

huis.<sup>14</sup> When  $M_s = \pm 1/2$ , the major component of the spin vector is in the  $xy$  plane and the nucleus will sense this component provided that the precession time of the spin vector about the  $z$  axis is long compared to the Larmor precession time of the nuclear spin. Oosterhuis estimates that the precession time will be  $10^{-8}$  sec or greater if the magnetic field along the  $z$  axis (due to neighboring magnetic dipoles in the lattice) is about 10 G; this is sufficiently long to observe magnetic broadening. If this explanation is correct, the phenomenon should be general for these high spin ferric

(14) W. Oosterhuis, Carnegie-Mellon University, private communication.

compounds with large positive  $D$ , and its extent will depend on the magnitude of the adventitious magnetic field along the  $z$  axis. One might suppose this broadening could be quenched by application of a modest external field ( $< 1000$  G), although attempts by Oosterhuis to observe such a quenching have so far been unsuccessful.<sup>14</sup>

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## Pyridinium Iodide Salts. Correlation of Experimental Parameters with Self-Consistent Extended Hückel (SCEH) Calculations

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**Abstract:** Pyridinium iodide salts possess an iodide to ring charge-transfer (CT) band; two such bands are generally observed in nonpolar solvents. Both the absolute and relative energies of these bands are sensitive to the nature and position of the substituent on the pyridinium ring, as well as to the nature of the solvent. Self-consistent extended Hückel (SCEH) calculations have been performed for the unsubstituted and the 2-, 3-, and 4-cyano (and acetyl) pyridinium ions. The calculated difference between the energy of the first (lowest) and second (next highest) vacant molecular orbital of the pyridinium ion is in good agreement with the observed separation of the two CT bands in methylene chloride. This supports other experimental results which indicate that the second CT band does not arise from the excited state ( $^2P_{1/2}$ ) of the iodine atom. These and other results of the calculation are discussed in terms of various experimental parameters.

The first (long wavelength) electronic absorption band of pyridinium iodide salts has been studied extensively. It arises from charge transfer from iodide to the pyridinium ion.<sup>1,2</sup> In nonpolar solvents a second CT band, at shorter wavelength than the first, is observed and has been ascribed to the first excited state of the iodine atom ( $^2P_{1/2}$ ).<sup>3</sup> Recent experimental results indicate that the second band may in fact result from charge transfer to the second vacant molecular orbital of the pyridinium ion.<sup>2,4</sup> We have therefore performed self-consistent extended Hückel (SCEH) calculations on various pyridinium ions and compared the results with experimental parameters including CT band energies.

### Calculations and Experimental

The calculations were performed by the method suggested by Harris<sup>5</sup> using a modified procedure of Kalman

(1) E. M. Kosower and J. A. Skorcz, *J. Amer. Chem. Soc.*, **82**, 2195 (1960).

(2) R. A. Mackay, J. R. Landolph, and E. J. Poziomek, *ibid.*, **93**, 5026 (1971), and references therein.

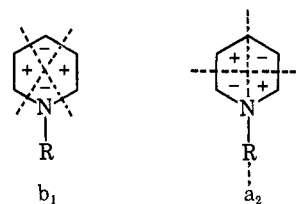
(3) E. M. Kosower, J. A. Skorcz, W. M. Schwarz, Jr., and J. W. Paton, *ibid.*, **82**, 2188 (1960).

(4) J. W. Verhoeven, I. P. Dirks, and Th. J. de Boer, *Tetrahedron*, **25**, 3395 (1969).

and Clarke.<sup>6</sup> All valence orbitals and electrons were included. The electron affinities of the pyridinium ions were taken as the negative of the ionization potential of the corresponding pyridinyl radicals. The band energies and the rate constants were determined in methylene chloride.<sup>2</sup>

### Results and Discussion

**Band Energies.** The lowest unoccupied molecular orbital (LUMO) in benzene is a doubly degenerate  $\pi$  orbital ( $E_{2u}$  in  $D_{6h}$ ) and on going to pyridine or pyridinium ion splits into  $b_1$  and  $a_2$  (in  $C_{2v}$ ). These orbitals are shown below. The dotted line indicates the nodes.



The lowest energy orbital has been assigned as  $b_1$  by Kosower and Poziomek on the basis of infrared

(5) F. E. Harris, *J. Chem. Phys.*, **48**, 4027 (1968).

(6) B. Kalman and G. Clarke, *ibid.*, submitted for publication.

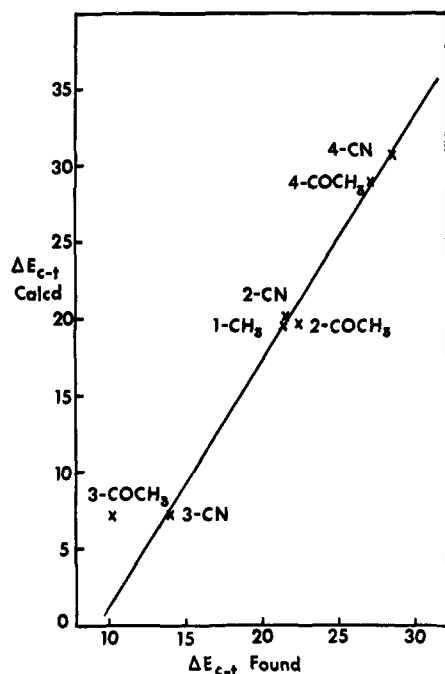


Figure 1. Plot of  $\Delta E_{CT}$  calculated vs. found ( $\text{kcal mol}^{-1}$ ). Data are contained in Table I.  $\Delta E_{CT}(\text{calcd}) = 1.60\Delta E_{CT}(\text{found}) - 14.8$ .

evidence<sup>7</sup> and by Verhoeven on the basis of some simple Hückel linear combination of atomic orbitals-molecular orbitals (LCAO-MO) calculations.<sup>8</sup> Our SCEH calculations confirm these assignments. Both orbitals are essentially  $\pi$  in character; the highest filled MO is mixed but is largely  $\sigma$  (in the plane). The energy separation between the  $b_1$  and  $a_2$  orbitals depends on the nature and position of the substituent on the ring. The first CT band arises from donation of an electron from iodide into the  $b_1$  orbital of the pyridinium ring. If the second band arises from donation into  $a_2$ , then the energy difference between the two observed CT bands ( $\Delta E_{CT}$ ) should be related to the energy difference between the  $a_2$  and  $b_1$  MO's.<sup>9</sup>

The geometry used for the 1-methyl group was such that one hydrogen atom is in the plane perpendicular to the ring passing through the nitrogen and the 4 position. Except for the acetyl substituents, the remaining geometry is fixed. The acetyl was positioned with the carbonyl oxygen in the plane of the ring.

As may be seen from the results in Table I, there is good qualitative agreement between the calculated and experimental values of  $\Delta E_{CT}$ . For all but the 3-substituted ions the quantitative agreement is excellent. The calculated values for the meta-substituted species are somewhat low, but still good considering that the energy gap is now fairly small.

A plot of the calculated  $\Delta E_{CT}$  vs. the experimental  $\Delta E_{CT}$  (data from Table I) is shown in Figure 1. The plot indicates that the calculated energy gap is linearly related to the experimental  $\Delta E_{CT}$  rather than equal to it, as suggested by the results for the unsubstituted and

(7) E. M. Kosower and E. J. Poziomek, *J. Amer. Chem. Soc.*, **86**, 5515 (1964).

(8) J. W. Verhoeven, Thesis, Laboratorium voor Organische Scheikunde der Universiteit van Amsterdam, 1969.

(9) Although these are orbital rather than state energies, it is to be expected that the additional terms will be largely self-cancelling in  $\Delta E_{CT}$  due to the nature of the transitions and the similarity of the two acceptor MO's.

Table I. Charge-Transfer Transition Energies for Several 1-Methylpyridinium Iodides

Ring substituent	$E_{c1}^a$	$E_{c2}^a$	$\Delta E_{CT}^b$	
			Found	Calcd
4-CN	58.2	85.3	27.1	29.0
4-COCH <sub>3</sub>	63.8	92.5	28.7	30.8
2-CN	59.8	81.2	21.6	20.1
2-COCH <sub>3</sub>	64.7	87.2	22.5	19.7
1-CH <sub>3</sub>	76.7	98.2	21.5	19.5
3-CN	65.0	79.0	14.0	7.2
3-COCH <sub>3</sub>	70.6	80.8	10.2	7.1

<sup>a</sup>  $E_{c1}$  and  $E_{c2}$  are the first and second CT band energies, respectively, in  $\text{kcal mol}^{-1}$  (precision  $\pm 0.2 \text{ kcal mol}^{-1}$ ; accuracy  $\pm 0.4 \text{ kcal mol}^{-1}$ ) as determined in  $\text{CH}_2\text{Cl}_2$ . <sup>b</sup>  $\Delta E_{CT}(\text{found}) = E_{c2} - E_{c1}$ .  $\Delta E_{CT}(\text{calcd}) = E(a_2) - E(b_1)$ , in  $\text{kcal mol}^{-1}$ .

2- and 4-substituted salts. This removes some of the apparent discrepancy in the case of the meta-substituted species. The 3-cyano substituent now correlates well with the other 2- and 4-substituents. On this basis the calculated  $\Delta E_{CT}$  for the 3-acetyl substituent, rather than being too low, now appears to be too high by about 5  $\text{kcal mol}^{-1}$ . It may also be noted that the slope of the line is not unity. The experimental  $\Delta E_{CT}$  values were measured in  $\text{CH}_2\text{Cl}_2$ , while the calculated energies should actually be compared with gas-phase values. This is an important consideration because of the large spectral solvent shifts of pyridinium iodide CT band energies and undoubtedly accounts in large part for the nonunity slope, and for some of the intercept as well. In addition, as noted previously,<sup>9</sup> orbital rather than state energies have been calculated. However, the iodine atom is left in the same state in each of the two transitions and the  $b_1$  and  $a_2$  MO's merge to a doubly degenerate MO as  $\Delta E_{CT}$  approaches zero. Thus, while the neglected coulomb and exchange integrals are not zero, they should be at least approximately equal. A more important consideration may be the geometry of the "pyridinyl radical" excited states. If there is no change in geometry, as implicitly assumed here, then a given  $\Delta E_{CT}$  should also be equal to the lowest energy electronic transition of the corresponding pyridinyl radical. The absorption spectra of some substituted pyridinyl radicals have been obtained recently.<sup>10</sup> The transition energies correlate with the  $\Delta E_{CT}$  values in support of our explanation of the nature of the CT bands. However, their magnitude is 1.5-1.7 times greater than the experimental  $\Delta E_{CT}$  values.

**Band Intensities.** The difference in energy between the  $^2P_{1/2}$  and  $^2P_{3/2}$  states of the iodine atom is 21.7  $\text{kcal mol}^{-1}$ . If the second CT band also arises from donation into the  $b_1$  orbital of the ring, but with the iodine atom being left in its first excited ( $^2P_{1/2}$ ) state, then in the absence of any strong interactions  $\Delta E_{CT}$  should be about 22  $\text{kcal mol}^{-1}$  regardless of the substituent. In other words,  $\Delta E_{CT}$  should be approximately independent of the acceptor, as is observed in alkali iodide CT spectra. In tropylium iodide, which has only one (doubly degenerate) acceptor orbital, two iodide to ring CT bands are observed in  $\text{CH}_2\text{Cl}_2$  with a  $\Delta E_{CT}$  of 19.9  $\text{kcal mol}^{-1}$ .<sup>11</sup> The spectra of tropylium chloride and bromide substantiate that the two bands do arise from the  $^2P_{1/2}$  and  $^2P_{3/2}$  states of iodine.<sup>12</sup> This is

(10) E. M. Kosower, E. J. Land, and A. J. Swallow, *J. Amer. Chem. Soc.*, **94**, 986 (1972).

(11) E. M. Kosower, *J. Org. Chem.*, **29**, 956 (1964).

in accord with the expectation that  $\Delta E_{CT}$  should not vary more than a few kcal mol<sup>-1</sup> from the gas-phase  ${}^2P_{1/2} - {}^2P_{3/2}$  separation. Thus, one should expect to observe *three*<sup>13</sup> CT bands in the pyridinium iodide spectra, one about 21 kcal mol<sup>-1</sup> higher than the first (lowest energy) band, and another varying between 10–30 kcal mol<sup>-1</sup> higher than the first depending on the substituent and its position. However, only two bands have been definitely observed.<sup>2</sup>

The energy difference for 2,4,6-trimethylpyrylium iodide CT bands (in CHCl<sub>3</sub>) was found to be 14.5 kcal mol<sup>-1</sup>.<sup>14</sup> Here, however, local transitions are close in energy to the CT bands and can interact with them. In particular, the  $n-\pi^*$  transition can interact with the CT band which leaves iodine in the  ${}^2P_{1/2}$  state, possibly giving it intensity and shifting it to lower energy. However, in contrast to the pyrylium ion, the pyridinium ion does not possess a lone pair of electrons and this interaction is not possible. Interaction with other (CT) excited states has been considered in a previous publication but this does not appear capable of providing a reasonable explanation.<sup>2</sup> Thus, the absence of the third band is puzzling. A possible explanation for the failure to observe this CT band is that it has been reduced in intensity due to what may be considered as a "ligand field" splitting of the iodine 5p orbitals by the pyridinium ion. The space part of the wave functions for the  ${}^2P_{3/2}$  and  ${}^2P_{1/2}$  states of iodine contains contributions from the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals. Assuming that the electron transferred from the iodide ion to the ring in the CT process is donated essentially from an iodine 5p orbital, the relative contribution of the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals to the overall transition dipole moment may be calculated. For a model in which the iodide ion is located on the  $z$  axis above the center of a "benzene" ring (idealized  $C_{6v}$  symmetry), the contribution of  $p_x$  and  $p_y$  are equal and very much greater than that of  $p_z$ .<sup>15</sup>

For zero ligand field splitting ( $\Delta$ ), the two CT bands, due to the iodine being left in the  ${}^2P_{3/2}$  and  ${}^2P_{1/2}$  states, are thus of comparable intensity. In the limit of  $\Delta \gg \zeta$  (spin-orbit coupling constant), the  ${}^2P_{3/2}$  and  ${}^2P_{1/2}$  states go over to two other states designated  ${}^2E$  and  ${}^2A$ , respectively. In  $C_{6v}$  symmetry, these are the  $E_1$  and  $A_1$  symmetry species. In the actual pyridinium ion the  $E_1$  state would be split by a small amount, but would still be approximately doubly degenerate. Thus, we have simply designated these states as  ${}^2E$  and  ${}^2A$ . The  ${}^2E$  state contains only  $p_x$  and  $p_y$ , while  ${}^2A$  only  $p_z$ . In this case, the CT transition leaving iodine in the  ${}^2A$  state has negligible intensity<sup>16</sup> compared to the lower energy transition which leaves iodine in the  ${}^2E$

state. There is some experimental support for this explanation from other CT spectra. In the case of tropylium iodide, the higher energy CT band is less intense than the lower energy one,<sup>11</sup> while for the bromide, both bands (although not completely resolved) are clearly of comparable intensity. The higher energy band is considerably less intense in 2,6-dichlorobenzylquinolinium iodide,<sup>17</sup> which might be expected to have a "ligand field strength" closer to that of the pyridinium ion. In the case of gaseous alkali iodide, both bands would, as observed, be expected to be of comparable intensity regardless of the value of  $\Delta$  due to the spherical symmetry of the acceptor orbital on the alkali metal ion. Thus, the relative intensities of the possible CT transitions between iodide ion and an acceptor will depend on the nature of the acceptor orbital(s), the geometry of the complex, and the ligand field strength of the acceptor species. Calculations are currently in progress to examine this effect on a more quantitative basis.

**Electron Affinity.** The electron affinity (EA) of the pyridinium ion has been taken as equal to the negative of the calculated ionization potential (IP) of the pyridiny radical. Although the calculation is capable of giving absolute values of the IP within 1.0–1.5 eV, the relative values for different positions of the same substituent are considerably better. A plot of  $E_{ct}$  vs. EA (data given in Table II) shows the correct general trend. The

Table II. Calculated Electron Affinities for Several 1-Methylpyridinium Iodides

Ring substituent	EA, <sup>a</sup> eV	$E_{ct}$ , <sup>b</sup> eV
1-CH <sub>3</sub>	7.83	3.32
3-CN	7.96	2.86
3-COCH <sub>3</sub>	8.54	3.06
2-COCH <sub>3</sub>	8.73	2.80
4-COCH <sub>3</sub>	8.76	2.78
2-CN	8.23	2.58
4-CN	8.32	2.52
Tr <sup>10c</sup>	8.85	2.16 <sup>d</sup>

<sup>a</sup> Electron affinity. <sup>b</sup> First CT band as observed in CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Tropylium ion. <sup>d</sup> Calculated from datum in ref 10.

individual correlations for the 2-, 3-, and 4-CN or COCH<sub>3</sub> substituted ions are quite good.

**Substituent Constants.** Correlation of  $\sigma$  substituent constants with  $E_{ct}$  (in CHCl<sub>3</sub>) has been reported by Kosower and Skorcz<sup>18</sup> for 4-CN-, 4-COCH<sub>3</sub>-, H-, 3-CH<sub>3</sub>-, and 4-CH<sub>3</sub>-substituted pyridinium iodides;  $\sigma^-$  values were used for the 4-substituents which are electron withdrawing. Similarly, there is a good correlation of  $\sigma$  substituent constants with  $E_{ct}$  (obtained in CH<sub>2</sub>Cl<sub>2</sub>) for the compounds listed in Table III.

Steric hindrance by a substituent toward iodide ion approaching the pyridinium ring would not be expected to vary appreciably with ring position. This allows an estimate of ortho  $\sigma^-$  values from CT transitions observed with the 2-substituted compounds. For example, the ortho  $\sigma^-$  values for 2-COOC<sub>2</sub>H<sub>5</sub>, 2-COCH<sub>3</sub>, and 2-CN as estimated from a plot of the data in Table

(12) K. M. Harmon, F. E. Cummings, D. A. Davis, and D. J. Diestler, *J. Amer. Chem. Soc.*, **84**, 3349 (1962).

(13) In fact, there should be four bands, the last corresponding to transfer of an electron into the second vacant MO of the pyridinium ring leaving the iodine in the  ${}^2P_{1/2}$  state. However, this band would be "buried" under the intense local transitions of the ring.

(14) A. T. Balaban, M. Mocanu, and Z. Simon, *Tetrahedron*, **20**, 119 (1964).

(15) Calculations show that this is still true even when the actual pyridinium ion is used and the iodide ion is located over the position of minimum electrostatic potential energy, which is somewhat displaced from the center of the ring.

(16) In the idealized case ( $C_{6v}$ ), zero intensity since the transition dipole moment connecting the  $\pi$  MO on the ring ( $E_2$  in  $C_{6v}$ ) with the  $p_z$  orbital on iodine ( $A_1$  in  $C_{6v}$ ) is zero. Thus, the same conclusion can be reached without calculation on the basis of group theoretical (symmetry) considerations provided that idealized symmetry is used.

(17) G. Briegleb, W. Jung, and W. Herre, *Z. Phys. Chem. (Frankfurt am Main)*, **38**, 253 (1963).

(18) E. M. Kosower and J. A. Skorcz, "Advances in Molecular Spectroscopy," Pergamon Press, New York, N. Y., 1962, p 413.

**Table III.** Comparison of the Energy of the First CT Band ( $E_{ct}$ ) of Various Pyridinium Iodides (in  $\text{CH}_2\text{Cl}_2$ ) with  $\sigma$  Substituent Constants and Calculated Charges ( $Q_N$ ) on the Pyridinium Nitrogen

Ring substituent	$E_{ct}^a$ kcal/mol	$\sigma_m^b$	$\sigma_p^b$	$\sigma_p^{-c}$	$Q_N^d$
H	76.7	0	0	0	1.00
3-CN	65.6	+0.56			1.54
2-CN	60.1				1.77
4-CN	58.5		+0.66	+1.00	1.57
3-COCH <sub>3</sub>	70.6	+0.38			1.29
2-COCH <sub>3</sub>	64.7				1.31
4-COCH <sub>3</sub>	63.8		+0.50	+0.87	1.37
4-CH <sub>3</sub>	80.7 <sup>e</sup>		-0.17		
3-CH <sub>3</sub>	78.0 <sup>e</sup>	-0.069			
3-COOC <sub>2</sub> H <sub>5</sub>	71.3	+0.37			
4-COOC <sub>2</sub> H <sub>5</sub>	65.2		+0.45	+0.68	
2-COOC <sub>2</sub> H <sub>5</sub>	67.8				

<sup>a</sup> Reference 2. <sup>b</sup> J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962, p 87. <sup>c</sup> H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953). <sup>d</sup> The calculated charges on nitrogen are normalized to the unsubstituted 1-methylpyridinium ion. <sup>e</sup> From  $\text{CHCl}_3$  data, ref 18, as "corrected" to  $\text{CH}_2\text{Cl}_2$ .

III are +0.48, +0.65, and +0.89, respectively. These fall in between the values of  $\sigma_p$  and  $\sigma^-$  for the corresponding para substituent.

A reasonable correlation also exists between  $\sigma$  values ( $\sigma_p$  and  $\sigma_m$ ) and the calculated charges on the nitrogen ( $Q_N$ ). However, from a plot of these data (given in Table III) and the calculated values of  $Q_N$  for the 2-substituents,  $\sigma_o$  for the CN appears to be larger than  $\sigma_{p-CN}$  while  $\sigma_{o-COCH_3}$  is less than  $\sigma_{p-COCH_3}$  and approximately equal to  $\sigma_{m-COCH_3}$ . Though the data are inter-

esting their interpretation in terms of the various possible effects is difficult to achieve satisfactorily without additional results with more compounds.

### Summary

SCEH calculations for 1-methylpyridinium ion and 2-, 3-, and 4-cyano- (and acetyl-) 1-methylpyridinium ions give data on energy differences between the lowest and next highest vacant molecular orbitals of the pyridinium ion which are in good agreement with the observed separation of the two pyridinium iodide CT bands in methylene chloride. This supports previous indications that the higher energy CT band results from charge-transfer to the second vacant molecular orbital of the pyridinium ion.

Calculated electron affinities of the pyridinium ions show expected trends in plots with the low energy pyridinium iodide CT transition. A reasonable correlation was also found to exist between  $\sigma$  values ( $\sigma_p$  and  $\sigma_m$ ) and the calculated charges on the pyridinium nitrogen.

A possible explanation for the failure to observe three CT bands has been proposed which, if valid, allows prediction of relative intensities from simple group theoretical considerations using idealized symmetry.

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## Unusually Weak Electronic Interaction between Two Aromatic Chromophores Less Than 10 Å Apart in a Rigid Model Molecule<sup>1</sup>

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**Abstract:** *p*-Dimethoxybenzene (D) and phenanthrene (P) chromophores have been attached to an inflexible  $\sigma$ -bond molecular frame composed of two norbornane and one cyclopropane rings. The two  $\pi$  systems in the model compound have a center-to-center separation of 9 Å and their orientation is fixed, mutually perpendicular, and nearly bisecting. The energy levels of D and P are appropriate for both singlet-singlet and triplet-triplet energy transfer from D to P. Each chromophore, when separately attached to the frame, emits easily detectable and characteristic fluorescence and phosphorescence. The absorption, emission, and excitation spectra of the model molecule in dilute solution closely resembled those of an equivalent equimolar mixture of the two chromophores. Since the D-P separation is well within ranges of efficient S-S and T-T transfer, it is obvious that the D-P relative orientation in the model compound is responsible for their weak interaction. Tentative explanations related to the exchange and resonance transfer concepts are offered. Special precautions have been taken to make sure that the spectrophotometric measurements were not altered by spurious light-induced reactions or eventual photo-products.

In a previous communication<sup>2</sup> we compared the absorption and emission spectra of model compound **1** with those of 3',6'-dimethoxybenzonorbornane (**2**) and

2,3-*exo*-(4',5'-methylene)phenanthrene-11'-spiro-1''-cyclopropane)bicyclo[2.2.1]heptane (**3**) which represent, respectively, the constituent *p*-dimethoxybenzene (D)

(1) Taken from the Ph.D. dissertation of D. S. C. Chang, George Washington University, 1970.

(2) (a) N. Filipescu, Symposium on Radiationless Transitions in

Molecules, Paris, France, May 1969; (b) N. Filipescu, J. R. DeMember, and G. R. Howard, *J. Chim. Phys. Physicochim. Biol.*, **67**, 84 (1970).