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Citation: *J. Chem. Phys.* **68**, 1857 (1978); doi: 10.1063/1.435908

View online: <http://dx.doi.org/10.1063/1.435908>

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Zero field optically detected magnetic resonance (ODMR) of dihydroporphin

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(Received 26 October 1977)

Zero field ODMR results are presented for the lowest triplet state T_0 of dihydroporphin free base (chlorin), representing the basic skeleton for many photosynthetic pigments. ISC rates are found to be $k_x = 435 \pm 35 \text{ sec}^{-1}$, $p_x = 62 \pm 13\%$; $k_y = 173 \pm 11 \text{ sec}^{-1}$, $p_y = 36 \pm 8\%$; $k_z = 23.4 \pm 0.7 \text{ sec}^{-1}$, $p_z = 2 \pm 0.5\%$; where k_x , k_y , k_z and p_x , p_y , p_z represent total decay rate constants and relative populating rates of spin levels $|x\rangle$, $|y\rangle$ and $|z\rangle$ of T_0 . Upon prolonged irradiation with 400 nm light, the central protons of dihydroporphin free base are rearranged, as is evident from the appearance of new zero field transitions; no shift in fluorescence spectra is observed during this phototransformation. ZFS shifts due to the effect of different crystal field orientation and H-H axis orientation have been obtained separately. The results are consistent with a model based on four possible orientations of a C_{2v} dihydroporphin molecule in a crystal site with twofold or lower symmetry.

I. INTRODUCTION

Following a preliminary study of chlorin free base¹ (systematic name: dihydroporphin free base) as a model compound of pheophytin we present in this paper a more detailed account of some new experimental results of the kinetics of the lowest triplet T_0 state of this compound. By improving the ODMR spectrometer w. r. t. a previous version² we could measure at higher optical excitation rate resulting in a higher S/N ratio, and allowing kinetic data to be determined over a range of light intensities. This enabled extrapolation of experimental decay constants to zero excitation rate, which is necessary for a precise determination of the correct decay constants of the T_0 spin states.^{3,4}

In addition, we have obtained reliable values for the relative populating rates of the three spin states of T_0 . Such measurements are of importance since they provide kinetic and static parameters of T_0 , bridging the gap between porphin free base, which has been thoroughly studied,^{4,5-7} and natural photosynthetic pigments, which are far less understood w. r. t. their electronic structure.

Similarly to what has been found in porphin free base^{4,7} chlorin free base exhibits a photoinduced rearrangement of the two central protons. There are interesting differences with porphin behavior, however, due to the asymmetric potential inside the chlorin ring, since this compound has one saturated pyrrole ring. (Fig. 1).

II. EXPERIMENTAL

Most of the experimental details have been described in previous papers.^{4,2} Some modifications will be described in this section. Unless stated otherwise, all experiments were carried out at 4.2 K.

For optimum S/N ratio we have used a 900 W Xenon arc (Osram XBO 900 W/2) as an excitation source and a dichroic mirror (Schott type 311) for the separation of

the blue excitation and red emission light. The ODMR transitions are detected by monitoring the dihydroporphin 0-0 fluorescence emission at 635 nm.^{8,5} For the selection of the blue excitation light we used either a combination of a 12 cm cuvette containing water and a Balzers interference filter (Filtraflex B 40) transmitting at 403 nm (bandwidth: 15 nm) or a 12 cm cuvette containing a CuSO_4 solution combined with Schott BG 12 and GG 395 filters. The latter combination has a bandwidth of 80 nm.

Two methods were used to determine the kinetics of the spin states of the lowest excited triplet state:

(i) Following Clarke,⁸ we used a microwave pulse long compared to the mean triplet state lifetime resulting in a simple exponential curve fitting, but requiring saturating microwave pulses.

(ii) The second method is due to Van Dorp *et al.*⁴ who used a relatively short (i. e., short compared to the lifetime of the fastest decaying T_0 spin state) microwave pulse; this method requires no saturating microwaves, but leads to a more complicated exponential curve fitting.³

In order to determine the mean triplet state decay constant we used fluorescence onset experiments at 77 K without microwaves or at 4.2 K with CW irradiation at two resonant microwave frequencies as described by Van Dorp *et al.*⁴ To switch the light on and off we used a Vincent Associates Uniblitz model 225 electronic shutter.

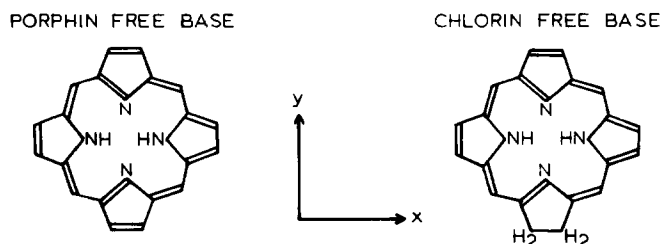


FIG. 1. Skeleton of porphin free base and chlorin free base. x , y , z defines the molecular axis system.

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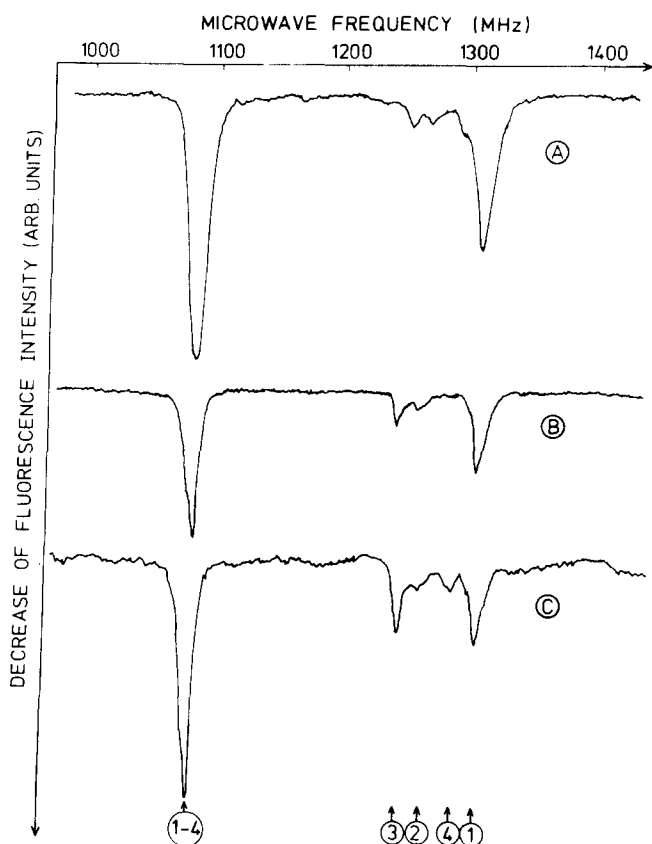


FIG. 2. Zero field ODMR spectra of chlorin free base in *n*-octane single crystal at 4.2 K. Spectrum A was taken <1 h after starting irradiation; B and C are taken 24 h apart. Detection wavelength/bandwidth: A: 635/1; B: 635/1; C: 635/10 nm. Microwavepower: A: 50; B: 10; C: 50 mW. Sweep rate: A: 80; B: 40; C: 40 MHz/s. Number of accumulated transients: A: 2⁹; B: 2¹⁴; C: 2⁸. Labels 1-4 refer to *D*+*E* resonances, mentioned in text. A, B, C have been recorded at different gain.

For those ODMR transitions, which were strong enough, frequencies were determined as follows: The change of fluorescence intensity $\Delta I_f(t)$ for both transitions was measured while stepwise varying the frequency in a small region (~ 10 MHz) around the frequencies which were already approximately known using pulsed microwaves following Clarke.⁸ The frequency where the amplitude $|\Delta I_f(t)|$ had a maximum was taken to be the frequency of the ODMR transition. In the following we will refer to this method as the "maximum response" method. The frequency of the microwave source was measured with a Systron-Donner 1017 series frequency meter with a model 1292A plug in. In this way, sizeable errors due to nonlinear calibration and systematic errors in markers produced by the swept microwave source, are avoided.

III. RESULTS

A. ODMR and optical spectroscopy

ODMR spectra of chlorin in *n*-octane at 4.2 K are presented in Fig. 2 A-C where Fig. 2 A is in close agreement with a previously published spectrum with lower *S/N* ratio¹ in which the transitions marked by 2

through 4 in the *D*+*E* region of Fig. 2 were not visible. Anticipating a discussion of spectra A-C, we assign transitions 1-4 to four physically different species 1-4, each with its own *D*+*E* and *D*-*E* transition. For the *D*-*E* region all species have their resonance within one ODMR peak, whereas in the *D*+*E* region they are resolved.

The spectra A-C are shown in the order of increasing time of exposure to exciting light in a band centered at 410 nm and halfwidth of ~ 30 nm. We did not carry out an accurate analysis of the slow changes of the ODMR spectra with time during continuous irradiation. Spectrum A was taken of a sample for which the product of excitation rate and exposure time was much smaller than for spectra B and C, which were taken ~ 24 h apart, whereas the excitation rate is estimated to be $R_{ex} \sim 500$ s⁻¹ per molec. A fourth spectrum taken 24 h after spectrum C was recorded, did not show detectable differences with spectrum C, all experimental conditions being identical. The spectra A-C have not been recorded at identical experimental conditions (see captions of Fig. 2 A-C). It was checked however, that these differences did not affect our conclusions. We have compared spectrum B with those observed at various detection wavelengths around the maximum of the 0-0 fluorescence band; no significant changes in relative intensity of transitions 1-4 were observed in the (*D*+*E*) region for different wavelengths within the 0-0 band.

It turns out that the ratio of the integrated total intensities in the *D*+*E* region 1-4 and the *D*-*E* integrated intensity does not vary in time within our accuracy of measurement between spectra A, B, and C, despite the major changes observed in the shape of the spectra in the *D*+*E* region: transitions of species 1 and 2 decrease in amplitude after prolonged irradiation, whereas 3 and 4 simultaneously increase. The 2*E* transition is not visible using single resonance ODMR, but can be obtained using double resonance with CW irradiation at $\nu(D+E)$ and sweeping through the region 10-1200 MHz.

The experimental amplitudes of the *D*-*E* and 2*E* transitions found in such an experiment are not equal, due to inhomogeneous broadening of the *D*+*E* transition. This is expected in the absence of FM modulation of the *D*+*E* resonance frequency. The frequencies for species 2 through 4 were obtained by interpolation between $\nu_1(D+E)$ and $\nu_1(D-E)$, where the subscript 1 refers to species 1; these frequencies were determined accurately as described in the previous section. The data are collected in Table I.

None of the transitions in the *D*+*E* region exhibits a significant change of its intensity if microwave power is increased from 1 to 50 mW. Even at power levels as low as 1 mW we find considerable saturation broadening. The smallest linewidth was measured at 80 μ W to be 6.8 MHz for the *D*-*E* transition and 4 MHz for the *D*+*E* transition which is the most intense ODMR transition at this power level. Special care was taken to ensure that intensity measurements were only made under saturating conditions.

Fluorescence spectra were identical to those previ-

TABLE I. Frequencies of chlorin ODMR transitions in *n*-octane/4.2 K.

Species	$\nu(D+E)$ (MHz) ^a	$\nu(D-E)$ (MHz)	$\nu(2E)$ ^b (MHz)
1	1308 ± 2	1085 ± 2	223 ± 3 ^c
2	1262 ± 3	1085 ± 2	174 ± 4
3	1246 ± 3 ^d	1085 ± 2	161 ± 4
4	1289 ± 3	1085 ± 2	204 ± 4

^aThe values of $\nu(D+E)$ and $\nu(D-E)$ of species 1 are somewhat (7 MHz) higher than previously reported,⁴ due to a systematic error in marker frequencies in the older measurements.

^bObtained from $\nu(D+E) - \nu(D-E)$.

^cAlso determined by double resonance to be 228 ± 5 MHz.

^dAlso determined with the maximum response method to be 1249 ± 2 MHz.

ously published¹ and did not change during experiments. A fluorescence excitation spectrum exhibits complete wavenumber mirror symmetry with the fluorescence emission spectrum in the 560–635 nm region.

B. Triplet state kinetics

From time dependent single resonance experiments, saturating either the $D+E$ or $D-E$ transition with a 1–2 ms microwave pulse following the method of Van Dorp *et al.*,⁴ or with a 50–100 ms microwave pulse following the method of Clarke *et al.*,⁸ the kinetic parameters of the lowest triplet state T_0 (species 1) were determined as collected in Table II. The data presented in this Table, column b, were obtained by taking the average of several measurements at frequencies at and close to the maximum of the ODMR profile. In separate experiments at 77 and 4.2 K, we determined the mean decay constant k_T of T_0 by the fluorescence-onset method⁴ also given in Table II. The errors given in Table II for k_i , k_j , and k_k were determined from the rms deviation between the experimental and calculated fluorescence transients. Errors in p_i , p_j , and p_k are quoted as standard deviations of the slope of the experimental decay rates vs light intensity. The errors in n_i , n_j , and n_k have been calculated as the rms sum of errors in k 's and p 's. The decay constants at finite light intensity are found to vary somewhat over the profile of the microwave transitions: in a region ± 3 MHz around the maximum of the profile, decay constants did not vary outside the accuracy of our measurements. At larger distance from the center of the transition, the decay constants eventually decrease to about 50% of the value measured at the top. This may be ascribed to a smaller optical excitation rate for molecules at the edge of the absorption band which also have slightly shifted zero field resonance positions. If this explanation is correct, these shifted resonances arise from molecules in different environments.

IV. DISCUSSION

The sequence of spectra shown in Fig. 2 A–C can be viewed to arise from a slow, light-induced transformation of a chlorin species (1) with resonance frequencies 1308 and 1085 MHz into a different species (3) with $\nu(D+E) = 1246$, $\nu(D-E) = 1085$ MHz.

After long periods of irradiation, both species reach ~ 50/50 equilibrium, as judged from their $D+E$ amplitudes in Fig. 2 C. A resonance due to a species labeled 2 with smaller amplitude appears to be always associated with the species 1 resonance; its time dependence and spectral characteristics are undistinguishable from those of species 1; a similar satellite at 1289 MHz (species 4) is associated with the species 3 resonance.

Ascribing the different $D+E$ resonances to different chlorin species, we have silently assumed that for a single molecule only three resonances can be observed at $\nu(D+E)$, $\nu(D-E)$, and $\nu(2E)$; the latter is commonly too weak to be observed for photosynthetic pigments. Satellites have been observed in ODMR, arising from nuclear quadrupole interaction,⁹ but their relative amplitudes do not change with time. Therefore, we assign the different $D+E$ resonances to different species, where species 1 through 4 have $D-E$ resonance frequencies equal to within the ~ 10 MHz linewidth at half height of the $D-E$ peak.

For porphyrin free base in *n*-octane, similar light-induced changes have been observed both by optical spectroscopy⁵ and magnetic resonance.⁶ There are some

TABLE II. Kinetic constants of the lowest excited triplet spin states of chlorin free base in *n*-octane/4.2 K.^a

	Decay rate constant (s ⁻¹)		Relative populating rates (%)		Method
		Method		Method	
k_i	174 ± 33	b	p_i	36 ± 8	c
	172 ± 11	c			
k_j	464 ± 60	b	p_j	62 ± 13	c
	406 ± 33	c			
k_k	23.9 ± 2.9	b	p_k	2 ± 0.5	c
	23.4 ± 0.7	c			
$k_T(4.2 \text{ K})$	221 ± 23	b	Steady state population		
	200 ± 12	c	n_i	0.47 ± 0.09	f
	370 ± 19	d	n_j	0.34 ± 0.06	f
$k_T(77 \text{ K})$	325 ± 17	e	n_k	0.19 ± 0.04	f

^aSpinstates are labeled $|i\rangle$, $|j\rangle$, and $|k\rangle$ in decreasing order of zero field energy; subscripts i , j , and k attached to the symbols k , p , and n , refer to these spin states; k_m ($m = i, j, k$) is the total rate constant (almost entirely being of non-radiative character) of spin state $|m\rangle$; similarly p_m and n_m refer to relative populating rates and steady state populations of $|m\rangle$.

^bDetermined following van Dorp's method.⁴

^cDetermined following Clarke's method.⁸

^dDetermined from fluorescence onset at 4.2 K with presence of CW microwave radiation at $\nu(D+E)$ and $\nu(D-E)$.

^eDetermined from fluorescence onset at 77 K (no microwaves present).

^fCalculated from k_m and p_m measured by method c.

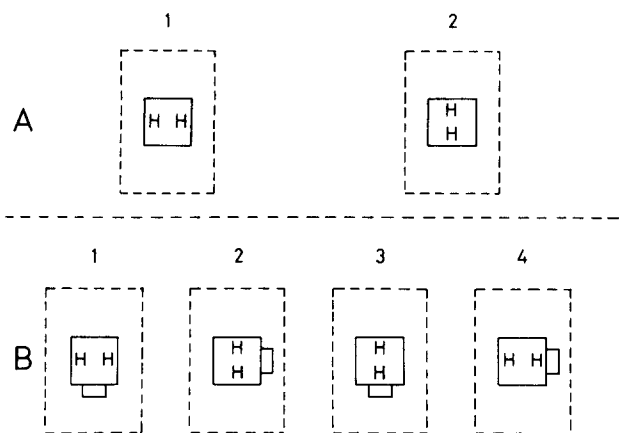


FIG. 3. (a) Porphin free base in a crystal site with lower than D_4 symmetry; (b) Chlorin free base in a similar crystal site. Skeletons of porphin and chlorin free base have been represented by fully drawn lines, the crystal environment by dashed lines. Rotated porphin/chlorin skeletons have been labeled by 1 and 2 in A and B, whereas rotation of protons within the chlorin skeleton results in 3 and 4 in diagram (b).

striking differences with the behavior of chlorin, however: for porphin in *n*-octane at 1.2 K, a quasiline fluorescence spectrum was observed,⁶ each fluorescence "line" being doubled with a splitting of $\sim 65 \text{ cm}^{-1}$. The ODMR spectrum⁵ exhibits similar doubling of $D-E$ and $D+E$ transitions; the correlation of each separate pair of $D-E$ and $D+E$ transitions and their associated fluorescence progressions with two physically distinct species (i. e., tautomers) has been convincingly demonstrated.⁵ Under broadband excitation, one observes both species by ODMR and fluorescence with almost equal amplitude. Photoinduced transformation of one species into the other can be achieved by selective optical absorption of one species, using laser irradiation.¹⁰ This photoautomerism involves a rotation of the H-H axis in porphin free base by 90° , as is confirmed by high field EPR.⁶

The possibility to distinguish porphin tautomers by different fluorescence and ODMR transitions is evident from Fig. 3(a), since the crystal field interacting with either the first excited singlet state (S_1) or the lowest excited triplet state (T_0) has lower than D_{4h} symmetry causing the energy of S_1 and zero field splitting (ZFS) of T_0 of both tautomers to be slightly different. For the ground state, the energy difference between both tautomers is apparently so small that they occur in equal statistical weight when a liquid solution of porphin in *n*-octane is slowly crystallized into a single crystal.

For chlorin free base we have a quite different situation as depicted in Fig. 3(b): the potential energy surface of the chlorin dianion skeleton after removal of the two inner protons has C_{2v} symmetry, thus making both tautomers to occur with unequal statistical weight in the groundstate if a solution of chlorin in *n*-octane is slowly crystallized. In fact, a previous study¹ has shown, that the tautomer with the H-H axis parallel to the pyrrole saturated bond is almost exclusively present in fresh samples of chlorin in *n*-octane single crystals. Now,

broadband excitation at $\sim 400 \text{ nm}$ of such a sample induces the transformation of one tautomer into the other, until a 50/50 mixture is reached. Prolonged broad band irradiation leaves this ratio unchanged, as found by comparing ODMR spectra. The constant integrated intensity in the $D+E$ region for different excitation periods relative to that of the $D-E$ transition provides another argument that the single tautomer which was originally present, is transformed into a second one until equilibrium is reached. When the exciting light is turned off, the proton pairs remain fixed in both positions, at least at 4.2 K.

Returning to Fig. 2 it can be understood why at least one of the chlorin ODMR resonances ($D+E$) is split into four different peaks after long periods of excitation, in contrast with porphin free base exhibiting only two resonances for the $D+E$ as well as the $D-E$ transition; note that two chlorin dianion skeletons obtained by removing two protons from chlorin free base and rotated by 90° about an axis perpendicular to the chlorin plane, within a crystal site with lower than fourfold symmetry, are physically nonequivalent (cf. Fig. 3(b) 1 vs 2, and 3 vs 4); each of the nonequivalent orientations may carry two protons with a H-H axis parallel or perpendicular to the in-plane C_2 axis of chlorin, yielding a total of four distinguishable chlorin molecules. The resonances 1-4 of Fig. 2 have been assigned to those four different chlorin molecules in Fig. 3(b), such that the pairs of resonances 1/3 and 2/4 result from a rotation of protons, whereas the pairs 1/2 and 3/4 arise from a rotation of the chlorin skeleton within the crystal lattice. Note that the splitting $\nu_1(D+E) - \nu_2(D+E) = 46 \text{ MHz}$ is very close to $\nu_4(D+E) - \nu_3(D+E) = 43 \text{ MHz}$, which is expected for the same crystal field acting on structurally similar tautomers.

If the previous assignment is correct, removing the orientational inequivalency of the chlorin skeleton within the crystal lattice by transformation of chlorin into porphin free base would cause the resonances 1 and 4 as well as 2 and 3 to coalesce. For the $D+E$ transitions of chlorin we obtain

$$\frac{1}{2} \{ \nu_1(D+E) + \nu_4(D+E) \} - \frac{1}{2} \{ \nu_2(D+E) + \nu_3(D+E) \} = 44 \text{ MHz} .$$

The splitting of the $D-E$ transitions is within the linewidth of $\sim 7 \text{ MHz}$. The pronounced difference between both splittings is very similar to that observed for porphin free base: 33 and 4 MHz, respectively⁵ and is also found in ODMR spectra of photosynthetic pigments in solid alkane matrices.¹¹ By inspection of Fig. 3 we may obtain the splitting of the $D+E$ resonances due to rotation of protons alone, i. e., in the absence of crystal field splittings: by rotation of the entire chlorin molecules, including protons in fixed positions, within the crystal site, symbolized by a rectangular box, we observe diagrams 1-4 to be transformed into each other as 1 \leftrightarrow 2 and 3 \leftrightarrow 4. Thus, the average values $\frac{1}{2}(\nu_1 + \nu_2)$ and $\frac{1}{2}(\nu_3 + \nu_4)$ represent resonances for which the effect of the orientation of the chlorin molecule within the lattice site, i. e., crystal field splittings, have been eliminated.

The difference $\frac{1}{2}(\nu_1 + \nu_2) - \frac{1}{2}(\nu_3 + \nu_4) = 18 \text{ MHz}$ represents the purely tautomeric splitting of $D+E$ resonances

for chlorin structures with the H-H axis parallel and perpendicular to the saturated pyrrole bond.

Averaging over both orientations of the H-H axis in the chlorin skeleton restores D_{4h} symmetry and one expects the molecule to become insensitive to the orientation within the crystalsite. This means that the average $\frac{1}{2}(\nu_1 + \nu_3)$ should approximately coincide with $\frac{1}{2}(\nu_2 + \nu_4)$ which is indeed found from Table I.

The absence of a resolved crystal field splitting in the fluorescence spectrum of chlorin is in striking contrast with the 65 cm^{-1} splitting observed throughout the porphyrin free base fluorescence spectrum.⁵ Such a splitting is also absent in the fluorescence excitation spectrum of chlorin. Probably one of the Q transitions (in our axis system, shown in Fig. 1, designated as Q_y , corresponding to Q_x in Goutermans work¹² hides in the 480 nm region which was not accessible under the conditions of our experiment. The Q_x fluorescence excitation spectrum is an almost perfect mirror image of the fluorescence spectrum. Although the different behavior of porphyrin and chlorin free base in n -octane single crystals is not yet understood, there is no doubt that both species previously denoted by 1 and 3, and their respective partners 2 and 4, all have fluorescence spectra coinciding to within experimental error.

Finally, we want to comment on the kinetic data, presented in Table II: The k values quoted in Table II exhibit some differences with previously published results.^{4,2} For $k_k (=k_z$ in the molecular axis system of Fig. 1) there is excellent agreement, whereas $k_i (=k_y)$ in Table II is equal within experimental error to the previously reported value. For $k_j (=k_x)$, however, the presently determined value is considerably higher than in Refs. 4 and 2. This is probably due to a 50 s^{-1} contamination, which we have found to interfere with the pure molecular decay, especially when using Clarke's method. By a proper fitting procedure, the interfering exponential could be eliminated. This has not been done with the older measurements, however.

We cannot exclude that the tabulated decay constants are contaminated by spin lattice relaxation; this contri-

bution can be shown to be small for the extrapolated values $\frac{1}{2}(k_i + k_k)$ and $\frac{1}{2}(k_j + k_k)$.³ The mean decay constant $k_T = \frac{1}{3}(k_i + k_j + k_k)$ calculated from the data of Table II following methods band c does not agree with the value obtained from fluorescence onset experiments at 4.2 and 77 K. The 4.2 K experimental value of k_T , obtained from double-resonance experiments may be too fast if saturation is incomplete, evidence for which has been found in Sec. III A. For the discrepancy between k_T obtained at 77 K and the calculated value $\frac{1}{3}(k_i + k_j + k_k)$ we do not have a satisfactory explanation.

Finally, we note that the spin state labels i , j , and k can be identified with y , x , and z as in Ref. 4.

ACKNOWLEDGMENT

Technical and computational assistance by Mr. P. Geerse, Mr. P. A. de Jager, and Mr. J. Meuleman is gratefully acknowledged.

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