines. $\lambda_{exc} = 632.8$ nm. The asterisk indicates lines characteristic of the solvent.

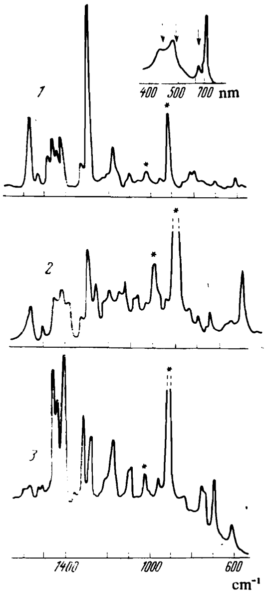

FIG. 2. Raman scattering spectra of monoanions of Co-PC excited in different absorption bands: 1—λ_{exc} = 441.6 nm, 2—λ_{exc} = 488.0 nm, 3—λ_{exc} = 632.8 nm. In the upper right hand corner are shown conditions of excitation.

scattering and which are forbidden in all the other types. We hope that such measurements in future, when a complete theory of the phenomenon will have been created, may turn out to be the point of departure in identifying vibrations and in determining the true molecular symmetry. Another characteristic feature has been established in the case of excitation of the polarization spectrum of the monoanions of Co-PC by radiation of wavelength of 441.6 nm. It has turned out that under these conditions the "anomalous" values of ρ are modified into values which do not fall outside the limits of the usual values. Analogous results have been obtained for related substances also in a number of other papers (cf., for example [20,21]). We shall return later to a discussion of the reasons for the appearance of strongly polarized lines.

Thus, it has been shown that a reversal of the magnitudes of ρ in individual cases can indeed be associated with a sharply resonant nature of excitation of spectra.

It was of considerable interest to intercompare RS spectra excited in different systems of electronic-vibrational absorption bands. We have succeeded to give the most complete solution of this problem in the case of the Co-PC monoanions. The spectra of their solutions recorded by us for three wavelengths of exciting light (441.6, 488.0 and 632.8 nm) are shown in Fig. 2. It can be seen that the intensity of a number of lines and the very fact of their appearance in the spectrum are determined by the region of the absorption spectrum into which the exciting radiation falls. In particular, the greatest sensitivity to these experimental conditions has been exhibited by the group of vibrations in the region of 1500–1433 and 1300–1335 cm^{-1} i.e., by just those vibrations the scattering tensors of which exhibit asymmetry.

Other results refer to a number of neutral molecules of PC, Co-PC, Fe-PC and Mg-PC. In this case we were able to excite their spectra by the same three radiations, but utilizing the crystalline state of the substance in samples prepared by the method of tablet formation with KBr. It turned out that under definite conditions lines were observed in the RS spectra of the compounds named above in the frequency region near 1610 cm^{-1} which correlated well with the bands of their infrared spectra. For example, in the case of Co-PC this corresponds to the excitation of RS by the first and by the second radiations.[9,10]

It is considered that the molecules of M-PC, as well as those of the metalloporphyrins related to them, have the symmetry D_{4h}. In the case of metals with filled shells (Mg, Be, Zn and others) the ground state of the molecules belongs to the symmetry type A_{1g}. From it transitions are allowed into the doubly degenerate state E_u. (For Co^{II}-PC and for its monoanions the symmetry of the electronic states is the same[22]).

The structured absorption band of greatest wavelength of neutral M-PC (similar to the one shown in Fig. 2) belongs to one of the transitions A_{1g}-E_u in which π-electrons take part (the π-π^*-transition). With respect to the band of M-PC of shortest wavelength in the region of 330 nm (not shown in the diagram) contradictory opinions have been expressed in the literature. The authors of the monograph[23] consider it to be an analog of the Soret band in porphyrins. Less definite still is the point of view concerning the nature and the origin of bands in the region of 400–500 nm observed in the spectra of the monoanions of Co-PC and Fe-PC, and also in the spectrum of neutral Fe-PC. In the opinion of some authors at least one of the bands in this region must be due to processes of charge transfer.[24-26]

There exist no direct data in the literature on the symmetry of the compounds under consideration in an excited electronic state. It is not very probable that it changes as a result of excitation. Under such conditions it is difficult to explain the high sensitivity of the incompletely symmetric vibrations to the frequency of exciting light outside the concepts of vibronic theory. However, an attempt to identify the interacting transitions encounters certain difficulties.

Vibrations characterized by the ability of mixing electronic states in the case of porphyrins belong to types b_{1g}, b_{2g}, a_{2g} and a_{1g}.[27] A condition for the vibrations to be active in mixing is the presence of a weak band and of a neighboring strong band of the same symmetry. This is realized in porphyrins in which the energy is borrowed from the Soret band. But in the spectra arising from transitions of M-PC the analogs of the Soret band have not been reliably established. However, it is clear that they are considerably weaker, and as a result of this mixing must also occur less effectively than in the case of porphyrins. The problem is further complicated if one takes into account other points of view concerning the nature of the bands in the region of 400–500 nm.

Thus, it is correct to assume rather that a careful study of RS using excitation over a broad range of frequencies of incident radiation, for example, with the aid of a continuously tunable laser, can give information concerning the nature of the dipole transition themselves, than that the latter can give information concerning manifestations of vibronic interaction in RS. But this must be preceded by the creation of a complete theory of RS of interacting electronic states.

The violation of alternative rules forbidding transitions for centrally symmetric molecules, such as molecules of M-PC, can in principle be associated with a distortion of their symmetry, i.e., with a deviation of the true symmetry from D_{4h}. But in the present case it can be also explained without assuming violation of symmetry from the point of view of vibron theory. The assumption that excited $\pi-\pi^*$ states are mixed can be immediately laid aside since the matrix elements determining this process vanish for the D_{4h} group.[28] But this is no longer so if one of the states being mixed belongs to types A_{1u}, A_{2u}, B_{1u}, B_{2u} or E_g. States due to $n-\pi^*$ transitions may be of such a nature. Therefore activation in the RS spectrum, excited by blue or green radiations, of vibrations that are intense in the infrared spectrum, i.e., the violation of the alternative rule forbidding transitions, can be associated with the fact that under these experimental conditions the radiations mentioned above resonate with some of the $n-\pi^*$ transitions of the pigment (forbidden because of symmetry, or polarized perpendicular to the plane). Effective mixing is here favored by the existence of closely situated levels for a $\pi-\pi^*$ transition (of the E_u type) which correspond to a long wavelength band and the analog of the Soret band. The possibility of the existence of $n-\pi^*$ states lying between the bands mentioned above is indicated by theoretical investigations and by some experimental data.[29,30] The likelihood of the interpretation proposed above is indirectly confirmed by the spectral manifestations of the capability for the mixing of $n-\sigma^*$ and $\sigma-\sigma^*$ states in halogen derivatives of methane.

We return to the problem of the polarization of lines in the RS spectra of metallic complexes of PC. The fact that a number of lines has a value of ρ unusually low for resonance conditions of excitation (0.17–0.24) can be easily explained taking into account the nature of the degeneracy of the upper state. With the aid of simple calculations it can be shown that in the absence of degeneracy ρ is equal to 0.33 for a fully symmetric vibration in the case of resonance, while in the case of double and triple degeneracy it is respectively equal to 0.125 and 0.[31] An intermediate value of ρ (between 0.33 and 0.125) can indicate a partial removal of degeneracy resulting from the effect of an intermolecular interaction (cf., [32]).

THE CASE OF RESONANCE. SYSTEM WITH ORBITALLY DEGENERATE UPPER AND LOWER STATES

We do not know of any neutral polyatomic molecules with a degenerate lower electronic state.3) However, general theoretical considerations show that monoanions of highly symmetric molecules (with rotational axes of third or higher orders) can have such a property. A portion of the results of an investigation of monoanions of coronen which is a representative of the given class of compounds and which moreover differs by degeneracy also of the first excited electronic state is shown in Fig. 3.

It can be seen that the RS spectrum of a solution of this substance in tetrahydrofuran (THF) excited by radiation of 488.0 nm contains both depolarized lines and also lines for which the values of ρ are contained within the limits 0.17–0.25. On addition to the solution of a small amount of dimethylformamide (DMFA) which has the ability of displacing from the solvation shell anti-cations of the metal[33,34] the value of ρ decreases appreciably for polarized lines, while one of the lines of the spectrum (of frequency of 1106 cm^{-1}) becomes reversely polarized ($\rho = 1.1 \pm 0.2$).

As is well known, the dispersion formula determining the matrix element of the polarizability tensor involves the amplitudes of the dipole transitions, and not their squares which are proportional to the probabilities of the transitions mentioned above. This circumstance is associated with the possibility for terms belonging to different intermediate states to interfere, i.e., to be amplified, weakened or mutually cancelled. In the case when the intermediate state is degenerate this interference of probability amplitudes becomes highly significant, since in the dispersion formula terms appear equal in absolute value.[3]

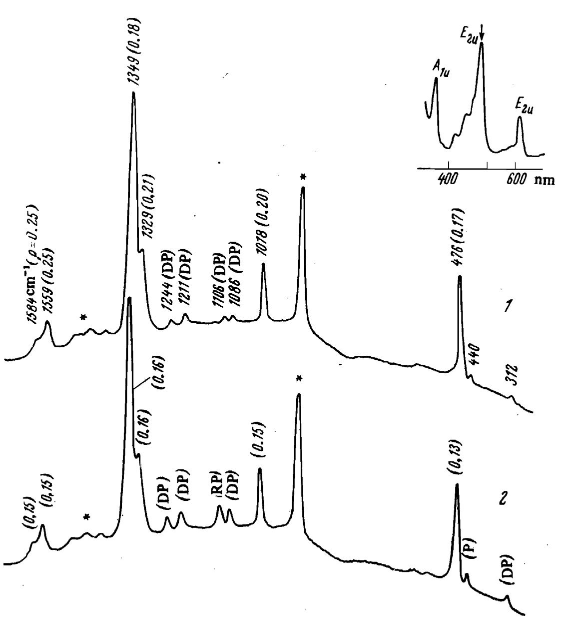

FIG. 3. Raman scattering spectra of monoanions of coronen: 1–solution in THF, 2–in THF + DFMA. At the peaks the frequency of the lines is indicated in cm^{-1}, and the values of ρ are given in brackets. (P-polarized, DP-depolarized, RP-reversely polarized lines). Asterisks indicate lines characteristic of the solvents. In the upper right hand corner are shown the symmetry of the electronic transition and the conditions of excitation of RS.

The degree of depolarization ρ of lines of resonant RS is very sensitive to interference. According to theoretical concepts external perturbations must have a particularly pronounced effect in this case. Their influence primarily amounts to the splitting of degenerate states as a result of which conditions for interference can be significantly changed. The significance of the latter circumstance near resonance is particularly great because even in the case of relatively small splitting of an initially degenerate intermediate state the changes in the denominators of the interfering terms become essentially different, and even a change in the sign of some of them becomes possible. Theory shows that for polarized lines this always leads to an increase in ρ.[3]

In the absence of anti-cations in the solvation shell of monoanions of coronen the external field in which they are situated is apparently isotropic. Corresponding to this exact degeneracy of electronic states occurs for stationary nuclei. The dynamic Jahn-Teller effect in the initial state for certain not completely symmetric vibrations can indeed lead under such conditions to a reversal of ρ,[6] and this is probably what is observed in the case of the 1106 cm^{-1} line.

It is natural to assume that the anisotropy of the

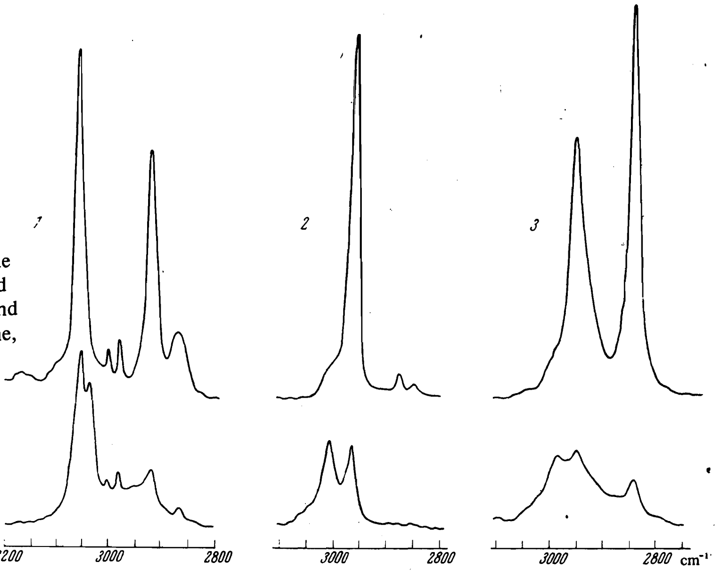

FIG. 4. Sections of the Raman scattering spectra in the region of the vibration frequencies of the C-H bonds. The upper spectra were excited without decomposition into polarized components, the lower correspond to the P components of the reverse direction of polarization. 1–toluene, 2–dichloroethane, 3–methyl alcohol.

field splitting the electronic levels of the initially degenerate ground and excited states is associated with the existence of antications in the solvation shell (solution in pure THF). As has already been noted, in accordance with theory this must lead to an increase in ρ for the polarized lines of the spectrum. On the other hand, under the conditions of the removal of degeneracy from the ground state the Jahn-Teller effect also ceases to be operative. These reasons then tentatively explain the changes described above in the RS spectrum of the monoanions of coronen situated in an isotropic external field.

Thus, the totality of the results obtained by us enables us to assert that simultaneous measurements of polarization characteristics and intensities of the RS lines give promise of turning into a powerful and universal method for the study of electronic-vibrational interactions in complex molecules, which to a significant degree complements the traditional methods of vibronic spectroscopy.

In conclusion we draw attention to the possible applications of the method of the decomposition of RS spectra into P components ("circular dichroism") to other problems. Often the resolution of a closely situated intense polarized and a weak depolarized line of RS encounters difficulties. In such cases success can be achieved by exciting the spectrum of the reversely polarized component. Three examples of such kind are illustrated in Fig. 4. The same situation exists also in the problem of the separation of lines of the purely rotational RS spectrum in gases from the very intense line of the exciting radiation. Finally, by measuring the magnitude of P one can as a result of recalculation obtain the value of the magnitudes of ρ. In a number of cases this enables one to achieve a significant increase in the accuracy of measurement.[3]

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[1] M. V. Vol'kenshteĭn, M. A. El'yashevich and B. I. Stepanov, Kolebaniya molekul (Molecular Oscillations) **2**, Gostekhizdat (1949).
[2] L. N. Ovander, Optika i spektroskopiya. II. Molekulyarnaya spektroskopiya (Optics and Spectroscopy. II. Molecular Spectroscopy) Publ. AN SSSR 1963, p. 139.
[3] G. Placzek, Rayleigh Scattering and Raman Effect (Russ. Transl. ONTIU, Kiev, 1935).
[4] G. Herzberg, Electronic Spectra and the Structure of Polyatomic Molecules (Russ. Transl., Mir, 1969).
[5] J. Koningstein, Optika i spektroscopiya (Optics and Spectroscopy) **35**, 260 (1973) [Opt. Spectrosc. **35**, 152 (1973)].
[6] M. S. Child and H. C. Longuet-Higgins, Trans. Roy. Soc. **254A**, 259 (1961).
[7] J. Tang and A. Albrecht, In the book: Raman Spectroscopy, ed. H. A. Szymanski, **2**, Plenum Press, N. Y. 1970, p. 33.
[8] É. M. Verlan, Candidate Dissertation, Kiev State University, 1967.
[9] Ya. S. Bobovich, I. V. Aleksandrov, V. G. Maslov and A. N. Sidorov, ZhETF Pis. Red. **18**, 175 (1973) [JETP Lett. **18**, 102 (1973)].
[10] I. V. Aleksandrov, Ya. S. Bobovich, V. G. Maslov and A. N. Sidorov, Optika i spektroskopiya (Optics and Spectroscopy) **37**, 467 (1974).
[11] M. M. Sushchinskiĭ, Spektry kombinatsionnogo rasseyaniya molekul i kristallov (Raman Scattering Spectra of Molecules and Crystals), Nauka, 1969.
[12] J. Brandmüller, K. Burhard, H. Hacker and H. Schrötter, Z. Angew. Phys. **22**, 177 (1967).
[13] E. de Boer, In the book: Advances in Organometallic Chemistry, ed. by F. G. A. Stone and R. West, **2**, Acad. Press, N. Y. 1964, p. 115.
[14] S. A. Akhmanov and N. I. Koroteev, Zh. Eksp. Teor. Fiz. **67**, 1306 (1974) [Sov. Phys.-JETP **40**, 650 (1975)].
[15] K. Kaya, N. Mikami, Y. Udagawa and M. Ito, Chem. Phys. Lett. **13**, 221 (1972).
[16] I. V. Aleksandrov, Ya. S. Bobovich and V. G. Maslov, ZhETF Pis. Red. **19**, 264 (1974) [JETP Lett. **19**, 157 (1974)].
[17] A. Gillem and E. Stern, Electronic Absorption Spectra of Organic Compounds (Russ. Transl., IIL, 1957).
[18] P. P. Shorygin, Usp. khim. **40**, 694 (1971).
[19] M. Ito, P. C. Huang and E. M. Kosower, Trans. Faraday Soc. **57**, 1662 (1961).

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1) It has been shown recently by the method of coherent active spectroscopy of Raman scattering that the vibration of frequency 1176 cm^{-1} corresponds to an asymmetric tensor [14].

2) In the text [16], incorrect values of the intensity have been given inadvertently for the lines of 606 and 1176 cm^{-1}.

3) It is possible that among them are certain molecules of coordination and metalloorganic compounds.

[20] T. G. Spiro and T. C. Strekas, Proc. Natl. Acad. Sci. USA **69**, 2622 (1972).

[21] L. A. Nafie, M. Pezolet and W. L. Peticolas, Chem. Phys. Lett. **20**, 563 (1973).

[22] M. Zerner and M. Gouterman, Theor. Chim. Acta **4**, 44 (1966).

[23] G. P. Gurinovich, A. N. Sevchenko and K. N. Solov'ev, Spektroskopiya khlorofila i rodstvennykh soedineniĭ (Spectroscopy of Chlorophyl and Related Compounds), Nauka i Tekhnika, Minsk, 1968.

[24] M. J. Cowan, J. M. Drake and R. J. P. Williams, Discuss. Faraday Soc. **27**, 217 (1959).

[25] B. W. Dale, Trans, Faraday Soc. **65**, 331 (1969).

[26] H. Kobayashi and J. Yanagawa, Bull. Chem. Soc. Japan **45**, 450 (1972).

[27] K. N. Solov'ev, Optika i spektroskopiya [Opt. Spectrosc. **10**, 389 (1961)].

[28] R. Hochstrasser, Molecular Aspects of Symmetry (Russ. Transl., Mir, 1968).

[29] A. M. Schaffer, M. Gouterman and E. R. Davidson, Theor. Chim. Acta 30, 9, (1973).

[30] A. N. Sevchenko, S. F. Shkirman, V. A. Mashenkov and K. N. Solov'ev, Dokl. Akad. Nauk SSSR **175**, 545 (1967) [Sov. Phys.-Dokl. **12**, 710 (1968)].

[31] D. G. Rea, J. Mol. Spectrosc. **4**, 499 (1960).

[32] I. E. Zalesskiĭ, V. N. Kotlo, K. N. Solov'ev and S. F. Shkirman, Zh. Prikl. Spektrosk. (J. Appl. Spectrosc.) **20**, 1010 (1974).

[33] J. Smid, In the book: Ions and Ion Pairs in Organic Reactions, ed. M. Szwarc **1**, 1972, N. Y., 85.

[34] K. S. Chen, S. W. Mao, K. Nakamura, N. Hirota, J. Amer. Chem. Soc. **93**, 6004 (1971).

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