BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 996—1004 (1972)

# Vibrational Analysis of Electronic Transition Bands of Coronene

Koichi OHNO, Takashi KAJIWARA, and Hiroo INOKUCHI

*The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo*

(Received September 10, 1971)

The fluorescence and absorption spectra of coronene dissolved in organic solvents were measured at room temperature. Their vibrational structures were analyzed by reference to the Raman lines of crystalline coronene measured by means of a He-Ne gas laser, and the observed transition energies were compared with the calculated ones. It was suggested that the p-band of the absorption spectrum of coronene (23000—27000 $cm^{-1}$) is composed of more than one electronic transition, in contrast with the case of benzene. The fluorescence and phosphorescence spectra of coronene in *n*-octane were also measured at 77°K, and their vibrational structures were successfully analyzed with some perturbing vibrations and a few totally-symmetric ones.

The absorption and emission spectra of the first singlet-singlet transition band of coronene in solution show distinct vibrational structures. Further, a good mirror-image correspondence between the intensities and positions of the vibrational peaks of the fluorescence spectra and those of the $\alpha$-band of the absorption spectra, both in solution and in vapor, was found. Therefore, it is possible to attempt the vibrational anaysis of the bands; such analysis has been carried out by Sidman,[1] Shpolskii,[2] and Mentzel and Zimmermann.[3] However, their results are somewhat tentative and insufficient because of the lack of Raman spectra and infrared absorption spectra of the hydrocarbon.

In order to analyze the vibronic structure, it is necessary to know the frequencies and symmetries of the intramolecular vibrations, which can be introduced from the observation of the Raman spectra. However, no complete measurement of the Raman spectra of coronene has yet been reported. Only one line has been found by Mentzel and Zimmermann;[3] its frequency is 1363 $cm^{-1}$ in a $CS_2$ solution and 1346 $cm^{-1}$ in a tetrahydrofuran (THF) solution. No other lines could be detected because of the poor solubility of coronene in the solvents. In this work, however, by means of a He-Ne gas laser as a light source, weak but refined Raman spectra of crystalline coronene could be obtained.

The first singlet-singlet transition band of coronene (23000—27000 $cm^{-1}$), with $\log \varepsilon = 2.5$[4] in the absorption spectrum, has been interpreted as a weakly-allowed electronic transition one, as was indicated by Brocklehurst and Bowen.[5] This concept is the same as for benzene, for both hydrocarbons, benzene and coronene, have a $D_{6h}$ symmetry. For benzene, the lowest one-electron transition is orbitally fourfold-degenerate in the Hückel MO calculation. The degeneracy is removed by electron-electron interactions; then, one degenerate $E_{1u}$ state and two nonde-

1) J. W. Sidman, *J. Chem. Phys.*, **23**, 1365 (1955).

2) E. V. Shpolskii and L. A. Klimova, *Soviet Physics*, Doklady 1, 782 (1956).

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

4) $\varepsilon$ is the extinction coefficient.

generate states, $B_{1u}$ and $B_{2u}$, are given.

The absorption and fluorescence spectra of benzene vapor have been vibrationally analyzed.[6] The emission spectrum of benzene arises from one quantum addition of an $e_{2g}$ vibration of 606 $cm^{-1}$ to the symmetry-forbidden 0—0 band. The main progression is obtained by several further quanta addition of an $a_{1g}$ vibration of 923 $cm^{-1}$. In coronene, as was reported by Brocklehurst and Bowen,[5] the vibrational structures of the fluorescence spectrum in heptane at −180°C are largely composed of several series of three bands. There are three remarkable series with interpeak distances of approximately 1360 $cm^{-1}$. This relation is common in the fluorescence spectrum and also in the α-band of the absorption spectrum, so it is possible to analyze the first singlet-singlet transition bands of coronene with some $e_{2g}$ and a few $a_{1g}$ vibrations, as in the case of benzene.

In this paper, the first singlet-singlet transition bands of coronene will be vibrationally analyzed by reference to the Raman lines of the crystalline sample. The above transition bands and the p- and β-bands of the absorption spectrum will also be analyzed using the transition energies calculated by means of the molecular obtital theory.[7-9] Further, the vibrational structures of the fluorescence and phosphorescence spectra of coronene in glassy *n*-octane (77°K) will be discussed.

## Experimental and Results

*1.1. Raman Spectra of Crystalline Coronene.* In order to analyze the vibronic structures of the electronic spectra of coronene, the Raman lines of crystalline coronene were measured by means of a laser Raman spectrometer with a He-Ne gas laser (Japan Electron Optics Laboratory Co.) attached. The He-Ne gas laser (15803 $cm^{-1}$) was operated at an output of 40 mW. The applied sample was crystalline powder of high-purity coronene.[10] A single crystal was not employed because the crystal form was of a needle-type, so the polarized Raman spectrum could not be measured.

Although a weak emission spectrum was overlapped on the Raman spectrum, several Raman lines were identified at room temperature and at the temperature of liquid nitrogen (listed in Table 1).

Because a coronene molecule has a $D_{6h}$ symmetry, the $e_{2g}$, $e_{1g}$, and $a_{1g}$ vibrations should be Raman-active. Among them, $a_{1g}$ vibrations are generally most intensive; therefore, it can be expected that most of the strong Raman lines obtained in the intramolecular vibration range belong to $a_{1g}$ except for one line of 369 $cm^{-1}$,[12] since, in the lower-frequency region, in general there is no totally symmetric vibration in a large aromatic hydrocarbon such as coronene.

Table 1. Raman lines of the crystalline coronene

| | RT | | 77°K | |
|---|---|---|---|---|
| Lattice vivration range | 40 $cm^{-1}$ | | 43 $cm^{-1}$ | |
| | 57 | | 52 | |
| | 87 | | 77 | |
| | | | 90 | |
| Intra-molecular vibration range | S | 369 $cm^{-1}$ | M | 369 $cm^{-1}$ |
| | W | 435 | M | 435 |
| | VS | 482 | VS | 487 |
| | W | 830 | M | 571 |
| | VS | 1354 | W | 828 |
| | VS | 1371 | S | 840 |
| | W | 1584 | VS | 1354 |
| | W | 1631 | VS | 1369 |
| | | | W | 1584 |
| | | | W | 1625 |
| | | | W | 1633 |

Among the observed lines, 1354 and 1371 $cm^{-1}$ are the most intensive lines in the intramolecular vibration range; they may correspond to 1363 $cm^{-1}$ measured in the $CS_2$ solution by Mentzel and Zimmermann. The complete assignments of the Raman lines have not yet been made because of overlapping with weak emission spectra and because of the difficulty of polarized-Raman-spectra measurements.

In the lattice vibration range, there is a drastic change in the structure of the Raman lines between room temperature and the temperature of liquid nitrogen (Fig. 1). There-

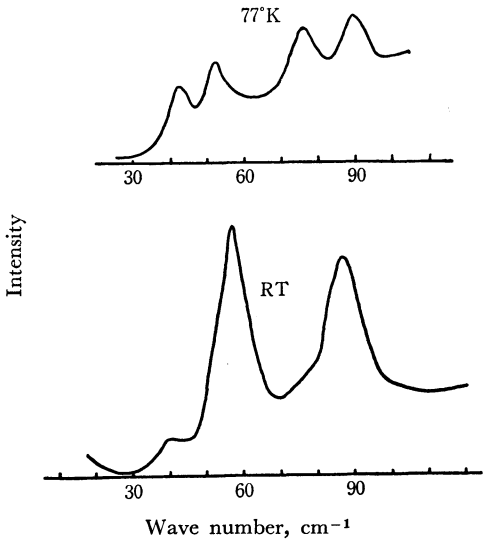


Fig. 1. The lattice vibration range of Raman spectra of coronene crystallites.

5) E. J. Bowen and B. Brocklehurst, *J. Chem. Soc.*, **1954**, 3875; **1955**, 4320.

6) H. Sponer, G. Nordheim, A. L. Sklar, and E. Teller, *J. Chem. Phys.*, **7**, 207 (1939).

7) N. S. Ham and K. Ruedenberg, *ibid.*, **25**, 1 (1956).

8) R. Hummel and K. Ruedenberg, *J. Phys. Chem.*, **66**, 2334 (1962).

9) H. Gutfreund and W. A. Little, *J. Chem. Phys.*, **50**, 4468 (1969); *Phys. Rev.*, **183**, 68 (1969).

10) The purification process has already been reported in another article.[11]

11) S. Iwahima, K. Ohno, T. Kajiwara, and J. Aoki, *Nippon Kagaku Zasshi*, **90**, 884 (1969).

12) See Sec. *2.1.*

fore, it seems that the phase transition takes place within the temperature range; the measurement of the heat capacity will now be undertaken.

*1.2. Absorption Spectra of Gaseous Coronene.* For understanding the optical properties of the coronene molecule, the absorption spectra of gaseous coronene are useful.[13] This seven-membered aromatic hydrocarbon, coronene, is very stable even at high temperatures of about 500°C, so that it was possible to obtain vapour phase enough to measure the absorption spectra. Purified coronene (46 mg) was enclosed in a cylindrical cell 3 cm in diameter and 30 cm in length *in vacuo*. The cell was placed in an electric furnace and heated to a constant temperature of 400°C in order to observe the α-band and to 250°C to observe the p-band. A tungsten lamp was used as the light source for the optical-absorption measurement. The most appropriate period of exposure was 20 min for the α-band observation and 10 min for the p-band observation, while the slit width of the spectrograph, a Spex Model 1700 III, was 100 μ. The relative intensities of the absorption peaks of the observed α-band are shown in Fig. 2.

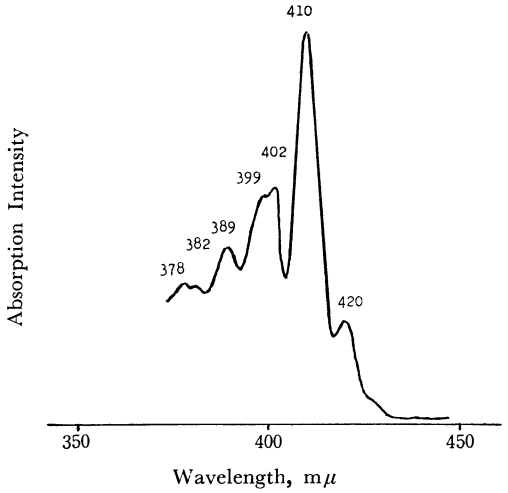


Fig. 2 The absorption spectrum of gaseous coronene.

As is shown in Table 2, the vibrational structure of the α-band of gaseous coronene is very similar to that of the benzene solution of coronene at room temperature reported by Clar,[14] while the p-band of the gaseous state is blue-shifted by a lack of solvent perturbation in comparison with that in solution. The fact that the α-band is hardly affected at all by the solvent supports the assignment of the band to an electronic transition from the $^1A_{1g}$ state to the $^1B_{2u}$ state which is symmetry-forbidden. The absence of the absorption peak at about 4270 Å in the gaseous phase, in contrast with its appearance in the benzene solution, suggests that the peak corresponds to that of the symmetry-forbidden transition.

*1.3. Absorption and Emission Spectra of Coronene in Solution.* The absorption and fluorescence spectra of coronene in solution were measured at room temperature. Fig. 3 and 4 show the absorption and emission spectra of coronene in THF. The peaks are named, as is shown in the figures,

13) J. Aihara, K. Ohno, and H. Inokuchi, This Bulletin, **43**, 2435 (1970).

14) E. Clar, "Polycyclic Hydrocarbons," Academic Press Inc., N. Y. (1964), p. 83.

Table 2. Absorption spectrum of gaseous coronene in comparison with the absorption spectra in benzene at room temperature

| | Vapor | In benzene | In benzene by Clar[14] |
|---|---|---|---|
| α-band | (4264 Å) a) | 4275 Å | 4280 Å |
| | 4200 | 4205 | 4200 |
| | 4104 | 4101 | 4100 |
| | 4022 | 4028 | 4020 |
| | 3980 | 3978 | 3965 |
| | 3890 | 3883 | 3880 |
| | 3820 | 3817 | 3815 |
| | 3780 | 3782 | 3780 |
| | | 3686 | 3685 |
| p-band | | 3560 | |
| | | 3474 | |
| | 3370 | 3412 | 3415 |
| | 3310 | 3359 | 3360 |
| | 3260 | 3311 | |
| | | 3258 | 3255 |
| | | 3193 | 3195 |
| | | 3150 | 3165 |

a) Very weak absorption was observed in the neighbourhood of 4264 Å, but it is impossible to determine the position exactly.

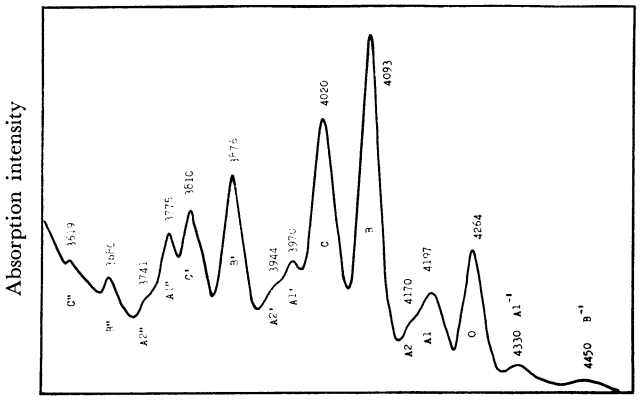


Fig. 3-1. The α-band of the absorption spectrum of coronene in THF at room temperature.

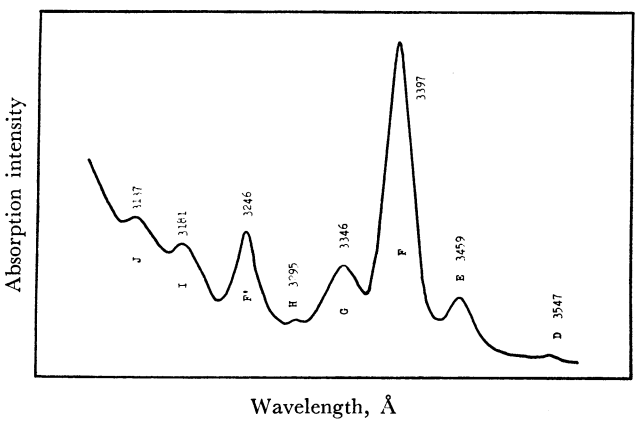


Fig. 3-2. The p-band of the absorption spectrum of coronene in THF at room temperature.

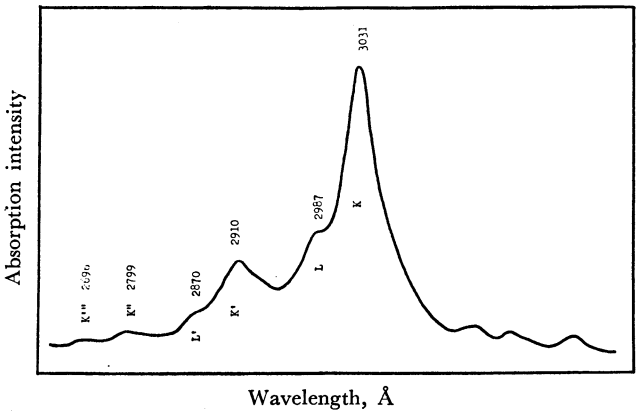


Fig. 3-3. The $\beta$-band of the absorption spectrum of coronene in THF at room temperature.

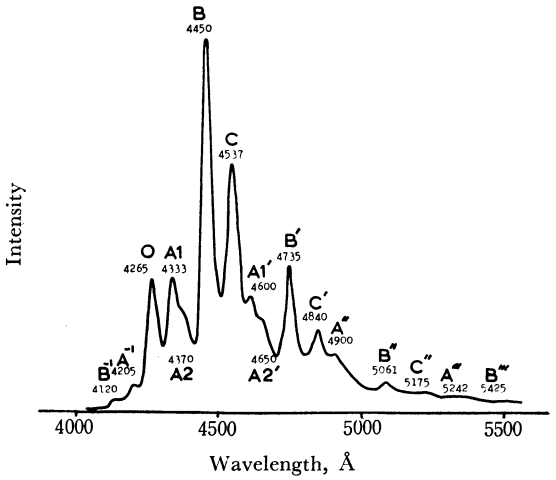


Fig. 4. The fluorescence spectrum of coronene in THF at room temperature.

according to the repeating structures and the mirror-image correspondence.

The vibrational structures of the fluorescence spectra of coronene in solution are composed of three ($A_1$, $B$, and $C$) or four series ($A_1$, $A_2$, $B$, and $C$), with a common interpeak distance, as in the case of the $\alpha$-band of the absorption spectra of coronene. Clearly, there is a good mirror-image correspondence between the fluorescence spectra and the $\alpha$-band of the absorption spectra. The mirror position at about 4270 Å (O-peak) coincides with the O-O position of the first singlet-singlet transition predicted by the absorption spectrum of gaseous coronene.

*1.4. Fluorescence and Phosphorescence Spectra of Coronene in* n*-Octane at 77°K.* As is well known, the quasi-linear spectra in $n$-paraffin at low temperatures give rather fine vibronic structures.[2,5] Therefore, the fluorescence and the phosphorescence spectra of high-purity coronene in $n$-octane were measured at 77°K in order to analyze the vibronic structures of the $^1A_{1g}$-$^1B_{2u}$ transition band and also the $^1A_{1g}$-$^3B_{1u}$ transition one. The resolving power of the spectra observed by means of a Spex 1700 III spectrograph are satisfactory (Fig. 5); for example, the line-widths at 4320 Å and at 4440 Å are about 4 Å (21 cm$^{-1}$). It is noted that the envelope of this fluorescence spectrum shows a very similar pattern ($A_1$, $A_2$, $B$, $C$, and their repetition) to that of the fluorescence bands in THF at room temperature. However, there exist some multiplicities. According to a recent report by Pfister,[15] the splittings are caused by many possible environments of a solute molecule dissolved in $n$-paraffin crystal. Although the number of possible sites depends, in general, upon the method of crystallization, in any of our measurements there were two possible sites for the case of coronene in $n$-octane; there exist two fluorescence origins, 23529 cm$^{-1}$ and 23495 cm$^{-1}$, but only one phosphorescence origin is observed, at 19399 cm$^{-1}$. However, if the other phosphorescence origin is assumed to be 19411 cm$^{-1}$, the vibronic bands can be divided into two series with similar vibronic patterns; one series starts from 19399 cm$^{-1}$, and the other, from 19411 cm$^{-1}$.

## Vibrational Analysis of the Spectra in THF

*2.1. First singlet-singlet Transition Bands.* The $\alpha$-band of the absorption spectrum shows a good mirror-image correspondence to the fluorescence spectrum. The O-peak (4264 Å in Fig. 3 or 4265 Å in Fig. 4) is in the mirror position. As has already been suggested, the O-peak corresponds to the 0—0 position of the transition between the lowest $^1A_{1g}$ state and the lowest $^1B_{2u}$ state, which is a symmetry-forbidden transition and which is allowed with a one-quantum addition of an $e_{2g}$ vibration. The main progressions are obtained by the further addition of several quanta of $a_{1g}$ vibrations.

Therefore, it is possible to analyze the vibronic structure of the first singlet-singlet transition with several $e_{2g}$ vibrations and a few $a_{1g}$ vibrations. The results of the analysis of the $\alpha$-band and the fluorescence spectrum of coronene in THF are shown in Table 3. The vibrational structure of the $\alpha$-band (or the fluorescence spectrum) is composed of four series ($A_1$, $A_2$, $B$, and $C$), with a common interpeak distance of about 1340—1370 cm$^{-1}$. The adding frequency $\nu_0$ ($a_{1g}$), reveals the existence of the totally

Table 3. Vibrational analysis of the $\alpha$-band and the fluorescence spectrum of coronene in THF

| | $\alpha$-band | | Fluorescence | | Assignment |
|---|---|---|---|---|---|
| | $\nu$ (cm$^{-1}$) | $\nu$-$\nu_{00}$ (cm$^{-1}$) | $\nu$ (cm$^{-1}$) | $\nu_{00}$-$\nu$ (cm$^{-1}$) | |
| $B^{-1}$ | 22470 | −980 | 24270 | −820 | $-\nu_3$ |
| $A^{-1}$ | 23095 | −355 | 23780 | −330 | $-\nu_1$ |
| O | 23450 | 0 | 23450 | 0 | $^1A_{1g}-^1B_{2u}$ |
| $A_1$ | 23825 | 375 | 23080 | 370 | $\nu_1(e_{2g})$ |
| $A_2$ | 23980 | 530 | 22880 | 570 | $\nu_2(e_{2g})$ |
| $B$ | 24430 | 980 | 22470 | 980 | $\nu_3(e_{2g})$ |
| $C$ | 24875 | 1425 | 22040 | 1410 | $\nu_4(e_{2g})$ |
| $A_1'$ | 25190 | 1740 | 21740 | 1710 | $\nu_1+\nu_0(a_{1g})$ |
| $A_2'$ | 25355 | 1905 | 21510 | 1940 | $\nu_2+\nu_0$ |
| $B'$ | 25800 | 2350 | 21120 | 2330 | $\nu_3+\nu_0$ |
| $C'$ | 26245 | 2795 | 20660 | 2790 | $\nu_4+\nu_0$ |
| $A_1''$ | 27490 | 3040 | 20410 | 3040 | $\nu_1+2\nu_0$ |
| $A_2''$ | 26730 | 3280 | 20130 | 3320 | $\nu_2+2\nu_0$ |
| $B''$ | 27175 | 3725 | 19760 | 3690 | $\nu_3+2\nu_0$ |
| $C''$ | 27630 | 4180 | 19320 | 4130 | $\nu_4+2\nu_0$ |
| $A_1'''$ | | | 19080 | 4370 | $\nu_1+3\nu_0$ |
| $B'''$ | | | 18430 | 5020 | $\nu_3+3\nu_0$ |

15) C. Pfister, *J. Chim. Phys.*, **67**, 418 (1970).

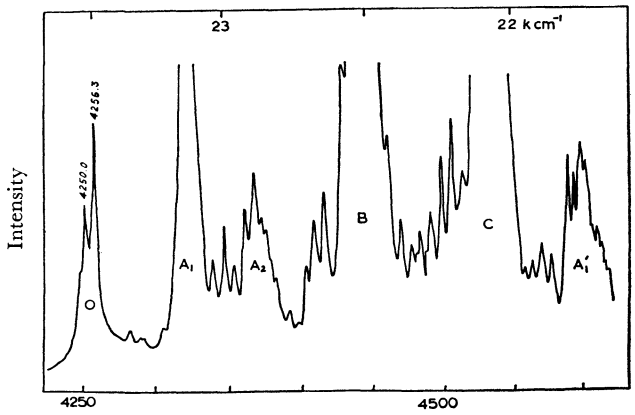


Fig. 5-1. Wavelength, Å

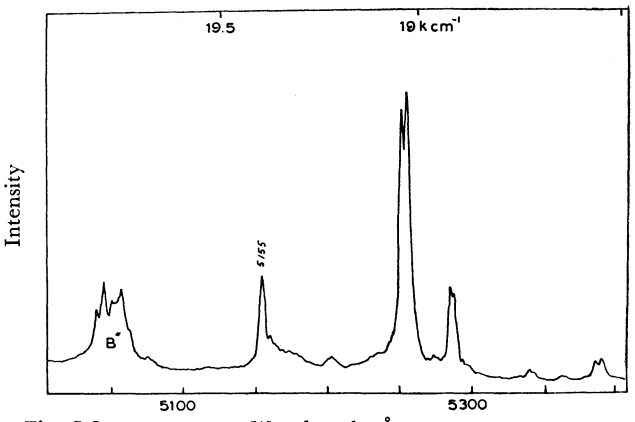


Fig. 5-3. Wavelength, Å

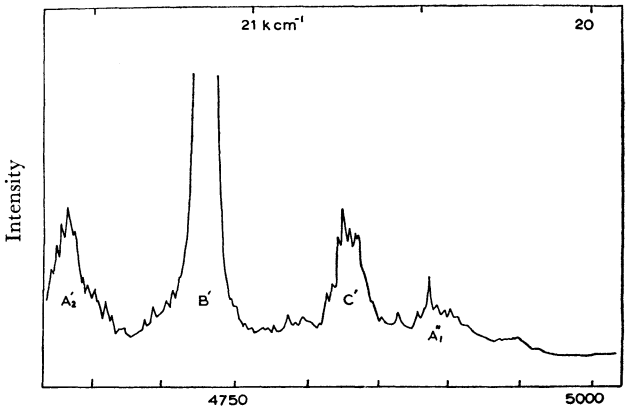


Fig. 5-2. Wavelength, Å

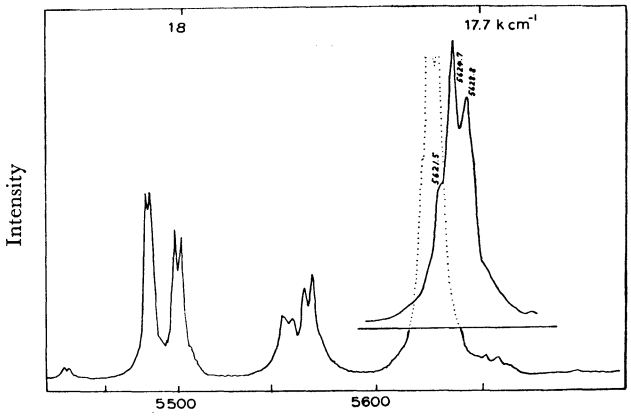


Fig. 5-4. Wavelength, Å

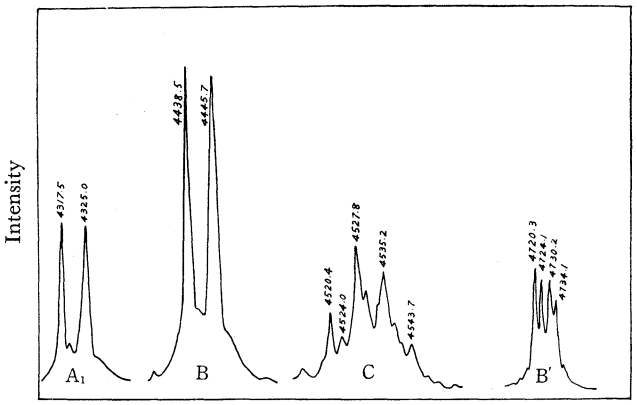


Fig. 5-5. Wavelength, Å

Fig. 5. The emission spectrum of coronene in *n*-octane at 77°K. Figure 5—5 shows the positions of peaks, $A_1$, B, C, and B′ illustrated in Fig. 5—1 and —2.

symmetric vibration of 1371 or 1354 $cm^{-1}$ found in the Raman spectrum of crystalline coronene by means of a He-Ne gas laser. This frequency also appears in both the p- and $\beta$-bands. $\nu_1$, $\nu_2$, $\nu_3$, and $\nu_4$ in Table 3 are perturbing vibrations belonging to $e_{2g}$. Among them, $\nu_1$ (375 $cm^{-1}$) corresponds to the Raman line (369 $cm^{-1}$), which may be one of the non-totally symmetric Raman active vibrations, $e_{2g}$ or $e_{1g}$, so that it is possible to predict that the Raman line (369 $cm^{-1}$) is an $e_{2g}$ vibration.

Two peaks ($A_1^{-1}$ and $B^{-1}$ of Fig. 3—1) apperaing on the longer-wavelength side of the $\alpha$-band, and also the two peaks, $A_1^{-1}$ and $B^{-1}$ of Fig. 4, on the shorter-wavelength side of the fluorescence spectrum, have almost identical frequency differences form the O-peak which correspond well to the frequencies of the perturbing vibrations, $\nu_1$ and $\nu_3$. As has already been indicated by Brocklehurst and Bowen,[5] these bands seem to be the hot bands of the lowest singlet-singlet transition, for these bands could not be observed at the temperature of liquid nitrogen in either the absorption or in the fluorescence spectra. Although the agreements in the vibrational analysis between the hot-band florescence and the $\alpha$-band are not adequate, these discrepancies can easily be understood by considering the reabsorption process.

Sidman[1] has assigned 990 $cm^{-1}$ (corresponding to $\nu_3$ in our assignment) to $\nu_1$ (370 $cm^{-1}$, $e_{2g}$)+$\nu$ (620

$cm^{-1}$, $a_{1g}$) but the absence of the 620 $cm^{-1}$ line in the Raman spectrum suggests that his assignment is not correct.

*2.2. p-Band.* In the p-band of the absorption spectrum, the values of log $\varepsilon$ range from 3 to 4.8 (Fig. 3—2). The intensity of the *D*-peak at 3547 Å is much weaker than that of any other peak in the p-band, while it is much stronger than the peaks in the $\alpha$-band. Therefore, this peak seems to belong to another electronic transition.

Taking the *E*-peak (Fig. 3—2) at 3459 Å (28910 $cm^{-1}$) as the 0—0 position, we can obtain exactly the same frequencies (Table 4) as in the vibrational analysis of the $\alpha$-band. In the p-band, the vibration of 530 $cm^{-1}$ is the most effective perturbing vibration, and the additional frequency is 1365 $cm^{-1}$.

The two peaks (I and J of Fig. 3—2) in the shorter-wavelength region of the p-band have an interpeak distance of 445 $cm^{-1}$, which corresponds to the frequency of 1420—975 $cm^{-1}$, but the interpeak distance between G and I is 1550 $cm^{-1}$, which has not yet appeared elsewhere. If I and J are the repeating structure of G and H with a one-quantum addition of a totally symmetric vibration of 1550 $cm^{-1}$, the repetition of the most intense peak, F, must appear at the 530+1550 $cm^{-1}$ position. Furthermore, although H is much weaker than G, J has an intensity almost comparable to that of I. Therefore, it is unreasonable to assign I and J to the repetition of G and H. It is, then, preferable to assume the existence of another electronic transition.[16] (Table 4)

Table 4. The vibrational analysis of the p-band of coronene in THF

| | $\nu(cm^{-1})$ | $\Delta\nu(cm^{-1})$ | Assignment |
|---|---|---|---|
| D | 28195 | | |
| E | 28910 | ( 0) | $^1A_{1g}-{}^1B_{1u}$ |
| F | 29440 | ( 530) | $\nu_5(e_{2g})$ |
| G | 29885 | ( 975) | $\nu_3(e_{2g})$ |
| H | 30330 | (1420) | $\nu_4(e_{2g})$ |
| F' | 30805 | (1895) | $\nu_5+\nu_0(a_{1g})$ |
| I | 31435 | | |
| J | 31880 | | |

Table 5. The vibrational analysis of the $\beta$-band of coronene in THF

| | $\nu(cm^{-1})$ | $\Delta\nu(cm^{-1})$ | Assignment |
|---|---|---|---|
| K | 32980 | 0 | |
| L | 33460 | 480 | $\nu_6$ |
| K' | 34350 | 1370 | $\nu_0(a_{1g})$ |
| M | 34890 | 1910 | $\nu_7$ |
| K'' | 35710 | 2730 | $2\nu_0$ |
| K''' | 37080 | 4100 | $3\nu_0$ |
| K'''' | 38460 | 5480 | $4\nu_0$ |
| N | 39600 | | |
| P | 42270 | | |
| Q | 43760 | | |
| R | 44480 | | |

16) This will be considered in Sec. 3.

*2.3. β-Band.* The $\beta$-band is clearly composed of an allowed transition, with log $\varepsilon$=5.4 at the most intensive absorption peak, which is assigned to the $^1A_{1g}$-$^1E_{1g}$ transition, as in the case of benzene. As is shown in Table 5, the vibrational structure of the $\beta$-band also reveals the totally symmetric vibration of 1370 $cm^{-1}$ which appears in the $\beta$-band, the p-band, and the Raman spectrum.

## 3. Comparison of Transition Energies between Calculated and Observed Values

The molecular orbitals of coronene and their energies were first calculated by Moffitt and Coulson[17] by means of the simple LCAO-MO method. According to their calculations, the highest occupied MO belongs to $e_{2u}$ and the lowest vacant MO belongs to $e_{1g}$, so that the lowest one-electron transition is orbitally fourfold degenerate, as in the case of benzene. The electron-electron interaction removes the fourfold

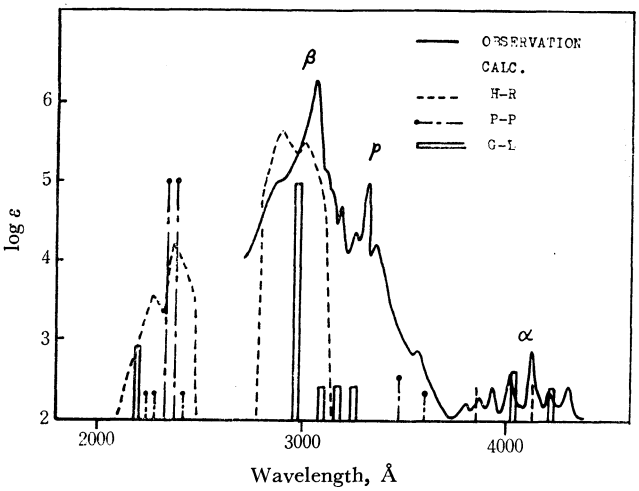


Fig. 6. The calculated and observed spectrum of coronene HR; Calculation by Hummel and Ruedenberg[8] P–P; Conventional Parier-Parr MO calculation[9] and G–L; Calculation by Gutfreund and Little.[9] The calculated spectral lines for forbidden transitions indicate their wavelength postitions only.

Table 6. The transition energy and the oscillator strength of coronene[a]

| | $\nu(cm^{-1})$ | $f$ |
|---|---|---|
| $^1B_{2u}$ | 24459 | 0.0000 |
| $^1B_{1u}$ | 27484 | 0.0000 |
| $^1A_{1g}$ | 31751 | 0.0000 |
| $^1A_{1g}$ | 32171 | 0.0000 |
| $^1A_{1g}$ | 32501 | 0.0000 |
| $^1E_{1u}$ | 33893 | 4.4 |
| $^3B_{1u}$ | 19762 | |

a) In this work Nishimoto-Mataga's electron repulsion integrals[18] are used as the bare Coulomb potential in the calculation of the effective interaction potential and 21 configurations are used in the CI calculation.

17) W. Moffitt and C. A. Coulson, *Proc. Phys. Soc.*, **60**, 21 (1948).
18) K. Nishimoto and M. Mataga, *Z. Physik. Chem.* (Frankfurt), **12**, 335; **13**, 140 (1957).

Table 7-a. The vibrational analysis of the fluorescence spectrum of coronene in *n*-octane at 77°K

| | $\nu$(cm$^{-1}$) | $\Delta\nu$(cm$^{-1}$) | Assignment |
|---|---|---|---|
| M | 23529 | 0 | I 0—0 ($^1B_{2u}-{}^1A_{1g}$) |
| M | 23495 | 34 | II 0—0 ($^1B_{2u}-{}^1A_{1g}$) |
| W | 23351 | 178 | I 178 |
| VW | 23310 | 219 | II 185 |
| VW | 23295 | 234 | |
| W | 23228 | 301 | |
| VS | 23162 | 367 | I 367 |
| W | 23145 | 384 | II 384 |
| VS | 23121 | 408 | II 374 |
| VW | 23100 | 429 | II 395 |
| M | 23042 | 487 | I 487 |
| M | 23001 | 528 | II 494 |
| M | 22959 | 570 | I 570 |
| M | 22929 | 600 | II 566 |
| M | 22897 | 632 | I 632 |
| M | 22862 | 667 | II 633 |
| VW | 22847 | 682 | I 682 |
| VW | 22815 | 714 | II 680 |
| W | 22766 | 763 | I 763 |
| VW | 22730 | 799 | II 765 |
| M | 22705 | 824 | I 824 |
| M | 22680 | 849 | I 849 (II 815) |
| M | 22640 | 889 | II 855 |
| M | 22582 | 947 | I 947 |
| VVS | 22528 | 1001 | I 1001 |
| VVS | 22494 | 1035 | II 1001 |
| M | 22424 | 1105 | I 1071 |
| M | 22376 | 1153 | I 1153 |
| M | 22336 | 1193 | II 1159 |
| W | 22321 | 1208 | I 1208 |
| M | 22306 | 1223 | I 1223 |
| W | 22279 | 1250 | II 1216 |
| M | 22274 | 1255 | II 1221 |
| M | 22242 | 1287 | I 1287 |
| M | 22205 | 1324 | II 1290 |
| M | 22163 | 1366 | I 1366 |
| S | 22122 | 1407 | I 1407 |
| S | 22104 | 1425 | I 1425 |
| VS | 22086 | 1443 | I 1443 (II 1409) |
| S | 22072 | 1457 | I 1457 (II 1423) |
| VW | 22056 | 1473 | |
| VS | 22051 | 1478 | II 1444 |
| M | 22036 | 1493 | II 1459 |
| M | 22024 | 1505 | I 1505 |
| S | 22009 | 1520 | I 1520 |
| M | 21988 | 1541 | II 1507 |
| M | 21973 | 1556 | II 1522 |
| W | 21956 | 1573 | I 1573 |
| M | 21930 | 1599 | II 1565 |
| M | 21901 | 1628 | I 1628 |
| M | 21867 | 1662 | II 1628 |
| M | 21815 | 1714 | I 367+1347 |
| M | 21796 | 1733 | I 367+1366 |
| M | 21772 | 1757 | II 374+1349 |
| M | 21753 | 1776 | II 374+1368 |
| W | 21716 | 1813 | I 1813 |
| W | 21701 | 1828 | I 487+1341 |
| VW | 21678 | 1851 | II 1817 |
| W | 21647 | 1882 | II 494+1354 |
| W | 21629 | 1900 | II 494+1372 |
| M | 21610 | 1919 | I 570+1349 |
| M | 21591 | 1938 | I 570+1368 |
| W | 21573 | 1956 | II 566+1356 |
| W | 21526 | 2003 | I 632+1371 |
| W | 21503 | 2026 | II 633+1359 |
| W | 21466 | 2063 | |
| W | 21450 | 2079 | |
| VW | 21419 | 2110 | |
| VW | 21409 | 2120 | |
| W | 21342 | 2187 | I 824+1363 |
| W | 21313 | 2216 | I 849+1367 |
| W | 21272 | 2257 | II 855+1368 |
| W | 21252 | 2277 | |
| VW | 21236 | 2293 | I 947+1346 |
| VW | 21211 | 2318 | I 947+1371 |
| S | 21184 | 2345 | I 1001+1344 |
| S | 21166 | 2363 | I 1001+1362 |
| S | 21142 | 2387 | II 1001+1352 |
| S | 21124 | 2405 | II 1001+1370 |
| VW | 21102 | 2427 | I 1071+1356 |
| VW | 21073 | 2456 | II 1071+1351 |
| VW | 21053 | 2476 | II 1071+1371 |
| W | 21028 | 2501 | I 1153+1348 |
| W | 21006 | 2523 | I 1153+1370 |
| W | 20958 | 2571 | I 1223+1348 |
| W | 20940 | 2589 | I 1223+1366 |
| W | 20894 | 2635 | I 1287+1348 |
| W | 20853 | 2676 | II 1290+1352 |
| W | 20777 | 2752 | I 1407+1345 |
| W | 20760 | 2769 | I 1425+1344 |
| M | 20741 | 2788 | I 1443+1345 (II 1409+1345) |
| M | 20725 | 2804 | I 1457+1347 |
| M | 20708 | 2821 | II 1444+1343 |
| M | 20693 | 2836 | II 1459+1343 |
| M | 20683 | 2846 | I 1505+1341 |
| VW | 20661 | 2868 | I 1520+1348 |
| VW | 20642 | 2887 | II 1507+1346 |
| W | 20614 | 2915 | II 1522+1359 |
| W | 20565 | 2964 | |
| W | 20511 | 3018 | |
| M | 20469 | 3060 | I 367+1347+1346 |
| W | 20448 | 3081 | I 367+1347+1367 |
| W | 20419 | 3110 | II 374+1349+1353 |
| W | 20400 | 3129 | II 374+1349+1372 |
| | 20280 | 3249 | |
| Broad | | | 570+2×1360 |
| | 20200 | 3329 | |
| VW | 19908 | 3611 | |
| W | 19841 | 3688 | I 1001+1344+1343 |
| M | 19822 | 3707 | I 1001+1362+1344 |
| W | 19798 | 3731 | II 1001+1352+1344 |
| M | 19771 | 3758 | II 1001+1370+1353 |
| W | 19701 | 3828 | |
| VW | 19592 | 3937 | |
| VW | 19535 | 3994 | |
| W | 19376 | 4153 | I 1457+1347+1349 |
| VW | 19361 | 4168 | |

Table 7-b. The vibrational analysis of the phosphorescence spectrum of coronene in *n*-octane at 77°K

| | $\nu$(cm$^{-1}$) | $\Delta\nu$(cm$^{-1}$) | Assignment |
|---|---|---|---|
| | (19411) | (−12) | I Assumed |
| S | 19399 | 0 | II $^3B_{1u}-{}^1A_{1g}$ |
| M | 19216 | 183 | II 183 |
| VS | 19047 | 352 | I 364 |
| VS | 19032 | 367 | II 367 |
| W | 18957 | 442 | |
| S | 18924 | 475 | I 487 |
| S | 18915 | 484 | II 484 |
| VW | 18875 | 524 | I 536 |
| W | 18758 | 541 | II 541 |
| W | 18727 | 672 | I 684 |
| W | 18716 | 683 | II 683 |
| W | 18650 | 749 | I 761 |
| M | 18570 | 829 | I 841 |
| M | 18553 | 846 | II 846 |
| M | 18447 | 952 | I 964 |
| M | 18435 | 964 | II 964 |
| VS | 18254 | 1145 | I 1157 |
| VS | 18245 | 1154 | II 1154 |
| VS | 18190 | 1209 | I 1221 |
| VS | 18175 | 1224 | II 1224 |
| S | 18005 | 1394 | I 1406 |
| S | 17992 | 1407 | II 1407 |
| S | 17972 | 1427 | I 1439 |
| S | 17960 | 1439 | II 1439 |
| W | 17789 | 1510 | |
| VVS | 17779 | 1620 | I 1632 |
| VVS | 17766 | 1633 | II 1633 |
| W | 17696 | 1703 | I 364+1351 |
| W | 17677 | 1722 | II 367+1355 |
| W | 17556 | 1843 | II 484+1359 |
| W | 17289 | 2110 | |
| W | 16883 | 2516 | II 1154+1362 |
| M | 16846 | 2553 | I 1221+1344 |
| W | 16628 | 2771 | I 1439+1344 |
| W | 16603 | 2796 | II 1439+1357 |
| W | 16412 | 2987 | II 1633+1354 |

degeneracy to give one degenerate $E_{1u}$ state and two nondegenerate states, $B_{1u}$ and $B_{2u}$.

The transition energies calculated by Ham and Ruedenberg[7] and those reported by Hummel and Ruedenberg[8] reproduce the experimental absorption spectra somewhat better than the conventional Pariser-Parr SCF-MO calculation, as is shown in Fig. 6.[19] The agreement with the experimental results has been considered plausible. By many authors, it has been assumed that the first weak band at 23400 cm$^{-1}$ might correspond to the 2600 Å band of benzene ($^1B_{2u}$); the band in the 29000 cm$^{-1}$ region, to the 2000 Å band of benzene ($^1B_{1u}$), and the most intensive band, at 33000 cm$^{-1}$, to the 1800 Å band of benzene ($^1E_{1u}$). However, these correspondences may not always be appropriate, because, in the case of coronene, a much larger number of electronic configurations must be considered in the CI calculation than in the case of benzene.

Recently, a more improved calculation has been presented by Gutfreund and Little.[9] In their calculation, the correlation effects of the $\pi$-electrons were considered carefully, and it was shown that the Coulomb interaction between $\pi$-electrons in a conjugated molecule is screened by the presence of other $\pi$-electrons and that, therefore, the bare Coulomb potential must be replaced by the appropriate effective interaction potential. The obtained transition energies for the low-lying singlet states of polycyclic hydrocarbons, such as coronene, tetracene, and pyrene, agreed plausibly with the absorption spectra experimentally obtained. In the case of coronene, the ambiguous p-band can be explained clearly by their calculation. According to their calculation, it seems that the conventional assignments are not appropriate; thus, it is preferable to conclude that the $\alpha$-band of coronene corresponds to the two forbidden transitions; the p-band, to the three forbid-

Table 8. The obtained fundamentals and Raman lines

| Fluorescence | | Phosphorescence | | Raman |
|---|---|---|---|---|
| I | II | I | II | |
| 178 cm$^{-1}$ | 185 cm$^{-1}$ | | 183 | |
| 367 | 374 | 364 | 367 | 369 |
| 384 | 395 | | | |
| | | | | 435 |
| 487 | 494 | 487 | 484 | 487 |
| | | 536 | 541 | |
| 570 | 566 | | | 571 |
| 632 | 633 | | | |
| 682 | 680 | 684 | 683 | |
| 763 | 765 | 761 | | |
| 824 | | | | 828 |
| 849 | 855 | 841 | 846 | 840 |
| 947 | | | | |
| | | 964 | 964 | |
| 1001 | 1001 | | | |
| | 1071 | | | |
| 1153 | 1159 | 1157 | 1154 | |
| 1208 | 1216 | | | |
| 1223 | 1221 | 1221 | 1224 | |
| 1287 | 1290 | | | |
| 1347 | 1349 | | | 1354 |
| 1366 | 1368 | | | 1369 |
| 1407 | (1409) | 1406 | 1407 | |
| 1425 | (1423) | | | |
| 1443 | 1444 | 1439 | 1439 | |
| 1457 | 1459 | | | |
| 1505 | 1507 | | | |
| 1520 | 1522 | | | |
| 1573 | 1565 | | | 1584 |
| 1628 | 1628 | | | 1625 |
| | | 1632 | 1633 | 1633 |
| 1813 | 1817 | | | |

19) The conventional Pariser-Parr MO calculation gives much larger transition energies.

den transitions, and the $\beta$-band, to the one allowed transition.

In the present work, we calculated the transition energies of coronene by the SCF-MO CI method, with effective electron repulsion integrals as in the Gutfreund and Little calculation. The calculated transition energies and oscialltor strengths are listed in Table 6. These results show that there are three states between $^1B_{1u}$ and $^1E_{1u}$, as in the results of Gutfreund and Little.[9] We found that the three states (31751, 32171, and 32501 $cm^{-1}$) belong to $^1A_{1g}$, so that the transitions between these states and the ground states ($^1A_{1g}$) are forbidden and vibronically allowed by $e_{1u}$ vibrations. Although the $e_{1u}$ vibrations are infrared-active, the infrared spectrum of coronene has not been measured; therefore, we cannot discuss further the vibronic structures of the p-band. In order to analyze the observed p-band, it would be desirable to determine the vibronic states by a calculation including the vibronic interactions among the three $A_{1g}$ states, the lowest $^1B_{1u}$ state, and the $^1E_{1u}$ state. Thus, we should prefer to suggest that the p-band is composed of more than one electronic transition.

## 4. Vibrational Analysis of Emission Spectra in *n*-Octane

The observed fluorescence and phosphorescence spectra of coronene in *n*-octane at 77°K were analyzed with reference to the results of the preliminary analysis reported in the Experimental and Results sections and with reference to the observed Raman lines. The assignments are shown in Table 7, while the obtained fundamentals are listed in Table 8. The fundamentals obtained from the phosphorescence spectrum agree well with those from the fluorescence one; most of the obtained Raman lines are also found in the fundamentals derived from the fluorescence spectrum. The adding $a_{1g}$ frequencies found in the fluorescence spectra are 1347 $cm^{-1}$ and 1366 $cm^{-1}$ in Series I, and 1349 $cm^{-1}$ and 1368 $cm^{-1}$ in Series II. These frequencies coincide well with the most intensive Raman lines, 1354 $cm^{-1}$ and 1369 $cm^{-1}$. The most effective perturbing fundamentals are 367, 1001, 1407, and 1443 $cm^{-1}$ in the fluorescence spectrum and 367, 484, 1154, 1224, 1407, 1439, and 1633 $cm^{-1}$ in the phosphorescence one. As was mentiaed in Sec. *2.1*, almost all of these should be $e_{2g}$ vibrations; however, 484 $cm^{-1}$, corresponding to the intensive Raman line, 487 $cm^{-1}$, may be an $a_{1g}$ vibration, since the 964 $cm^{-1}$ observed in the phosphorescence spectrum approximately equals $484 \times 2 = 968$ $cm^{-1}$.

The authors wish to thank Professor Mitsuo Ito, Tohoku University, and Dr. Toru Yokoyama, Japan Optics Laboratory Co., for their kind cooperation in making the Raman-spectrum measurements. The authors are also indebted to Professor Satoshi Iwahima, Meisei University, for preparing the high-purity coronene used for the spectroscopical measurements.