BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 685—689 (1969)

Zeeman Effect of Phosphorescence. II. Intensity Considerations on Pyrazine Phosphorescence

Tohru AZUMI, Mitsuo ITO and Saburo NAGAKURA

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

(Received August 10, 1968)

The Zeeman splitting of pyrazine phosphorescence is observed. The amount of splitting is 1.4 cm^{-1} under the magnetic field of 15 kilogauss. This magnitude is just what one expects for the free spin, which means that the zero-field splitting parameters are small compared with the observed splitting. On the assumption of random orientations of the pyrazine molecules in the sample, the phosphorescence intensities from the three split subcomponents are expected to be in the ratio of $13g_1 : 16g_0 : 13g_{-1}$ where g's represent populations. This expectation is roughly manifested in the experimental observation. Finally, the theoretical calculation of the zero-field splitting parameters, D and E, is attempted, and the results are interpreted in terms of the experimental data.

Phosphorescence of organic molecules was interpreted by Terenin[1] and by Lewis and Kasha[2] to be the multiplicity forbidden emission; namely, for majority of organic molecules where the ground state is singlet, Jablonski's "phosphorescent state"[3] was identified as the triplet state. Since then, considerable efforts have been devoted to date to substantiate the mechanism suggested by these authors. It is at present the usual notion that the triplet nature of the phosphorescent state is fairly well established. However, it seems not unworthy to recall these efforts and to judge how much the usually accepted notion is founded.

Probably, the most direct works reported so far along this line are the measurements of paramagnetic susceptibility[4] in earlier days and the recent ESR measurements of the excited triplet state.[5] These works have revealed that the triplet state is produced by irradiation of solid solution of organic molecules by ultraviolet light and that it decays in a manner nearly identical to phosphorescence. The triplet state is considered simultaneously the phosphorescent state because of the *approximate* identity of the decay mode. Other evidence which shows the spin forbidden character of the phosphorescence comes from the heavy-atom effect, both intramolecular and intermolecular: McClure[6] found that the

---

[1] A. Terenin, *Acta Physicochem. USSR*, **18**, 210 (1943).

[2] G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).

[3] A. Jablonski, *Z. Physik*, **94**, 38 (1935).

[4] G. N. Lewis and M. Calvin, *J. Am. Chem. Soc.*, **67**, 1232 (1945).

[5] C. A. Hutchison and B. W. Mangum, *J. Chem. Phys.*, **29**, 952 (1958); J. H. van der Waals and M. S. de Groot, *Mol. Phys.*, **2**, 333 (1959); W. A. Yager, E. Wasserman and K. M. R. Cramer, *J. Chem. Phys.*, **37**, 1148 (1962).

[6] D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

introduction of heavy atoms such as halogen and sulfur to hydrocarbon molecules decreases the phosphorescence lifetime considerably, and that this lifetime decrease is quantitatively explained by the increase of spin-orbit coupling in the presence of heavy atom. The decrease of the phosphorescence lifetime in the heavy atom containing solvents is also interpreted by McGlynn[7] in a similar manner.

As is seen in the two examples cited above, the phosphorescence *lifetime* data have frequently been presented as evidence supporting the identity of the phosphorescent state to the triplet state. However, conclusions based on lifetime data are not unique, and can not be served as a conclusive evidence. For, it is not certain whether the phosphorescent state is simultaneously the triplet state itself or is a certain kinetically rate-limiting state or species produced *via* the triplet state. In view of the long lifetime of the triplet state and its potency to photochemical reactions this suspicion does not seem too unrealistic. A pertinent example is delayed thermal fluorescence,[8] or *alpha*-phosphorescence[9] in the widely used, but somewhat misleading, terminology.[10] This emission consists of thermal excitation to the singlet excited state followed by fluorescence emission. Even though its lifetime is identical to that of the phosphorescence, the emission starts out actually from the singlet state and not from the triplet state.

As described above many experiments carried out to date do not necessarily present conclusive evidence of the triplet nature of the phosphorescence. One might suppose that a Zeeman splitting of the phosphorescence would provide the most unambiguous verification of the triplet nature of the phosphorescent state. This experiment was already suggested by Weisman and Lipkin[16] in 1942; however, no attempts have been reported to date. The lack of such attempts is probably due to the difficulty in observing the phosphorescence spectrum sharp enough to resolve the Zeeman slpitting.

As reported in a previous paper[17] we have succeeded to observe the Zeeman splitting of the phosphorescence of pyrazine crystal. The pyrazine crystal was chosen because it emits fairly intense and quite sharp phosphorescence at 4.2°K. Moreover, for n,π^* triplet excited states of aza-aromatics ESR measurements have never been succeeded, and the phosphorescence measurements under magnetic field are likely to be the only means of identifying the three spin subcomponents. The present paper concerns the detailed analyses of this observation.

Experimental

Pyrazine was purified by repeated (seven times) sublimations in vacuum between room temperature and the dry ice temperature. After the final step of sublimation, the sample was transferred to a quartz cell and the cell was sealed off. All procedures were carried out in vacuum and a contact with air was rigorously avoided.

The emission was taken at 4.2°K in a polycrystalline form. A liquid helium cryostat was placed between the poles of a JEOL JM210 magnet. The magnetic field applied was 15400 gauss. Excitation was effected to the region of $^1B_{2u}(\pi,\pi^*)$ excited state with light from a 500 W high pressure mercury lamp passed through a following filter combination: (1) Toshiba's glass filter UV-D2, (2) 1 cm path of 10^{-3}M K_2CrO_4 aqueous solution, and (3) 1 cm path of $NiSO_4$ and $CoSO_4$ mixed aqueous solution (0.55M and 0.15M, respectively). Because of the geometrical limitations a phosphoroscope was not used. The emission spectrum thus obtained was identical to that obtained with a Becquerel type phosphoroscope and without any filters. The emission was photo graphed on a Kodak 103a-F plate in the second order of a 1200 grooves/mmg rating (blaze at 5000 Å) mounted on a Spex Spectrometer Model 1700-II.

Results

The detailed analyses of the phosphorescence spectrum as well as of the singlet to triplet absorption spectrum will be published elsewhere. Our

---

[7] S. P. McGlynn, M. R. Reynolds, G. W. Daigre and N. Christodouleas, *J. Chem. Phys.*, **66**, 2499 (1962); S. P. McGlynn, J. Daigre and F. J. Smith, *ibid.*, **40**, 507 (1964).

[8] S. P. McGlynn, T. Azumi and M. Kinoshita, "The Molecular Spectroscopy of the Triplet State," Prentice Hall, New Jersey (1968).

[9] G. N. Lewis, D. Lipkin and T. T. Magel, *J. Am. Chem. Soc.*, **63**, 3005 (1941).

[10] There have been numerous terminologies for this process and is sometimes confusing. In earlier days Pringsheim[11] merely called this process "phosphorescence," while Förster[12] called it "high temperature phosphorescence." Terminologies used in recent days are: "*alpha*-phosphorescence" by Lewis, Lipkin, and Magel,[9] "E-type delayed fluorescence" by Parker and Hatchard,[13] "slow fluorescence" by Windsor,[14] and "*alpha*-delayed fluorescence" by Lower and El-Sayed.[15] We use the term "delayed themal fluorescence" following the suggestion of Ref. 8.

[11] P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, New York (1949).

[12] Th. Förester, "Fluoreszenz Organischer Verbindungen," Vandenhoeck Ruprecht, Göttingen (1951).

[13] C. A. Parker and C. G. Hatchard, *Trans. Faraday Soc.*, **57**, 1894 (1961).

[14] M. W. Windsor, "Physics and Chemistry of the Organic Solid State," Vol. 1, Interscience Publishers, New York (1964).

[15] S. K. Lower and M. A. El-Sayed, *Chem. Revs.*, **66**, 199 (1966).

[16] S. I. Weisman and D. Lipkin, *J. Am. Chem. Soc.*, **64**, 1916 (1942).

[17] T. Auzmi, Y. Udagawa, M. Ito and S. Nagakura, *J. Chem. Phys.*, **47**, 4850 (1967).

[18] M. Ito and T. Shigeoka, *ibid.*, **44**, 1001 (1966).

interest is now focussed on the four emission lines near the onset of the spectrum which are quite sharp and intense, and are consequently suited to Zeeman effect experiments. The group of these four lines are repeatedly found in progressions of 606, 759, 953, and 1254 cm^{-1}. In view of the agreement of these progressions with the Raman frequencies,[18] the above mentioned four lines are interpreted to be due to pyrazine.[19] The effect of magnetic field on these lines is shown in Fig. 1.

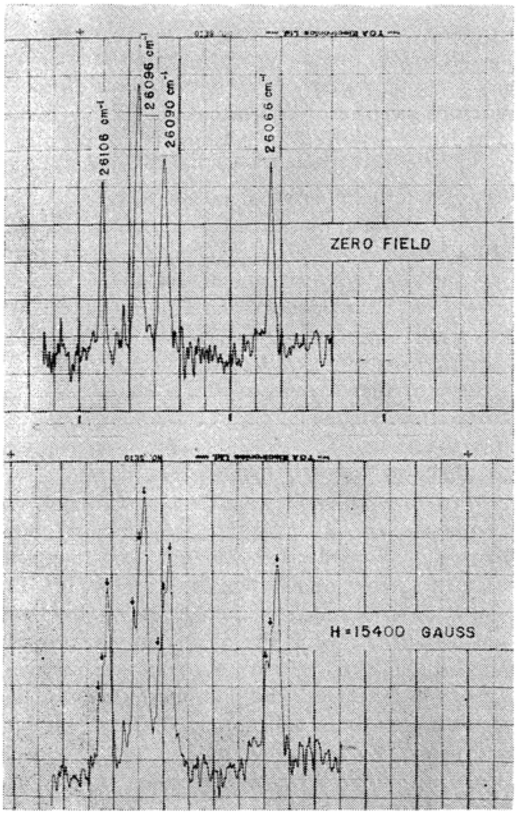

Fig. 1. Zeeman effect of the phosphorescence of pyrazine crystals.

It is immediately clear that magnetic field splitts the emission lines into the three subcomponents, as are indicated by arrows. For all the four lines, separation between two nearest subcomponents is approximately 1.4 cm^{-1}. Also, Fig. 1 clearly indicates that the lower energy subcomponent emitts more intensely than the higher one. This marked difference in intensity might at first seem quite natural in view of the population differences. However, noting that the phosphorescence intensities are determined not only by population but also, more importantly, by the matrix elements connecting the upper and the lower levels, one needs to consider further. The following discussion concerns this point.

Discussion

In analyzing the above results we have, in principle, to consider the effect of magnetic field on the triplet excitons. However, the nature of the triplet excitons is not sufficiently enough understood for pyrazine crystal to warrant detailed analysis. Further, it is believed that the intermolecular interaction is not very significant as compared with the effect of magnetic field. Hence, as a preliminary approach, in the following, we neglect any intermolecular interaction.

Let the lowest triplet state be produced by an excitation of an electron from a molecular orbital ϕ_a to a molecular orbital ϕ_b.[20] We choose the following zeroth order triplet eigenfunctions:

$$\begin{aligned} |T_x\rangle &= 2^{-1/2}(|\bar{\phi}_a\bar{\phi}_b| - |\phi_a\phi_b|) \\ |T_y\rangle &= 2^{-1/2}(|\bar{\phi}_a\bar{\phi}_b| + |\phi_a\phi_b|) \\ |T_z\rangle &= 2^{-1/2}(|\phi_a\bar{\phi}_b| + |\bar{\phi}_a\phi_b|) \end{aligned} \tag{1}$$

The Hamiltonian for Zeeman effect is represented by

$$\mathscr{H} = g\beta\mathrm{H}(lS_x+mS_y+nS_z) + DS_z^2 + E(S_x^2-S_y^2) \tag{2}$$

where l, m, and n are direction cosines of molecular axes, x, y, and z, respectively, with the field direction, and D and E are the zero-field splitting parameters. The displacement of the triplet levels due to (2) should be asymmetric because of the terms involving D and E. However, as pointed out above, within the accuracy of our experiments both the higher and the lower energy subcomponents are displaced from the middle component by 1.4 cm^{-1}. Furthermore, the amount of 1.4 cm^{-1} is just one expects from the term $g\beta\mathrm{H}$ under the magnetic field of 15400 gauss. It is consequently assumed that the terms involving D and E may be neglected. The eigenvectors $|T_1\rangle$, $|T_0\rangle$, and $|T_{-1}\rangle$ are then easily obtained as

$$\begin{pmatrix} |T_1\rangle \\ |T_0\rangle \\ |T_{-1}\rangle \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{1-l^2}{2}} & \frac{n+ilm}{\sqrt{2(1-l^2)}} & \frac{-(nl+im)}{\sqrt{2(1-l^2)}} \\ l & im & n \\ \sqrt{\frac{1-l^2}{2}} & \frac{n-ilm}{\sqrt{2(1-l^2)}} & \frac{-(nl-im)}{\sqrt{2(1-l^2)}} \end{pmatrix} \begin{pmatrix} |T_x\rangle \\ |T_y\rangle \\ |T_z\rangle \end{pmatrix} \tag{3}$$

For the spin-forbidden phosphorescence to be observed, there must be a singlet state, or states, which may mix with the lowest triplet state by

---

[19] These lines, however, do not coincide with the onset of the singlet to triplet absorption. Detailed examinations have revealed that these are due to the pyrazine molecule at some crystalline defects. T. Auzmi, Y. Nakano and M. Ito, to be published.

[20] Here, configuration interactions with other singly excited or with doubly excited configurations are not considered. However, the inclusion or them does not alter the conclusions.

spin-orbit interaction, and further may have a dipole allowed transition to the ground state. Alternatively, one may consider a mechanism in which the singlet ground state mixes with a triplet state by the spin-orbit interaction. However, as far as group theoretical cansiderations are concerned, these two mechanisms result in identical conclusions; hence, in the following treatment, only the perturbation to the lowest triplet state is considered. Spin-orbit interaction is, in general, expressed as the sum of one-electron and two-electron operators;[21] however, only the former is considered here. Specifically,

$$\mathscr{H}_{\mathrm{so}} = \sum_i \xi_i l_i s_i \tag{4}$$

Restricting the spin-orbit interaction to one-electron operator, the singlet state which may mix with the triplet state is only of the type

$$|S\rangle = 2^{-1/2}(|\phi_a\bar{\phi}_c| + |\phi_c\bar{\phi}_a|) \tag{5}$$

here the molecular orbital ϕ_c is chosen so that the transition between $|S\rangle$ and the ground state is dipole-allowed. The matrix elements for the spin-orbit interaction are now readily obtained as follows:

$$\begin{aligned}\langle S|\mathscr{H}_{\mathrm{so}}|T_x\rangle &= -(h/4\pi)\xi\langle\phi_c|l_x|\phi_b\rangle\\ \langle S|\mathscr{H}_{\mathrm{so}}|T_y\rangle &= \ i(h/4\pi)\xi\langle\phi_c|l_y|\phi_b\rangle\\ \langle S|\mathscr{H}_{\mathrm{so}}|T_z\rangle &= -(h/4\pi)\xi\langle\phi_c|l_z|\phi_b\rangle\end{aligned} \tag{6}$$

In the expansion of the integrals over *molecular orbitals* in (6) in terms of integrals over *atomic orbitals*, we choose to neglect all multi-center integrals other than the one-center terms. With this approximation, and further if the molecular axes are chosen[22] as shown in Fig. 2, it is immediately clear that the first and the third integrals in (6) necessarily vanish since the operator l transform like rotation. It is, therefore, concluded that only the $|T_y\rangle$ component is emissive.

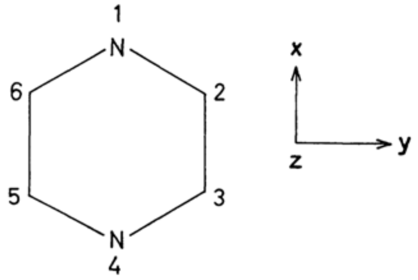

Fig. 2. Molecular axes and the numbering of atoms in pyrazine molecule.

Let the phosphorescence intensities from the three subcomponents, $|T_1\rangle$, $|T_0\rangle$, and $|T_{-1}\rangle$ be denoted by I_1, I_0, and I_{-1}. Then from (3)

$$I_1 : I_0 : I_{-1} = [(1-m^2)/2]g_1 : m^2g_0 : [(1-m^2)/2]g_{-1} \tag{7}$$

where g_1, g_0, and g_{-1} denote the population of the three subcomponents.

The relationship expressed by (7) may be verified using an oriented sample; this is the subject we are presently attempting to work. In the present case, however, the sample is polycrystalline and the above relationship can not be used as it is. In what follows intensity relationship is derived on the assumption that our polycrystalline sample is randomly oriented. The discussion closely follows that of photoselection by Albrecht.[24] Two sets of coordinates are defined, the laboratory-fixed set (a, b, c) and the molecule-fixed set (x, y, z). Assigning these a common origin we then specify the orientation of a molecule in using Eulerian angles θ, ϕ, and ψ. The cosines of the angles between the axes of the two sets of coordinates are denoted by t_{ax}, *etc.*

Let unpolarized exciting light be incident along b axis onto the ac face, and the phosphoresecnce is viewed also along b axis. In our experimental setup the magnetic field is applied along c axis, and therefore $m^2 = t_{cy}^2$. The exciting light is absorbed mainly to $^1B_{2u}(\pi,\pi^*)$ state (y axis). As determined by Krishna and Goodman,[25] phosphorescence is polarized along x axis. In the case of $^1B_{2u}(\pi,\pi^*)$ excitation, the probability that a single molecule at θ, ϕ, and ψ is photoselected is $(t_{ay}^2+t_{cy}^2)/2$, while the probability of viewing the phosphorescence with unpolarized light is $(t_{ax}^2+t_{cx}^2)/2$. Then, the phosphorescence intensities from the three subcomponents are expressed as:

$$\begin{aligned}I_1 : I_0 : I_{-1} = {} & g_1(t_{ay}^2+t_{cy}^2)(t_{ax}^2+t_{cx}^2)(1-\tfrac{1}{2}t_{cy}^2) :\\ & g_0(t_{ay}^2+t_{cy}^2)(t_{ax}^2+t_{cx}^2)t_{cy}^2 :\\ & g_{-1}(t_{ay}^2+t_{cy}^2)(t_{ax}^2+t_{cx}^2)(1-\tfrac{1}{2}t_{cy}^2)\end{aligned} \tag{8}$$

This expression should be integrated over the Eulerian angles

$$\int_0^{\pi}\sin\theta\,d\theta\int_0^{2\pi}d\phi\int_0^{2\pi}d\psi$$

The final results for $^1B_{2u}(\pi,\pi^*)$ excitation is

$$I_1 : I_0 : I_{-1} = 13g_1 : 16g_0 : 13g_{-1} \tag{9}$$

Similarly for $^1B_{1u}(n,\pi^*)$ excitation,

$$I_1 : I_0 : I_{-1} = 8g_1 : 5g_0 : 8g_{-1} \tag{10}$$

If these ratios are calculated with the Boltzmann distribution at 4.2°K for three substates that are 1.4 cm^{-1} apart successively,

---

[21] H. A. Kramers, "Quantum Mechanics," North-Holland Publishing Co., Amsterdam (1957).

[22] This choice of axes, which is different from that of Mulliken's recommendation,[23] is convenient since the familiar form of Eq. (2) is consistent with the condition, $D > 3E > 0$.

[23] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1997 (1955).

[24] A. C. Albrecht, *J. Mol. Spectry.*, **6**, 84 (1961).

[25] V. G. Krishna and L. Goodman, *J. Chem. Phys.*, **36**, 2217 (1961).

$$I_1 : I_0 : I_{-1} = 1.0 : 0.76 : 0.38 \quad \text{for } {}^1\mathrm{B}_{2u}(\pi,\pi^*) \text{ excitation} \tag{11}$$

and

$$I_1 : I_0 : I_{-1} = 1.0 : 0.39 : 0.38 \quad \text{for } {}^1\mathrm{B}_{1u}(n,\pi^*) \text{ excitation} \tag{12}$$

It is, at this stage, impossible to obtain the accurate intensity ratio from Fig. 1, for there is, to a certain extent, a band overlap, and also the ordinate in the microphotometer tracing is not calibrated to intensity scale. Moreover, our polycrystalline sample can not be expected to be perfectly random. Yet, it is evident from Fig. 1 that the intensity relationship is more in conformity with the ${}^1\mathrm{B}_{2u}$-(π,π^*) excitation, which is just we expect from our experimental condition. (*vide supra*).

Conclusions and Remarks

The Zeeman splitting of the phosphorescence was observed for pyrazine and thereby the triplet nature of the phosphorescence is definitely substantiated. The observed intensities of the three phosphorescence subcomponents are roughly in agreement with theoretical predictions. It may also be concluded that the population of the three triplet subcomponents is governed by the Boltzmann distribution at 4.2°K.

In the above discussions we have adopted a number of approximations. In the first place our discussion is confined to the case of the pyrazine solution in which solutes are oriented randomly. Although this treatment is in principle unjustified for polycrystalline sample, it may be justified in rough estimates. More detailed analysis on triplet excitons are the subject of future investigations. We have further neglected the zero-field splitting parameters, D and E. This approximation was based on our experimental data on energy splitting. However, it is not immediately certain if this assumption is also valid when intensities are evaluated in a manner discussed above. Unfortunately, there have not been any ESR observations for pyrazine triplet state, and no data are available, at present, for the zero-field splitting parameters. In view of the lack of data, theoretical evaluations of these values are of interest and are attempted in Appendix.

We wish to express our appreciation to Professor Shigeo Shionoya and his associates for their kindness in letting us use the magnet and the cryostat. We are also grateful to Mr. Yasuo Udagawa for experimental assistance and for stimulating discussions.

Appendix

Calculations of the Zero-Field Splitting Parameters. The purpose of this calculation is to obtain an order of magnitude of D and E values, and hence, semi-empirical approach is adopted.

The molecular orbitals are obtained by the usual Pariser-Parr-Pople method. The coordinates of atoms in pyrazine molecule are taken from the results of an X-ray analysis by Wheatley.[26] Ionization potentials and electron affinities are taken from the table of Pilcher and Skinner.[27] Zero-differential overlap is assumed throughout and penetration integrals are neglected. Two-center repulsion integrals are calculated by uniformly charged sphere model formula given by Pariser and Parr.[28] Core resonance integrals between adjacent atoms are chosen to proportional to overlap integrals, and

$$\begin{aligned}\beta_{\mathrm{CC}} &= -2.526\,\mathrm{eV}\\ \beta_{\mathrm{CN}} &= -2.162\,\mathrm{eV}\end{aligned} \tag{A1}$$

The lowest vacant SCF molecular orbital, π_4^*, thus obtained[29] is

$$\pi_4^* = -0.5349(\chi_1+\chi_4) + 0.3270(\chi_2+\chi_3+\chi_5+\chi_6) \tag{A2}$$

where χ_r is $2p\pi$ atomic orbital on rth atom and where numbering of atoms is shown in Fig. 2.

The lowest triplet state may be successfully expressed by a single configuration of the type (n_-,π_4^*), where n_- represents the minus combination of the two nitrogen nonbonding orbitals. Only configuration which has the same symmetry species with this is of the type (n_+,π_6^*), but because it locates at higher energy, the mixing may well be neglected.

The one-center integrals are computed exactly from the SCF atomic orbitals expanded in Slater orbitals by Clementi and Roothaan[30] by means of analytical formulas given by Higuchi.[31] The final results are[32]

$$D = 0.31\,\mathrm{cm}^{-1} \text{ and } E = 0.01\,\mathrm{cm}^{-1}.$$

The value of D thus obtained is a little larger than the D values for π,π^* triplet states of aromatic hydrocarbons, and is roughly in the same order of magnitude as those of n,π^* ground state obtained experimentally[33,34] and theoretically.[31] It is consequently believed that the calculated values are not much off.[35] If this asertion is correct, the zero-field splitting is not very significantly small compared with the Zeeman splitting, and might be observed in a high resolution work.

---

26) P. J. Wheatley, *Acta Cryst.*, **10**, 182 (1957).

27) G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).

28) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

29) The computations were carried out with a HITAC 5020 in Computer Center, The University of Tokyo. We are grateful to Mr. Fumihiko Hirota in this laboratory for a computer program for SCF.

30) E. Clementi and C. C. J. Roothaan, *Phys. Rev.*, **127**, 1618 (1962).

31) J. Higuchi, *J. Chem. Phys.*, **38**, 1237 (1963).

32) The use of a single Slater orbital, the exponent being determined by the Slater recipe, in calculating the one-center terms yields: $D=0.16\,\mathrm{cm}^{-1}$ and $E=0.02\,\mathrm{cm}^{-1}$.

33) A. M. Trozzolo, R. M. Murray and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4990 (1962).

34) G. Smolinsky, E. Wasserman and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3220 (1962).

35) Rough estimate given by Sternlicht yields: $D=2E=0.78$. H. Sternlicht, *J. Chem. Phys.*, **38**, 3216 (1963).