-A091 714   CALIFORNIA UNIV LOS ANGELES DEPT OF CHEMISTRY   F/G 7/4
ANALYSIS OF SPECTRAL DIFFUSION OF LOCALIZED TRIPLET SPIN TRANSI--ETC(U)
NOV 80 A R BURNS, M A EL-SAYED, J C BROCK   N00014-75-C-0602
LASSIFIED TR-36   NL

|OF|

END
DATE
FILMED
81-1
DTIC

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0602

Task No. NR 056-498

TECHNICAL REPORT NO. 36

ANALYSIS OF SPECTRAL DIFFUSION OF LOCALIZED TRIPLET SPIN TRANSITIONS WITHIN AN INHOMOGENEOUS PROFILE

by

A. R. Burns and M. A. El-Sayed
Department of Chemistry
University of California
Los Angeles, CA 90024

and

J. C. Brock
Molecular Chemistry and Physics Section
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91103

Prepared for Publication

in

Chemical Physics Letters

November 1, 1980

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) UNCLASSIFIED

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER
Technical Report No. 36

2. GOVT ACCESSION NO.
AD-A091

3. RECIPIENT'S CATALOG NUMBER
714

4. ~~TITLE (and Subtitle)~~
(6) Analysis of Spectral Diffusion of Localized Triplet Spin Transitions Within an Inhomogeneous Profile

5. ~~TYPE OF REPORT & PERIOD COVERED~~
(9) Interim Technical Report,

6. ~~PERFORMING ORG. REPORT~~ NUMBER

7. ~~AUTHOR(s)~~
(10) A. R. Burns, M. A. El-Sayed ~~and~~ J. C. Brock

8. CONTRACT OR GRANT NUMBER(s)
(15) N00014-75-C-0602

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Regents of the University of California
University of California, 405 Hilgard Ave.
Los Angeles, California 90024

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
NR-056-498

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research
Chemistry Branch
Arlington, Virginia 22217

(11) 1 Nov 80

12. REPORT DATE
November 1, 1980

13. NUMBER OF PAGES
19

14. MONITORING AGENCY NAME & ADDRESS ~~(If different from Controlling Office)~~
Office of Naval Research
Branch Office
1030 East Green Street
Pasadena, CA 91106

(12) 24

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
This document has been approved for public release and sale; distribution of this document is unlimited.

(14) TR-36

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES
Accepted for publication in Chemical Physics Letters

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
spectral diffusion
hole burning
homogeneous line width
triplet state

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
The observation of rapid changes in the lineshape of a hole burned in the spectral profile of a zero-field triplet spin transition indicates that spectral diffusion processes are occurring. A kinetic model which quantitatively reproduces the hole lineshape changes is used to calculate a spectral diffusion rate constant. The diffusion rate constant depends not only on the frequency shift (i.e., energy mismatch), but also on whether the excited molecule is deuterated, which suggests that the energy-conserving spin-flipping processes responsible for the homogeneous width are also responsible for spectral diffusion within the inhomogeneous profile.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

472255

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

"ANALYSIS OF SPECTRAL DIFFUSION OF LOCALIZED TRIPLET SPIN TRANSITIONS WITHIN AN INHOMOGENEOUS PROFILE"

A.R. Burns* and M.A. El-Sayed
Department of Chemistry, University of California, Los Angeles, CA 90024
and
J.C. Brock**
Molecular Chemistry and Physics Section, Jet Propulsion Laboratory,
California Institute of Technology, Pasadena, CA 91103

---

*Present Address: Sandia Laboratories, Division 4216, Albuquerque, NM 87185.

**NRC-NASA Resident Research Associate
Present Address: TRW, Inc., 1 Space Park, Redondo Beach, CA 90278.

ABSTRACT

The observation of rapid changes in the lineshape of a hole burned in the spectral profile of a zero-field triplet spin transition indicates that spectral diffusion processes are occuring. A kinetic model which quantitatively reproduces the hole lineshape changes is used to calculate a spectral diffusion rate constant. The diffusion rate constant depends not only on the frequency shift (i.e., energy mismatch), but also on whether the excited molecule is deuterated, which suggests that the energy-conserving spin-flipping porcesses responsible for the homogeneous width are also responsible for spectral diffusion within the inhomogeneous profile.

1. INTRODUCTION

In recent years many important features of energy exchange in molecular crystals have been revealed by monitoring the loss of phase coherence induced in zero-field triplet spin transitions using techniques such as spin-locking [1,2] and spin echoes [3-6]. Loss of phase memory is caused by energy fluctuations resulting from changes in the environment surrounding an excited system. Energy transfer between distinct sites in a lattice can induce a loss of spin coherence as shown by Fayer and Harris [2]. Botter, et al. [7], reported that the decay of stimulated echoes in an exciton band was due to wavevector excursions induced by defect and phonon scattering, and were able to determine that the frequency of the energy fluctuations decreased as their magnitude increased. In cases where there is no energy transfer, such as when triplet excitations are localized in deep, "guest" molecule trap sites, the phase memory decay time is still found to be orders of magnitude faster than the radiative lifetime or spin-lattice relaxation time [3,5]. The loss of phase memory in these dilute spin systems is thus a result of spectral diffusion processes, which modulate the triplet spin sublevel energies by way of fluctuating local fields.

Fluctuations in the local fields surrounding the excited molecule can be caused by phonon interactions at that site in the lattice. However, it is also thought that the perturbation of the triplet energies may be due to the coupling of the electronic excitation to an oscillating nuclear field through the hyperfine interaction [5]. In their thorough study of spectral diffusion at deep trap sites in chemically-mixed crystals, Van 'T Hof and Schmidt [8] demonstrated that a change in environmental nuclear magnetic moments, brought about by the dueteration of the guest and/or host molecules, directly influenced the decay time of Hahn spin echoes. They concluded that the spectral diffusion is caused at least in part by rapid, energy-conserving spin flips of the host nuclei. This mechanism has been the subject of a number of theoretical treatments [9-12], and was recently shown to be operative in the dephasing of optical transitions ($^3H_4 \leftrightarrow {}^1D_2$ transition of Pr^{3+} in LaF_3) [3,14].

The effects of spectral diffusion in isolated molecule systems such as 1,2,4,5-tetrachlorobenzene (TCB) in durene are not limited to the destruction of phase coherence. In fact, when a hole is burned into the inhomogeneous spectral profile of the TCB triplet spin transition, spectral diffusion will cause the hole to broaden in time. This was first observed indirectly by Leung and El-Sayed [15], when the application of a continuous fixed-frequency microwave source resulted in a "steady-state" hole that was broadened by spectral diffusion. Later, Pitts and El-Sayed [16], demonstrated that the broadening of the hole-width can be time-resolved by using a short (10 μsec) pulse of fixed frequency, followed by a short probe pulse which sweeps the transition and maps out the spectral profile. The shape of the hole was found to be a function of the time delay between the two pulses.

In this paper, we report that the time-resolved hole-burning experiment can be performed in a quantitative manner; that is, the time evolution of the hole shape can be used to determine a spectral diffusion rate constant as a function of the energy shift experienced by the triplet spin system. The spectral diffusion rate constant is then analyzed in terms of the same processes that cause a loss of phase coherence.

2. EXPERIMENTAL

Single crystals of zone-refined $\underline{h}_{14}$-durene containing either 1% M/M $\underline{h}_2$-TCB (1,2,4,5-tetrachlorobenzene) or 1% M/M $\underline{d}_2$-TCB were grown from the melt. The experimental arrangement is essentially the same as that described in detail by Pitts and El-Sayed [16]. All the experiments were conducted at temperatures below 2.0 K and were monitored by observing phosphorescence intensity changes at the electronic origin (3780 Å) of the TCB guest molecule [17]. Since the radiative relaxation rates for the τ_y and τ_z sublevels are much faster than the third τ_x sublevel [18], only the $2|E|$, $\tau_y \leftrightarrow \tau_z$, transition was monitored. The resonant microwave field was delivered by a slow wave helix suitable for optical detection.

The hole-burning experiment is carried out as follows. Two 5 μsec microwave pulses are delivered to the sample at a repetition rate of 10 Hz. The pulses are separated by a variable delay time and are both 80 mW at the helix. The first pulse is from a fixed-frequency source and is used to burn the hole, while the second pulse is from a source which sweeps through the $2|E|$ transition. The phosphorescence response is photon-counted for 1 msec after the second pulse and is sent to a multichannel analyzer. The memory address of the analyzer was advanced through 512 channels as the microwave field of the second pulse was sweeping; in this way, one spin transition spectral profile, with a hole burned into it, was stored in the first 512 channels. In the next 512 channels, the experiment was repeated with the fixed frequency pulse inhibited. Thus a second spin-transition spectral profile, with no hole burned in it, was stored. The frequency resolution for each spectrum was approximately 12 KHz per channel. For each time delay between the microwave pulses, the signals contained in the 1024 channels was averaged for 64 sweeps; the results are similar to those shown in fig. (1).

Each 512 channel spectrum was transferred to a PDP 11/45 computer for data storage and analysis. The computer subtracted the unburned spectrum from the burned spectrum and analyzed the resulting lineshape of the hole (which was generally smoothed for visual clarity). The data file for the unburned spectrum was also transferred to an IBM 360 computer for use as the asymmetric, inhomogeneous lineshape in the kinetic model described in section 4.

3. RESULTS

The time evolution of a hole burned into the |2E| transition of $\underline{h}_2$-TCB in durene can be seen in fig. (2A). The linewidth (FWHM) of the hole when there is no delay time between the two microwave pulses (the sweeping pulse immediately follows the fixed frequency pulse), is generally about 0.73 MHz at the 80 mW power level. Breiland *et al.* [5], report a T_2 time of 4 μsec for the Hahn spin echo decay in this crystal (homogeneous linewidth of 80 KHz); thus the initial width of the hole is clearly power broadened. This was confirmed by the fact that the hole widths can be decreased by lowering the power level of the pulses. Pitts and El-Sayed [16] were able to obtain hole-widths which were close to the homogeneous lifetime limit; however this was after great difficulty with signal-to-noise problems. Thus it was in the best interests of this experiment to sacrifice the ability to approach the narrower linewidth determined by the homogeneous lifetime [16,19,20] in order to obtain optimum signal-to-noise ratios and time resolution for *changes* in the lineshape due to spectral diffusion.

The hole width was determined for a number of delay times (e.g. 50, 100, 200, 400 sec). One can see in Fig. (2A) that after 400 μsec the hole has spread out to a width of 1.1 MHz (FWHM) and has lost 30% of its "depth". However, the total area of the hole has changed very little on this time scale. This is exactly the kind of behavior one expects if the frequency of the saturated spin transitions are modulated during the 400 μsec delay by spectral diffusion. The short timescale and conservation of hole area are features that rule out any contribution by feeding or decay processes of the triplet spin sublevels to the evolution of the hole shape.

The hole depicted in fig. (2A) was burned at the maximum of the inhomogeneous profile. When a hole was burned in the wings of the profile, the time evolution showed not only a broadening and a filling in of the hole, but also a noticeable shift in the location of the hole towards the maximum of the line. Thus it appears that the local fields tend to evolve towards the most probable value, which is the value at the maximum of the inhomogeneous spectral line profile.

4. KINETIC MODEL

Under conditions of constant triplet excitation and decay, the steady state populations of the τ_y and τ_z sublevels are given by:

$$(1) \qquad Y = \frac{C_y(K_z + K_{SLD}) + K_{SLD}C_z}{(K_z + K_{SLD})(K_y + K_{SLU}) - K_{SLU}K_{SLD}}$$

$$(2) \qquad Z = \frac{C_z(K_y + K_{SLU}) + K_{SLU}C_y}{(K_z + K_{SLD})(K_y + K_{SLU}) - K_{SLU}K_{SLD}}$$

K_y and K_z are rate constants for the decay of the two spin sublevels to the ground state (28.0 sec^{-1} and 26.0 sec^{-1}, respectively [18]). K_{SLU} and K_{SLD} are the rate constants for upward ($\tau_y \rightarrow \tau_z$) and downward ($\tau_z \rightarrow \tau_y$) spin-lattice relaxation, and are expected to have values of less than 5 sec^{-1} at temperature below 2.0 K [21]. Spin-lattice relaxation between τ_y or τ_z and the third sublevel τ_x is neglected. These rate constants are assumed to be independent of the local field; that is, they are constant at any particular site in the inhomogeneous profile. C_y and C_z are the total feeding rates to the sublevels, where C_y:C_z is roughly 1:4 [22]. As will be shown below, feeding to a particular site is assumed to be simply the product of the total feeding rate and the site probability given by the inhomogeneous line shape.

The inhomogeneous lineshape, which is obtained experimentally as described in section 2, determines a set of weighting factors A_i, where A_i is the value for the i^{th} site or isochromat. It should be emphasized that A_i refers to the probability of a certain site in frequency space. The population of each isochromat is therefore given by the products of the sublevel populations, Y and Z, and the normalized weighting factors. Thus in the equations below, y_i is the population of the τ_y sublevel of the i^{th} isochromat, and z_i is the population of the τ_z sublevel of the i^{th} isochromat:

(3) $$y_i = A_i Y$$

(4) $$z_i = A_i Z$$

(5) $$\sum_{i=1,n} A_i = 1$$

In this way, one may divide up the total spin sublevel populations given by equations (1) and (2) into two sets of n isochromats. Neighboring isochromats are separated by a frequency difference $\Delta\omega$, which corresponds to the experimental resolution (12 kHz per channel).

A Lorentzian "hole" centered at the j^{th} isochromat, which has a zero-field frequency of ω_j, is introduced into the inhomogeneous profile by altering the spin sublevel populations, y_i and z_i, around this site in frequency space. The new sublevel populations, y_i^* and z_i^*, are just linear combinations of the steady-state populations as shown below:

(6) $$y_i^* = D_i z_i + (1 - D_i) y_i$$

(7) $$z_i^* = D_i y_i + (1 - D_i) z_i$$

$$D_i = D\left(\frac{G^2}{(\omega_i - \omega_j)^2 + G^2}\right)$$

The initial half-width G of the hole can be set equal to the experimentally observed value when there is a negligible delay time between the two microwave pulses, while the depth D of the hole can be set anywhere from 0 to 1. Thus if $D = 0.5$, then $y_j^* = z_j^*$ at $t = 0$, whereas $y_i^* \simeq y_i$ and $z_i^* \simeq z_i$ if $\omega_i << \omega_j$ or $\omega_i >> \omega_j$.

To monitor the hole profile as is done experimentally, the "unburned" spectrum must be subtracted from the "burned" spectrum, as shown below in equation (9). This difference x_i is evaluated at each site or isochromat by calculating the relative population difference between the sublevels y_i^* and z_i^* (burned spectrum) and the steady-state relative population difference (unburned spectrum). The relative changes are normalized by the lineshape weighting factor A_i of that site:

$$x_i(t) = [\frac{y_i^*(t) - z_i^*(t)}{y_i^*(t) + z_i^*(t)} - \frac{Y - Z}{Y + Z}]A_i \tag{9}$$

The t = 0 values of y_i^* and z_i^* are given by equations (6) and (7). The time evolution of the isochromat populations is a function of the rate constants given in equations (1) and (2) and a new rate constant K_{SDF}, which corresponds to the rate at which the frequency of the zero-field transition is shifted by an amount ω_s. In our model, a change in frequency ω_s, induced by spectral diffusion processes, is equivalent to the situation where the i^{th} isochromat has a population feeding term which is proportional to the $(i - m)^{th}$ and $(i + m)^{th}$ isochromat populations and the corresponding relative lineshape weighting factors. The value of m (1,2,...) determines the size of the frequency shift; that is, $\omega_s = m\Delta\omega$. Thus the time dependences of the sublevel populations are given by:

$$\begin{aligned} \frac{dy_i^*}{dt} &= -y_i^*(t)\,(K_y + K_{SLU} + K_{SDF}) + z_i^*(t)\,K_{SLD} + C_yA_i \\ &\quad + [y_{i-m}^*(t)\,(\frac{A_i}{A_i + A_{i-2m}}) + y_{i+m}^*(t)\,(\frac{A_i}{A_i + A_{i+2m}})]K_{SDF} \end{aligned} \tag{10}$$

$$\begin{aligned} \frac{dz_i^*}{dt} &= -z_i^*(t)\,(K_z + K_{SLD} + K_{SDF}) + y_i^*(t)\,K_{SLU} + C_zA_i \\ &\quad + [z_{i-m}^*(t)\,(\frac{A_i}{A_i + A_{i-2m}}) + z_{i+m}^*(t)\,(\frac{A_i}{A_i + A_{i+2m}})]K_{SDF} \end{aligned} \tag{11}$$

The decay of an isochromat population due to spectral diffusion is two-fold, since the frequency change $\omega_s = m\Delta\omega$ can be negative or positive. For instance, part of the $(i - m)^{th}$ population undergoes a positive frequency change and decays into the i^{th} isochromat with a probability given by $A_i/(A_i + A_{i-2m})$. Similarly, part of the $(i - m)^{th}$ population undergoes a negative frequency change and decays into the $(i - 2m)^{th}$ isochromat with a probability of $A_{i-2m}/(A_i + A_{i-2m})$. Thus the relative lineshape weighting factors are at the heart of the model, for they reflect the probability of a population increase of a particular isochromat on the basis of the value of the local field it represents. For the special cases at the edges of the line, where $i \leqslant 2m$ and $(512 - i) \leqslant 2m$, m is systematically reduced. Also, the kinetic model does not require knowledge of the absolute orders of magnitude of the feeding constants C_z and C_y, since the population difference between the two levels of any particular isochromat is normalized anyway.

Numerical integration of equations (10) and (11) for specific delay times t was performed for n = 500 isochromats with a predictor-corrector subroutine (DREBS) provided by the IBM 360 IMSL library. Thus a total of 1000 coupled differential equations were integrated over each time interval of interest. Evaluation of equation (9) at time t then yields the time-resolved lineshape of the hole, as shown in fig. (2B). A comparison with the experimental time evolution of the hole lineshape can be easily accomplished through an analysis of the width (FWHM), depth, and area. Thus the value of K_{SDF}, for a particular frequency change ω_s which best fits the experimental parameters can be determined.

5. DETERMINATION OF THE SPECTRAL DIFFUSION RATE CONSTANT

In the manner outlined in the previous section, the value for the spectral diffusion rate constant K_{SDF} is determined as a function of the jump in frequency of the zero-field transition. Of course, in the actual experiment, changes in frequency are not restricted to a particular value. However, the dependence shown can be perturbed by the hyperfine interaction with the host nuclear spins. The deuteration of the guest molecule reduces the hyperfine interaction [8] between the guest nuclei and the triplet spins. This is evidenced by the "static" shift in the 2|E| zero-field frequency from the $\underline{h}_2$-TCB value of 1744 MHz to $\underline{d}_2$-TCB value of 1822 MHz. (The inhomogeneous linewidth was found to change very little upon dueteration: FWHM = 3.5 MHz for $\underline{h}_2$-TCB, FWHM = 3.4 MHz for $\underline{d}_2$-TCB). Thus deuteration not only changes the static zero-field frequency but also reduces the strength of the coupling between the triplet spins and the oscillating field produced by the nuclear spins of the host.

It is interesting that the magnitude of the reduction of K_{SDF} (factor of eight) upon dueteration of the guest appears to be about the same as the magnitude of reduction of the Hahn spin echo decay rate (factor of 6) measured in the quinoline/durene crystals Van 'T Hof and Schmidt [8], even though there are more protons (or deuterons) on the quinoline molecule (C_9NH_7). We also observed, just as Van 'T Hof and Schmidt did, that at temperatures below 2.0 K, there appears to be no K_{SDF} temperature dependence. The latter observation thus indicates that the host nuclear spin-flipping process which is causing the fluctuations in the local fields surrounding the triplet spin must be an energy-conserving spin-spin relaxation.

To conclude, we would like to point out another interesting feature of the hole-burning results. Hu and Hartman [12] developed a model whereby they could relate the time dependence of Hahn spin echo decays to an average nuclear flipping rate W of the host spins and a guest frequency-shifting term $\Delta\omega^*_{1/2}$ (HWHM), which is related to W in various ways, depending on whether the time scale of the Hahn echo experiment is fast or slow relative to W. Van 'T Hof and Schmidt [8] found that the echo decay times for the quinoline in durene crystals were roughly exponential and that $2W \simeq 0.25\ \Delta\omega^*_{1/2}$. The frequency shift $\Delta\omega^*_{1/2}$ of the guest triplet spins caused by the flipping host nuclear spins was in turn related to the echo decay time T_2 by the function $\Delta\omega^*_{1/2} = 2\pi^{1/3}/T_2$. We can follow in the footsteps of Van 'T Hof and Schmidt and calculate W and $\Delta\omega^*_{1/2}$ for the $\underline{h}_2$-TCB in durene crystal from the 4 μsec T_2 time measured by Breiland *et al*. [5] Thus if $T_2 = 4$ μsec, then $\Delta\omega^*_{1/2} \approx 117$ KHz; when one locates this frequency shift on the curve in fig. (3), the best-fit value of K_{SDF} is 1.5×10^4 sec^{-1}. This is remarkably close to the calculated nuclear flipping rate $W = 0.125\ \Delta\omega^*_{1/2} = 1.46 \times 10^4$ sec^{-1}. Thus it does indeed appear that the time evolution of a hole burned in the inhomogeneous profile of triplet spins is intimately related to the nuclear spin-flipping processes which determine phase memory time.

ACKNOWLEDGMENTS

We would like to thank Henry Brenner for stimulating discussions. J.C. Brock is grateful to the National Research Council for support as an NRC-NASA Resident Research Associate. We would like to thank the Office of Naval Research for support of this work and the UCLA Office of Academic Computing for the grants of computer time on the IBM 360.

REFERENCES

[1] C.B. Harris, R.L. Schlupp, and H. Schuch, Phys. Rev. Letters 30 (1973) 1019.

[2] M.D. Fayer and C.B. Harris, Phys. Rev. B 9 (1974) 748.

[3] J. Schmidt, Chem. Phys. Letters 14 (1972) 411.

[4] W.G. Breiland, C.B. Harris, and A. Pines, Phys. Rev. Letters 30 (1973) 158.

[5] W.G. Breiland, H.C. Brenner, and C.B. Harris, J. Chem. Phys. 62 (1975) 3458.

[6] B.J. Botter, D.C. Doetschman, J. Schmidt, and J.H. Van der Waals, Mol. Phys. 30 (1975) 609.

[7] B.J. Botter, A.I.M. Dicker, and J. Schmidt, Mol. Phys. 36 (1978) 129.

[8] C.A. Van 'T Hof and J. Schmidt, Mol. Phys. 38 (1979) 309.

[9] J.R. Klauder and P.W. Anderson, Phys. Rev. 125 (1962) 912.

[10] W.B. Mims, K. Nassau, and J.D. McGee, Phys. Rev. 123 (1961) 2059.

[11] W.B. Mims, Phys. Rev. 168 (1968) 370; also in: Electron Paramagnetic Resonance, ed. by S. Geschwind (Plenum Press, New York, 1968) pp. 263-351.

[12] P. Hu and S.R. Hartman, Phys. Rev. B 9 (1974) 1.

[13] R.G. De Voe, A. Szabo, S.C. Rand, and R.G. Brewer, Phys. Rev. Letters 42 (1979) 1560.

[14] S.C. Rand, A. Wokaun, R.G. De Voe, and R.G. Brewer, Phys. Rev. Letters 43 (1979) 1868.

[15] M. Leung and M.A. El-Sayed, Chem. Phys. Letters 16 (1972) 454.

[16] William M. Pitts and M.A. El-Sayed, "Optical Detection of Spectral Diffusion of the Triplet State Zero-Field Transition Energy", Mol. Crys. Liq. Crys., in press.

[17] A.H. Francis and C.B. Harris, J. Chem. Phys. 57 (1972) 1051.

[18] W.G. Breiland and C.B. Harris, Chem. Phys. Letters 18 (1973) 309.

[19] P.E. Jessop, T. Muramoto, and A. Szabo, Phys. Rev. B 21 (1980) 926.

[20] Harmen de Vries and Douwe A. Wiersma, J. Chem. Phys. 72 (1980) 1851.

[21] H. Schuch and C.B. Harris, Z. Naturforsch 30a (1975) 361.

[22] W.M. Pitts and M.A. El-Sayed, Chem. Phys. 19 (1977) 289.

FIGURE CAPTIONS

Fig. (1) (A): First 512 channels of 1024 channel signal averager after 64 sweeps. A hole appears at 1744.08 MHz because a 5 μsec microwave pulse, fixed at that frequency, immediately preceeds the 5 μsec sweeping pulse. The delay time between the 80 mW pulses is less than 1.0 μsec.

(B): Second 512 channels of signal averager after 64 sweeps. The fixed frequency pulse is inhibited, thus the steady-state "unburned", asymmetric lineshape of the transition appears.

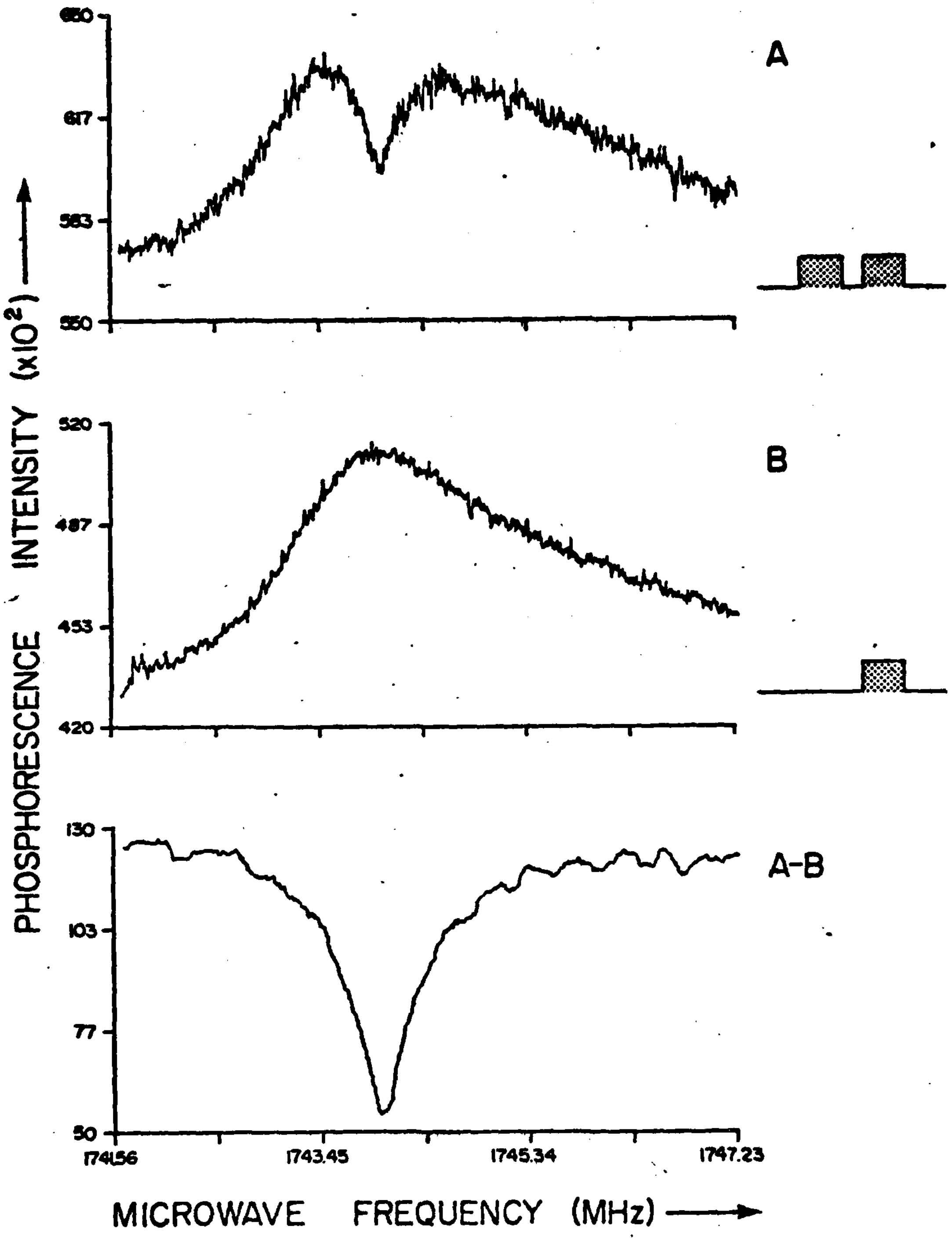
(A-B): Computer substraction of data set B from set A, resulting in the profile of the burned hole. The difference spectrum is also smoothed by the computer (5-point smooth).

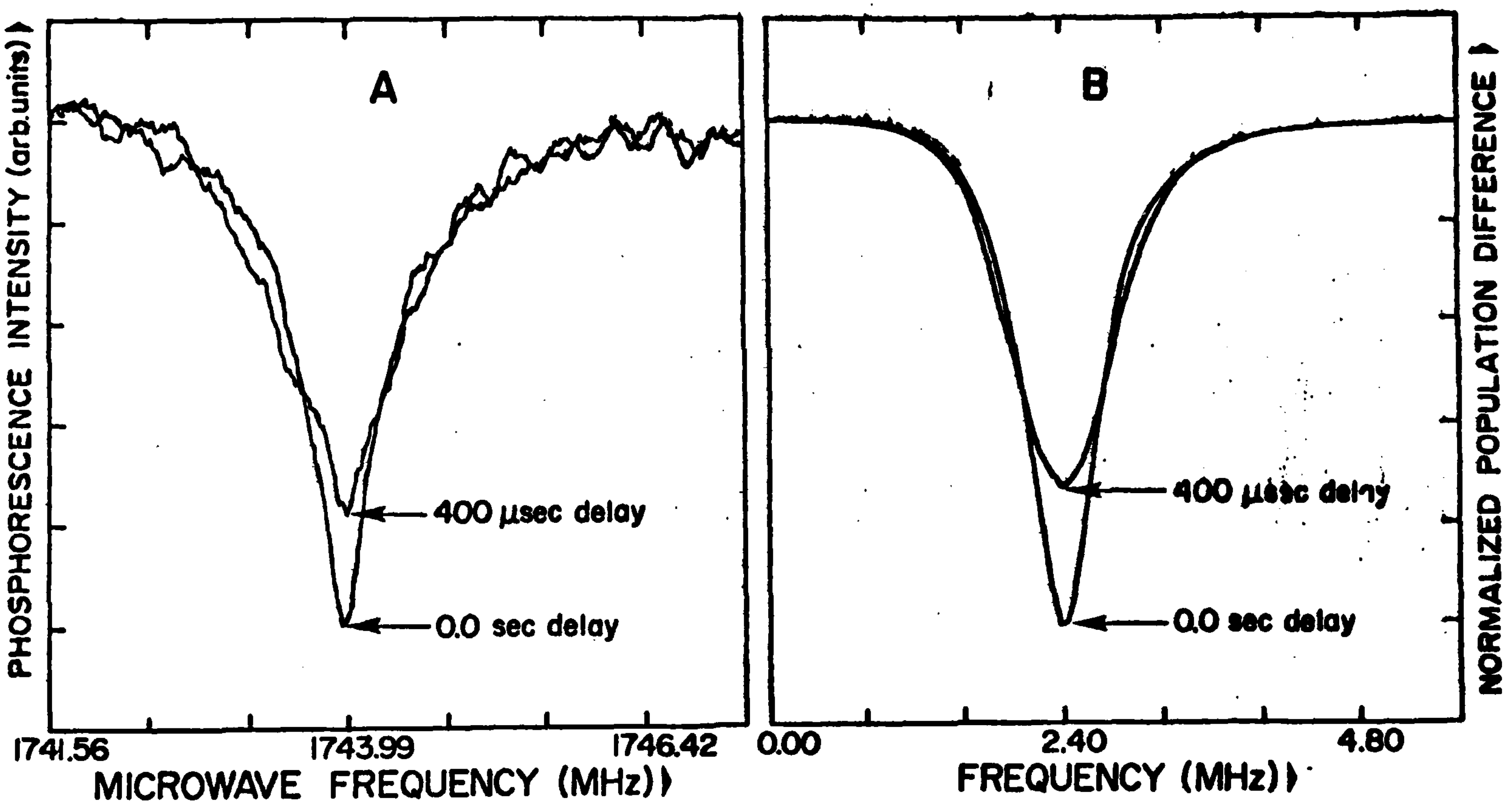
Fig. (2) (A): Comparison of hole profiles at different delay times between the fixed and sweeping microwave pulses. The deeper, narrower hole is the "initial" lineshape at 1.0 μsec or less delay time. The shallower, wider hole is a result of a 400 μsec delay time. Both hole profiles were obtained by the method depicted in Fig. (1).

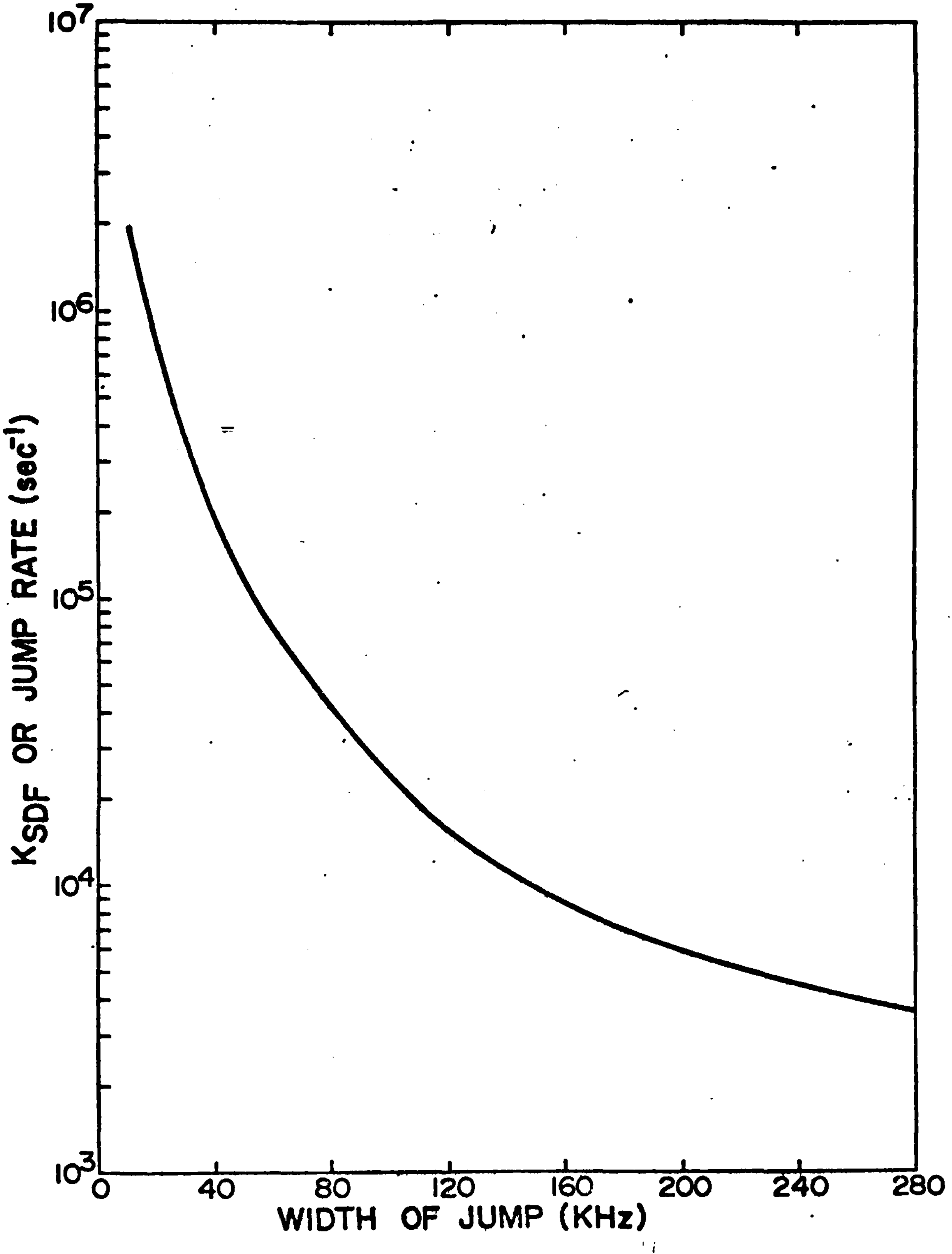
(B): Time development of hole lineshape calculated using the kinetic model described in the text. The initial hole linewidth was matched to the experimentally observed width at the minimum delay time between the microwave pulses.

Fig. (3): Spectral diffusion rate constant K_{SDF} as a function of the frequency shift ω_s of the zero-field spin transition. The dependence is calculated from the time-resolved hole profiles for $\underline{h}_2$-TCB in durene.

HOLE-BURNING IN THE 2|E| TRANSITION OF
1% SYM-TETRACHLOROBENZENE IN DURENE




A
B
PHOSPHORESCENCE INTENSITY (arb.units)
400 μsec delay
0.0 sec delay
1741.56
1743.99
1746.42
MICROWAVE FREQUENCY (MHz)
NORMALIZED POPULATION DIFFERENCE
400 μsec delay
0.0 sec delay
0.00
2.40
4.80
FREQUENCY (MHz)


10^7
10^6
10^5
10^4
10^3
K_SDF OR JUMP RATE (sec^-1)
0
40
80
120
160
200
240
280
WIDTH OF JUMP (KHz)

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1
ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1

	No. Copies
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Dr. Rudolph J. Marcus Office of Naval Research Scientific Liaison Group American Embassy APO San Francisco 96503	1
Mr. James Kelley DTNSRDC Code 2803 Annapolis, Maryland 21402	1

TECHNICAL REPORT DISTRIBUTION LIST, 051A

	No. Copies
~~Dr. M. A. El-Sayed~~ ~~Department of Chemistry~~ ~~University of California, Los Angeles~~ ~~Los Angeles, California 90024~~	1
Dr. E. R. Bernstein Department of Chemistry Colorado State University Fort Collins, Colorado 80521	1
Dr. C. A. Heller Naval Weapons Center Code 6059 China Lake, California 93555	1
Dr. J. R. MacDonald Chemistry Division Naval Research Laboratory Code 6110 Washington, D.C. 20375	1
Dr. G. B. Schuster Chemistry Department University of Illinois Urbana, Illinois 61801	1
Dr. A. Adamson Department of Chemistry University of Southern California Los Angeles, California 90007	1
Dr. M. S. Wrighton Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Dr. M. Rauhut Chemical Research Division American Cyanamid Company Bound Brook, New Jersey 08805	1
Dr. J. I. Zink Department of Chemistry University of California, Los Angeles Los Angeles, California 90024	1
Dr. D. Haarer IBM San Jose Research Center 5600 Cottle Road San Jose, California 95143	1
Dr. John Cooper Code 6130 Naval Research Laboratory Washington, D.C. 20375	1
Dr. William M. Jackson Department of Chemistry Howard University Washington, DC 20059	1
Dr. George E. Walraffen Department of Chemistry Howard University Washington, DC 20059	1

LME