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On the Emission of Naphthalene and Some of its Derivatives in the Crystalline State

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Abstract—The emission spectra of pure 1-methylnaphthalene and 1,6-dimethylnaphthalene at 77 °K and the emission spectra from sublimation flakes of naphthalene and 2,6-dimethylnaphthalene at room temperature have been measured. The spectrum of 1-methylnaphthalene, which is cooled down rapidly to 77 °K, is exactly of excimer type. The emission of 1,6-dimethylnaphthalene at 77 °K has a broad band in the lower energy region and is also attributed to an emission from the excimer. Three kinds of naphthalene crystals have been grown by sublimation: (A) normal crystals, (B) crystals whose emission intensities decrease to one fifth by the irradiation of the exciting light, (C) crystals whose emission intensities increase to four times by irradiation. The emission intensity of a sublimation flake of 2,6-dimethylnaphthalene increases up to three times by exposure to exciting light. Under a microscope it has been observed that: (1) naphthalene crystals B have many wrinkles in the surface; (2) naphthalene crystals C show generation of bubbles by irradiation of the exciting light; (3) an irradiated surface of 2,6-dimethylnaphthalene crystal is prohibited from making evaporation pits and shows a clear surface. And also the mechanism of these phenomena is described as an effect of displacements of excited molecules in defect regions in a crystal.

1. Introduction

On the experiment of the concentration quenching of the fluorescence in the solution of naphthalene,(1) the behavior of relative quantum yield showed the existence of the excited complex with a sufficient life time to undergo complex fluorescence at room temperature. At moderate low temperature the emission spectrum of its concentrated solution(2) displays the broad and structureless emission band in the lower energy region, so-called excimer fluorescence. This type of emission was observed first by Förster and Kasper(3,4) in the solution of pyrene, and they attributed this phenomena to the association of electronically excited and unexcited molecules. At very low temperature, the solvent freezes and encounters in the solute molecules in solution (which are responsible for the formation of the excimer state) do not occur, so the observation of excimer has not been performed in general except in special cases.(10,17,18) While, in the crystalline state the emission from crystals of pyrene,(5) perylene,(6) etc. are also of excimer type. These molecules form crystals in which the molecules are crystallized in sandwich-like pairs. On the other hand, crystalline naphthalene and anthracene, etc. display monomer-like emission spectra, whereas the molecular planes of nearest neighbors in these crystals are oriented nearly perpendicular to each other. However at high pressure(7,8) these crystals also show excimer emission. These excimers act as traps for the migrating electronic excitation energy in the crystal.

In this paper the author will report the observed results on excimer type emission of α-substituted naphthalene in the frozen state at 77 °K and also report phenomena for changes in intensity of the emission of crystalline β-substituted naphthalenes at room temperature by the exposure of exciting light, which seem to predict displacements of excited molecules due to the force similar to the excimer binding.

2. Experimentals

The materials (except naphthalene) were obtained from Tokyo Kasei Ltd. 1-methylnaphthalene (1-MN) and 1,6-dimethylnaphthalene (1,6-DMN) were purified by adsorption chromatography with alumina and silica-gel. 2,6-dimethylnaphthalene (2,6-DMN) was purified by zone refining (80 passes). Naphthalene (Ishizu Pharmaceutical Co. Ltd.; extra-pure grade) was refluxed with sodium and then zone refined (200 passes). The liquid samples in a quartz tube (inside dia. 3 mm) were out-gassed several times and sealed off. The samples were cooled by the two different methods as follows: (1) The sample tube was immersed swiftly in the liquid nitrogen (rapid freezing), (2) The sample tube was cooled in the liquid nitrogen step by step; it was put into a Dewar bottle for a moment and then withdrawn. After this process was repeated several times, the sample was finally put into the Dewar (slow freezing). Sublimation flakes of naphthalene and 2,6-DMN were prepared in a glass tube of 3 cm diameter and 40 cm length with one end closed and the other end stuffed loosely with cotton. Naphthalene was sublimated by three different methods. (A) A sublimation tube was mounted inside a furnace which maintained a slow temperature gradient from the melting point of the sample at the inner end to room temperature at the outer end (method A). (B) The second method is as follows: $\frac{1}{5}$ part of the length of the sublimation tube was inserted in the furnace which is inclined at about 30° with the desk. Temperature of the furnace was raised slowly for one hour from room temperature to the melting point of the sample and then kept at this temperature for one hour. Crystals grown on the cotton stuff were used. Thickness of the crystals was $\sim 50\,\mu$ (method B). (C) In the third method the mounting of the sublimation tube in the furnace was the same as that in method B. The sublimation tube was heated slowly to 70 °C, taking one hour, and then taken out from the furnace. After the temperature of the furnace was raised to the melting point of naphthalene the sublimation tube was again mounted. Crystals of $20 \sim 10\,\mu$ thick were grown upon nuclei grown while the temperature of the sublimation tube had been low. For the purpose of examining the effect of oxygen an evacuated sample tube with naphthalene was prepared. A silica tube of 1 cm inner dia. and 25 cm length was evacuated after exchanging air in the sample by nitrogen gas with repetition of melting and sealed off. One end of the tube was heated by the sublimation method B, and a crystal grown on the wall of the tube in the other end was used for experiments. Crystals of 2,6-DMN were grown by methods A and C. The emission spectra were detected by Hitachi 139 grating spectrometer (Hamamatsu-denshi R-106 photomultiplier). The monochromatized exciting light was obtained from a 500 W xenon lamp or 100 W super-high pressure mercury lamp by using Hitachi G-2 monochrometer. In the case of drawing decay and growth curves of naphthalene crystal, a crystal was irradiated on the front surface and the emission was measured at two wavelength regions by two detecting systems.

3. Results

A. 1-METHYLNAPHTHALENE

The emission spectra at 77 °K of pure 1-MN frozen by the two different methods are shown in Fig. 1 together with the molecular emission spectrum in ethanol at 77 °K (A: slow freezing; B: rapid freezing; the dotted line: in ethanol). The sample of rapid freezing has a broad and structureless emission peaking at 25970 cm^{-1}. On the other hand the sample of slow freezing shows a structured emission and a slight shift from the molecular emission spectrum. Figure 2(a) is a photomicrograph of 1-MN at 77 °K by rapid freezing and (b) by the slow freezing, respectively. In Fig. 2(b) (slow freezing) lines that run diagonally in the photograph seem to be boundaries of crystals. On the other hand in Fig. 2(a) (rapid freezing) large crystals as observed in Fig. 2(b) cannot be found.

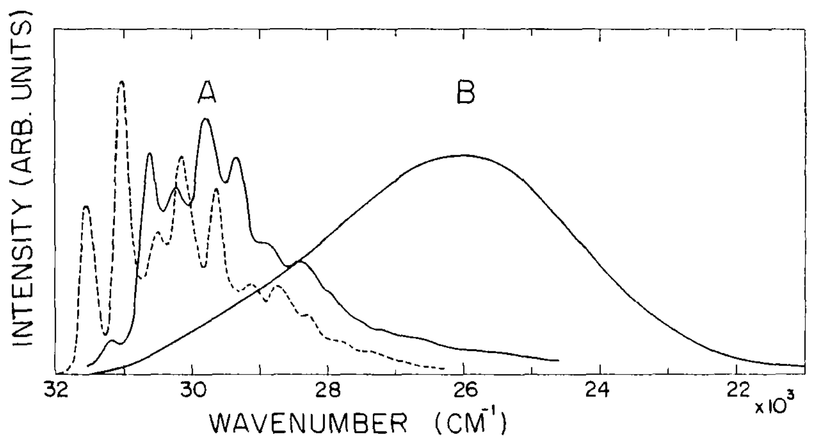

Figure 1. Emission spectra from pure 1-methylnaphthalene at 77 °K by (A) slow freezing, (B) rapid freezing. The dotted line: the molecular fluorescence spectrum in ethanol at 77 °K.

B. 1,6-DIMETHYLNAPHTHALENE

The emission spectrum of crystalline 1,6-DMN at 77 °K is shown in Fig. 3 together with that at 205 °K. This material does not show a complete excimer emission even in the case of rapid freezing. Figure 4 shows a photomicrograph of 1,6-DMN at 77 °K by rapid freezing.

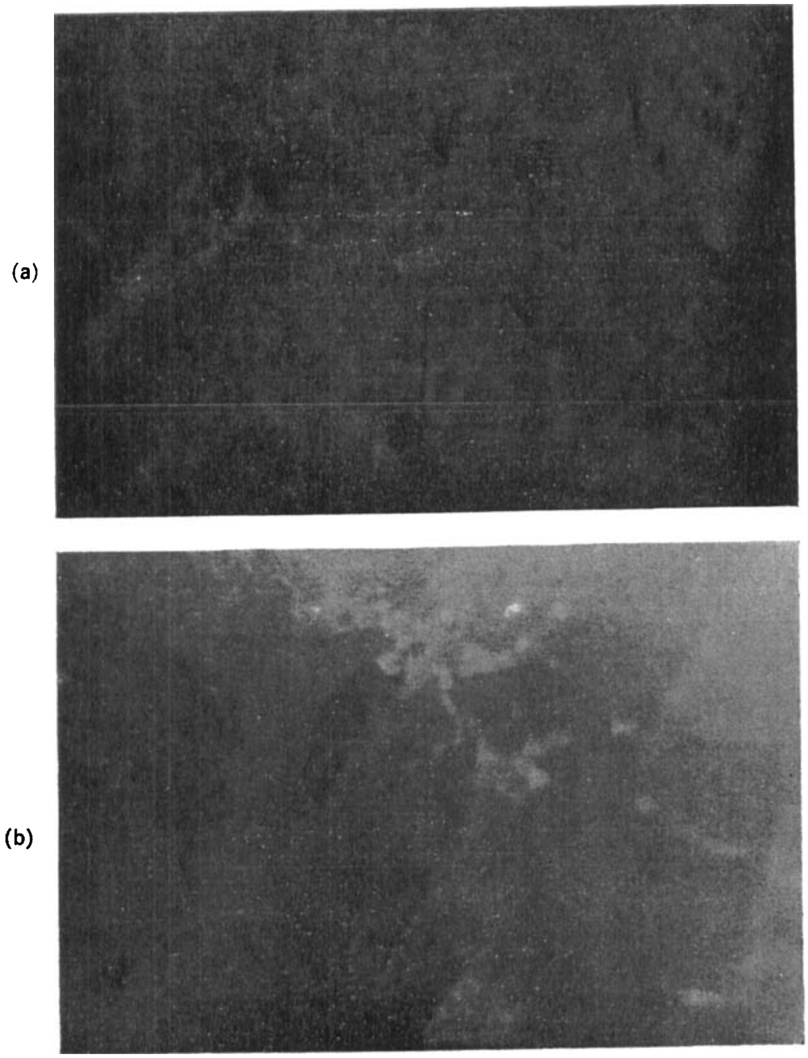

Figure 2. Crystal of 1-methylnaphthalene at 77°K (38 ×)
(a) by the rapid freezing, (b) by the slow freezing.

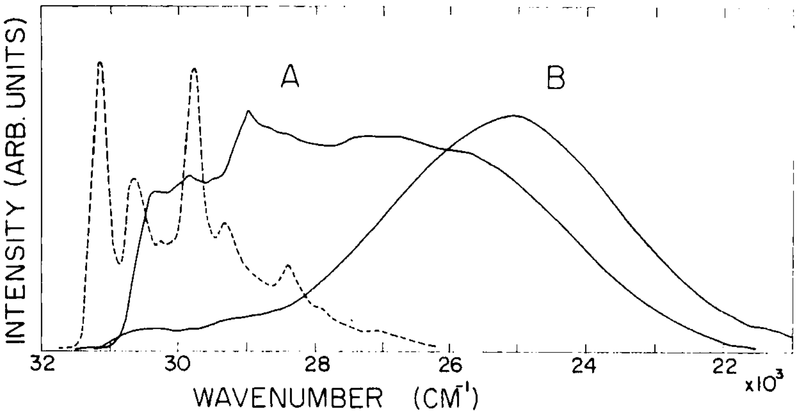

Figure 3. Emission spectra from pure 1,6-dimethylnaphthalene (A) at 77°K (B) at 205°K. The dotted line: the molecular fluorescence spectrum in ethanol at 77°K.

Figure 4. Crystal of 1,6-dimethylnaphthalene at 77°K by rapid freezing (38×).

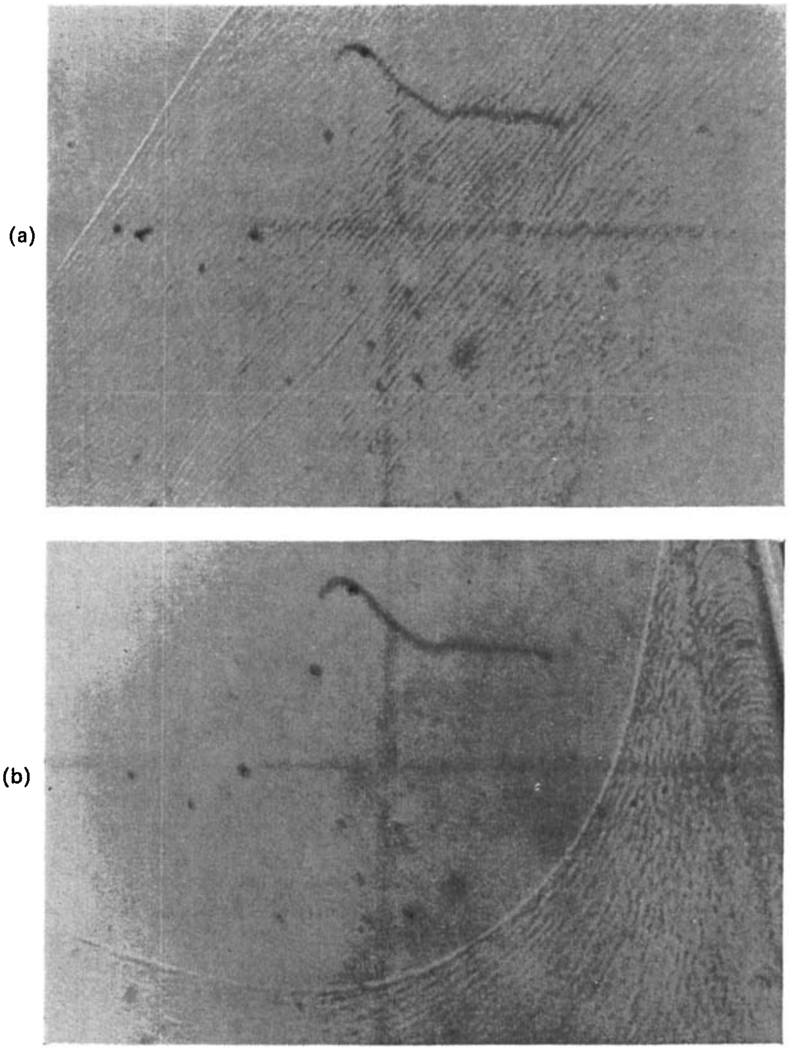

Figure 5. The surface of a naphthalene crystal grown by method B (95 ×). (a) The photograph gives many wrinkles where the emission spectrum shows spectrum B in Fig. 6. The left top portion of the photograph, which makes a clear appearance, shows spectrum A in Fig. 6 by excitation. The boundary between the above two portions looks a straight line. (b) Curved boundary of the two portions. The bottom portion has spectrum B in Fig. 6.

In the photograph, 1,6-DMN differs from 1-MN, growth of some large crystals is observed in the rapid freezing. At 205 °K the spectrum is exactly of excimer type. The excitation spectrum for the 26320 cm^{-1} emission of crystalline 1,6-DMN at 77 °K is the same as that at 205 °K.

C. NAPHTHALENE CRYSTAL A AND CRYSTAL B

Figure 5 shows a photomicrograph of surface of naphthalene crystal grown by method B (crystal B). In the photograph many wave-like wrinkles are observed. The left top portion in Fig. 5(a) and the top portion in Fig. 5(b) give clear appearances within the present method of observation. Curve A in Fig. 6 is the spectrum of a crystal grown by method A. The emission spectrum obtained by exciting on a crystal B surface where many wrinkles exist is shown in curve B (Fig. 6). The spectrum of the clear portion of crystal B is the same as that of crystal A. By irradiation of the exciting light on the surface of crystal A or crystal B visual change could not be found within the present magnification. Comparison with spectrums A and B in Fig. 6 predicts that the emission band lower than 29580 cm^{-1} of B is the same as that of A, but the emission

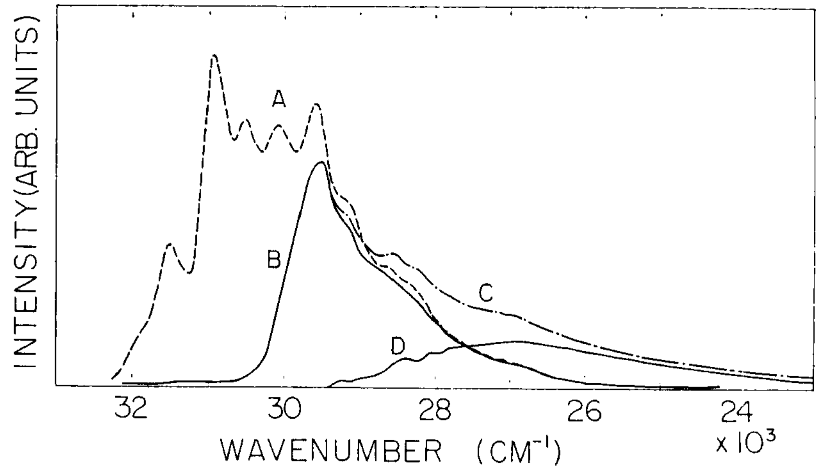

Figure 6. Emission spectra from sublimation flakes of naphthalene at room temperature (A) — — — as grown by method A, (B) by the excitation on a portion of crystal surface which has many wrinkles as Fig. 5, (C) — · — after two hours irradiation on a crystal surface having spectrum B (the intensity is normalized to spectrum B, (D) Difference between curve C and curve B.

band higher than 29580 cm^{-1} disappears in spectrum B. The intensity of 29580 cm^{-1} emission of spectrum B in a crystal B decreases remarkably during the exposure of the exciting light of 34480 cm^{-1}, while the intensity of emission increases in far lower energy than that of main emission peak, which is about one fiftieth of that of main emission. Figure 7 shows a typical decay of the emission intensity at 29580 cm^{-1} and growth of the emission at 24390 cm^{-1} of a sublimation flake B by the irradiation of exciting light. By irradiation the spectrum of crystal B slightly changes in the lower energy region. Curve C in Fig. 6 indicates a spectrum of post-irradiated crystal B, in which the intensity is normalized to curve B. The difference between curves, B and C is curve D, and it gives the change of the spectrum by irradiation. A freshly sublimated

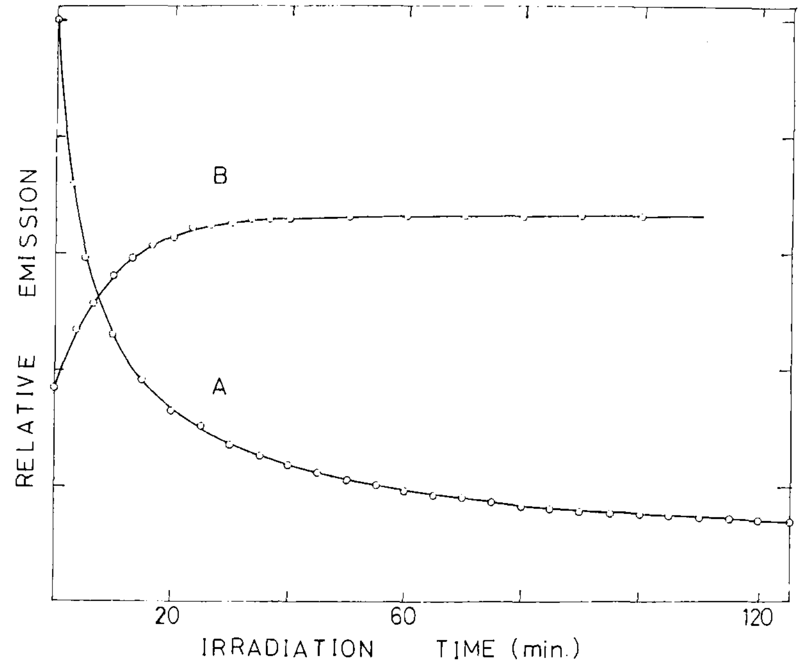

Figure 7. (A) Decay of the emission at 29580 cm^{-1} under the exposure of 34480 cm^{-1} on a portion of crystal where the emission spectrum is spectrum B in Fig. 6. (O: experimental value). The solid curve is calculated according to Eq. (3). (B) Increase of emission at 24390 cm^{-1} measured simultaneously with the decay curve (A) (O: experimental value). The solid curve is plotted according to the function $(1 - e^{-bt})$ correspondingly $b = 0.105$.

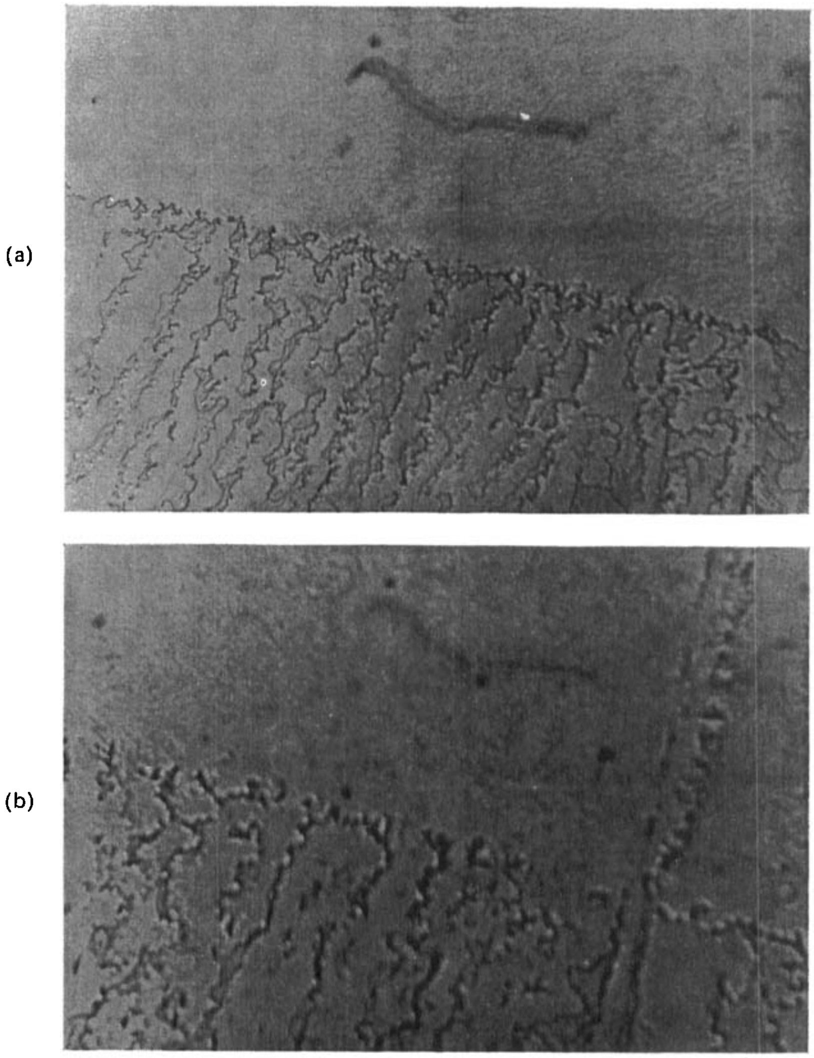

Figure 8. Change by irradiation of the exciting light on a naphthalene crystal grown by method C (95 ×). (a) irradiated for 5 min and exposed to air at room temperature by 30 min. The bottom half of the photograph is the irradiated portion and the top half is the unirradiated. (b) Further exposed to air for 15 min after (a). Evaporation pits appear distinctly at unirradiated surface.

crystal grown by method A also shows a decay and growth of intensity and the observed result fits the same kind of theoretical relations as that of crystal B. However the decay is more moderate than that of crystal B. The intensity of emission decreases by from 10 to 30% of the pre-irradiated intensity from crystal to crystal. Crystal grown in a evacuated tube also showed the spectrum B and the same decay and growth of emission intensity as a sublimation flake grown by the method B.

D. Naphthalene Crystal C

The third kind of crystal grown by method C is described. This kind of crystal evaporates rapidly. Under the microscope, twenty-minutes exposure to air at room temperature allows us to observe evaporation pits. By irradiation of the exciting light many small bubbles appear under microscope, and grow and aggregate together. Figure 8 shows changes by irradiation of the exciting light on a surface of crystal C after irradiation for 5 min and exposure to air at room temperature for 30 min. The bottom portion of the photograph is the irradiated surface and the remaining portion is the unirradiated one. In the irradiated portion aggregated bubbles are created and in the unirradiated surface many evaporation pits appear after 30 min exposure to air. The emission intensity and spectrum of crystal C change by irradiation of the exciting light. Figure 9 shows a change in the emission intensity at 29580 cm^{-1} from a crystal C by the exciting light of 34480 cm^{-1}. Rapid growth of the emission follows on the heels of a small fall and after taking maximum value, it decreases gradually. Change of emission intensity occurs mainly in the spectral region lower than 29580 cm^{-1} and that higher than 29580 cm^{-1} is almost unchanged. The emission spectrum of this kind of crystal at maximum intensity is shown in Fig. 10. This spectrum has an intermediate character between A and B in Fig. 6.

E. 2,6-Dimethylnaphthalene

Crystals of $1 \sim 5\,\mu$ thickness were grown by method C. These crystals evaporate rapidly. By exposure to air at room temperature evaporation pits appear under microscope. Irradiation of the exciting light upon a crystal changes the nature of the surface into the one that does not show any evaporation pit. Figure 11 shows a

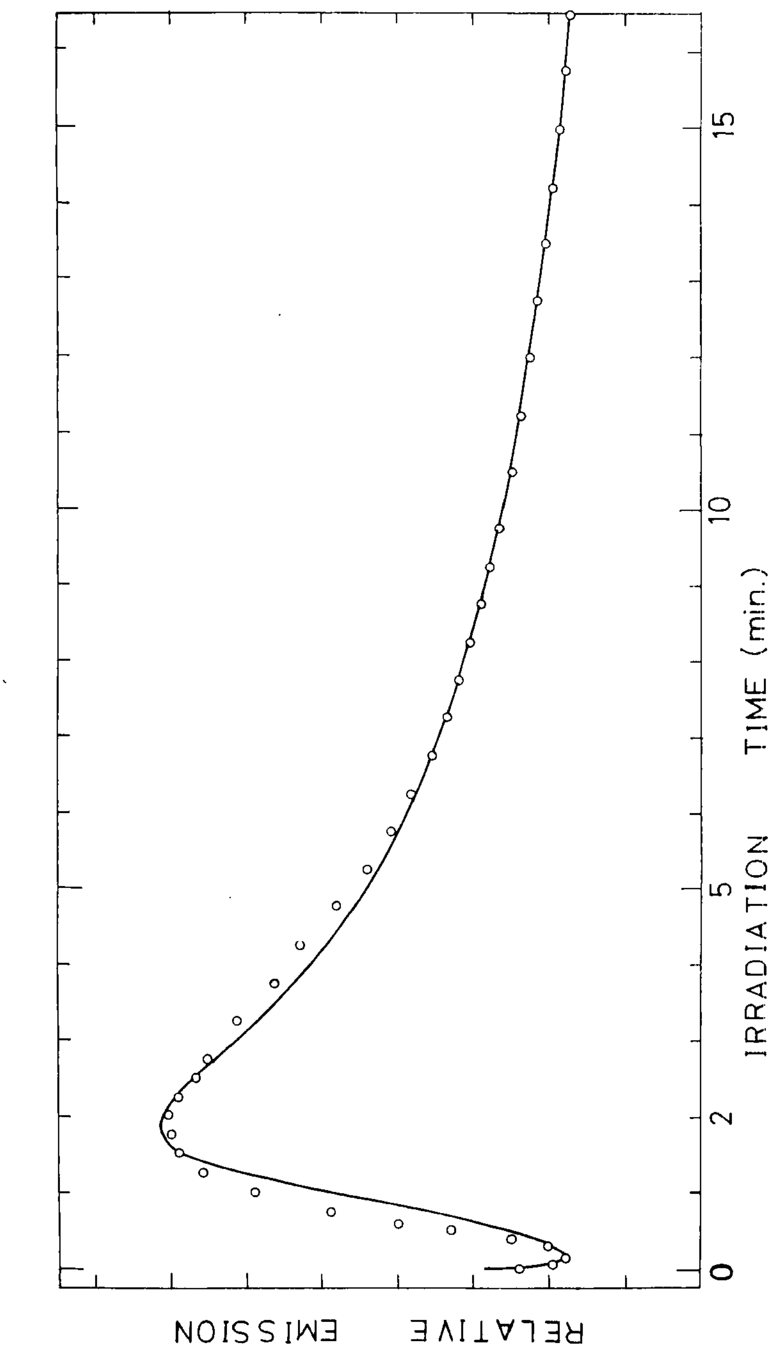

Figure 9. Change of the emission intensity at 29580 cm^{-1} from a sublimation flake of naphthalene grown by method C under the exposure of 34480 cm^{-1} light (O: experimental value). The solid curve is drawn according to Eq. (6).

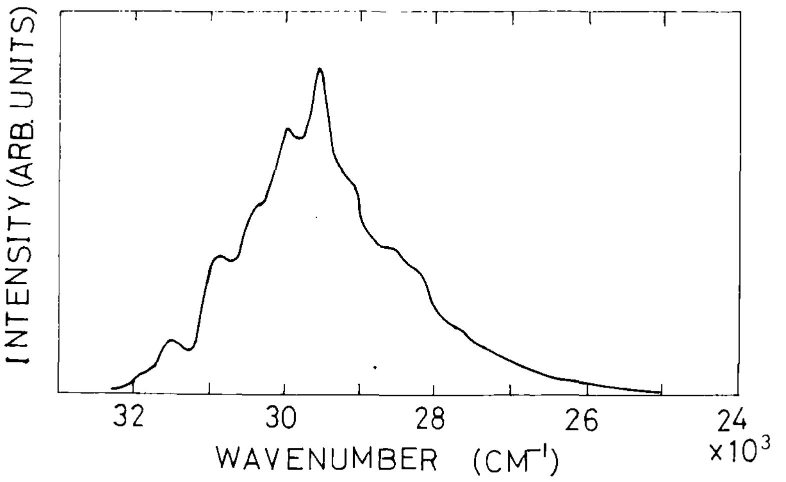

Figure 10. Emission spectrum at room temperature from a sublimation flake of naphthalene grown by method C at maximum intensity.

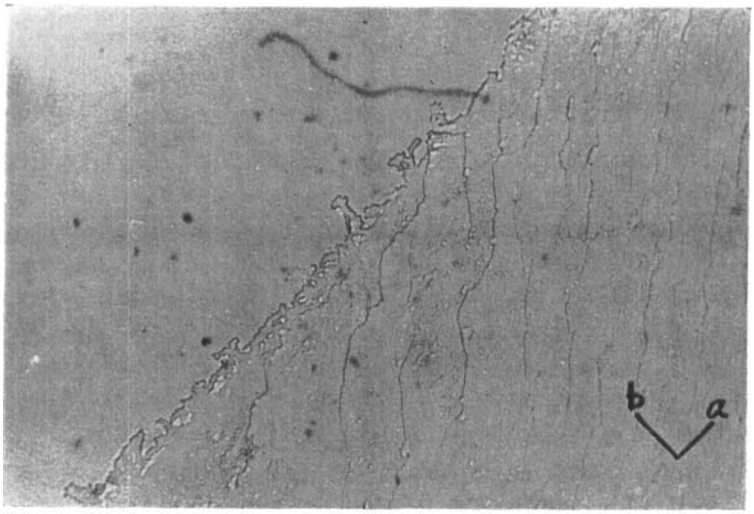

Figure. 11 Change by the irradiation of the exciting light on a 2,6-dimethylnaphthalene crystal grown with the method C (95 x): irradiated by 5 min and exposed to air at room temperature by 30 min. The left top half of the photograph is irradiated surface which looks clear. The right bottom portion is unirradiated where evaporation pits appear.

surface of 2,6-DMN crystal which was exposed to air by 30 min after 5 min irradiation. In the unirradiated surface evaporation pits appear but, on the other hand, the irradiated surface looks clear. These crystals sublimate out about ten hours after exposure to air and at this time irradiated surfaces are clearly left and evaporate out lastly. The intensity of emission increases and the spectrum turns from A in Fig. 12 into B gradually by the irradiation of the exciting light of 34480 cm^{-1}. After the irradiation the intensity of emission grows up to three times as great as that before irradiation and a new emission band appears around 29940 cm^{-1}. A typical increase of emission intensity at 29100 cm^{-1} by the irradiation is shown in Fig. 13. Crystals grown by method A also show the growth of emission intensity, however the velocity of increase in emission intensity is slower than that by method C. Crystals which had the spectrum A and had been left at room temperature for a month after the sublimation showed three times the growth of emission intensity by irradiation.

Discussion

1. 1-METHYLNAPHTHALENE AND 1,6-DIMETHYLNAPHTHALENE

The emission spectrum of 1-methylnaphthalene by slow freezing is that of crystal.†

On the other hand, the spectrum by rapid freezing is of excimer type. Observations with microscope indicate that slow freezing allows the growth of large crystals, but by rapid freezing crystallization of molecules does not afford to completely go on and so the aggregate by the rapid freezing would contain a large number of defects of the crystal. In the defect regions displacements of excited molecules are allowed to compose excimers. In the case of slow freezing crystallization seems to prevent the displacement of excited molecules. The peak of spectrum B locates at 25970 cm^{-1} which is 770 cm^{-1} higher than that of excimer in solution. This shift may indicate that the interaction of the two molecules of an excimer in solid, which depends upon both the configuration and intermolecular distance, is

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† The spectrum was that referred to in Ref. 9. The energy and intensity of O, O-band and other six peaks consist with those of the crystal spectrum in Ref. 9.

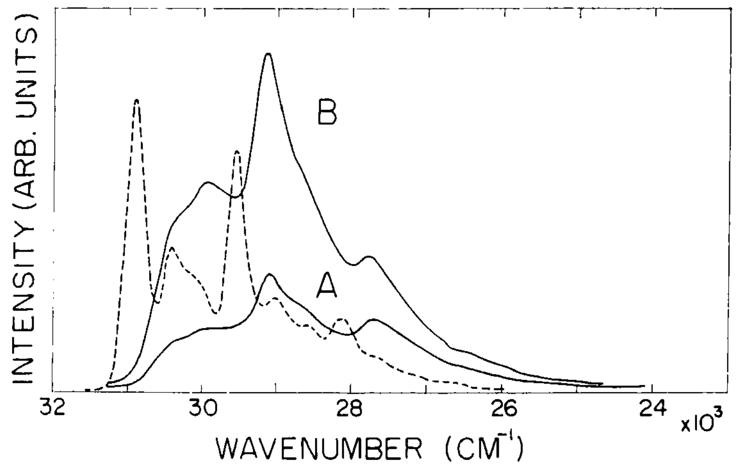

Figure 12. Emission spectra at room temperature from a sublimation flake of 2,6-dimethylnaphthalene grown by method C: (A) before irradiation (B) after one hour irradiation of the exciting light of 34480 cm^{-1}. The dotted line: the molecular fluorescence spectrum in ethanol at 77 °K.

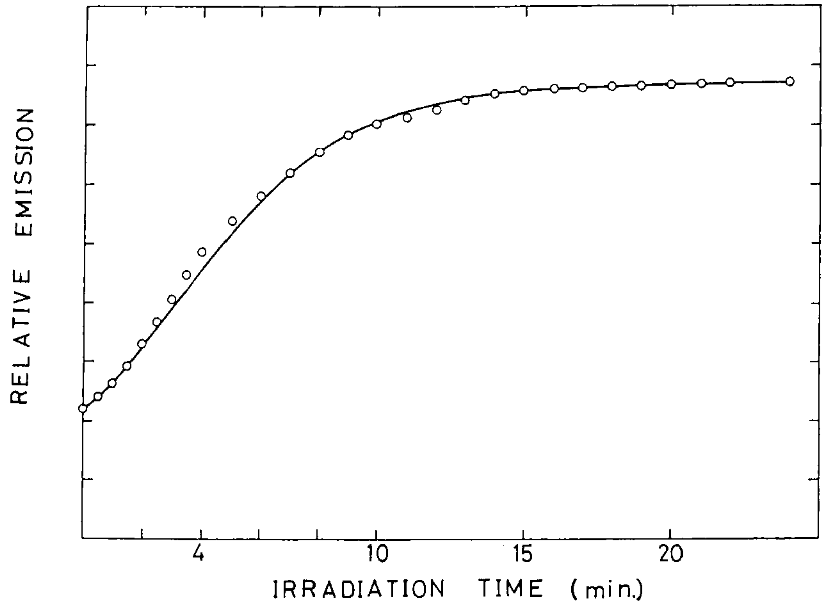

Figure 13. Increase of emission at 29100 cm^{-1} of a sublimation flake of 2,6-dimethylnaphthalene grown with method C under the exposure of exciting light of 34480 cm^{-1} (O: experimental value). The solid curve is calculated according to Eq. (5).

more weak than that in solution. 1,6-DMN, unlike from 1-MN, does not show a complete excimer emission by even rapid freezing. This result is consistent with the fact that growth of some large crystals is found in the photomicrograph (Fig. 4). At 205 °K the number of molecules capable of displacements to compose an excimer seems to increase due to weakening of a restrictive force in the crystal lattice. The peak of spectrum B in Fig. 3 lies at 25000 cm^{-1} which is 150 cm^{-1} higher than that of an excimer in solution.(16) The value of 150 cm^{-1} is rather a small one compared with 6000 cm^{-1} shift of excimer peak from the monomer emission. This fact may allow us to suppose that an excimer in solid at 205 °K is a similar species to that in solution.

At 77 °K the center of broad emission shifts to higher energy by 1000 cm^{-1} or more. This shift may be regarded as corresponding to the 770 cm^{-1} shift in the case of 1-MN by rapid freezing. The excimer fluorescence of naphthalene at 77 °K has been reported in rigid matrix.(10) In cyclohexane solution the slow freezing is a more favorable cooling method for observation of the excimer emission in marked contrast to the case of 1-MN in this paper. Because in rigid matrix, educing solute molecules from the solvent by the slow freezing and aggregating it are essential for producing excimer. On the other hand, in pure solid it seems necessary to produce a sufficient amount of defects of lattice by rapid freezing.

2. Naphthalene Crystal B

In the case of β-substituted naphthalene in the solid state, the behavior of the emissions are completely different from those of α-substituted naphthalenes. There is a phenomenon that the emission intensities of sublimation flakes change on the exposure of the exciting light at room temperature. In 2,6-DMN and naphthalene crystal C the intensities of the emission increase, on the other hand that of naphthalene crystal B decreases. In both naphthalene and 2,6-DMN crystals, the emission spectra and distinction of decay or growth of its intensities and extent of it seem to depend upon a condition under which the crystal has grown. And naphthalene crystals which show spectrum B (Fig. 6) in one part and spectrum A in another part of one crystal can be obtained. These facts suggest that these phenomena might be connected with imperfections in the crystal. Observations of evaporation pits of naphthalene crystals by simple evaporation(11) and a study of dislocations(12) using a chemical etchant have been reported. According to the above consideration, let us compare spectrum B to spectrum A in Fig. 6. The fact that in spectrum B the higher energy region is quenched may be considered as an effect of crystal imperfections. Crystals which show spectrum B might contain a larger number of crystal imperfections than that of spectrum A.† This consideration is consistent with the fact that many wrinkles are observed in the surface of a crystal B.

By the excitation a force between excited and unexcited molecules takes place and gives rise to rearrangements of molecules in imperfection regions of a crystal, in which molecules aggregate so as to allow displacement upon excitation. The association between excited and unexcited molecules in concentrated solution of naphthalene and its derivatives is well known.(16) In the case of 1-MN, occurrence of displacements of excited molecules in the crystalline state is ensured by the observation of excimer emission for a sample of rapid freezing in the present experiment. First the growth of 24390 cm^{-1} emission band of naphthalene crystal B is considered. If in some crystal imperfection whose total number is initially given, emission centers having an emission band at some energy region will grow in proportion to the number of imperfections that exist at a time t. The emission intensity at that energy increases in proportion to the function $(1-e^{-bt})$. Experimental points of the growth of 24390 cm^{-1} emission fits to curve B in Fig. 7 corresponding $b = 0.105$. Second we consider the decay curve of the emission at 29580 cm^{-1}. If a crystal contains the number n of quenching center for the emission of crystal, the relative intensity of emission is expressed as

$$I/I_0 = \frac{1}{1+nK} \tag{1}$$

where K is constant. If quenching centers create in proportion to a number of the remaining imperfections capable of producing a

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† The emission spectrum of naphthalene crystal at room temperature was referred to in Refs. 13 and 14. The emission spectrum of 2,6-DMN crystal at 4.2°K appears in Ref. 15 and main emission bands consist with the present spectrum B in Fig. 12. The fluorescence spectra of solutions of 1-MN, 1,6-DMN and 2,6-DMN were referred to those in Ref. 9 and close agreements between the two were obtained.

center, time dependent relation for emission intensity should be expressed as

$$I(t) = \frac{1}{1+D(1-e^{-bt})} \tag{2}$$

where D and b are constants.

Now we must take into account a quenching of 29580 cm^{-1} emission band by the center which has an emission band around 24390 cm^{-1}. This center will grow with the same time constant as that of growth of 24390 cm^{-1} emission. However, the intensity of this emission is only one part in fifty of the 29580 cm^{-1} emission, therefore we could not attribute its center to be main source for quenching of 29580 cm^{-1} emission, even if a low emission efficiency of the center is taken into consideration. Then we must introduce another kind of quenching center. In the case that a crystal contains two kinds of crystal imperfections, and in each imperfection one kind of quenching center, creates with a different time constant, a change of emission intensity as:

$$I(t) = \frac{1}{1+D(1-e^{-bt})+D'(1-e^{-b't})} \tag{3}$$

A typical experimental result of decay in emission intensity fits successfully to the solid curve calculated for Eq. (3) corresponding to $D = 0.606$, $b = 0.105$, $D' = 7.680$, $b' = 0.10172$. Thus we conclude that a naphthalene crystal B contains two kinds of imperfections and by irradiation a number of quenching centers increases by the limit determined by the total number of each kind of imperfections. One of two kinds of quenching centers has a broad emission peaking a 26900 cm^{-1}. This emission is like, to that extent, the spectrum at high pressure(8) or the excimer emission in solution. However the peak of this emission lies higher by 1350 cm^{-1} than that in solution. Its value is still more than 770 cm^{-1} in the case of 1-MN.

3. 2,6-Dimethylnaphthalene Crystal

In 2,6-DMN crystals, contrary to naphthalene crystals B, emission intensity increases by irradiation. On the exposure of the exciting light upon a 2,6-DMN crystal, creation of evaporation pits is prohibited and rapid evaporation is halted. These facts suggest a possibility that in imperfection regions where evaporation pits will originate, displacements of molecules upon excitation lead to the disappearance of imperfections. As a result, the number of defects decreases and so radiationless consumption of excitation energy decreases. In this manner the increase in intensity of the emission occurs in a crystal of 2,6-DMN. The appearance of the emission band around 29940 cm^{-1} by irradiation, which is assigned to the crystal emission,(15) adds to the above interpretation. If the number of quenching centers which are initially given over a crystal decreases proportionately with the number of centers that exist at a time t, the time-dependent relation of emission intensity is represented as

$$I(t) = \frac{1}{1+D\,e^{-bt}} \tag{4}$$

where D and b are constants.

For the purpose of adjusting the initial rising of increase curve to the experimental points in Fig. 13, a correction term which means a small amount of creation of quenching center must be introduced. Thus the following expression is obtained :

$$I(t) = \frac{1}{1+D(1-e^{-bt})}\, X\, \frac{1}{1+D'\,e^{-b't}} \tag{5}$$

where $D = 0.05$, $b = 3.0$, $D' = 2.675$, $b' = 0.34$.

In Eq. (5), the first term represents a small amount of rapid creation of quenching centers and the second term expresses increase of emission intensity by the disappearance of imperfections in the crystal.

4. NAPHTHALENE CRYSTAL C

Now we consider the third kind of naphthalene crystal (crystal C). The emission intensity of this kind of crystal increases and then decreases. It seems appropriate to consider that in this phenomenon the increase of emission occurs through the same mechanism as in 2,6-DMN and the decrease arises from the same reason as in naphthalene crystal B. Namely simultaneously with disappearance of imperfections, creation of quenching centers occurs upon excitation. As seen in 2,6-DMN, disappearance of imperfections, not accompanied by a large amount of quenching centers, gives rise to an increase in all the spectral region. The fact that increase of emission in naphthalene crystal C occurs only in the energy region lower than 29580 cm^{-1} can be explained with the above interpretation. Contrast with the clear appearance of the surface with irradiation in 2,6-DMN, creation of bubbles occurs in naphthalene crystal C. This phenomenon seems to be caused from displacements of molecules for creating quenching center (seemingly strong interacting molecules) at imperfection region of crystal where displacement of molecules is more intense than in the case of naphthalene crystal B. Change of emission intensity at 29580 cm^{-1} can be approximately described by the following relation,

$$I(t) = \frac{1}{1 + D(1 - e^{-bt}) + D'(1 - e^{-b't})} X \frac{1}{1 + D'' e^{-b''t}} \tag{6}$$

where $D = 250.0$, $b = 0.006$, $D' = 2.0$, $b' = 4.5$, $D'' = 16.0$, $b'' = 2.7$. The above equation is a better approximate expression than the following:

$$I(t) = \frac{1}{1 + D(1 - e^{-bt}) + D'(1 - e^{-b't}) + D'' e^{-b''t}} \tag{7}$$

This fact suggests the disappearance of imperfection which might mean in this case ones that lie at the boundary of the microcrystal, occurs somewhat in a macroscopic scale, on the other hand creation of a quenching center occurs in a microscopic scale.

The reason why quenching centers are created in naphthalene crystal by irradiation and not in 2,6-DMN may depend upon a character of molecule. One reason may be that a strong interacting molecule of 2,6-DMN is more unstable than that of naphthalene due to the steric hindrance of the two methyl groups. In the case of anthracene two kinds of dimer were observed and both of these have been suggested to be important as a crystal defect.(17,18) The studies in anthracene, though anthracene is photochemically more active than naphthalene, may be helpful for an investigation about the structure of defect or quenching centers in naphthalene crystal.

Conclusions

Emission spectra of four naphthalenes in the crystalline state with variation of conditions of crystallization have been measured. Crystals which seem to include rather many imperfections showed the excimer emission in α-substituted naphthalenes and showed partically quenched emissions whose intensities changed under excitation in naphthalene or 2,6-DMN. It has been described that the molecules at an imperfection region of crystal composes a sandwich dimer reversibly upon excitation in α-substituted naphthalenes. On the other hand, in a 2,6-DMN crystal disappearance of imperfections occurs irreversibly and consequently the emission intensity increases. In naphthalene crystal B creation of quenching centers originates and so the emission intensity decreases. In naphthalene crystal C, both disappearance of imperfections and creation of quenching centers start simultaneously and as a result the emission intensity increases and after that decreases.

REFERENCES

1. Dammers-De Klerk, A., *Mol. Phys.* **1**, 141 (1958).
2. Döller, E. and Förster, Th., *Z. Phys. Chem.* **31**, 274 (1962).
3. Förster, Th. and Kasper, K., *Z. Phys. Chem. NF.* **1**, 19 (1954).
4. Förster, Th. and Kasper, K., *Z. Electrochem.* **59**, 976 (1955).
5. Ferguson, J., *J. Chem. Phys.* **28**, 765 (1958).
6. Tanaka, J., *Bull. Chem. Soc. Japan* **36**, 1237 (1963).
7. Schnaithmann, R. and Wolf, H. C., *Z. Physik, Chem.* (Frankfurt) **31**, 274 (1962).
8. Jones, P. F. and Nicol, M., *J. Chem. Phys.* **43**, 3759 (1965).
9. Wolf, H. C., *Z. Naturforsch.* **10a**, 270 (1955).
10. Kawakubo, T., Okada, M. and Shibata, T., *J. Phys. Soc. Japan* **21**, 1469 (1966).
11. Sears, G. W., *J. Chem. Phys.* **37**, 2155 (1962).
12. McGhie, A. R., Reucroft, P. J. and Labes, M. M., *J. Chem. Phys.* **45**, 3163 (1966).
13. Zima, V. L. and Faidysh, A. N., *Optics and Spectro.* **19**, 203 (1966).
14. Reed, C. W. and Lipsett, F. R., *J. Mol. Spect.* **11**, 139 (1963).
15. Benarroche, M., *Ann. Phys.* (Paris) **2**, 27 (1967).
16. Aladekomo, J. B. and Birks, J. B., *Proc. Roy. Soc.* A **284**, 551 (1965).
17. Chandross, E. A. and Ferguson, J., *J. Chem. Phys.* **45**, 3554 (1966).
18. Chandross, E. A., Ferguson, J. and McRae, E. G., *J. Chem. Phys.* **45**, 3546 (1966).