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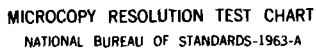
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4. TITLE (and Subtitle) Intermolecular Energy Transfer between the Individual Zero-Field Levels of Triplet Traps in an Orientationally Disordered Solid		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
7. AUTHOR(s) Hansjorg S. Niederwald and M. A. El-Sayed		6. PERFORMING ORG. REPORT NUMBER
PERFORMING ORGANIZATION NAME AND ADDRESS Regents of the University of California University of California, 405 Hilgard Ave. Los Angeles, CA 90024		8. CONTRACT OR GRANT NUMBER(s) N00014-83-K-0341
CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Branch Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research Branch Office 1030 East Green Street Pasadena, CA 91106		12. REPORT DATE February 5, 1985
		13. NUMBER OF PAGES 21
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Published J. Phys. Chem. <u>88</u> , 5775 (1984).		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Energy Transfer Mechanisms Zero-field levels Optical detection.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The zero-field transitions and levels of the phosphorescing triplet state of the traps in the orientationally disordered crystal of 1-bromo-4-chloro-naphthalene (BCN) are assigned by using phosphorescence-microwave double resonance techniques at 1.8 K. The relative population of the different zero-field levels are determined at different delays after singlet-singlet excitation and as a function of the energy of the emitting traps within the inhomogeneously broadened bands. For the same delay, the population of the radiating level is found to have a maximum which is at a lower energy within.		

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TECHNICAL REPORT NO. 44

Intermolecular Energy Transfer between the Individual Zero-Field Levels
of Triplet Traps in an Orientationally Disordered Solid

by

Hansjorg S. Niederwald and M. A. El-Sayed

Prepared for Publication

in the

Journal of Physical Chemistry

University of California
Department of Chemistry and Biochemistry
Los Angeles, California 90024

February 5, 1985

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INTERMOLECULAR ENERGY TRANSFER BETWEEN THE INDIVIDUAL ZEROFIELD LEVELS
OF TRIPLET TRAPS IN AN ORIENTATIONALLY DISORDERED SOLID

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Abstract

The zerofield transitions and levels of the phosphorescing triplet state of the traps in the orientationally disordered crystal of 1-bromo-4-chloronaphthalene (BCN) are assigned by using phosphorescence-microwave double resonance techniques at 1.8 K. The relative population of the different zerofield levels are determined at different delays after singlet-singlet excitation and as a function of the energy of the emitting traps within the inhomogeneously broadened bands. For the same delay, the population of the radiating level is found to have a maximum which is at a lower energy within the inhomogeneous profile than that for the dark level. This observation is contrary to predictions based on one-dimensional exchange mechanisms and might suggest the involvement of dipole-dipole coupling for the triplet-triplet energy migration at the relatively large distances involved in the energy transfer between the traps.

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INTRODUCTION

Intermolecular triplet-triplet energy transfer in the orientationally oriented solid of 1-bromo-4-chloronaphthalene (BCN) has recently been studied by using time-resolved laser phosphorescence line narrowing techniques.⁽¹⁻³⁾ This was carried out at 4.2 K within the inhomogeneous profile of the 0,0 band of the lowest energy singlet-triplet absorption. The temporal profile of the laser excited donors is examined from which the transfer mechanism is concluded. The results can be summarized as follows:

1. The transfer rate increases rapidly as the donor energy (laser frequency) increases. This was described in terms of an increase in the density of the acceptors, which are BCN molecules with energies lower than that for the donor.
2. The one-dimensional exchange mechanism is found to account for the data until the acceptor density falls below ~ 5 mole %.
3. The temporal results at low acceptor concentrations (low laser frequency) could be described in terms of a 3-dimensional dipole-dipole coupling.
4. At still lower concentrations, the trap emission of the crystal is observed. The emission profile was theoretically described^(2b) in terms of an emission from excited molecules in the crystal whose radiative probability is comparable to or larger than their transfer probability.

In the present study, we extend the energy transfer studies to longer times, i.e., we examine energy transfer between the so-called trapped molecules. Furthermore, using phosphorescence-microwave double resonance techniques, we examine the time dependence of the populations of the

different zerofield levels of molecules with different energies within the inhomogeneous profile of the "trap" emission. The results suggest that for the same delay after singlet-singlet excitation, the radiative spin levels seem to shift the maximum of their population distribution to lower energies more than that for the dark spin level. This result is inconsistent with the one-dimensional exchange mechanism and can better be described in terms of a dipole-dipole coupling for the triplet-triplet energy transfer between the low density trap molecules.

EXPERIMENTAL

The BCN was synthesized from 1-amino-4-chloronaphthalene by a Sandmeyer reaction. The material was extensively zone refined. Durene was purified by sublimation. The MIDP and the phosphorescence measurements were carried out at a temperature of 1.8 K. Phosphorescence spectra were recorded with a 1-m Jarrell-Ash monochromator with 0.5 Å resolution. The delayed spectra were taken with a Princeton Applied Research 162 boxcar averager. The light source was a 100 W mercury lamp used with a NiSO₄ aqueous solution and Schott UG 11 filter combination, passing mainly the 313 nm line to excite the sample.

Microwave Induced Delayed Phosphorescence (MIDP) experiments⁽⁵⁾ were done monitoring the 0,0 band (and sometimes the 0,0-234 cm⁻¹ vibronic band) of the phosphorescence emission. A Hewlett Packard 8690 Sweep Oscillator with 8699B and 8693A plug-in units was used as a microwave source with an Alto Scientific microwave amplifier. The microwave frequency was determined by the use of a Hewlett Packard 8557 spectrum analyzer. The microwave power was brought by a coaxial cable to a helix surrounding the sample.

The lifetimes of the triplet sublevels were also determined by the MIDP techniques.⁽⁵⁾ The principle of this method is to determine the height of the leading edge of the MIDP signal as a function of delay time relative to the closing time of the shutter in the excitation light path. The slope of the resulting curve yields the decay constant of the long-lived level. The radiative lifetime of the short-lived level is determined from the decay of the microwave induced signal.

An electromechanical shutter was driven at a frequency of approximately 1 Hz. Data were acquired with a Biomation 805 waveform recorder, processed on an Apple II plus computer.

RESULTS

a) The zerofield transitions in BCN

Figure 1 shows the MIDP signals of the three zerofield transitions of BCN in a BCN crystal. It was not possible to obtain cw-PMDR spectra of these transitions. The strongest and sharpest one is the transition at 1.05 GHz, the one at 3.16 GHz is weaker and the one at 4.24 GHz is very hard to detect, most probably due to its large hyperfine broadening. The signals are the optical response to a microwave sweep at 2.5 MHz per ms which passes through resonance approximately 100 ms after closing of the shutter.

For a 10^{-3} molar solution of BCN in durene we find, within experimental error, the same transition frequencies as in neat BCN.

b) Lifetimes

The lifetime of the radiative level of each of the 1.05 and 3.16 GHz transitions is found to be the same and has the value of 10 ms. For the level involved in the 3.16 GHz transition, a lifetime of 50 ms was

determined, while in the 1.05 GHz transition a lifetime of 140 ns was found. Thus the 4.24 GHz transition connects the 50 ns and the 140 ns levels. It was, however, not possible to determine these lifetimes because of the weak signal of this transition.

Similar measurements for a 10^{-3} molar solution of BCN in durene resulted in about 20% longer lifetimes, which can be partly blamed on the external heavy atom effect in neat BCN.

The above results are summarized in Table 1.

c) Phosphorescence Spectra

In Figure 2, three phosphorescence spectra are shown. On the top, the phosphorescence of neat BCN under cw excitation is shown which is in agreement with previously published spectra.⁽⁴⁾ The middle spectrum is that for neat BCN which was taken 70 ns after excitation. The gate on the boxcar averager was 5 ns. The most significant difference between the cw and the delayed spectrum is the relative intensities of the 0,0 band at approximately 4950 Å and the (0,0-321 cm⁻¹) vibronic band at approximately 5030 Å. The vibronic band is a factor of two weaker at 70 ns delay, indicating a large part of its radiation originates from a spin level which has a shorter lifetime than that giving the radiation of the 0,0 band. The spectrum at the bottom was taken from a BCN solid solution in durene. The relative intensity of the different bands is the same in durene as in neat BCN; however, the bandshapes are different. The bands are narrower and the peaks are slightly shifted to the red (by around 2 Å) in durene host.

d) The 0,0 Band Position and Line Shape

Figure 3 shows the inhomogeneous lineshape of the 0,0 band of the phosphorescence emission, taken under four different conditions. Curve a shows the cw intensity distribution. Curves b and c show the height of the leading edge of the MIDP signal of the 1.05 GHz zf transition, which is proportional to the population of the nonradiative zf level after 70 ms delay time (curve b) and after 130 ms delay time (curve c). Curve d is derived from the phosphorescence spectrum taken after 70 ms delay, which is the middle spectrum in Fig. 2. The 0,0 band in this spectrum reflects the population of only the zf level with the 50 ms radiative lifetime. The population of the 10 ms radiative level after 70 ms delay is practically zero.

The curves in Fig. 3 are normalized to the same amplitude, although the original relative intensities vary from 1 for the cw spectrum to 0.1 for the MIDP curves and to 0.01 for the delayed spectrum.

There is a significant red-shift by $1.5 \text{ \AA}$ and a slight narrowing by about 10% for the MIDP curves with respect to the cw spectrum. The MIDP curves after 70 ms and 130 ms are nearly identical. The delayed phosphorescence spectrum is red shifted by $2.5 \text{ \AA}$ with respect to the cw curve and by $1 \text{ \AA}$ with respect to the MIDP curves. As the observed peak shifts to the red, it becomes more asymmetric with a steeper, sharper long-wavelength edge.

DISCUSSION

a) Assignment of the Zerofield Levels

Group theoretical and detailed experimental analysis of C_{2v} dihalonaphthalene(6) predicts that the 0,0 band originates from the τ_L

zf level, the false origin built on an out-of-plane vibration of the halogen originates via vibronic-spin orbit coupling from the τ_M zf level. The τ_N is expected to be dark. These results are in agreement with the results of Figs. 2b and c if the 10 ms is assigned to the τ_M level and the 50 ms to the τ_L level. A delay of 70 ms greatly reduces the intensity of the 0,0-234 cm^{-1} vibronic band. A good fraction of the intensity of this band is expected to originate from τ_M . Thus the 10 ms radiative lifetime must be τ_M . Of course the 140 ms must be the dark level which is predicted to be τ_N . From this assignment, the transition at 1.05 GHz is $\tau_N \leftrightarrow \tau_M$, that at 3.16 GHz is $\tau_M \leftrightarrow \tau_L$ and that at 4.24 GHz is $\tau_N \leftrightarrow \tau_L$. These results are similar to those observed for 1-iodonaphthalene.⁽⁷⁾ This is not surprising, since the spin orbit coupling of bromines, having spin orbit factors much larger⁽⁸⁾ than chlorine, would dominate the radiative properties of the zf levels in BCN.

b) Triplet-Triplet Energy Transfer Between the BCN Traps

The application of the MIDP method to the inhomogeneously broadened phosphorescence lineshape bears two interesting aspects. First, it is possible to measure the triplet state energy distribution after appropriate delay times at which the population of one of the radiative levels has been completely depopulated. The other point is that the energy distribution of the nonradiative level is measured as well by using MIDP techniques. A comparison can thus be made of the energy distribution in the different (radiative and dark) zf levels. Differences can then be described in terms of the differences in the energy transfer mechanisms involved.

Figure 3 summarizes the results. Figs. 3a is the energy distribution in a cw experiment and reflects the populations of the radiating levels, τ_L and τ_M . Fig. 3d shows the energy distribution of the radiating level(s) of trap molecules 70 ms after excitation. Since τ_M has a 10 ms lifetime, this distribution reflects the trap population of the longer lived radiating level, τ_L . Due to energy transfer to lower energy trap molecules, the distribution shows a shift of its maximum to lower energy. Curve b shows the distribution of the traps in the τ_N level after 70 ms. The shift in the maximum in this curve (from the cw maximum) is found to be less than that for curve d. This suggests that the population of the radiating level, τ_L , transfer energy to the lower traps in 70 ms more effectively than that for the dark level, τ_N . Furthermore, the energy distribution of molecules in the dark level is found not to shift any further if a delay of 130 ms (Fig. 3c) is used instead of 70 ms (curve 3b).

One-dimensional exchange interaction is expected to have the same transfer probability for the different zerofield levels. This is due to the conservation of the spin angular momentum in triplet-triplet energy transfer⁽¹⁰⁾ and the fact that molecules along the one-dimensional chain have parallel magnetic axes. This would lead to the same shift in the maximum of the energy distribution with time, independent of the zf level.

One possible explanation for the above observations could be that the switching in energy transfer mechanism from short-range transfer to

long-range transfer⁽²⁾ is only possible for the radiative sublevels. The nonradiative sublevel may only be capable of short-range energy transfer. Thus for the $\langle T_N \rangle$ ensemble, energy transfer comes to an end, as soon as there are no more energy acceptors present within the exchange critical radius, which is undoubtedly smaller than that for the dipole coupling.

ACKNOWLEDGMENT

We wish to thank Dr. H. P. Krimmer for the synthesis of the BCN. H.S.N. gratefully acknowledges the Deutsche Forschungsgemeinschaft for a research fellowship during 1983-1984. We thank Mr. T. Corcoran for careful reading of the manuscript. The support of the Office of Naval Research is also acknowledged.

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TABLE 1: Summary of the Zerofield Transitions and Lifetimes for the
Lowest Triplet State of 1-Bromo-4-Chloronaphthalene Traps
in Neat Crystals and in Durene at 1.8° K

	Lifetimes/ms		Transition Frequencies/GHz	
	neat BCN	BCN in durene	τ_L	τ_M
τ_L	50 $\pm$ 10	65 $\pm$ 10	-	-
τ_M	10 $\pm$ 2	12 $\pm$ 2	3.16 $\pm$ 0.01	-
τ_N	140 $\pm$ 20	180 $\pm$ 20	4.24 $\pm$ 0.02	1.05 $\pm$ 0.01

Figure Captions

- Fig. 1 MIDP signals of the three zerofield transitions of BCN in a neat BCN crystal, detected at $4348 \text{ \AA}$. The microwave frequency was swept at $2.5 \text{ MHz per millisecond}$; the sweep passed through resonance at about 100 ms after closing off the excitation light. The transition at 1.05 GHz is the strongest and narrowest one. The one at 4.24 GHz is the broadest and weakest one; it is shown on a larger time scale. The 1.05 GHz and 3.16 GHz MIDP signals decay with a 10 ms lifetime, the 4.24 GHz with about 50 ms lifetime. Sample temperature was 1.8 K .
- Fig. 2 Phosphorescence spectra of a neat BCN crystal under cw-excitation (top), of the same crystal, taken with a boxcar averager 70 ms after closing off the excitation light (middle) and of a 10^{-3} molar solid solution of BCN in durene (bottom). Sample temperature was 1.8 K . Excitation source was the 313 nm line of a 100 W Hg-lamp . The major difference between the cw spectrum and the delayed spectrum is in the relative intensities of the $0,0$ band and the $0,0 - 321 \text{ cm}^{-1}$ band. The lines in the middle and bottom spectra are slightly narrower and red shifted by $1-2 \text{ \AA}$.
- Fig. 3 Inhomogeneous lineshape of the $0,0$ phosphorescence transition at 1.8 K , taken under four different conditions. Curve a shows the cw intensity distribution, curves b and c show the height of the leading edge of the MIDP signal at 1.05 GHz , which is

proportional to the population of the τ_N sublevel, after 70 ms (b) and 130 ms (c) delay time. Curve d is derived from the delayed spectrum in the middle part of Fig. 2 and represented the population of the τ_L sublevel. With the red shift, the curves b, c and d also get slightly narrower and asymmetric. As Figs. b and d show, the distribution of sublevel τ_L (lifetime 50 ms) at 70 ms is relaxed to lower energies than the distribution of sublevel τ_N (lifetime 140 ms) at the same delay time.

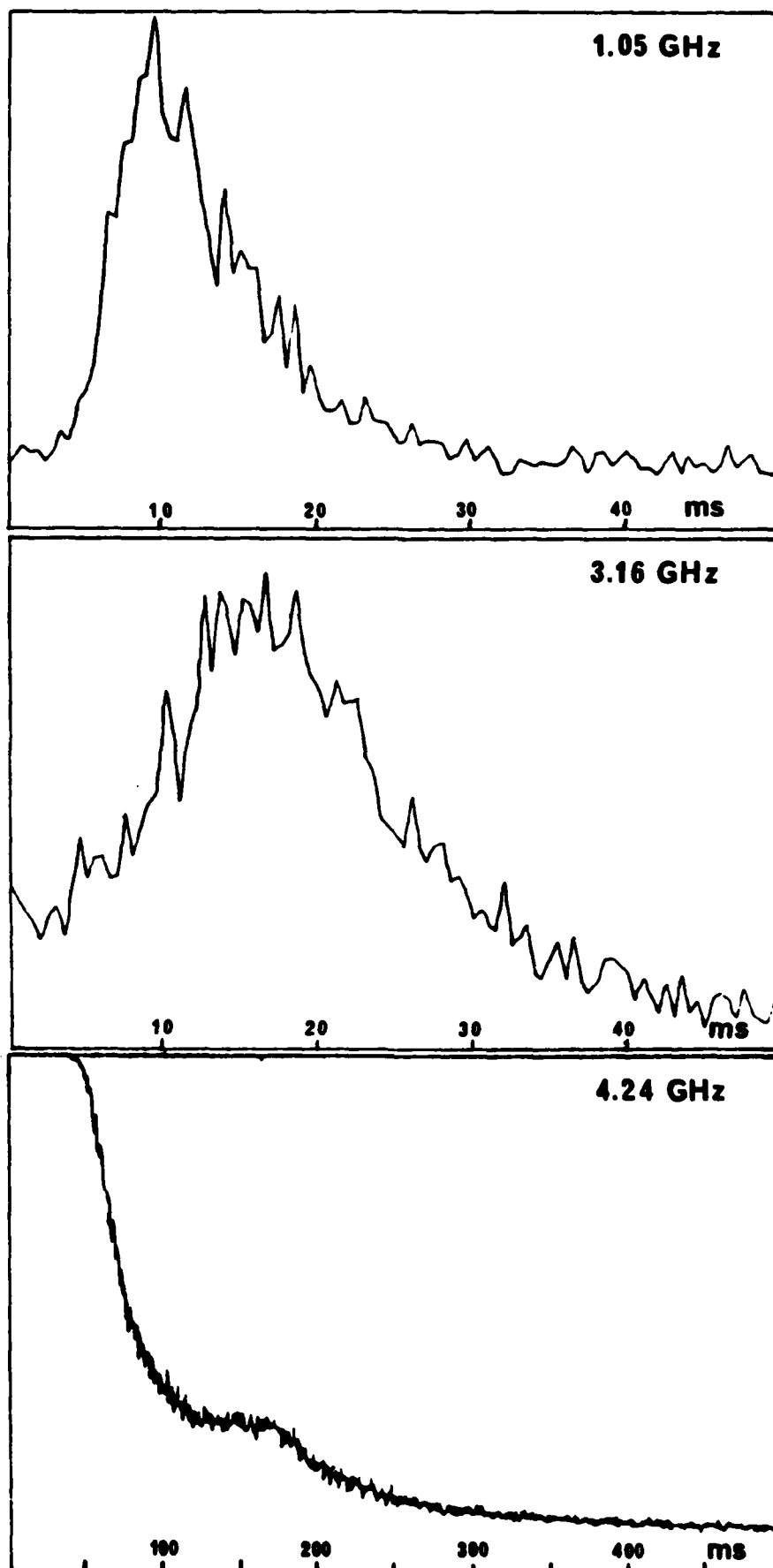


Fig. 2

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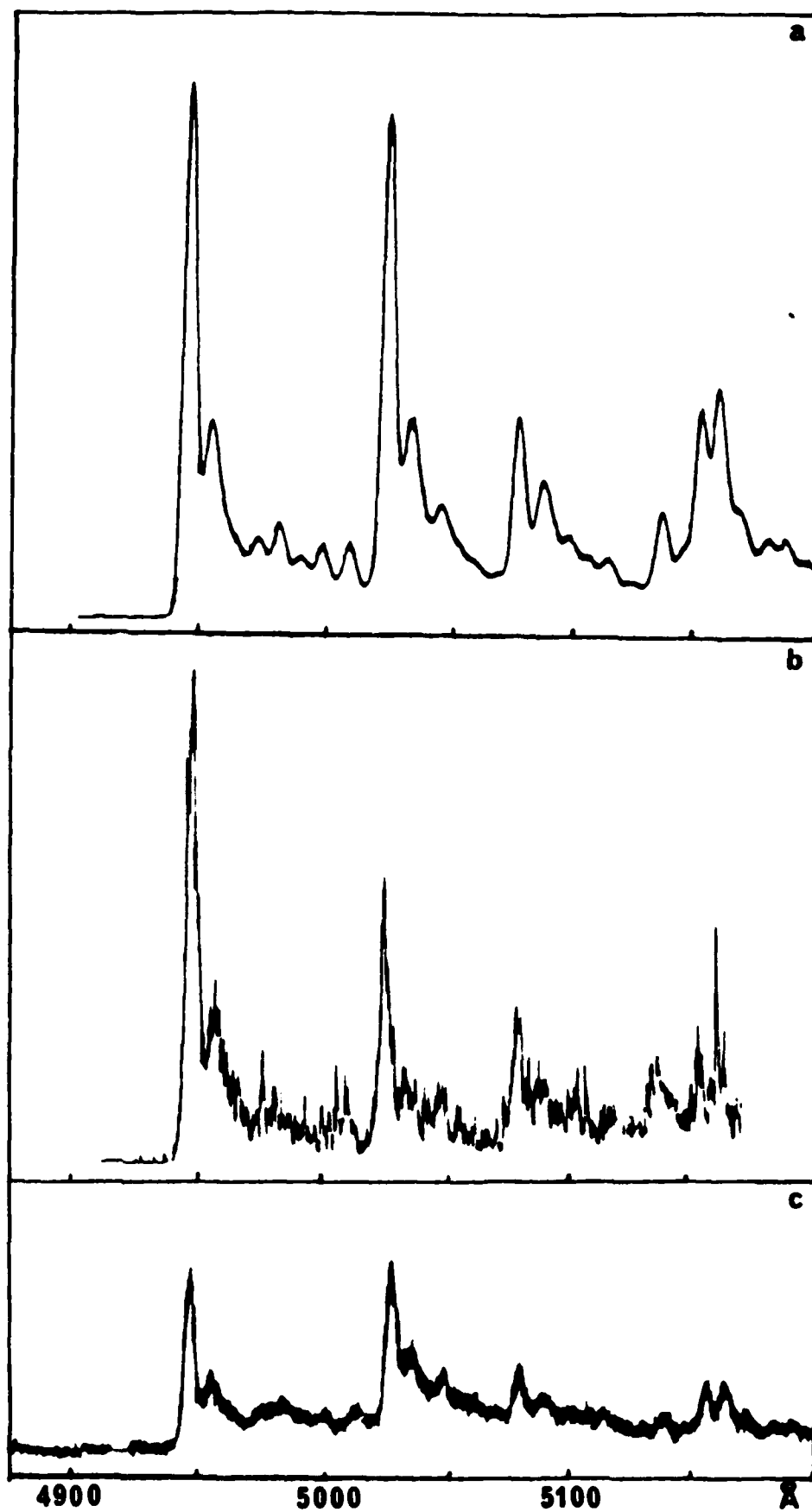
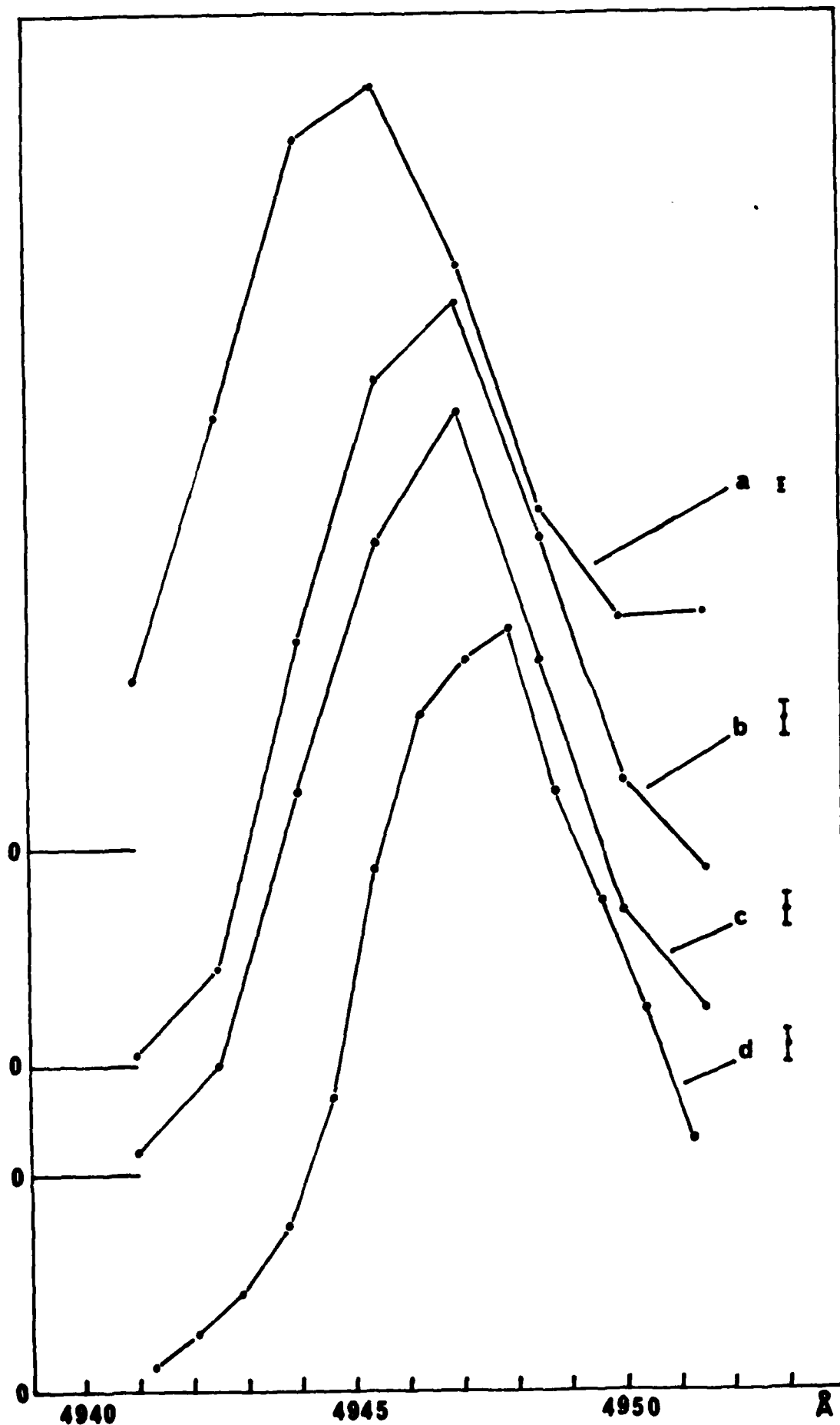


Fig 3

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