Acknowledgment. The authors are indebted to K. Funabashi for many discussions which have been of great assistance.

References and Notes

(1) International Atomic Energy Agency Fellow, on leave of absence from the "Ruder Boskovic" Institute, Zagreb, Yugoslavia.
(2) The research described herein was supported by the Division of Basic Energy Sciences of the U.S. Department of Energy. This is Document No. NDRL-1790 from the Notre Dame Radiation Laboratory.
(3) J. W. Hunt and W. J. Chase, *Can. J. Chem.*, **55**, 2080 (1977).
(4) D. Razem, W. H. Hamill, and K. Funabashi, *Chem. Phys. Lett.*, in press.
(5) D. Razem and W. H. Hamill, *J. Phys. Chem.*, **81**, 1625 (1977).
(6) This was originally an assumption, partially supported by plots of C_{37} vs. T as in Figure 1. Later experiments in methanol covered the range 298–80 K for seven electron acceptors. There was no measurable change in C_{37} below 125 K for any, and none below 150 K for three of these systems. Using measured values of $C_{37}{}^0$ the function $C_{37}-C_{37}{}^0$ obeys the Arrhenius dependence.
(7) R. L. Bush and K. Funabashi, *J. Chem. Soc., Faraday Trans. 2*, **73**, 274 (1977).
(8) J. A. Ward and W. H. Hamill, *J. Am. Chem. Soc.*, **87**, 1853 (1965).
(9) K. Hiraoka and W. H. Hamill, *J. Chem. Phys.*, **57**, 3870 (1972). There are additional unpublished results for ethanol supporting the resonance based on retarding potential spectra of back-scattered electrons.
(10) A. Mozumder and J. L. Magee, *J. Chem. Phys.*, **47**, 939 (1967).
(11) W. F. Schmidt and A. O. Allen, *J. Chem. Phys.*, **52**, 4788 (1970).
(12) K. Harada, M. Irie, and H. Yoshida, *Int. J. Radiat. Phys. Chem.*, **8**, 331 (1976).
(13) T. Shida and W. H. Hamill, *J. Am. Chem. Soc.*, **88**, 3689 (1966).
(14) I. A. Taub and K. Eiben, *J. Chem. Phys.*, **49**, 2499 (1968).
(15) T. Ichikawa and H. Yoshida, *Int. J. Radiat. Phys. Chem.*, **8**, 391 (1976).
(16) Evidence for both activated and activationless localization in aqueous solids appears in Figure 10 of a recent report by G. V. Buxton and K. G. Kemsley, *J. Chem. Soc., Faraday Trans. 1*, **71**, 568 (1975).

Heavy Atom Effects on the Phosphorescent Triplet States of Several Aromatic Molecules

Karen J. Latas and A. M. Nishimura*

Department of Chemistry, Wichita State University, Wichita, Kansas 67208

(Received June 25, 1977; Revised Manuscript Received November 28, 1977)

Publication costs assisted by the National Institutes of Health and the Petroleum Research Fund

Phosphorescence microwave double resonance techniques were used to observe the effects of inter- and intramolecular heavy atom perturbation on naphthalenes and quinolines. In order to observe intramolecular heavy atom perturbation in naphthalene, the 1 position was chlorinated whereas on quinoline, the chlorine was substituted on the 2, 4, and 8 positions. The effects of external perturbation were studied using 1,2,4,5-tetrachlorobenzene (TCB) as a host single crystal, while substituted single crystals of durene were grown to represent the least interactive matrix. The changes in the zero field splitting of these guest–host systems were interpreted in terms of the second-order spin–orbit contribution to the zero field splitting parameters. Relative radiative rate and total decay rate constants from the phosphorescent triplet state were interpreted in terms of out-of-plane vibronic coupling to the radiative process in these aromatic molecules.

Introduction

Heavy atom effects have been a subject of interest to researchers in triplet state spectroscopy for many years.[1-3] Interpretation has been limited to spectral properties such as vibrational analysis of the phosphorescence spectra and lifetime data at 77 K. With the use of the phosphorescence microwave double resonance (PMDR) method, a powerful and sensitive tool in the study of molecular perturbations, several workers have gained a better understanding of intra- and intermolecular heavy atom effect in several azanaphthalenes.[4,5]

In this paper we shall present a systematic study on the effect of chlorine substitution in aromatic molecules, viz., naphthalene and quinoline, and the effects of externally chlorinated solvents on the lowest phosphorescent triplet state of these molecules. The changes in the zero field splittings and the phosphorescence relaxation parameters due to intra- and intermolecular heavy atom perturbation are interpreted in terms of the changes in the parameters relative to the parent molecules, naphthalene and quinoline.

Experimental Section

The guest molecules studied were naphthalene, 1-chloronaphthalene, quinoline, isoquinoline, 2-chloroquinoline, 4-chloroquinoline, 8-chloroquinoline, and quinoxaline. These molecules were purchased commercially, and purified by multiple vacuum distillation or sublimation at reduced pressures. The hosts were durene and tetrachlorobenzene (TCB) which were purified by extensive zone refining under an inert atmosphere for an equivalent of over 300 passes after recrystallization from ethanol. The single crystals of the host were grown with guest concentrations of less than 0.05% mole/mole in the standard Bridgemann furnace. Single crystals were cut and shaped to fit a slow wave helix which was then immersed in the liquid helium cryostat. Further details of the PMDR apparatus were described in previous work.[6,7]

The microwave zero field transition was observed by the microwave induced delayed phosphorescence (MIDP) technique as described by van der Waals et al.[8,9] The microwave sweep was calibrated with an EIP microwave frequency counter and reproducibility of the detected transition was determined to be approximately ±5 MHz. In several cases, two of the zero field transitions could be observed by the MIDP methods, but the third transition was observed by continuous pumping of a different transition with another microwave generator while the third resonance was swept (vide infra).

For phosphorescence decay measurements a vibronic band of the phosphorescence (usually the 0, 0 band) was isolated with a spectrometer slit width of ≤ 100 cm^{-1}. The filtered Hg excitation source was extinguished in about 2 ms by an electronically controlled shutter.

0022-3654/78/2082-0491$01.00/0

TABLE I: Phosphorescence Origin, Zero Field Splitting Frequencies in MHz (±10 MHz), Total Phosphorescence Rate Constants (±10%) in s^{-1}, and Relative Radiative Rate Constants (±20%) for Naphthalenes and Quinolines as Determined by Microwave Induced Delayed Phosphorescence at 1.4 K[a,b]

Guest	Host	Durene	Tetrachlorobenzene
Naphthalene	0,0 (cm^{-1})	21300	20695
	Transitions	3420[c]	3428
		2548	2521
		822	905
	k_z	0.65[d]	2.9
	k_y	0.40	2.1
	k_x	0.15	0.28
	k_z^r		1.5
	k_y^r		1.0
	k_x^r		<0.10
1-Chloronaphthalene	0,0 (cm^{-1})	20490	20410
	Transitions	3398	3343
		2528	2570
	k_z	7.0	7.1
	k_y	2.3	2.5
	k_x	0.28	0.42
	k_z^r	30	1.3
	k_y^r	1.0	1.0
	k_x^r	0.50	<0.10
Isoquinoline	0,0 (cm^{-1})	20940	20880
	Transitions	3335[e]	3325
		2655	2630
	k_z	3.0[f]	3.9
	k_y	2.9	4.6
	k_x	0.38	0.70
	k_z^r	1.0	1.0
	k_y^r	2.9	1.3
	k_x^r		<0.10
Quinoline	0,0 (cm^{-1})	21882[g]	21556
	Transitions	3585[e]	2530
		1005	
	k_z	3.1[h]	3.4
	k_y	0.32	1.1
	k_x	0.19	0.58
	k_z^r	28	0.5
	k_y^r	1.0	1.0
	k_x^r	0.70	<0.10
2-Chloroquinoline	0,0 (cm^{-1})	22200	22130
	Transitions	3670	3620
		2510	2580
		1060	
	k_z	2.3	4.0
	k_y	4.2	4.8
	k_x	0.21	0.33
	k_z^r	0.50	1.0
	k_y^r	1.0	1.5
	k_x^r	<0.10	<0.10
4-Chloroquinoline	0,0 (cm^{-1})	21540	21230
	Transitions	3548	3485
		2540	2560
	k_z	8.7	8.8
	k_y	1.8	4.4
	k_x	0.25	0.86
	k_z^r	20	10
	k_y^r	1.0	1.0
	k_x^r	<0.10	0.10
8-Chloroquinoline	0,0 (cm^{-1})	20840	20830
	Transitions	3380	3300
		2520	2468
		850	
	k_z	10	11
	k_y	8.2	12
	k_x	0.30	0.56
	k_z^r	1.2	1.0
	k_y^r	1.0	1.0
	k_x^r	<0.10	<0.10

[a] Relative radiative rates in several cases are rough estimates, since conditions necessary as described in ref 3 and 12 were not strictly met. [b] For most of these molecules spin axes may differ from each other. Strict correlation between the spin axes of the various molecules is not implied. [c] From ref 15. [d] From ref 26. [e] From ref 8. [f] From ref 8. [g] From ref 25. [h] From ref 9.

The kinetic relaxation parameters of the total phosphorescence decay constants were obtained by several methods. The decay measured subsequent to continuous wave excitation and shutter closure was recorded repetitively on a Tracor-Northern Model NS 570 signal averager. The accumulated 2048 data points were transferred directly into a Varian Model 620 minicomputer interfaced to a visual display. Using a linear regression program the three decays were computer fit to an equation describing the decay of the phosphorescence intensity.[10] Additionally, all of the data were analyzed by a program using the Newton–Raphson nonintegral method of curve fitting with approximated gradients on an IBM 360 computer and were found to be consistent with the direct analysis using the regression analysis on the minicomputer.[11]

The kinetic data were found to be self-consistent with kinetic parameters obtained via MIDP techniques as well as high temperature decay measurements in which the helium level was allowed to fall below the sample. The sample temperature was estimated to be roughly 10 K and the data yielded a single exponential curve which represented an average of the individual rate constants from the sublevels. These values agreed well with the rate constants observed using a xenon flash lamp excitation of 10 μs duration. Relative radiative rates were determined by MIDP techniques and/or by adiabatic rapid passage techniques as described by Harris and Hoover.[12]

Results and Discussion

The zero field splittings and the energies of the phosphorescence 0,0 bands for the various naphthalene, chloronaphthalene, quinoline, isoquinoline, and chloroquinolines in the two hosts durene and TCB are shown in Table I. The axis system was chosen such that x is out of plane and z lies along the in-plane long axis. For the molecules which were studied, the guest $^3\pi,\pi^*$ phosphorescent state was energetically red shifted in TCB as compared to durene host from about 10 to 300 cm^{-1} depending on the guest molecule. This is consistent with the energy lowering of the excited Franck–Condon state and is due primarily to the enhanced dipole–dipole interaction in the excited state.[13]

The relaxation rate parameters from the lowest triplet state are shown in Table I.[14] These include the total phosphorescent decay and the relative radiative rate constants. The relative energy orderings have been assumed to be unchanged in different hosts and are extrapolated from studies on naphthalenes,[15] quinoline,[16] isoquinoline,[16] and quinoxaline.[17] In several cases where only one of the zero field transitions could be observed,

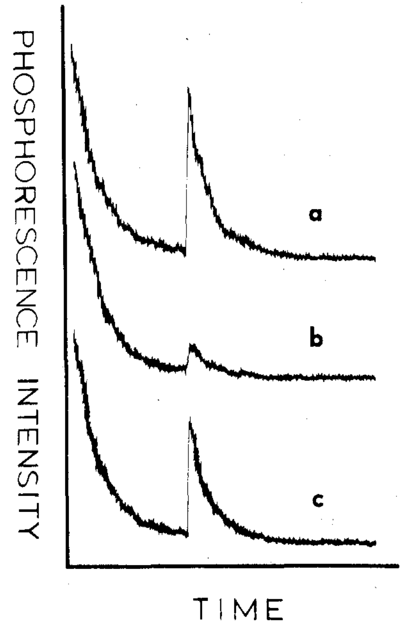


Figure 1. Microwave induced delayed phosphorescence (MIDP) signals in 2-chloroquinoline in a durene crystal. (a) MIDP when the 2610-MHz transition is swept, subsequent to extinguishing the optical pumping light. (b) Same as in (a), except the 3670-MHz resonance is simultaneously saturated by frequency modulation. (c) Same as in (a), except the 1060-MHz transition is continuously saturated.

the other resonance frequencies were determined by a method involving the simultaneous application of two microwave frequencies upon the sample analogous to electron–electron double resonance as described by Kuan et al.[18]

2-Chloroquinoline in durene represents one such case in which only one transition was observed with the MIDP technique. The transition occurred at 2610 MHz and corresponds to the $|D| - |E|$ splitting. Analysis of a single MIDP decay gave a rate constant of 4.2 s^{-1}, while the slope of the echo heights, as a function of time when the transition was swept, was 0.21 s^{-1}. Careful analysis of the phosphorescence decay after shuttering the light used to continuously pump the triplet state showed a third rate constant of 2.3 s^{-1}. Thus the relative energy ordering of the triplet state could be either t_m:t_f:t_s or t_m:t_s:t_f, where the subscript f, m, and s refer to the triplet sublevels corresponding to the fast, middle, and slow rate constants.

Shown in Figure 1 are the oscilloscope traces of MIDP pulses in which the transition not detectable by usual MIDP was frequency modulated and continuously saturated at approximately 100 Hz while the observed 2610-MHz transition was swept to yield the MIDP signal. These are shown along with the usual MIDP echo in which only the 2610-MHz transition was swept. In both cases where the 1060- and 3670-MHz transitions were continuously saturated, the echo of the 2610-MHz transition yielded a less intense echo, as compared to the echo obtained by sweeping through the 2610-MHz transition alone. If the continuously swept microwave power was off resonance, no effect on the MIDP echo was observed when the 2610-MHz transition was swept. The fact that the echo was affected to a greater extent upon the continuous saturation of the 3760-MHz transition than when the 1060-MHz transition was continuously saturated indicated that the 3670-MHz transition must connect the spin state corresponding to the *slow* rate constant with another sublevel, in this case, the one corresponding to the middle rate constant. Thus the relative energy ordering of the triplet state for 2-chloroquinoline must be t_m:t_f:t_s.

TABLE II: Ratio of Total Phosphorescence Decay Rate Constants of Various Chlorinated Quinolines and Quinoline in Durene Measured at 1.4 K (See Text)

	Relative rate constants for sublevel		
Guest molecule	τ_z	τ_y	τ_x
2-Chloroquinoline	0.75	13	1.1
4-Chloroquinoline	3.1	5.6	1.3
8-Chloroquinoline	3.2	25.6	1.0

TABLE III: Relative Total Phosphorescence Decay Rate Constants of Various Naphthalenes and Quinolines in 1,2,4,5-Tetrachlorobenzene to the Same Guest Molecules in Durene Host Single Crystals Measured at 1.4 K (See Text)

	Relative rate constants for sublevel		
Guest molecule	τ_z	τ_y	τ_x
Naphthalene	4.5	5.3	1.9
1-Chloronaphthalene	1.0	1.1	1.5
Isoquinoline	1.0	1.6	1.8
Quinoline	1.1	3.4	3.1
2-Chloroquinoline	1.7	1.1	1.6
4-Chloroquinoline	1.0	2.4	3.4
8-Chloroquinoline	1.1	1.5	1.9

TABLE IV: Total Phosphorescence Rate Constants for the Chlorinated Quinolines in Durene Host Relative to the Rate Constants for Quinoline in 1,2,4,5-Tetrachlorobenzene Measured at 1.4 K (See Text)

	Relative rate constants for sublevel		
Guest molecule	τ_z	τ_y	τ_x
2-Chloroquinoline	0.68	2.8	0.36
4-Chloroquinoline	2.6	1.2	0.43
8-Chloroquinoline	2.9	5.5	0.51
1-Chloronaphthalene[a]	2.4	1.1	1.0

[a] The analogous ratio for the rate constants of 1-chloronaphthalene in durene and naphthalene in tetrachlorobenzene.

In addition, the MIDP echo pulse height shown in Figure 1b represents the relative populations in the slower of the two coupled sublevels. The relative populations, in turn, are functions of the rate of decay from the less active sublevel. In one case (cf. Figure 1b) the slowest of the sublevels was coupled to a second sublevel by the saturating microwave power at 3610 MHz thereby affecting the MIDP echo height when the 2610-MHz transition was swept. Alternatively, when the 1060-MHz transition was saturated continuously, the MIDP echo height reflected the rate constant of the middle rate constant (cf. Figure 1c). Thus the ratio of log of echo heights with and without the continuous saturating microwave power roughly represents the ratio of the rate constants. Accounting for the fact that the population must be averaged over *two* sublevels during the decay in the echo involving continuous saturation, the analysis of the echo heights shows a ratio of 0.4:1:0.08, whereas the continuous wave decay data shows 0.5:1:0.05 for k_m:k_f:k_s. Quantitative analysis of the pulse heights as a function of time should yield even better agreement.

The use of this simultaneous continuous saturation and MIDP method allows the determination of the relative energy orderings of the triplet state sublevels in cases where MIDP method alone fails to produce echoes. In addition, the analysis of the decays of the single MIDP pulses while continuously saturating another transition gave good agreement with the kinetic data obtained by

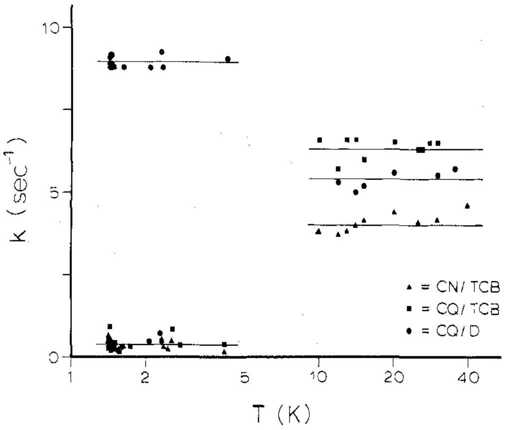


Figure 2. Phosphorescence rate constants of 1-chloronaphthalene (▲) and 8-chloroquinoline (■) both in 1,2,4,5-tetrachlorobenzene and 8-chloroquinoline in durene (●) as a function of temperature. The rate constants from individual sublevels converge to an average of the three rate constants at high temperatures (>10 K) due to spin-lattice relaxation. The extremely rapid convergence to the average decay value at roughly 10 K is probably due to the seventh power dependence on temperature of the indirect Raman process in the spin-lattice relaxation.

continuous wave excitation methods.

Tables II-IV were shown to emphasize internal, external, and competitive heavy atom effects, respectively. In Table II, the ratios are shown of the total phosphorescence rate constants of the chloroquinolines relative to quinoline in durene single crystals, i.e. k_i^{tot}(2-, 4-, or 8-chloroquinoline in durene host)/k_i^{tot}(quinoline in durene host). The subscript i corresponds to the x, y, z principal axes. In Table III the total rate constants of a particular guest molecule in durene host are compared to the rate constants found for the same molecule in TCB, i.e. k_i^{tot}(guest in durene host)/k_i^{tot}(guest in TCB host). Finally in Table IV, the ratios of the total phosphorescence decay rate constants of chloroquinoline in durene relative to the rate constants of quinoline in TCB are shown, i.e., k_i^{tot}(2-, 4-, or 8-chloroquinoline in durene host)/k_i^{tot}(quinoline in TCB host). Table IV reveals the competitive strengths of the internal to external heavy atom effect. If the ratio is greater than unity, the internal heavy atom effect is predominant, whereas a ratio less than unity would indicate a large external heavy atom perturbation. The data shown in Tables II-IV indicate a large sensitivity and selectivity of the interaction due to intramolecular heavy atom effect.

Implicit in the above phosphorescence decay analysis is the assumption that the spin-lattice relaxation is slow compared to the decay rates such that the relaxation effects can be neglected. Figure 2 shows the decay rate constants as a function of temperature. The guest-host systems were chosen to represent the largest spin-orbit interactions due to internal and external heavy atoms and consequently should reflect the largest spin-lattice relaxation rates which are encountered in this study. As the relaxation rates become comparable or exceed the decay rates, the observed decay rate constants converge to an apparent "high temperature" rate constant which is the average of the three individual rates from the sublevels. The assumption made in the decay analysis appear to be valid, since the decay rate constants do not vary from 1.4 K, the temperature at which the experiments were done, to about 5 K.

The magnitude of spin-lattice relaxation necessary to cause an averaging of the decay rates can be obtained as follows. The rate change in the populations for a simplified two level system when the excitation light is shuttered can be written as: $\dot{N}_1 = -(k_1 + W)N_1 + WN_2$ and analogously for $\dot{N}_2$ where k_1 is the phosphorescence decay constant and W is the spin-lattice relaxation rate constant between the two levels. The intensity of the phosphorescence is proportional to $I \propto \sum_i f_i k_i^r N_i$ where f_i is the Franck-Condon factor, k_i^r is the radiative rate, and N_i is the population in the ith sublevel. Thus the rate change in the population from solutions to the simultaneous differential equations will yield the decay rate for the phosphorescence intensity. The resulting expression shows that the onset of the averaging of the rate constants occurs when the spin-lattice relaxation is of the order of 10^{-1} as large as the faster decay constant.

Past workers have postulated various mechanisms for the deactivation processes in aromatic hydrocarbons.[19-22] The principle relaxation route is the coupling of $^1\sigma,\pi^*$ and/or $^1\pi,\sigma^*$ with τ_z and τ_y of the lowest triplet state via the orbital angular momentum component along z and y, respectively. A weaker spin-orbit coupling between two π,π^* rates gives τ_x its singlet character or the singlet character for τ_x may be derived from vibronic interaction. *Radiative relaxation from τ_y is strictly symmetry forbidden* by first-order spin-orbit coupling scheme. The in-plane spin axes of quinoline was shown by Vincent and Maki[15] to be rotated by ~13° from the durene axes and τ_y would therefore be expected to gain radiative strength especially in the chlorinated quinolines. In addition, from Table I, it is evident that the proximity of the chlorine relative to the nitrogen in chloroquinolines is important in enhancing the radiative strength of τ_y. This is evident when comparing the large increase in k_y in 8-chloroquinoline where the chlorine is directly along the y axis, whereas in 4-chloroquinoline, although the chlorine is also along y, the effect on k_y is much smaller. The indication is that the chlorine spin-orbit interaction in the 8 position enhances the interaction of the excited n,π^* state with the lowest $^3\pi,\pi^*$ state. Thus the relaxation mechanism for the radiative process is facilitated by the operation of the angular momentum operator in the spin-orbit coupling scheme. Such interaction is facile due to the proximity and favorable orientation of the halogen and the nitrogen.

Close examination of the phosphorescence spectra of the chlorinated quinolines reveals an intense band situated roughly 260 cm^{-1} from the 0,0 band. In some cases, this 260-cm^{-1} band is more intense than the phosphorescence origin and is attributed to the asymmetric out-of-plane vibration due to the C-Cl group.[20] Previous workers have attributed this mode to be the cause of radiative strength for the τ_y sublevel via spin-orbit vibronic coupling.[5] This is reflected by the larger increase in k_y (as compared to k_z and k_x) of the chlorinated quinolines in durene relative to quinoline in the same host (cf. Table II).

In a study of heavy atom effects in quinoxaline, Lin demonstrated that there are three mechanisms for external heavy atom effects. The mixing of the phosphorescent triplet state of the guest molecule with its singlet state, with the excited singlet state of the host, or with a created charge-transfer state of the $^1\pi,\sigma^*$ type in which the π electron of the guest is promoted to a σ^* orbital of the host.[5] The first two mechanisms would affect the relaxation rate constants of τ_z and τ_y via spin-orbit interaction, but the τ_x sublevel would not be affected. The third mechanism would be less selective and the data in Table IV are consistent with this interpretation. The decay rate constants in Table III show that in almost all cases the external heavy atom effect is largest for τ_x as evidenced by the largest relative ratio.

Yamaguchi et al. have postulated that for quinoxaline in TCB the chlorine atoms of TCB could roughly reside spatially coincident with the naphthalene when looked down the axis perpendicular to the molecular plane.[4] Crystallographic data do not show such large overlap of the guest and host molecules if the guest molecule were substitutionally replaced.[23,24] Additionally, if such overlap did exist, the decay rate constants for the quinoline in TCB should be comparable to that for 2-chloroquinoline in durene. Also, the decay rate for naphthalene in TCB should compare with those for 1-chloronaphthalene in durene. The data in Table I show that although the effect of the chlorinated host is similar to that of the chlorinated guest, the internal heavy atom effect is more pronounced than the external effect as reflected in the increase in k_z and k_y (also, see Table IV).

From Table I, the $|D|$ and $|E|$ values for a particular guest molecule decreased in durene compared to the same guest molecule in 1,2,4,5-tetrachlorobenzene host. The only exception was the increase in the $|E|$ value for naphthalene in durene relative to the chlorinated benzene host. The difference in $|D|$ value could be attributed to either a distortion in the excited state of the guest in one or both of the hosts due to the crystallographic differences in the two crystals, or an effect on the zero field splitting due to spin–orbit contribution from external heavy atom effect. Our study here does not preclude either interpretation. Considering the low symmetry of chloronaphthalene, quinoline, and chloroquinoline, the decrease in $|E|$ may be attributed to the less anisotropic crystal fields arising from the external heavy atom of the chlorinated host. Conversely, the increase in $|E|$ for a very symmetric molecule like naphthalene may be due to a more anisotropic environment in the tetrachlorobenzene host.

Acknowledgment. We thank the National Institutes of Health (GM 21770) for support in this research. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. The liquid helium used in this study was kindly provided by the Kansas Refined Helium Co.

References and Notes

(1) S. P. McGlynn, T. Azumi, and M. Kinoshita in "Molecular Spectroscopy of the Triplet State", Prentice Hall, Englewood Cliffs, N.J., 1969.
(2) J. B. Birks in "Photophysics of Aromatic Molecules", Wiley, New York, N.Y., 1970.
(3) R. H. Hofeldt, R. Sahai, and S. H. Lin, *J. Chem. Phys.*, **53**, 4512 (1970); *Trans Faraday Soc.*, **67**, 1690 (1971).
(4) S. Yamaguchi, K. Matsuzaki, and T. Azumi, *J. Lumin.*, **12/13**, 369 (1976).
(5) C. T. Lin, *J. Lumin.*, **12/13**, 375 (1976).
(6) K. A. Martin, G. Moller, and A. M. Nishimura, *J. Phys. Chem.*, **80**, 2788 (1976).
(7) G. Moller and A. M. Nishimura, *J. Phys. Chem.*, **81**, 147 (1977).
(8) J. Schmidt, W. S. Veeman, and J. H. van der Waals, *Chem. Phys. Lett.*, **4**, 341 (1969).
(9) J. Schmidt, D. A. Antheunis, and J. H. van der Waals, *Mol. Phys.*, **22**, 1 (1971).
(10) R. K. Power, "An Active Data Analysis Program", to be submitted to VOICE, Varian Minicomputer Users' Software Library.
(11) M. J. D. Powell, *Comp. J.*, **8**, 303 (1965).
(12) C. B. Harris and R. J. Hoover, *J. Chem. Phys.*, **56**, 2199 (1972).
(13) R. S. Becker in "Theory and Interpretation of Fluorescence and Phosphorescence", Wiley, New York, N.Y., 1969.
(14) We are grateful for the assistance in decay data analysis by P. C. Saint-Erne, A. Habash, and G. Cherry.
(15) C. A. Hutchison, Jr., and W. Mangum, *J. Chem. Phys.*, **34**, 908 (1961).
(16) J. S. Vincent and A. H. Maki, *J. Chem. Phys.*, **42**, 865 (1965).
(17) J. S. Vincent and A. H. Maki, *J. Chem. Phys.*, **39**, 3088 (1963).
(18) T. S. Kuan, D. S. Tinti, and M. A. El-Sayed, *Chem. Phys. Lett.*, **4**, 507 (1970).
(19) D. S. McClure, *J. Chem. Phys.*, **20**, 682 (1952).
(20) T. Pavlopoulos and M. A. El-Sayed, *J. Chem. Phys.*, **41**, 1082 (1964).
(21) M. S. de Groot, I. A. M. Hesselmann, J. Schmidt, and J. H. van der Waals, *Mol. Phys.*, **15**, 17 (1968).
(22) W. S. Veeman and J. H. van der Waals, *Mol. Phys.*, **18**, 63 (1970).
(23) G. Gafner and I. H. Herbstein, *Acta Crystallogr.*, **13**, 702, 706 (1960).
(24) F. H. Herbstein, *Acta Crystallogr.*, **18**, 997 (1965).
(25) V. Ermolaev and I. Koltyar, *Opt. Spectrosc.*, **9**, 183 (1960).
(26) M. Schwerer and H. Sixl, *Chem. Phys. Lett.*, **2**, 14 (1968); *Z. Naturforsch. A*, **24**, 952 (1969).

COMMUNICATIONS TO THE EDITOR

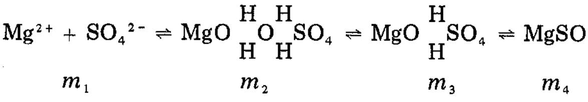
Comment on "A High-Pressure Laser Raman Spectroscopic Investigation of Aqueous Magnesium Sulfate Solutions"

Publication costs assisted by the University of California, San Diego

Sir: Chatterjee, Adams, and Davis[1] report a $\Delta\bar{V}° = -20$ cm^3/mol for the volume change of dissociation of $MgSO_4$ contact ion pairs. They conclude that their results in 2 M $MgSO_4$ solutions do not agree with the values of $\Delta\bar{V}°$ obtained by others.[2-4] From pressure–conductance data a value of $\Delta\bar{V}° = -7.3$ cm^3/mol[3] and $\Delta\bar{V}° = -7.7$ cm^3/mol[4] was obtained from two independent investigations.

The purpose of this letter is to show that their results are consistent with the other work with which they claim disagreement. Their work is in rough agreement with pressure–acoustic work of Fisher.[5]

The reaction of interest is the three-step multistate dissociation model developed by Eigen and Tamm[2] to explain ultrasonic absorption relaxation spectra at atmospheric pressure:



$$\underset{m_1}{\mathrm{Mg^{2+} + SO_4^{2-}}} \rightleftharpoons \underset{m_2}{\mathrm{MgO\underset{H\ H}{\overset{H\ H}{O}}SO_4}} \rightleftharpoons \underset{m_3}{\mathrm{MgO\underset{H}{\overset{H}{\ }}SO_4}} \rightleftharpoons \underset{m_4}{\mathrm{MgSO_4}} \qquad (1)$$

In this model three ion pairs forms exist and the contact ion pair concentration is m_4.

The molal dissociation constant is

$$K_m = \frac{m\alpha^2 f_\pm{}^2}{1-\alpha} = \frac{m_1{}^2 f_\pm{}^2}{m_2 + m_3 + m_4} = \frac{K_{12}K_{23}K_{34}}{1 + K_{34} + K_{23}K_{34}} \qquad (2)$$

where the K_{ij} are the equilibrium constants for the various steps. The conventional $\Delta\bar{V}°$ is obtained from the equation

$$\partial \ln K_m/\partial p = -\Delta\bar{V}°/RT \qquad (3)$$

The relationship between the various $\Delta\bar{V}_{ij}$ and K_{ij} Eigen and Tamm obtained from acoustic data and K_m and $\Delta\bar{V}°$ obtained from pressure–conductance work has been discussed by Fisher.[5,6] The Eigen and Tamm model does in fact predict[2,5] a large decrease with pressure of the con-

0022-3654/78/2082-0495$01.00/0