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- ⁵ W. J. Hooker and R. C. Millikan, *J. Chem. Phys.* **38**, 214 (1963).
- ⁶ W. A. Rosser, Jr., R. D. Sharma, and E. T. Gerry, *J. Chem. Phys.* **54**, 1196 (1971).
- ⁷ W. A. Rosser, Jr., A. D. Wood, and E. T. Gerry, *J. Chem. Phys.* **50**, 4996 (1969).
- ⁸ Y. Sato and S. Tsuchiya, *Chem. Phys. Letters* **5**, 293 (1970).
- ⁹ R. A. Svehla, NASA Tech. Rept. **R-132** (1962).
- ¹⁰ Y. Sato, S. Tsuchiya, and K. Kuratani, *J. Chem. Phys.* **50**, 1911 (1969).
- ¹¹ R. L. Taylor and S. Bitterman, *J. Chem. Phys.* **50**, 1720 (1969).
- ¹² D. J. Seery, "Intramolecular Energy Transfer in CO₂," Paper presented at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 1971.
- ¹³ C. B. Moore, *Fluorescence*, edited by G. G. Guilbault (Marcel Dekker, New York, 1967), p. 133.
- ¹⁴ R. D. Sharma and C. A. Brau, *Phys. Rev. Letters* **19**, 1273 (1967).
- ¹⁵ B. H. Mahan, *J. Chem. Phys.* **46**, 98 (1967).
- ¹⁶ J. C. Stephenson, R. E. Wood, and C. B. Moore, *J. Chem. Phys.* **48**, 4790 (1968).
- ¹⁷ D. Rapp, *J. Chem. Phys.* **43**, 316 (1965).

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Mixed Magnetic and Electric Dipole Transition in *s*-Triazine*

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We have shown that the radiation pattern for absorption to the lowest energy excited singlet state of *s*-triazine corresponds to that of a mixed electric and magnetic dipole transition. This was done by demonstrating, for the first time with an organic, the classic procedure of obtaining absorption coefficients for different k , $\hat{\epsilon}$, and \hat{H} for a uniaxial arrangement of molecules. We find the 30 014 cm⁻¹ transition of *s*-triazine to be 26% magnetic and 74% electric dipole, hence the state symmetry is ¹*E* in the crystal field, and ¹*E*' in the free molecule (*D*_{3h}).

INTRODUCTION

The radiation patterns for pure multipoles—electric dipole or quadrupole, magnetic dipole, etc.—are well understood. However among organic chromophores there are few well-characterized magnetic dipole transitions and no well-characterized mixed electric and magnetic dipole transitions. There are more magnetic dipole transitions known in the spectra of rare earths and transition metal ion complexes, and the classic optical absorption anisotropy technique¹ of distinguishing electric and magnetic dipole transitions has been applied to uniaxial systems containing such ions.² Wide angle interference methods³ have also been used to expose the character of the emitted radiation from rare-earth ions. For optically active complex ions and molecules there are indirect methods to identify magnetic dipole transitions that in effect depend on knowing the ratio of the squared rotational strength to the extinction coefficient.^{4,5}

The same interaction that gives rise to the magnetic dipole transition to $n\pi^*$ states of ketones⁶ is also expected to occur in $n \rightarrow \pi^*$ transitions in *N*-heterocyclics; namely one-center matrix elements, $\langle p_x | l_z | p_y \rangle$. These magnetic dipole transitions have not yet been seen nor characterized, perhaps because the usual methods of characterization would require inherently asymmetric molecules containing nitrogen $n \rightarrow \pi^*$ transitions as their lowest excited states. Neither for the case of carbonyl compounds nor for the case of *N*-heterocyclics has there been a direct spectroscopic

identification of the magnetic dipole moment for a single vibronic transition. In the present note we describe such an identification for a mixed electric and magnetic transition.

s-Triazine is expected to have three $n\pi^*$ states of symmetry *E*'', *A*₂'', and *A*₁'' (symmetry group *D*_{3h}) arising from promotions from the degenerate pair (*e*') of nonbonding orbitals into the degenerate pair (*e*'') of antibonding π orbitals. One of these states, *E*'', should undergo only magnetic dipole transitions to the ground (*A*₁') state. In the *s*-triazine crystal⁷ the molecular symmetry becomes *D*₃ and there is mixing induced by the crystal field of the *D*_{3h} states *E*' and *E*'' which both become *E* in *D*₃. The *E* state is both electric and magnetic dipole allowed. A quite comparable result could obtain when a chromophore such as a C_{2v} carbonyl is part of a molecule where the carbonyl site symmetry is lower than C_{2v}.

MIXED ELECTRIC AND MAGNETIC DIPOLE RADIATION

In the semiclassical theory the transition moment between two states 0 and *f* is proportional to:

$$\langle f | \sum (1 - i\mathbf{k} \cdot \mathbf{r}) \nabla_A | 0 \rangle, \quad (1)$$

where \mathbf{k} is the propagation vector, and \mathbf{r} represents the position vector of an electron ($\sum \boldsymbol{\sigma}$ is the electric dipole operator). ∇_A is the gradient taken in the direction of the vector potential (i.e., if the electric vector of the light is along *x*, then $\nabla_A = \partial/\partial x$). The sum

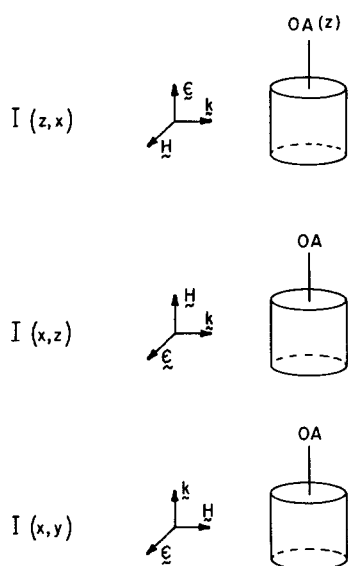


FIG. 1. Orientations of propagation vector (\mathbf{k}), magnetic vector (\mathbf{H}), and electric vector (\mathbf{E}) with respect to uniaxial crystal axes.

is over all electrons. The first term gives electric dipole and the second gives magnetic dipole and electric quadrupole transitions. Higher terms in the expansion of $\exp(i\mathbf{k}\cdot\mathbf{r})$ are omitted, and in what follows the electric quadrupole transitions are also neglected. The absorption intensity is proportional to the transition moment squared, and from (1) it follows that:

$$|m_f(\hat{E}, \hat{H})|^2 = |\boldsymbol{\mu}_{0f} \cdot \hat{E} - i\mathbf{m}_{0f} \cdot \hat{H}|^2 \quad (2)$$

where $m_f(\hat{E}, \hat{H})$ is the transition moment for radiation defined by the unit vectors \hat{E} and \hat{H} of the electric

and magnetic fields. $\boldsymbol{\mu}_{0f}$ and \mathbf{m}_{0f} are the electric and magnetic transition dipole moments.

For a doubly degenerate state with components f_x and f_y , where x and y are arbitrary orthogonal molecule-fixed axes that transform as partners in an E representation, the total absorption intensity $[I(\hat{E}, \hat{H})]$ is given, in terms of transition moments, as:

$$I(\hat{E}, \hat{H}) = |m_{f_x}(\hat{E}, \hat{H})|^2 + |m_{f_y}(\hat{E}, \hat{H})|^2 \quad (3)$$

It is now readily shown that the total absorption intensity is dependent only on the angles that \hat{E} and \hat{H} make with the z (perpendicular to xy plane) molecule-fixed axis; since $|\mu_{0x}| = |\mu_{0y}| \equiv \mu$, and $|m_{0x}| = |m_{0y}| \equiv m$, we have:

$$I(\hat{E}, \hat{H}) = \mu^2 \sin^2 \theta_{Ez} + m^2 \sin^2 \theta_{Hz} \quad (4)$$

The simple physical result is that when the electric (magnetic) vector of the light is parallel to z only magnetic (electric) dipole absorption is seen. In addi-

TABLE I. Observed absorption optical densities for various \hat{k} , \hat{E} , and \hat{H} orientations. Refer to Fig. 1 for definition of $I(\hat{E}, \hat{H})$.

$I(\hat{E}, \hat{H})$	Optical density per millimeter
$I(x, y)$	0.95 ± 0.05
$I(z, x)$	0.25 ± 0.02
$I(x, z)$	0.64 ± 0.04
$I(z, x) + I(x, z)$	0.89 ± 0.05

tion, the condition:

$$I(z, x) + I(x, z) = I(x, y) \quad (5)$$

can be experimentally checked, and represents an important property of the radiation pattern.

EXPERIMENTAL RESULTS

Single crystals of *s*-triazine of high purity and good optical quality were melt grown and cut into sections roughly 1 mm thick. The uniaxial structure is known to be transformed into a monoclinic form⁸ on cooling below $\sim 213^\circ\text{K}$ but the present study and other spectroscopic results^{9,10} indicate that the influence of the uniaxial-to-monoclinic distortion is not significant. The crystals were oriented at 4.2°K as shown in Fig. 1. The propagation vector \hat{k} and the direction of the \hat{E} and \hat{H} fields of the radiation are shown in the diagram. Optical densities were measured using a Jarrell-Ash Czerny-Turner-Fastie spectrometer at a resolving power of 1:50 000. The absorption band studied is about 3 cm^{-1} wide at 4.2°K (i.e., at least six times the resolvable increment). The data shown in Table I refer to the lowest energy singlet band that we assume to be the 0, 0-band of a singlet system (probably the

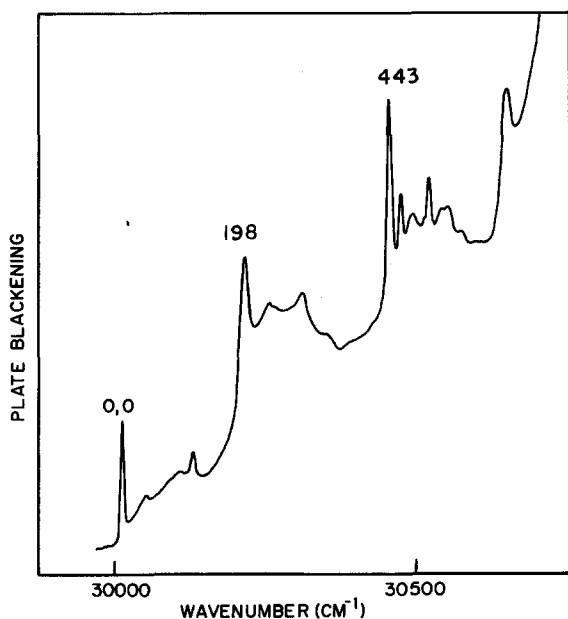


FIG. 2. Absorption spectrum of the first singlet system of *s*-triazine. The 0, 0-band is the band studied in this work.

lowest excited singlet state) of *s*-triazine. Figure 2 shows some of the bands from the first singlet system, and the origin at 30 014 cm⁻¹ is identified. These data (Table I) clearly show that the transition is not of purely electric dipole type, and since the condition of Eq. (5) is met within experimental error, we conclude that the transition is of mixed type.

The magnetic dipole transition represents 26% of the total intensity. We note that the data in Table I are given as optical density per mm for a 3 cm⁻¹ wide absorption line: accordingly the absorption coefficient is extremely small. For the 30 014 cm⁻¹ line we find $f=5\times 10^{-9}$, and in practical terms the transition has about the same strength as the singlet-triplet absorption of pyrazine.

DISCUSSION

This study proves that the lowest singlet state of *s*-triazine is *E*-type, and in view of its magnetic dipole activity it is *E''* type in *D*_{3h} symmetry. After the present results were obtained we verified the *E''* nature of the lowest singlet by observations of magnetic field and electric field splittings⁹ of the 30 014 cm⁻¹ transition. Our results also show that the low symmetry site field of the monoclinic phase is not sufficient to split significantly the *E* state.

In view of the stronger vibrationally induced absorption built on the magnetic dipole origin we have no way of measuring the total magnetic dipole transition moment for the ¹*E''*←¹*A*₁' transition. If the 0, 0-band contains at least 10⁻⁴ of the total intensity of ¹*E''*←¹*A*₁' (Fig. 2 shows that the low-frequency vibronic origins are not more than two orders of magnitude stronger than the zero band) the spontaneous lifetime of ¹*E''*→¹*A*₁' fluorescence would be greater than 3×10⁻⁵ sec: The lifetime associated with the magnetic dipole emission would be at least 10² longer than this.

In previous work^{10,11} we have identified an *nπ** triplet state at 28 935 cm⁻¹ of type ³*A*₁''. With a singlet

state ¹*E''* at 30 014 cm⁻¹ we are faced with the possibilities that either ³*A*₁' is not the lowest triplet state, or that a ³*E''* state lies within the gap of 1079 cm⁻¹ between ¹*E''* and ³*A*₁''. In addition to these features we have observed crystal absorption bands (singlets) polarized out-of-plane in the region 30 731 cm⁻¹ indicating the presence of a ¹*A*₂' state. In other words the energy spread of the *E''*, *A*₁'', and *A*₂' *nπ** states is extremely narrow. These results are, apart from specific detail, in general accord with theoretical predictions.¹²

The expected natural radiative lifetime for the fluorescence ¹*E''*→¹*A*₁' is so long that we would anticipate relatively effective radiationless transitions from ¹*E''* into lower triplet states and into the ground state, when *s*-triazine is in the condensed phase. The pathways for deactivation of ¹*E''* may be quite different in a collision free system, and internal conversion to the ground state may then become relatively more effective. These remarks assume that the energy levels have comparable relative spacings in the gas and the crystal.

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¹ See for example: D. S. McClure, *Electronic Spectra of Molecules and Ions in Crystals* (Academic, New York, 1959), p. 87.

² E. V. Sayre, K. Sancier, and S. J. Freed, *J. Chem. Phys.* **23**, 2060 (1955).

³ (a) P. Selenyi, *Ann. Physik*, **35**, 444 (1911). (b) S. Freed and S. I. Weissman, *Phys. Rev.* **60**, 440 (1941).

⁴ W. E. Moffitt, *J. Chem. Phys.* **25**, 1189 (1956).

⁵ S. F. Mason, *Quart. Rev. Chem. Soc.* **17**, 20 (1963).

⁶ S. F. Mason, *Mol. Phys.* **5**, 343 (1962).

⁷ P. J. Wheatley, *Acta Cryst.* **8**, 224 (1955).

⁸ P. Coppens and T. M. Sabine, *Mol. Cryst.* **3**, 507 (1968).

⁹ Robin M. Hochstrasser and Ahmed H. Zewail, *Chem. Phys. Letters* **11**, 157 (1971).

¹⁰ Robin M. Hochstrasser and Ahmed H. Zewail, *J. Chem. Phys.* **55**, 5291 (1971).

¹¹ Robin M. Hochstrasser and T. S. Lin, *Symp. Faraday Soc.* **3**, 100 (1969).

¹² J. S. Brinen and L. Goodman, *J. Chem. Phys.* **31**, 482 (1959).