# Magnetic Circular Dichroism of Excimer Molecules

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The magnetic circular dichroism of excimer absorption bands is used to obtain the first direct information about the angular momentum and angular momentum coupling schemes of excimer molecules.

In this paper we report on the first studies of the magnetic circular dichroism (MCD) of excimer absorption bands in gases. These studies can be used to obtain information about the angular momentum quantum numbers and coupling schemes (Hund's case $a$, $b$, $c$, etc.) of the excimer molecules, information of a type which has heretofore eluded experimental study.

A typical excimer system, which we shall use for illustrative purposes, is the cesium-argon molecule. The lowest energy levels of this molecule are sketched in Fig. 1 versus the internuclear separation $R$. The name excimer stems from the fact that attractive excited-state potential curves exist, e.g., the curves labeled $n$ and $d$ in Fig. 1, while the ground-state potential curve is repulsive except for a shallow van der Waals minimum. Thus, bound excited molecules can emit radiation while making a transition to a dissociative ground state. The resulting continuous emission and absorption bands have attracted much attention in recent years. Efficient visible and ultraviolet lasers can be constructed with rare-gas–halide excimers.[1] The excimers are also of considerable interest in their own right since it is now possible to make detailed calculations[2,3] of potential curves, transition moments, and other properties of excimer molecules, especially for the alkali–rare-gas systems in which a single valence electron is involved.

Current experimental methods for investigating excimer molecules are limited. Line structure does not exist in most cases and so the powerful methods of discrete spectral analysis cannot be applied. With certain approximations, it is possible to deduce potential curves from studies of the temperature dependence of excimer emission and absorption bands, and Gallagher and co-workers[4] and others have used this method to obtain detailed information about alkali–rare-gas potential curves.

So far there has been no experimental method to obtain information about the axial angular momentum and the angular momentum coupling schemes of excimer molecules. Measurements of the magnetic circular dichroism of an excimer band, that is the difference $\Delta k$ in the attenuation coefficients for right- and left-circularly polarized light propagating along a large magnetic field $H$, can provide important information about
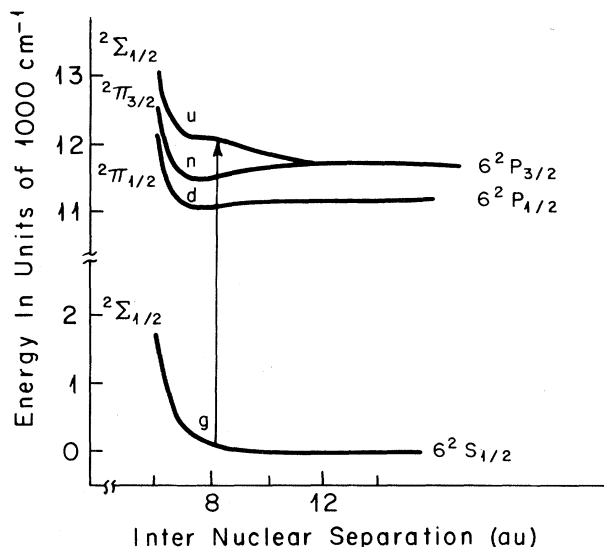


FIG. 1. Representative potential curves for CsAr excimer molecules (from Ref. 2).

the angular momenta of excimer molecules. Of-
ten one can make unambiguous qualitative conclu-
sions about an excimer molecule (e.g., the coup-
ling scheme is more nearly Hund's case $c$ rather
than Hund's case $a$) by simple inspection of the
MCD spectrum. Within the framework of the
classical Franck-Condon prinicple, which we
shall use in all subsequent analysis, one can show
that the MCD for an excimer absorption band with
an excited state $e$ is

$$\Delta k_e = \mu_B H \left( \frac{1}{h} \frac{\partial}{\partial \nu} A_e k_e + \sum \frac{B_{ee'} k_e}{E_e - E_{e'}} + \frac{C_e k_e}{\kappa T} \right). \quad (1)$$

The dimensionless coefficients $A$, $B$, and $C$ in
Eq. (1) correspond to the terms $a$, $b$, and $c$ origi-
nally introduced by Serber.[5] The $A$ term can be
nonzero if either the ground state or the excited
state of the optical transition is degenerate. The
$B$ term is due to the magnetic-field–induced ad-
mixture of other states $e'$ to the upper state $e$ of
the optical transition. The $C$ term can be present
if the ground state is degenerate, and this term
is due to the magnetic-field–induced polarization
of the ground state. The excited-state energies
$E_e$ and $E_{e'}$ in Eq. (1) are assumed to be functions
of the internuclear separation $R$, and we assume
that each optical frequency $\nu = c/\lambda$ corresponds to

one or more values of $R$.

As discussed by Gallagher and co-workers,[4] the
mean attenuation coefficient $k$ is

$$k_e = [\text{Cs}][\text{Ar}] \frac{16\pi^3}{3h\lambda} |p_{ge}|^2 R^2 \frac{dR}{d\nu} \exp(-E_g/\kappa T), \quad (2)$$

where the square of the electric dipole moment

$$|p_{ge}|^2 = |p_{0,ge}|^2 + |p_{\pm 1,ge}|^2 \quad (3)$$

is the sum of a longitudinal part $p_{0,ge}$ and a trans-
verse part $p_{\pm 1,ge}$, which are defined by

$$p_{\sigma,ge} = \langle g, \Omega_g | p_\sigma | e, \Omega_g - \sigma \rangle, \quad (4)$$

with the second quantum numbers in Eq. (4) denot-
ing the projection of the total electronic angular
momentum along the internuclear axis. We as-
sume that $\Omega_g$ is positive. The electric dipole
operators in the molecule-fixed frame are

$$p_0 = p_\zeta; \quad p_{\pm 1} = \mp (1/\sqrt{2})(p_\xi \pm i p_\eta). \quad (5)$$

The general theory of MCD was discussed by
Serber[5] and more recently by other authors in
connection with the condensed phase.[6] In the case
of continuous excimer bands we may write down
simple formulas for the MCD coefficients of Eq.
(1). For example, in the case of the state $u$ of
Fig. 1, which is associated with the blue wing of
the $D_2$ line of the cesium-argon system, we find

$$C_u = [- |p_{1,gu}|^2 \mu_{0,gg} + 2 \text{Re}(p_{1,gu} p_{0,gu}^* \mu_{1,gg})] |p_{gu}|^{-2} \mu_B^{-1}, \quad (6)$$

$$A_u = - C_u + [|p_{1,gu}|^2 \mu_{0,uu} + 2 \text{Re}(p_{0,gu} p_{1,gu}^* \mu_{1,uu})] |p_{gu}|^{-2} \mu_B^{-1}, \quad (7)$$

$$B_{un} = [- 2 \text{Re}(p_{0,gu} p_{1,gn}^* \mu_{1,nu}^*)] |p_{gu}|^{-2} \mu_B^{-1}. \quad (8)$$
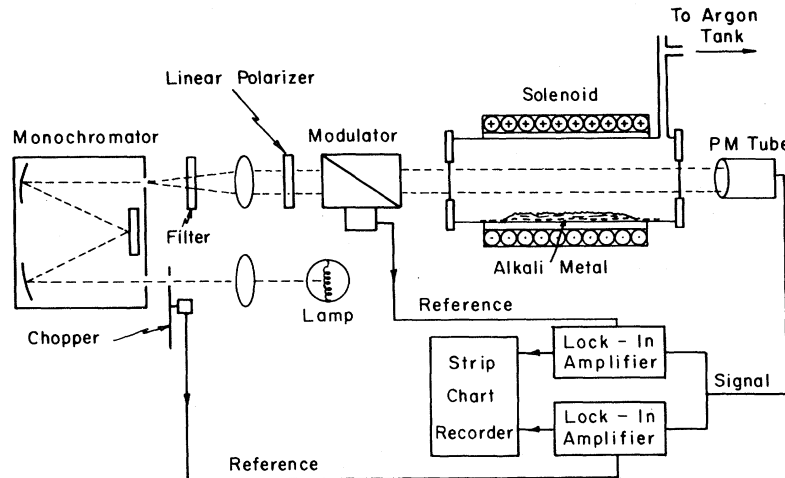


FIG. 2. Experimental apparatus.

Here the matrix elements of the magnetic dipole moment operator

$$\vec{\mu} = -\mu_B(\vec{L} + 2\vec{S}) \qquad (9)$$

are defined in analogy with Eq. (4). Other $B$ coefficients, e.g., $B_{ud}$, are combined with larger energy denominators in Eq. (1) and so we have limited our attention to $B_{un}$.

The utility of MCD stems from the great sensitivity of the coefficients $A$, $B$, and $C$ to the angular momentum coupling scheme in the molecule. For example, for the state $u$ of Fig. 1 formulas (6)–(8) lead to the following limiting cases: Hund's case $a$,

$$A_u, \ B_{un}, \ C_u = 0, \ 2, \ 0; \qquad (10)$$

and Hund's case $c$,

$$A_u, \ B_{un}, \ C_u = -1, \ \tfrac{8}{3}, \ -1. \qquad (11)$$

Of course, Hund's case $a$ is a $^2\Sigma_{1/2}$ state while Hund's case $c$ is a $^2P_{3/2,\,1/2}$ state quantized along the internuclear axis.

The experimental arrangement is shown in Fig. 2. Light from an intense lamp (tungsten-iodine or xenon arc) is chopped at 193 Hz and detected with a lock-in amplifier after passing through a sample cell and a monochromator (Spex 1700-111). The 193-Hz signal is a measure of the mean transmitted intensity $I$. The same light is alternately right- and left-circularly polarized at a frequency of 50.3 kHz by means of a piezoelectric birefringent modulator. The 50.3-kHz signal $\Delta I$ is a measure of the MCD, and one can easily show that

$$\Delta k = \Delta I / lI, \qquad (12)$$

where $l$ is the path length through the vapor. The cell is a 1.25-m stainless-steel pipe with an internal mesh of stainless steel which is soaked with 110 g of cesium metal. Pyrex windows are attached at each end of the cell. The cell is heated by noninductively wound Nichrome resistance heaters, and care is taken to ensure a uniform temperature distribution over the central region of the cell. Argon gas at pressures up to 10 atm can be admitted to the cell. The cell is contained in a solenoid, 0.85 m in length, which produces a magnetic field of 2700 G.

We have measured MCD for many excimer bands of the CsAr system and one example is shown in Fig. 3. This excimer band, which is associated with the state $u$, has been studied in absorption by Chen and Phelps[7] and in emission by Hedges, Drummond, and Gallagher.[4] It has also been the subject of several theoretical calculations.[2,3] The
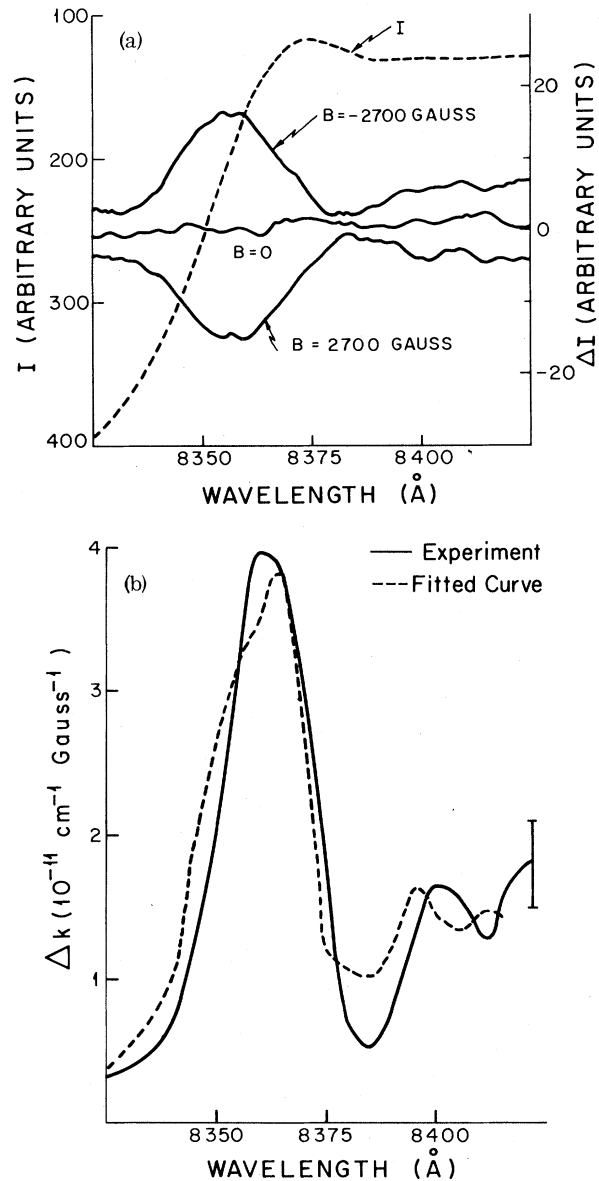


FIG. 3. (a) Raw experimental data as traced from a chart recording for the $g \rightarrow u$ transition of Fig. 1. There is no 50.3-kHz signal (the MCD signal, $\Delta I$) at zero magnetic field, which indicates that $\sigma_+$ and $\sigma_-$ light are attenuated equally in the absence of an external magnetic field. The noise on the 193-Hz signal (the mean transmitted intensity $I$) is too small to reproduce. (b) Experimentally measured MCD and fitted curve, Eq. (13), for data of (a). $T = 119$ °C; $[Cs] = 4.36 \times 10^{13}$ cm$^{-3}$; $[Ar] = 1.36 \times 10^{20}$ cm$^{-3}$; $H = 2700$ G.

band has a pronounced satellite due to an extremum in the difference potential, $E_u - E_g$.

The dashed curve in Fig. 3(b) is a least-squares

fit of the MCD data by a function of the form

$$\Delta k = N(\alpha c \, dk/d\nu + \beta k), \tag{13}$$

where $N$ is a dimensionless constant and

$$\alpha = -0.67 \text{ cm}^{-1}; \quad \beta = 0.011. \tag{14}$$

Comparing Eq. (13) with Eq. (1) we conclude that $\alpha$ is a measure of the $A$ term in Eq. (1) which cannot be zero and which must be of opposite sign to the sum of the $B$ and $C$ terms. From Eqs. (10) and (11) we immediately conclude that the $u$ state is poorly described by Hund's case $a$ and that the opposite signs of $\alpha$ and $\beta$ in Eq. (14) imply that the $B$ term is more important than the $C$ term, which has the same sign as the $A$ term.

While the fact that the state $u$ of Fig. 1 is not well described by Hund's case $a$ is to be expected, since the fine-structure splitting of the $6P$ state of cesium is comparable to the energy shifts of the excimer state, we should emphasize that the data of Fig. 3 are the first experimental evidence concerning the angular momentum coupling scheme of any excimer molecule.

We mention several other interesting results which follow from our studies of the MCD of CsAr. More details about the data and their analysis will be published elsewhere. We find that the yellow-green band[8] assigned to the transition $6S\,^{2}\Sigma_{1/2} \rightarrow 7S\,^{2}\Sigma_{1/2}$ at 0.56 $\mu$m shows no trace of an MCD signal. The designation $^{2}\Sigma_{1/2}$ for the upper state is therefore a very good approximation. The excimer bands associated with the $6S$-$5D$ state of cesium near 0.68 $\mu$m are devoid of MCD in the prominent blue wing and exhibit strong MCD in the red wings. Thus, the assignment of blue and red wings to $^{2}\Sigma$ and $^{2}\Pi$ transitions is well justified by MCD data.

We have also measured the Faraday rotation of the bands discussed in this paper and we have verified that the Faraday rotation signals are Kramers-Kronig transforms of the MCD signals. However, the Faraday rotation signals are less convenient than MCD signals because there is usually a large background rotation due to absorption bands well outside the spectral region of interest.

In summary, we have used magnetic circular dichroism to obtain the first direct experimental information about the angular momentum quantum numbers and coupling schemes of excimer molecules. A rich MCD spectrum exists which will add greatly to our understanding of excimer molecules.

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