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Absorption Spectra of Gaseous Benzo[*g*,*h*,*i*]perylene and Coronene

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The gas-phase spectra of typical polycyclic aromatic hydrocarbons benzo[*g*,*h*,*i*]perylene and coronene, were measured. These data can be used as criteria for the solvent shifts and the molecular excitons.

One of the most refined analytical approaches to the molecule is to examine the gaseous behaviour of the isolated molecule. The conventional way of doing so is to make an experimental determination of the electronic transition energies. Further, the gas-phase spectra play an important role in the estimation of the energies in the crystalline phase and in solution.

For these purposes, several absorption spectra have been obtained for the vapours of various aromatic compounds.[1,2] However, in spite of many investigations, the absorption spectra have not been measured for benzo[*g*,*h*,*i*]perylene and coronene, which are typical higher polycyclic aromatic hydrocarbons. The latter is a famous example of the Shpolskii effect.[3]

We overcame the experimental difficulties resulting mainly from their lower volatility, and we succeeded in measuring their absorption spectra by the aid of a powerful electric furnace.[4]

This paper will report the optical absorption band positions of compounds, benzo[*g*,*h*,*i*]perylene and coronene, in the near-ultraviolet region, and will compare these results with the solution data.

Experimental

Benzo[*g*,*h*,*i*]perylene (Benzoperylene). The absorption spectra of benzo[*g*,*h*,*i*]perylene (Fig. 1) in the gas phase were observed as follows: Below 3.2×10^4 cm^{-1}, an Aminco 4-8401 monochromator was used. Above 3.2×10^4 cm^{-1}, a Cary recording spectrophotometer 14 was employed. The light sources were a 300-W tungsten lamp and a hydrogen discharge tube. Sodium and mercury lamps were employed to calibrate the spectral wavelengths.

The optical cell used was a Pyrex one, 30 cm in length, and also a silica cell, 2 cm long. A small quantity of benzoperylene crystals was placed in the cell, which was then evacuated to less than 10^{-5} mmHg pressure. The absorption coefficients of both compounds range from 10^2 to 10^4.[5] Therefore, the temperature must be varied widely in order to obtain the appropriate concentration of the gaseous specimen for observing their absorption spectra. In the case of coronene, the temperature ranges from 250 to 450°C.

When the absorption spectra of benzoperylene in the longer-wavelength region were observed, the Pyrex cell was maintained in a 50-KW electric furnace equipped with a temperature controller because the cell had to be kept at a fairly high temperature. To detect the spectra in the shorter-wavelength region, a small 80-W furnace for heating the cell was placed in the spectrophotometer. The spectra were taken after the specimen had been kept at the chosen temperature for at least 20 min. No condensation of the sample on the windows was detected during the measurement. The blank determination for the spectra was done by carefully cleaning and replacing the cell without changing the optical arrangement.

Benzo[*g*,*h*,*i*]perylene used was a synthetic one, prepared by Iwashima; it was purified by the chromatographic method.[6]

Coronene. For spectral measurements, a Spex spectrograph equipped with a 300-W tungsten lamp was used. The spectra were recorded photographic sheet films, Fuji Neopan SS. The spectral response on the films was determined by means of a Shimadzu microdensitometer. Iron lines were used for the wavelength calibration.

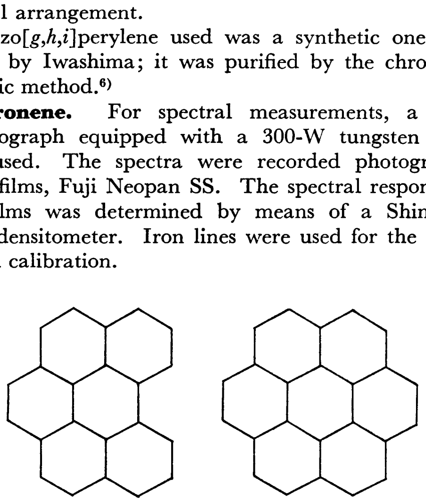

Fig. 1. Benzo[*g*,*h*,*i*]perylene and coronene.

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1) T. Kitagawa, *J. Mol. Spectry.*, **26**, 1 (1968).

2) G. C. Morris, *Australian J. Chem.*, **17**, 1288 (1964).

3) E. V. Shpolskii, *Soviet Phys. -Usp.*, **2**, 51 (1959).

4) N. Wakayama and H. Inokuchi, This Bulletin, **40**, 2267 (1967).

5) E. Clar, Polycyclic Hydrocarbons, Vols. 1 and 2, Academic Press Inc., New York (1964).

6) S. Iwashima, K. Ogino, T. Kajiwara and J. Aoki, *Nippon Kagaku Zasshi*, **89**, 1157 (1968).

The cell used for coronene was a Pyrex one used to measure the absorption spectra of benzoperylene vapour; the 50-kW furnace was also employed. The third band could not be observed because of the limitation of the optical absorption of the Pyrex cell.

Coronene (Fig. 1) used was a commercial one; it had been purified by recrystallization from xylene and by sublimination *in vacuo.*

For a complete investigation of absorption spectra of coronene, thirty hours were needed, but measurements of such a long duration scarcely affected the sample at all.[*2]

Results

The gaseous absorption spectra of benzoperylene are shown in Figs. 2, 3, and 4, which correspond to the region of the first, second, and third electronic transitions respectively. The spectra in an n-hexane solution were added for the sake of comparison. Table 1 gives the absorption bands observed in the various phases.7)

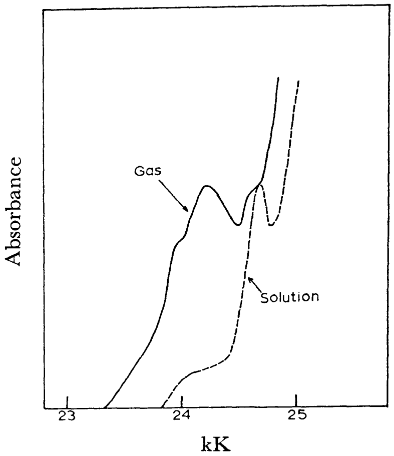

Fig. 2. Absorption spectrum of the α-band of benzo[*g,h,i*]perylene.

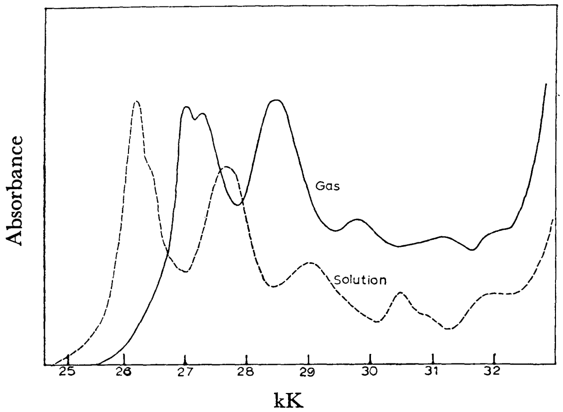

Fig. 3. Absorption spectrum of the p-band of benzo-[*g,h,i*]perylene.

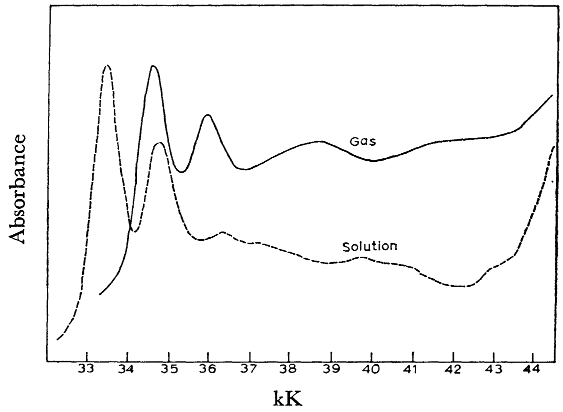

Fig. 4. Absorption spectrum of the β-band of benzo[*g,h,i*]perylene.

This compound has been subjected to scarcely experimental or theoretical treatments for the determination of its electronic transition energies, except for the case of the fluorescence spectra in the condensed phases.8) As to benzoperylene, the best, and almost the only calculations, have been those of Hummel and Rüdenberg's, whose results are also listed in Table 1.9)

Figures 5 and 6 show the spectra of gaseous coronene in the first two transition regions. The density on the films is plotted against the wave-numbers. Table 2 shows the bands of coronene which appeared in the various phases. The recent Pariser-Parr calculations for coronene are also listed.10)

TABLE 1. ABSORPTION BANDS OF BENZO-[*g, h, i*]PERYLENE

Band	Gas phase (cm^{-1})	n-Hexane solution (cm^{-1})	Crystal10) (cm^{-1})	Theoretical9) (cm^{-1})
α-Band	24230	24690	21685	26847 (f=0.008)
p-Band	27025	26075	24185	27077
	27315	~26460		(f=0.525)
	28490	27610	25560	
	29815	29015	26955	
	~31200	30415	28170	
β-Band	34565	33410		37239
	35880	34735		(f=2.084)

[*2] We also tried to detect the absorption spectrum of gaseous violanthrene B. This attempt was unsuccessful because of its thermal instability. In comparison with the other polycyclic aromatics, coronene is one of the most stable hydrocarbons.

7) J. Tanaka, This Bulletin, **38**, 86 (1965).

8) B. C. Mukherjee and S. C. Ganguly, *Proc. Phys. Soc.*, **83**, 93 (1954).

9) R. L. Hummel and K. Rudenberg, *J. Phys. Chem.*, **66**, 2334 (1961).

10) J. E. Bloor and B. R. Gilson, *Theoret. Chim. Acta*, **8**, 35 (1967).

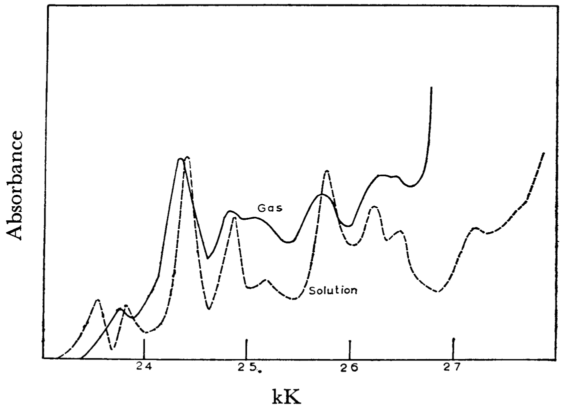

Fig. 5. Absorption spectrum of the α-band of coronene.

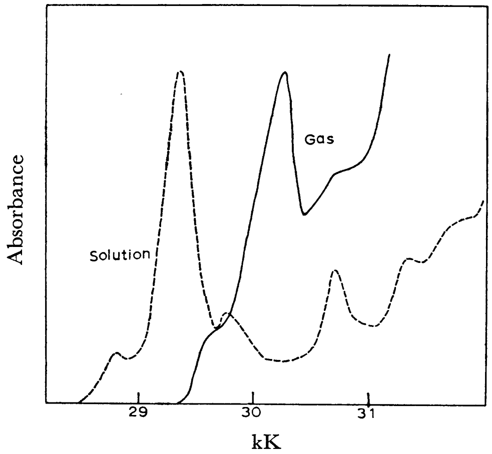

Fig. 6. Absorption spectrum of the p-band of coronene.

TABLE 2. ABSORPTION BANDS OF CORONENE

Band	Gas phase (cm^{-1})	Benzene solution (cm^{-1})	Crystal[7] (cm^{-1})	Analysis[15] (cm^{-1})	Theoretical[10] (cm^{-1})
α-Band	—	23365	21800	ν_{00}	24985 (f=0)
	23756	23810	22130	$\nu_{00}+350$	
	24366	24390	—	$\nu_{00}+350+650$	
	24832	24875	23250	$\nu_{00}+1450$	
	~25150	25220	—	$\nu_{00}+1450+350$	
	25727	25775	24140	$\nu_{00}+350+650+1350$	
	26178	26210	24620	$\nu_{00}+1450+1350$	
	~26450	26455	—	$\nu_{00}+1450+1600$	
p-Band	~29700	28780	27200		35190
	30250	29285	28350		(f=2.113)
	~30700	29760	30090		
		30720	31850		
		31300			
		31600			
β-Band		32787	32985		
			33570		
			36440		

Discussion

The first transition bands of these compounds, *i. e.*, the α-bands according to Clar's notation, have very weak oscillator strengths, f. ($f=0.008$ for benzoperylene and $f=0$ for coronene.[9]) Especially, the first singlet-singlet transition of coronene is forbidden by symmetry, but it is slightly allowed by vibrational perturbations, as in the case of benzene.[10]

Accordingly, it is the vibronic bands coupled with asymmetric vibrations that appeared with the stronger intensities. The 0–0 band is very weak, and it completely disappears in the gas phase. In both cases, the extinction coefficients are of the order of 10^2 in the solution.[5]

To aid the analysis of these bands, the behaviour in various solvents was taken into consideration. According to McRae's theory of the solvent effect, the molecule is affected by the interaction between the induced dipoles in the following way:[11]

$$h\Delta\nu = A\frac{n^2-1}{2n^2+1} \qquad (1)$$

where $h\Delta\nu$ is the spectral shift, where A is a constant characteristic of the transition of the solute, and where n is the refractive index of the solvent. The solvent-shifts are plotted for various kinds of solvents in Figs. 7 and 8.[12] As to benzoperylene, Eq. (1)

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[11] E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

[12] H. Matsushita, *Nippon Kagaku Zasshi*, **84**, 110 (1963).

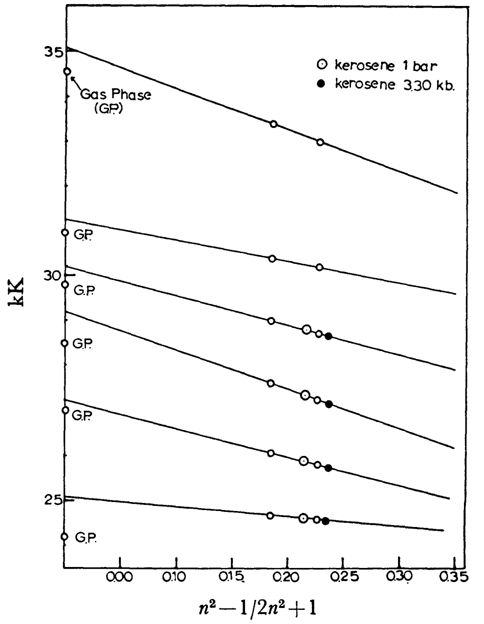

Fig. 7. Solvent effect for benzo[*g,h,i*]perylene.

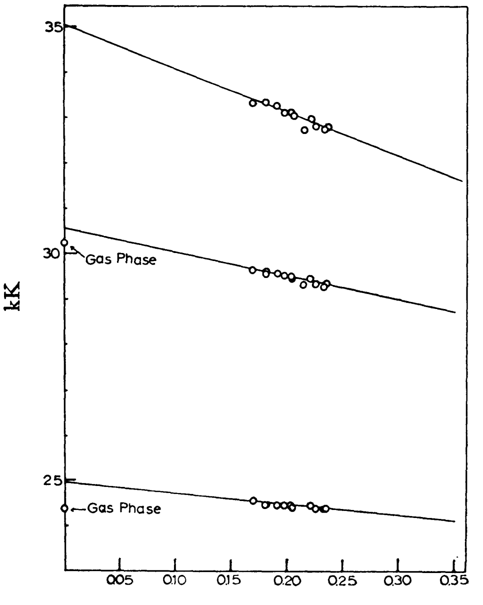

Fig. 8. Solvent effect for coronene.

is valid for the non-polar solvents, since it has a permanent dipole in the ground state.

The values extrapolated to the point of origin approximately indicate the positions of the spectra in the gaseous phase, but they generally exceed them to some extent. The discrepancies of the α-band are the greatest in both cases. The transitions with such small transition dipoles should not be expressed simply by Eq. (1), since the apparent amount becomes larger than the actual value, indicated by the abbreviation employed in the derivation of Eq. (1).[12,13]

The difference between the α-bands of benzoperylene in the gas phase and in solution is 460 cm^{-1}, while that of coronene is very little; the difference in f-values is thus reflected. This phenomenon is based on the fact that the solvent-shift is linearly correlated with the oscillator strength of the band to the second order of perturbation.[13]

However, the gaseous spectra became more diffuse than those in solution. This fact is the opposite of the general tendency, especially in the case of small molecules.

This line broadening can be explained if the following phenomenon is taken into consideration: in the first place, the thermal population can be considered in the vibrationally-excited states in the electronic ground state, which causes the hot bands in the excited states. The thermal energy kT amounts to 500 cm^{-1} when the α-band of coronene is measured. Considerable modes of fundamental vibration are obscured by this effect. This seems to have a very great effect on the line broadening. The relaxation process due to the intermolecular collisions may also be effective, thus reducing the lifetime of each vibronic band.

Coronene has many vibronic bands in the condensed phase, even at room temperature; this is rare among higher polycyclic aromatic hydrocarbons. These vibronic structures are reproduced in the gaseous spectrum. The redistribution of the oscillator strengths among the vibronic bands are not very distinguishable. The vibrational spacings are not changed. Several vibrational progressions, with fundamentals of 365, 650, 1440 cm^{-1}, *etc.*, are observed. These lines can be assigned by the aid of the studies in the rigid solution.[14,15]

From the two distinct lines, 4104 Å and 3887 Å, the location of the 0–0 band of coronene was deduced to be at 23390 cm^{-1}.

The second-transition bands of benzoperylene and coronene are called p-bands by Clar; they are theoretically-allowed transitions.[9,10] These two transitions have very similar red shifts in going from vapour to solution; the transitions amount to about 1000 cm^{-1}, corresponding to the fact that both transitions have nearly the same strong oscillator strengths (f= 2.08—2.20).

The spectrum of benzoperylene consists of four main peaks. The redistributions of the intensities were clearly observed in the passage from gas to solution. The shoulder on the band at 26075 cm^{-1} in solution grew into a distinct peak in the gas phase. The second vibronic peak augmented its intensity

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13) Y. Ooshika, *J. Phys. Soc. Japan*, **9**, 591 (1954).

14) E. G. Moisya, *Opt. Spectry.*, **21**, 59 (1966).

15) N. Mentzel and H. Zimmermann, *Ber. Bunsenges. Phys. Chem.*, **67**, 582 (1963).

in comparison with the other bands. The solvent effect of this band is apparently twice as large as those of the others. The pressure effect on these bands is consistent with the behaviour mentioned above.[16]

It is likely, in view of only the intensities and the shifts of the absorption spectra, that the *p*-band of benzoperylene consists of two or more transitions. However, theoretical studies do not suggest that there exists another transition near the 27025 cm^{-1} band system.[9] Therefore, the most reasonable interpretation should be based on the assumption that there are two (or more) vibrational progressions, beginning at 27025 cm^{-1} and 27315 cm^{-1}. When these progressions are very similar to each other, the overlapped band shapes are probably directly dependent on the difference in the solvent effects of the two progressions. The apparent peaks even in the same transition will sometimes behave differently, as in the case of benzoperylene.

It may be remarked incidentally that the pressure shifts can be explained in terms of the change in the refractive index of the solvent due to the applied pressure. In Fig. 7, the spectral shifts induced by the pressure of 3.30 kb are also plotted, along with the linear relationship of the solvent effect expressed by Eq. (1); all the evidence points to the same *n*-value, 1.501. This interpretation is slightly different from the popular explanation based on the change in the density of the solvent.[17] Therefore, it must be further examined both experimentally and theoretically.

In the case of coronene's *p*-band, one main peak and two subsidiary shoulders were detected. No other vibrational structure was observed. The behaviour in this region seems unchanged, except for the shifts of the spectral lines.

The third-transition system of benzoperylene, which is ordinarily called the β-band, begins at 34565 cm^{-1} in the gas phase. This intense system shifts to an energy lower by as much as 1165 cm^{-1}. The β-band of coronene may be supposed, on the basis of the solvent-shifts, to be located at about 35000 cm^{-1}.

The comparison of the gaseous spectra with those in crystalline states will be made elsewhere.

It is a pleasure to acknowledge our helpful and stimulating discussion with Drs. Takashi Kajiwara, Ichimin Shirotani, and Tadayoshi Sakata of the Institute for Solid State Physics, The University of Tokyo, during the course of this work.

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[16] T. Kajiwara, Thesis, University of Tokyo (1969).

[17] W. W. Robertson, D. E. Weigand, Jr., and F. A. Matsen, *J. Mol. Spectry.*, **1**, 1 (1957).