

Optical, magnetic resonance, and ENDOR studies of the $\pi\pi^*$ triplet state of benzophenone in mixed crystals

Robin M. Hochstrasser, Gary W. Scott, and Ahmed H. Zewail

Citation: *The Journal of Chemical Physics* **58**, 393 (1973); doi: 10.1063/1.1678937

View online: <http://dx.doi.org/10.1063/1.1678937>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/58/1?ver=pdfcov>

Published by the **AIP Publishing**

Articles you may be interested in

[Optically detected magnetic resonance studies of photoexcited 17O-benzophenone. Orbital rotation in the lowest triplet state](#)

J. Chem. Phys. **76**, 2275 (1982); 10.1063/1.443300

[An ENDOR study of the geometry of the lowest triplet state of benzil](#)

J. Chem. Phys. **71**, 1070 (1979); 10.1063/1.438472

[Optically detected magnetic resonance spectra of the lowest triplet states of benzophenone, 13C-benzophenone, and three 4,4'-dihalobenzophenones](#)

J. Chem. Phys. **66**, 5339 (1977); 10.1063/1.433896

[Optical and Magnetic Field Studies of the Lowest Triplet State of the Pyrazine Crystal](#)

J. Chem. Phys. **53**, 2676 (1970); 10.1063/1.1674390

[ESR of the Triplet State of Benzophenone](#)

J. Chem. Phys. **51**, 451 (1969); 10.1063/1.1671749



AIP Applied Physics Reviews

NEW Special Topic Sections

NOW ONLINE
Lithium Niobate Properties and Applications:
Reviews of Emerging Trends

AIP | Applied Physics
Reviews

only at the x -axis and not over an appreciable range of angle about \hat{x} because of overlapping.

With the notable exception of this very last case, the pair hyperfine structures were fitted, within the uncertainty of their measurement, by a spin Hamiltonian which was of the form of the last two terms of (1) but with the k -sums running over the 16 indexes of the protons of the pair and with the A_k component values⁵ for the isolated molecule replaced by values one half as large. This result is to be expected on the basis of the spin exchange model in the limit of infinite exchange and of negligible interaction between the electron spin on one molecule and the proton spins on the other.

In that case in which H_0 was set parallel to the x -axis of one molecule, the hyperfine splitting of the EPR pair line had approximately twice the value given by the hyperfine spin Hamiltonian which is described above and which fitted the hyperfine patterns observed along the principal axes of the pair spectra, i.e., they had approximately the isolated molecule value.

ENDOR frequency scans were made with H_0 fixed in direction and magnitude at the values required for EPR of the pairs for the microwave carrier frequency being used. At K-band H_0 was varied over a range, $\sim 0.24\pi(43^\circ)$, of angle about \hat{x} for one molecule, and at X-band by $\sim 0.10\pi(18^\circ)$ about \hat{x}^* for the pair. In

both cases the observed ENDOR originated from that electron spin state of the pair which was approximately describable as the strong field state, $M_S=0$.³ The ENDOR frequencies and the small but measurable angular variations of ENDOR frequency agreed with the pair hyperfine spin Hamiltonian mentioned above, even for that case in which H_0 was parallel to \hat{x} for one molecule at K-band frequencies and which showed the anomalous EPR hyperfine structure. The reason for this apparent anomaly is not yet understood.

We thank Dr. Marvin D. Kemple for discussions of this work.

* This research has been supported by the National Science Foundation.

† This research has been supported by the United States Atomic Energy Commission.

‡ Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

§ Some of the equipment used in this work was supplied by the Advanced Research Projects Agency and by the National Science Foundation under the materials science research program.

¹ M. Schwoerer and H. C. Wolf, *Mol. Cryst.* **3**, 177 (1967).

² M. Schwoerer and H. C. Wolf, *The Triplet State*, edited by A. B. Zahlan (Cambridge U. P., Cambridge, 1967), p. 133.

³ C. A. Hutchison Jr., *The Triplet State*, edited by A. B. Zahlan (Cambridge U. P., Cambridge, 1967), p. 63.

⁴ S. C. Abrahams, J. M. Robertson, and J. G. White, *Acta Cryst.* **2**, 233, 238 (1949).

⁵ P. Ehret and H. C. Wolf, *Z. Naturforsch.* **23a**, 1740 (1968).

Optical, magnetic resonance, and ENDOR studies of the $n\pi^*$ triplet state of benzophenone in mixed crystals*

ROBIN M. HOCHSTRASSER,† GARY W. SCOTT,‡ AND AHMED H. ZEWAIL

Department of Chemistry and Laboratory for Research on the Structure of Matter, The University of Pennsylvania, Philadelphia, Pennsylvania 19104

We wish to report our preliminary results of optical spectra, phosphorescence, EPR, and ENDOR spectra of the $n\pi^*$ lowest triplet state of benzophenone in a mixed crystal. Despite previous optical^{1,2} and magnetic³⁻⁵ measurements on excitons and traps in neat benzophenone crystals, there are no previous studies of essentially isolated benzophenone molecules in a well-defined dilute mixed crystal system. Such new results are important in establishing the spin distribution in a prototype $n\pi^*$ state, the effects of nuclear motion on the fine structure constants, and the possible influence of spin-orbital coupling energies on the zero-field splitting of carbonyl $n\pi^*$ states.

The experiments refer to single crystals of 4,4'-dibromodiphenylether (DDE) containing $\approx 10^{-2}$ mole per mole of benzophenone. The host is optically transparent in the region of the guest $n\pi^*$ electronic states. The sharp (≈ 3 cm⁻¹) and well polarized optical spectra of the guest, and the results of the low field

EPR experiments indicate that we have a substitutional solid solution in agreement with expectations based on the similar geometries of host⁶ and guest⁷ molecules. The observed phosphorescence zero-zero band and the zero-field splittings as obtained by optical detection of magnetic resonance (ODMR) at zero field are given in Table I for various isotopically substituted benzophenones. Table I also contains these parameters for some benzophenones in perdeuterobenzophenone. All the DDE mixed crystal ODMR transitions corresponded to a decrease in the benzophenone phosphorescence.

Mixed crystals of ¹²C- and ¹³C-benzophenone in DDE were oriented conoscopically according to the published structure data^{6,8} and an H_0 field of 100 ± 1 G was rotated in the **ab** and **bc** crystal planes: **c** corresponds to the molecular two-fold axis and **b** makes $\pm 1^\circ 40'$ with the lines of ring centers within the two magnetically equivalent molecules. The DDE crystal

TABLE I. Zero-field splittings and observed phosphorescence origin energies of isotopically substituted benzophenone $n\pi^*$ triplets in mixed crystals at $\sim 1.7^\circ\text{K}$.

Guest	Host	$T_1 \rightarrow S_0$ origin (vac cm^{-1})	$ (D-E)/h _{\text{peak}}$ (MHz)	$ (D+E)/h _{\text{peak}}$ (MHz)	$ 2E/h _{\text{peak}}$ (MHz)
$\text{C}_6\text{H}_6^{12}\text{COC}_6\text{H}_6$ (^{12}C -benzophenone- h_{10})	DDE	23 578.0	5225.82 ± 0.33	4182.06 ± 0.21	1043.76 ^a
$\text{C}_6\text{H}_6^{13}\text{COC}_6\text{H}_6$ (^{13}C -benzophenone- h_{10})	DDE	23 586.1	5217.20 ± 0.16	4171.16 ± 0.30	1046.04 ^a
		23 577.9 ^c			
$\text{C}_6\text{D}_6^{12}\text{COC}_6\text{H}_6$ (^{12}C -benzophenone- d_6)	DDE	23 595.4	5236.02 ± 0.36	4199.55 ± 0.10	1036.47 ^a
$\text{C}_6\text{D}_6^{13}\text{COC}_6\text{H}_6$ (^{13}C -benzophenone- d_{10})	DDE	23 612.8	5245.74 ± 0.05	4215.32 ± 0.17	1030.5 ^b
$\text{C}_6\text{H}_6^{12}\text{COC}_6\text{H}_6$	$\text{C}_{12}\text{D}_{10}^{12}\text{CO}$	24 191.7	5173.29 ± 0.48	3932.46 ± 0.17	1240.76 ± 0.13
$\text{C}_6\text{H}_6^{13}\text{COC}_6\text{H}_6$	$\text{C}_{12}\text{D}_{10}^{12}\text{CO}$	24 199.8	5163.17 ± 0.24	3919.57 ± 0.18	1243.63 ± 0.20
		24 191.8 ^c			

^a Not observed.

^b Observed by electron-double resonance only. See Ref. 3.

^c Identified as ^{12}C -benzophenone by emission intensity and characteristic EPR.

space group is $Ccc(C_{2v}^{13})$ and there are four C_2 symmetry molecules per unit cell. Both sets of magnetically inequivalent molecules were observed in the ab plane, thereby fixing the angle between y of one of the molecules and b at $20^\circ \pm 2^\circ$ which is in reasonable agreement with the EPR of neat benzophenone.⁹ The relative signs of D and E are determined by these experiments and since the sign of D is known from optical spectra^{1,10} we conclude that $D/h = -4703.94 \pm 0.27$ MHz, $E/h = +521.88 \pm 0.27$ MHz for ^{12}C -benzophenone- h_{10} implying the energy ordering $T_z > T_y > T_x$ of spin states.

The isotope effects on D and E have the signs expected from the change in rms displacement from equilibrium (^{13}C), and the change in π spin density at the carbonyl carbon due to the isotope effect on the rms torsional displacement from equilibrium (d_{10}). Isotope effects on the anharmonicity and on the spin-orbital coupling of $^3n\pi^*$ with nearby $^3\pi\pi^*$ states via L_z would be expected to give contributions having opposite signs from those observed. The ^{13}C zero-field hyperfine shift of the T_z doublet state is computed from following data to be $+0.14$ MHz.

For the $^3n\pi^*$ state of ^{13}C -benzophenone- h_{10} (but not for ^{12}C -benzophenone) in DDE, with \mathbf{H}_0 parallel to \mathbf{a} , a hyperfine splitting of ≈ 10.5 MHz was observed. By mounting a larger rf coil coaxially with the slow wave helix, several ENDOR transitions could be studied for ^{12}C - and ^{13}C -benzophenone- h_{10} in DDE whilst rotating \mathbf{H}_0 in the ab and bc planes. Changes of intensity at the peak of the 4 GHz transition (observed by modulating the microwave power at 80 Hz and detecting changes in the 0-0 or 0-1 carbonyl stretch phosphorescence bands) were monitored while sweeping the cw ENDOR source. The ^{13}C ENDOR was discerned by its absence in ^{12}C spectra while the persistent ENDOR transitions may be due to protons.

The ^{13}C ENDOR frequencies (extrema, $\pm 7^\circ$) are for $\mathbf{H}_0 \parallel \mathbf{z}$, 5.31 ± 0.15 MHz; for $\mathbf{H}_0 \parallel \mathbf{x}$, 5.81 ± 0.05 MHz; and for $\mathbf{H}_0 \parallel \mathbf{y}$, 2.5 ± 0.5 MHz. Neglecting the

nuclear Zeeman effects the ^{13}C hyperfine tensor elements¹¹ are therefore: $|A_{xx} + iA_{xy}|/h = 43.66 \pm 0.36$ MHz, $|A_{yy} + iA_{xy}|/h = 23.4 \pm 4.7$ MHz, and $|A_{zz}|/h = 11.24 \pm 0.56$ MHz. $|A_{xy}|/h < 4$ MHz.

The anisotropic portion of the hyperfine tensor can be used to expose features of the n and π electron distributions: The dominant contributions to the electron-nuclear coupling are the one-center interaction of the nuclear spin with carbon p_x and p_y electrons and the two center coupling with p_x and p_y electrons on oxygen. If we assume that the π -electron spin densities at the carbonyl carbon and oxygen are in the same ratio as in formaldehyde,¹² and that the anisotropic A tensor elements are determined by the aforementioned one center terms as computed by Smith *et al.*¹³ and two center terms computed for oxygen Slater orbitals, and that other interactions are small, then we find the fraction α of π -electron spin density on the carbonyl to be $0.84 \leq \alpha \leq 1.00$. From these assumptions we conclude also that the n -electron spin density on oxygen is less than or equal to 0.64 thus confirming the significant n -electron delocalization predicted by Hoffman and Swenson.¹⁴

The optical spectrum provides values for the carbonyl stretch (1170 cm^{-1} for ^{12}C) and for the symmetric torsional mode (90 cm^{-1} for h_{10}) in the $^1n\pi^*$ state. The frequency of the torsional mode is decreased from that in the ground state (102 cm^{-1}) contrary to expectations based on model calculations of the potential curves,¹⁴ but our assignments are necessarily tentative at this point.

Further optical and ENDOR studies of this system are in progress and a fuller account of the above results will be forthcoming.

* This research was supported in part by a Public Health Grant GM12592, and in part by NSF/MRL.

† J. S. Guggenheim Fellow.

‡ N.S.F. post-Doctoral Fellow 1971-72, N.I.H. post-Doctoral Fellow 1972-73.

¹ R. M. Hochstrasser and T. S. Lin, *J. Chem. Phys.* **49**, 4929 (1968).

² S. Dym, R. M. Hochstrasser, and M. Schafer, *J. Chem. Phys.* **48**, 646 (1968).

³ I. Y. Chan and J. Schmidt, *Symp. Faraday Soc.* **3**, 156 (1969); W. S. Veeman and J. H. Van der Waals, *Chem. Phys. Letters* **7**, 65 (1970).

⁴ M. Sharnoff, *Phys. Rev. Letters* **27**, 576 (1971).

⁵ C. J. Winscom and A. H. Maki, *Chem. Phys. Letters* **12**, 264 (1971).

⁶ J. Toussaint, *Bull. Soc. Roy. Sci. Leige* **15**, 86 (1946).

⁷ E. B. Fleischer, N. Sung, and S. Hawkinson, *J. Phys. Chem.* **72**, 4311 (1968).

⁸ We are indebted to Mr. Henry Katz for confirming the assignment of axes from the x-ray reflection data of these crystals.

⁹ M. Sharnoff, *J. Chem. Phys.* **51**, 451 (1969).

¹⁰ The sign of E from the optical work¹ is not certain since it depends on assignments from imperspicuous Stark-Zeeman transitions. The negative sign of D is proven.

¹¹ C. A. Hutchison Jr., J. V. Nicholas, and G. W. Scott, *J. Chem. Phys.* **53**, 1906 (1970).

¹² J. M. Foster and S. F. Boys, *Rev. Mod. Phys.* **32**, 303 (1960).

¹³ W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, *Phys. Rev.* **115**, 1546 (1959).

¹⁴ R. Hoffman and J. R. Swenson, *J. Phys. Chem.* **74**, 415 (1970).

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 58, NUMBER 1

1 JANUARY 1973

Relation of temperature dependence of heavy-atom chemical shifts to absolute values of σ_p

THOMAS H. BROWN AND SHEILA M. COHEN

Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680

(Received 13 September 1972)

For many applications the impossibility of direct measurement of absolute chemical shifts by the NMR experiment poses no problems and the determination of shifts relative to some reference compound is adequate. On the other hand, for comparison with theoretical calculations, the conversion of measured shifts to an absolute scale is of interest. With particular reference to transition metal atoms, knowledge of the position of the unshifted resonance¹ is valuable in selecting reliable references for estimating Knight shifts^{2,3} and in deducing absolute values for gyromagnetic ratios and hence magnetic moments.⁴ In this Communication, we report on a new procedure for placing the paramagnetic contribution, σ_p , to measured shifts on an absolute basis; this method, which exploits the temperature sensitivity of transition-metal chemical shifts, further provides the means for deducing relative values of the diamagnetic contribution, σ_d .

Heavy-metal chemical shifts, as well as the considerable sensitivity of these shifts to temperature, are largely determined by σ_p . Unfortunately, cobalt (III) complexes appear to be unique amongst transition-metal compounds in that Co(III) chemical shifts are linearly proportional through the σ_p term to the reciprocal of the corresponding crystal-field splittings Δ according to the Griffith and Orgel expression.⁴⁻⁷ Consequently, although the unshifted Co(III) resonance position can be estimated by extrapolation to that σ value for which $1/\Delta=0$, this procedure is not generally applicable to other transition elements, presumably because of variations amongst complexes of a given ion of the product of $\langle 1/r^3 \rangle_{av}$, for the valence electrons, with the so-called orbital-reduction factor.^{6,8}

The alternative NMR method based on temperature dependency measurements, being free of these restrictions, holds promise of broad applicability. The essential temperature independence of the diamagnetic

contribution to the total shift has been established.⁹ It is meaningful to rewrite an expression given by Benedek⁹ *et al.* in a form that emphasizes the observation that the temperature coefficient for the *total* chemical shift $d\bar{\sigma}/dT$, where $\bar{\sigma} = \sigma_d + \bar{\sigma}_p$ and the thermal average is indicated, is linearly proportional to σ_p at all but the lowest temperatures (Fig. 1 insert):

$$d\bar{\sigma}/dT = \sigma_p k K(\omega_0, \omega_N) \Delta^{-1} [1 - (1/12)(\hbar\omega_0/kT)^2],$$

where ω_0 and ω_N are harmonic oscillator frequencies in the ground and upper electronic states, respectively, and $K(\omega_0, \omega_N)$ is a function of ω_0 and ω_N only. The expectation is therefore that extrapolation to the σ value at which the temperature sensitivity of the chemical shift just vanishes will provide an independent estimate of σ_p and consequently establish a relative scale for σ_d .

Initial results for the ¹⁹⁵Pt nucleus, shown in Fig. 1, indicate that temperature dependency of chemical-shift measurements do provide a useful new tool for obtaining reasonable experimental estimates of absolute values of σ_p . The method depends upon the recognition that all the temperature sensitivity of the chemical shift resides in the paramagnetic contribution and that extrapolation to $d\sigma/dT=0$ then establishes the $\sigma_p=0$ position. Using a reasonable but otherwise arbitrary reference, one can construct a preliminary curve, each point of which represents measured $d\sigma/dT$ vs observed chemical shift for a given member of a series of complexes of the heavy metal. Since both the $d\sigma/dT$ and the slope of this curve are effectively independent of the particular reference frequency used, the extrapolation defines the position of the unshifted resonance for the series and allows a curve of the type shown in Fig. 1 to be drawn. For the two isomeric series considered here, the positions of the unshifted ¹⁹⁵Pt resonances are different by an amount that may