# Measurement of the Dipole Moments of Excited States and Photochemical Transients by Microwave Dielectric Absorption<sup>T</sup>

## Richard W. Fessenden,\* Paul M. Carton, H. Shimamori,<sup>‡</sup> and Juan C. Scalano<sup>§</sup>

Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556 (Received: March 22, 1982; In Final Form: June 7, 1982)

Time-resolved changes in microwave dielectric absorption have been used to study transients formed by laser flash photolysis. Details of the method and apparatus are given. Applications both to the measurements of the dipole moments of transients and to decay kinetics are given. The dipole moments of the lowest triplet states of a number of aromatic compounds (mostly ketones) have been measured in benzene solution at room temperature. States of  $n\pi^*$  character generally possess smaller dipole moments than the corresponding ground states while states of  $\pi\pi^*$  character (for example, fluorenone) have larger values than the ground state. The triplets of 4-(dimethylamino)benzaldehyde and 4,4'-bis(dimethylamino)benzophenone have rather high values of dipole moment (10.5 and 8.4 D, respectively) showing their charge-transfer character. The triplet state of benzil was found to have zero or near-zero dipole moment, thus confirming that the triplet state is of a trans structure. Several radical systems were also investigated. It was found that hydrocarbon peroxyl radicals are quite polar so that their formation by reaction of the hydrocarbon radical with oxygen could readily be followed and the rate constant measured.

## Introduction

A previous communication<sup>1</sup> described measurement of the dipole moment of a transient radical by means of changes in microwave dielectric absorption. That experiment involved a steady-state method using modulated light for radical production. It was estimated, however, that detection of a species produced by a pulse methodfor example, by a laser flash-should also be possible. The predicted sensitivity was  $2 \times 10^{14}$  molecules if the dipole moment changed from 0 to 4 D and microsecond time resolution was involved. This number of molecules is easily produced by a laser of modest energy. The present paper details the apparatus and the considerations necessary to make the method quantitative. Results will be given on the dipole moments of a number of photochemical transients including both triplet states and radicals. Some kinetic applications will also be discussed. The initial work involves transients with lifetimes longer than 100 ns because of sensitivity and time response limitations. Improvements to allow study of singlet states with 10-ns lifetime should be possible.<sup>2</sup>

The absorption of microwave energy has been used for some time to study conductance in solids, liquids, and gases. Chemical applications have involved the study of electron attachment in various gases,<sup>3,4</sup> electron and hole mobility and reaction kinetics in liquids,<sup>5</sup> and electron mobilities in ice.<sup>6</sup> Another mechanism of absorption of microwave energy is dielectric loss, the basis of the present work. Although the apparatus used for measuring dielectric loss is similar to that used in some conductance studies, the basic experiment is rather different in that no motion of free ions is involved. The major cause of microwave absorption for liquids is dielectric relaxation in which dipolar molecules reorient in times comparable to the period of the probing microwaves. Any changes in dipole moments or rotational correlation times can be expected to change the microwave absorption, and quantitative measurements should allow determination of, for example, the change in dipole moment. In the present work, the chemical changes are brought about by a laser flash which converts a certain number of ground-state molecules to excited states (triplets in this work) or produces a pair of free radicals. Since the initial molecule which is transformed also may absorb microwave energy, one must always consider its disappearance as well as the formation of the new state. Thus, changes in dipole moment are usually the quantity determined.

Dipole moments of transients are of interest because they provide important information on electronic and geometrical structure just as for stable molecules. Several methods have been used for such measurements. Precise measurements are possible if Stark splittings can be measured. This method has been applied<sup>7,8</sup> to a few triplet states in crystals but has not been applied generally. More commonly, the dipole moment has been measured by means of solvent shifts in electronic spectra (solvatochromism) or by means of electrochromic effects. Several reviews describe these methods more fully.<sup>9,10</sup> In these latter cases, the reduction of observations to dipole moments is complex and involves a number of assumptions. The present method will be found to be more direct.

(7) R. M. Hochstrasser and L. J. Noe, J. Mol. Spectrosc., 38, 175 (1971).

(9) N. G. Bakhshiev, M. I. Knyzhanashii, V. I. Minkin, O. A. Osipov, and G. V. Saidov, Russ. Chem. Rev. (Engl. Transl.), 38, 740 (1969). (10) W. Liptay, Excited States, 1, 129 (1974).

<sup>&</sup>lt;sup>†</sup>This is Document No. NDRL-2333 from the Notre Dame Radiation Laboratory.

<sup>&</sup>lt;sup>†</sup>Present address: Department of Environmental Safety Engineering, Fukui Institute of Technology, Fukui 910, Japan.

<sup>&</sup>lt;sup>§</sup>Division of Chemistry, National Research Council, Ottawa, Canada K1A 0R6.

<sup>(1)</sup> R. W. Fessenden, P. M. Carton, H. Paul, and H. Shimamori, J. Phys. Chem., 83, 1676 (1979).

<sup>(2)</sup> In a very recent paper (J. M. Warman, M. P. deHaas, A. Hummel, C A. G. O. Varma, and P. H. M. VanZeyl, Chem. Phys. Lett., 87, 83 (1982)) microwave dielectric absorption changes with  $\sim$ 10-ns resolution have been reported. That work has not yet been developed to the stage of giving quantitative values of dipole moments. (3) See, for example, R. W. Fessenden and J. M. Warman, Adv. Chem.

Ser., No. 82, 222 (1968).

<sup>(4)</sup> R. W. Fessenden and K. M. Bansal, J. Chem. Phys., 53, 3468 (1970)

<sup>(5)</sup> P. P. Infelta, M. P. de Haas, and J. M. Warman, Radiat. Phys. Chem., 10, 353 (1977).

<sup>(6)</sup> J. B. Verberne, H. Loman, J. M. Warman, M. P. de Haas, A. Hummel, and L. Prinsen, *Nature (London)*, **272**, 343 (1978); J. M. Warman, M. P. de Haas, and J. B. Verberne, *J. Phys. Chem.*, 84, 1240 (1980).

<sup>(8)</sup> S. J. Sheng and M. A. El-Sayed, Chem. Phys., 20, 61 (1977).



Figure 1. Block diagram of the dielectric absorption apparatus. See the text for further description. The output of the signal amplifier is normally fed to a transient digitizer and processed by an on-line computer.

Most of the existing dipole moment data pertain to excited states observed optically, and almost no data exist on radicals. However, considerable detail is known about certain aspects of the electronic structures of radicals through hyperfine splittings. A body of data on the dipole moments would thus provide an additional probe of their electronic structure.

### **Experimental Apparatus**

The apparatus which has been used is similar to the microwave portion of an ESR spectrometer or to apparatus developed to measure microwave conductivity in condensed phases. It can be considered as a microwave analogue of an optical absorption apparatus with a resonant microwave cavity taking the place of a multiple-pass absorption cell. The block diagram is shown in Figure 1. The signal source is a 40-mW klystron at about 9.2 GHz. There is a main signal arm (center) as well as two other arms to provide automatic frequency control (AFC, lower) and bias to the main detector (upper). The signal in the main arm passes through an attenuator and circulator to the cavity. Any reflected wave is sent by the circulator to the main detector. The phase in the AFC arm is set to give a dispersion curve as the klystron frequency is swept through the cavity resonance; the signal in the bias arm is set to be in phase with an absorption signal. Normal operation has the cavity (with sample tube in place) exactly matched to the waveguide by means of an adjustable coupling iris and screw so that no power is reflected at the center of the cavity resonance. The automatic frequency control holds the klystron frequency at the center of cavity resonance for minimum noise from the detector. The bias power is then adjusted to give the desired detector diode current and the bias phase adjusted to give minimum noise (indicating a phase corresponding to absorption). About 5-mW power is incident on the cavity.

The signal amplifier was similar to that used in timeresolved ESR experiments<sup>11</sup> and had a rise time of about 200 ns. The other main factor limiting the time response is the so-called ringing time of the cavity. For a (loaded) cavity Q of 2000 the time constant due to this effect is 100 ns so the amplifier is the limiting factor. (Subsequent experiments with a lower Q cavity and a faster amplifier have shown a 30-ns rise time.) The output of the amplifier was connected to a Tektronix R7912 digitizer interfaced to the laboratory's PDP 11/55 computer as described by Encinas and Scaiano.<sup>12</sup> This system allowed averaging the results of multiple experiments, correction for base line, and on-line analysis for first-order formation or decay rates. A Molectron UV-400 nitrogen laser (337 nm) with nominal 3-mJ energy per pulse and 10-ns pulse length was used to irradiate the sample.

A drawing of the microwave cavity used for these experiments is shown in Figure 2. The cavity is rectangular with an inner cross section of  $0.4 \times 0.9$  in. (the standard for X-band waveguide) and operates in the TE<sub>102</sub> mode. The sample cell of  $3 \times 7$  mm (inside dimension) fused silica tubing is placed at the maximum in the microwave electric field (with the cell and solvent present). A 0.86-cm hole in the thick end plate allows the laser light to enter without loss of microwave energy. The sensitivity of the apparatus to changes in the sample is not uniform over the sample volume but will depend on the electric field strength in the volume element considered. To a first approximation the field strength is constant along the cell axis and varies as  $\sin(\pi x/l)$  in the other two directions. The center of the cell is located near the maximum of this function in both

<sup>(11)</sup> N. C. Verma and R. W. Fessenden, J. Chem. Phys., 65, 2139 (1976).

<sup>(12)</sup> M. V. Encinas and J. C. Scaiano, J. Am. Chem. Soc., 101, 2146 (1979).



**Figure 2.** Drawing of the microwave cavity and cell used in these experiments. The internal dimensions are  $1.02 \times 2.29 \times 4.00$  cm with the cell axis at 0.32 cm from the end. With the fused silica cell (3  $\times$  7 mm internal dimension) in place and filled with benzene the resonant frequency is about 9150 MHz.

directions to minimize any changes in sensitivity. In addition, the position of the light beam is not changed during a series of experiments. The main variation will be with samples of different absorbance—those with high optical density will experience most photochemistry in a layer at the front of the cell while those with lower values will have it distributed along the light path. The fact that the thickness of the cell along the light beam is only 3 mm avoids any large effects. In actual practice, the signal amplitude from our standard remained constant to approximately  $\pm 10\%$  over months; measurements at different times on a given day agreed to within about 5%.

## Materials

Unless otherwise mentioned the compounds studied were obtained from Aldrich Chemical Co., Inc. and used as received. Benzophenone and naphthalene were from Eastman Organic Chemicals and were recrystallized from ethanol; benzil and fluorenone were from Aldrich and were recrystallized from ethanol. Acetophenone was Fisher Certified or Baker Analyzed; benzaldehyde was Fisher Certified or Mallinckrodt. The 9,10-phenanthrenequinone was from Aldrich and was stated to be free of anthraquinone. It was recrystallized and sublimed. Xanthone and Michler's ketone were Fluka, AG "purissimum"; the latter was recrystallized and sublimed. Duroquinone was from Sigma Chemical Co. and durohydroquinone was from Pfaltz and Bauer. The 2,5-dimethyl-2,4-hexadiene was from K and K Laboratories. The benzene was mainly Aldrich Gold Label as was *n*-decane. Benzene for some experiments was dried by passage through an alumina column. Cyclohexane and carbon tetrachloride were Fisher Certified ACS Spectranalysed. Unless specified all solutions were deoxygenated by bubbling with argon.

The quantum yield of disappearance of diphenylcyclopropenone was determined by comparison to the yield of production of acetophenone from valerophenone in benzene solution ( $\phi = 0.30$ ).<sup>13</sup> Both samples were exposed to a known number of pulses from the nitrogen laser. The yield of acetophenone was determined by gas chromatography. Disappearance of diphenylcyclopropenone was determined by the decrease in absorbance of the solution at 347 nm. The product, diphenylacetylene, does not absorb appreciably at this wavelength. Linearity in the disappearance to over 75% reaction was found. On the basis of these measurements, the quantum yield of disappearance of diphenylcyclopropenone is  $1.00 \pm 0.03$ .

It was also necessary to determine quantum yields for formation of the triplet states of several compounds. These measurements were made in the way described by Das et al.<sup>14</sup> The triplet energy was transferred to 1-methylnaphthalene, and the absorbances were compared to that obtained with acetophenone ( $\phi = 1.0$ ).

### Theory

The presence of polar molecules in a nonpolar solvent has two effects on the dielectric properties, namely, an increase in the dielectric constant and introduction of a dielectric loss. Although either effect could be the basis of a method to detect transients, it is easier to detect absorption of energy with high sensitivity and so the loss was used. The dielectric loss,  $\epsilon''$ , for a dilute solution of a polar solute in a nonpolar solvent is<sup>15</sup>

$$\epsilon'' = (\epsilon_0 + 2)^2 \frac{4\pi n\mu^2}{27kT} \frac{\omega\tau}{1 + \omega^2\tau^2} \tag{1}$$

where  $\epsilon_0$  is the dielectric constant of the solvent, *n* is the number of solute molecules per cm<sup>3</sup>,  $\mu$  is the dipole moment of the solute,  $\omega$  is the angular frequency of the electric field,  $\tau$  is the rotational relaxation time, *k* is Boltzmann's constant, and *T* is the temperature. This function can be rewritten as

$$\epsilon'' = A[S]\mu^2 g(\tau) \tag{2}$$

where  $A = (\epsilon_0 + 2)^2 (4000\pi)/(27kTN)$  (N = Avogadro'snumber), [S] is the solute concentration (molar), and  $g(\tau) = \omega \tau/(1 + \omega^2 \tau^2)$ . To produce a loss,  $\omega$  of the electric field must match the relaxation time  $\tau$  so that  $\omega \tau \sim 1$ . However, the function of  $\omega \tau$  is not a strongly peaked one and loss will exist over a range of frequencies. The relaxation time of typical molecules of molecular weight about 150 in solvents such as benzene or cyclohexane are such that 9 GHz is near the maximum in the relaxation function. Thus, near maximum sensitivity will be obtained with such a frequency. (This frequency was chosen because of the availability of microwave components used in ESR spectrometers.) Any mismatch between  $\omega$  and  $\tau$  can readily be accommodated by the methods to be described and only a corresponding decrease in sensitivity will result.

Equation 1 represents the behavior for a rigid molecule with a single rotational relaxation time. The usual behavior even for a rigid molecule reflects a distribution of relaxation times so that the factor  $g(\tau)$  should not be taken too literally. In many cases, comparisons will be made between ground and excited states of the same molecule so that the same  $g(\tau)$  should describe both. If the direction of the dipole in the molecule changes or if there are contributions to the relaxation from internal rotations as well

<sup>(13)</sup> P. J. Wagner, P. A. Keslo, A. E. Kemppainen, J. M. McGrath, H. N. Scott, and R. G. Zepp, J. Am. Chem. Soc., 94, 7506 (1972).
(14) P. K. Das, M. V. Encinas, R. D. Small, Jr., and J. C. Scaiano, J.

<sup>(14)</sup> P. K. Das, M. V. Encinas, R. D. Small, Jr., and J. C. Scaiano, J. Am. Chem. Soc., 101, 6965 (1979).

<sup>(15)</sup> See, for example: C. P. Smyth, "Dielectric Behavior and Structure", McGraw-Hill, New York, 1955, p 64; C. J. F. Böttcher, "Theory of Electric Polarization", Elsever, Amsterdam, 1952, eq 10.102.

as from an overall rotation, then more care will be necessary in interpreting the results.

If a sample of a solution with a given value of dielectric loss  $\epsilon''$  is placed in a microwave cavity, the loss can be expressed as<sup>16,17</sup>

$$L = \int_{\text{sample}} \epsilon''(E)^2 \, \mathrm{d}v / \int_{\text{cavity}} (E)^2 \, \mathrm{d}v$$
$$= \epsilon'' \eta \tag{3}$$

where  $\eta$  is a filling factor similar that used in ESR but involving the microwave electric field. The meaning of the loss L will become clearer below.

It is appropriate next to consider the behavior of the cavity. Initially the coupling of microwave energy into the cavity is adjusted by means of an adjustable iris so that at the frequency of the cavity resonance no power is reflected; i.e., all power incident on the cavity is absorbed. If either the microwave frequency or the absorption of power in the cavity is changed, then some power will be reflected. From the definition of the reflection coefficient, the ratio of the electric field amplitude in the reflected wave,  $V_r$ , to that in the incident wave,  $V_0$ , is<sup>16,18,19</sup>

$$\frac{V_{\rm r}}{V_0} = \frac{1 - Y_{\rm c}}{1 + Y_{\rm c}} = \frac{1 - Q_{\rm x}/Q_0 - jB}{1 + Q_{\rm x}/Q_0 + jB}$$
$$= \frac{1 - \beta^{-1} - jB}{1 + \beta^{-1} + jB}$$
(4)

where  $Q_0$  is the unloaded cavity Q,  $Q_x$  is the Q due to the external coupling,  $\beta^{-1} = Q_x/Q_0$ ,  $B = Q_x(\omega - \omega_0)/\omega_0$  with  $\omega_0$ the resonant frequency (angular units),  $\omega$  is the actual frequency, and  $j = (-1)^{1/2}$ . When a dielectric is introduced into the cavity, a shift in resonace frequency occurs and a term is added to  $1/Q_0$ ; that is,  $\omega_0$  becomes  $\omega_0'$  and  $1/Q_0$  becomes  $1/Q_0 + L$  (where L is given in eq 2). Equation 4 then becomes

$$\frac{V_{\rm r}}{V_0} = \frac{1 - \beta^{-1} - \beta^{-1} Q_0 L - jB'}{1 + \beta^{-1} + \beta^{-1} Q_0 L + jB'}$$
(5)

where the prime on B indicates that the resonance frequency has been changed. This equation can be interpreted in several ways. The quantities  $Q_0$  and  $\omega_0$  can refer to the empty cavity, to the cavity with cell and solvent, or to the cavity with cell, solvent, and solute before irradiation. It is best for the purposes at hand to take the situation with cell and solvent as the reference. In many experiments (e.g., with ketones) the solute produces a loss before irradiation and the amount of loss is changed by photochemical transformation of a fraction of the solute. Adjustment of the cavity coupling for minimum reflected power with sample in place means adjusting  $\beta$  (through  $Q_x$ ) so that  $1 - \beta^{-1} - \beta^{-1}Q_0L = 0$  and  $1 + \beta^{-1} + \beta^{-1}Q_0L =$ 2. In addition, the klystron frequency is adjusted to be at the center of cavity resonance so B = 0. The photochemical change will change L to  $L + \Delta L$  and B from 0 to  $\Delta B$ . The reflected amplitude will be

$$\frac{V_{\rm r}}{V_0} = \frac{-\beta^{-1}Q_0\Delta L - j\Delta B}{2 + \beta^{-1}Q_0\Delta L + j\Delta B} \tag{6}$$

The changes  $Q_0 \Delta L$  or  $\Delta B$  are small compared with the

other quantities so that the denominator is not changed significantly. In addition, the use of a biased detector provides for response to only the component of  $V_r$  in phase with the microwave bias signal. This component is

$$\Delta V_{\rm r}/V_0 = -\beta^{-1}Q_0 \Delta L/2 \tag{7}$$

It is not convenient to measure  $\Delta V_r$  on an absolute basis because the detector diode efficiency varies with conditions such as the current through it. It is sufficient to note that the output of the detector diode  $V_s$  will be proportional to  $\Delta V_r$  for the small values of that quantity which will be encountered. If conditions such as cell size and position are kept constant, it is possible to compare values of  $V_s$ for two systems, one of which serves as a reference. Combination of eq 2, 3, and 7 leads to

$$\frac{V_{s1}}{V_{s2}} = \frac{\beta_1^{-1} \Delta([S_1]\mu_1^{-2})g(\tau_1)}{\beta_2^{-1} \Delta([S_2]\mu_2^{-2})g(\tau_2)}$$
(8)

where the quantities A,  $\eta$ , and  $Q_0$  have cancelled. (It is assumed that the differences in samples are not sufficient to change the distribution of fields inside the cavity and hence to change  $\eta$ .) The only quantities to be determined are  $\beta^{-1}$  for the two solutions and values of  $g(\tau)$ . It is important to point out that  $g(\tau)$  is not considered as one of the properties changed in the photochemical reaction because those to be considered, for example, excitation of a ketone to its triplet state, the size of the molecules, and hence their tumbling rates, will not change significantly. One should also note the dependence of observed signal on the change in the square of the dipole moment. Thus a 1-D change in moment is much easier to detect in a large moment than in a small one.

The unknown quantities in eq 8 are the values of  $\beta^{-1}$  and  $g(\tau)$ . As we will be using them, these quantities refer to the reference and sample solutions before irradiation. Therefore, it is possible to make static measurements. Since it is easier to make absolute power measurements, it is necessary to modify eq 5 to give the power reflected from the cavity rather than the amplitude:

$$\frac{P_{\rm r}}{P_0} = \frac{|V_{\rm r}|^2}{|V_0|^2} = \frac{(1 - \beta^{-1} - \beta^{-1}Q_0L)^2 + B'^2}{(1 + \beta^{-1} + \beta^{-1}Q_0L)^2 + B'^2}$$
(9)

Rearrangement of this equation gives

$$f(P_{\rm r}/P_0) = [1 \pm (P_{\rm r}/P_0)^{1/2}]^{-1} = \frac{1}{2} + \frac{\beta^{-1}}{2} + \frac{\beta^{-1}}{Q_0}L/2$$
(10)

if measurement of the incident and reflected powers is made at the center of cavity resonance where B' = 0. The signs in eq 10 are for over- or undercoupling, respectively. Measurement is carried out with a simplified microwave circuit consisting of a klystron, an attenuator, a 3-dB directional coupler, a circulator, and the same cavity and coupling iris as used in the photolysis experiment. Two power meters were used to measure incident and reflected power simultaneously.<sup>20</sup> The loss, L, will again be given by  $\eta A \mu^2 g(\tau)[S]$  so that the slope of a plot of  $f(P_r/P_0)$  against [S] will give

$$(1/2)\beta^{-1}Q_0\eta A\mu^2 g(\tau) = C$$
(11)

The quantity  $\beta^{-1}$  will be near 1.0 and can be eliminated by use of the value of the intercept of such a plot.<sup>21</sup> Figure 3 shows the behavior of  $f(P_r/P_0)$  for successive concentrations of benzophenone in benzene. The value of C for

<sup>(16)</sup> J. C. Slater, Rev. Mod. Phys., 18, 441 (1946), especially Chapter III.

<sup>(17)</sup> C. P. Poole, Jr., "Electron Spin Resonance", Wiley-Interscience, New York, 1967, p 586. (18) J. C. Slater, "Microwave Electronics", Van Nostrand, New York,

<sup>1950,</sup> Chapter V. (19) A. F. Harvey, "Microwave Engineering", Academic Press, New

York, 1963, p 200.

<sup>(20)</sup> Incident power was measured with a Hewlett-Packard 431B power meter with X486A thermistor mount; for reflected power, a 435A power meter and a 8481A power sensor were used. (21) The result is  $\beta^{-1} = 2(\text{intercept}) - 1$ .



**Figure 3.** Plot of the appropriate function of reflected power as a function of concentration of benzophenone in benzene. The linear behavior demonstrates that the loss is proportional to concentration as expected. The slope measures how much loss is produced by a given concentration. The small intercept of 1.015 shows that the cavity was not exactly critically coupled with only the benzene solvent present. The uncorrected slope is 22.8 and the slope corrected for critical coupling is 22.2 M<sup>-1</sup>.

this curve is 22.2. Within the range of compounds and solvents studied, the values of C have not been greatly different and have varied only over a factor of 2-3. (Note that the value for a given compound and solvent is a function of the cell geometry and  $Q_0$  but that ratios for two compounds do not depend on these quantities.) If the values of  $\mu$  are known for two compounds, the quotient of the C values gives the relative values of  $g(\tau)$ 

$$(\mu_2^2/\mu_1^2)C_1/C_2 = g(\tau_1)/g(\tau_2) \tag{12}$$

Equation 11 represents the situation when the value of  $\beta^{-1}$  is adjusted so that the cavity is matched with a sample of pure solvent. In the transient experiment represented by eq 8 the cavity is matched with the solute also present. Hence, the values of  $\beta_i^{-1}$  in eq 8 must be so calculated. The condition is that the right side of eq 10 should equal unity. The corresponding value is  $\beta^{-1} = (1 + 2C[S])^{-1}$ .

The final equation for our purposes is determined by multiplying both sides of eq 8 by  $C_2/C_1$  to get

$$\frac{C_2 V_{s1}}{C_1 V_{s2}} = \frac{\beta_1^{-1} \Delta[\mathbf{S}_1] \Delta(\mu_1^{\ 2}) / \mu_1^{\ 2}}{\beta_2^{-1} \Delta[\mathbf{S}_2] \Delta(\mu_2^{\ 2}) / \mu_2^{\ 2}}$$
(13)

Depending upon the particular situation this equation can be interpreted in slightly different ways. In the work to be presented, a constant-intensity laser flash is used so that the ratio  $\Delta[S_1]/\Delta[S_2]$  includes differences in quantum yields and absorbances. The reference compound transforms from a polar molecule to nonpolar products so that  $\Delta(\mu_2^2)/\mu_2^2 = 1$ . If the reaction under study represents excitation of a ketone to a triplet state, then the reference for the dipole moment of the triplet is that of the ground state through the term  $\Delta(\mu_1^2)/\mu_1^2$ .

## **Results and Discussion**

Several different types of chemical systems have been studied by this method and will be described. A major portion of the work has involved the determination of the dipole moments of triplet states. Various systems with triplet lifetimes between 70 ns and about 10  $\mu$ s are covered. Several radical reactions were also studied, including formation of durosemiquinone, which was used in the initial report.<sup>1</sup> The first discussion will be of the reference reaction.



Figure 4. Time dependence of the output of the dielectric absorption apparatus for solutions of diphenylcyclopropenone (■) and Michier's ketone (O) in benzene. Note that the curve for diphenylcyclopropenone represents a decrease in loss and would normally be plotted as a negative-going step. The curve for Michier's ketone does represent an increase in loss corresponding to an increase in dipole moment. The rise time is determined by the amplifier.

Reference Compound. After some searching, an excellent reference compound has been found in diphenylcyclopropenone (DPCP). This compound reacts by

$$c_{e}H_{5} - c = c_{e}H_{5} \xrightarrow{\hbar\nu} c_{e}H_{5}c \equiv cc_{e}H_{5} + co$$

to give essentially nonpolar products (the moment of CO is only 0.1 D). As described above, the quantum yield of this reaction is 1.0 for irradiation at 337 nm. The dipole moment of DPCP is reported<sup>22</sup> to be 5.1 D and so a very large signal should be obtained. In time-resolved experiments, only a single rapid step change in properties is observed in both optical and dielectric experiments. Figure 4 shows the dielectric absorption signal observed upon photolysis of a 3 mM solution in benzene. Note that it has been inverted for comparison with the other signal (to be discussed below) so that it represents a decrease in dielectric loss. The rise time of 300 ns represents the response of the amplifier and no decay is seen in other experiments out to 100  $\mu$ s. It is reasonable to presume that the photochemical change is that represented by the reaction. Since the products are essentially nonpolar, the change in loss (or detected signal) for a given extent of photochemical reaction should be exactly the same as for the same decrease in concentration by dilution. This concept was used in deriving the equations in the previous section. As already mentioned,  $\Delta(\mu^2)/\mu^2$  for this compound in eq 13 can be taken to be 1.

Results for Triplet States. A number of aromatic compounds (mostly ketones) have been examined with the object of determining the dipole moments of their lowest triplet states. Most were examined in benzene solution. The concentrations were adjusted to give an optical density of about 1 in the cell used (3-mm path length). In the case of acetophenone the concentration needed to produce such an optical density was so high that the starting solution had too large a dielectric loss and a lower optical density had to be used. Typical curves representing the change in dielectric loss for formation of the triplet states of several ketones are shown in Figures 4 and 5. The amplitude scale is absolute millivolts from our apparatus. Although various other factors must be included to get the

<sup>(22) &</sup>quot;Tables of Experimental Dipole Moments", Vol. II, Rahara Enterprises, El Cerrito, CA, 1974.

TABLE I:	Dipole	Moments o	of Trit	olet States <sup>a</sup>
TUDUNT	DIDOLC .	MOHIGING (		JIEU QUAUES

molecule	state	$\mu_{g},^{b}$ D	$\mu_{\mathbf{T}}, \mathbf{D}$	$g(\tau)^c$	$\phi_{ ext{isc}}$	
benzophenone	nπ*	2.98	2.1	1.47	1.0 <sup>d</sup>	
acetophenone	$n\pi^*$	2.95	2.4	1.34	1.0 <sup>d</sup>	
benzaldehyde	$T_1 + T_2$	3.0	~3.0	1.09		
fluorenone	$\pi\pi^*$	3.35	4.7	1.63	0.93 <sup>d,e</sup>	
xanthone <sup>f</sup>	$\mathbf{T}_1 + \mathbf{T}_2$	3.0 <sup>g</sup>	3.27	1.96	0.97 <sup>h</sup>	
Michler's ketone	$\pi \pi * (C \hat{T}) (+ T_2)$	5.3	8.4	0.80	$1.01^{i}$	
2,5-dimethoxybenzaldehyde	ππ*	3.0 <sup>/</sup>	4.5	1.91	$0.89 \pm 0.05^k$	
4-(dimethylamino)benzaldehyde	$\pi\pi^*(CT)$	5.6 <sup>j</sup>	10.5	1.11	$0.96 \pm 0.05^{k}$	
benzil	$n\pi^*$	$3.75^{l}$	~0	1.30	$0.92^{d}$	
4,4'-dimethoxybenzil		m	$0.4\mu_{\sigma}$	n	$1.03 \pm 0.05^{k}$	
furil		$3.2^{o}$	1.5	0.96	$1.01 \pm 0.05^k$	
9,10-phenanthrenequinone	$n\pi^*$	5.6	5.0	1.06	1.0 <sup>p</sup>	
1,4-diazanaphthalene	$\pi\pi^*$	0.5	2.3	$1.15^{q}$	$0.5 < \phi \le 1.0^r$	

<sup>a</sup> Values in Debye; measured in benzene solution. <sup>b</sup> Value from ref 22 unless otherwise specified. <sup>c</sup> Relative to diphenylcyclopropenone as determined from the slope of plots like Figure 3 and the dipole moments as in eq 12. <sup>d</sup> A. A. Lamola and G. S. Hammond, J. Chem. Phys., 43, 2129 (1965). <sup>e</sup> L. J. Andrews, A. Deroulede, and H. Linschitz, J. Phys. Chem., 82, 2304 (1978). <sup>f</sup> Measured in CCl<sub>4</sub>. <sup>g</sup> Z. Aizenshtat, E. Klein, H. Weiler-Feilchenfeld, and E. D. Bergmann, Isr. J. Chem., 10, 753 (1972). <sup>h</sup> Reference 30. <sup>i</sup> D. I. Schuster, M. D. Goldstein, and P. Bane, J. Am. Chem. Soc., 99, 187 (1977). <sup>j</sup> P. Suppan, J. Mol. Spectrosc., 30, 17 (1969). <sup>k</sup> This work. <sup>l</sup> C. C. Caldwell and R. J. W. LeFèvre, J. Chem. Soc., 1614 (1939); C. W. N. Cowper and A. P. Thurston, J. Chem. Soc., Perkin Trans. 2, 106 (1972). <sup>m</sup> Not reported. <sup>n</sup> The relative C value (eq 12) is 0.83. <sup>o</sup> P. H. Cureton, C. G. LeFèvre, and R. J. W. LeFèvre, J. Chem. Soc., 4447 (1961). <sup>p</sup> J. S. M. Boleij and H. J. T. Bos, Recl. Trav. Chim. Pays-Bas, 91, 1212 (1972); J. F. Brennan and J. Beutel, J. Phys. Chem., 73, 3245 (1969). <sup>q</sup> Because of the small moment, a C value was determined for quinoline ( $\mu = 2.2$ ) and the  $g(\tau)$  value assumed to be the same. <sup>r</sup> The lower limit is based on the value for pyrazine of 0.33. The calculated  $\mu_{\rm T}$  is for  $\phi = 1.0$ .



Figure 5. Time dependence of the output of the apparatus for solutions of fluorenone (O), benzophenone ( $\Box$ ), and benzil ( $\Delta$ ). Positive values represent increased loss.

change in dipole moment, the amplitudes shown give a qualitative idea of the changes observed. The curve for Michler's ketone in Figure 4 (increase in dielectric loss) shows that the rise time is the same as that for DPCP and is, therefore, governed by the amplifier. The decay is that of the triplet and can be caused by the natural decay rate, quenching by impurities, and also triplet-triplet quenching as the concentrations are rather high. The three curves in Figure 5 show decreases in dielectric loss for benzophenone and benzil and an increase for fluorenone. A number of other compounds were also studied.

That the curves do indeed relate to the triplet states was demonstrated by the effects of known triplet quenchers and experiments where nonpolar triplet states should be formed. Although 10 mM benzophenone in benzene gave the signal of  $\sim 200$  mV shown in Figure 5, a sample to which naphthalene had also been added showed no appreciable signal above the noise of about 5 mV. A sample of anthracene in benzene behaved similarly. In both cases optical absorption measurements show that a large yield of the appropriate hydrocarbon triplet is rapidly formed. Since both the ground states and the triplets of these aromatic hydrocarbons are nonpolar, no signal is produced. A sample of the benzene solvent itself gave no signal.

These experiments put an upper limit on any spurious effects such as heating of the solution or cavity or two photon processes which might produce a signal similar to that attributed to the triplet states. More quantitative studies were carried out on benzil by quenching with 2,5dimethyl-2,4-hexadiene. This symmetrically substituted diene does not possess cis and trans isomers and so avoids any contribution to the signal associated with its isomerization. Solutions of 6 mM benzil in benzene with a series of concentrations of diene were run in the dielectric experiment and the decay lifetimes determined by fitting an exponential to the observed signal decay. A similar series of experiments were carried out optically by monitoring the triplet-triplet absorption at 450 nm. The first-order disappearance rate constants obtained from these experiments are plotted in Figure 6. Data of both types fit quite well on the same plot. (The slope of the least-squares line corresponds to  $6.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .) The agreement shows that both experiments are examining the same species, namely, the lowest triplet state.

Data like that in Figure 5 were obtained for a number of molecules. The amplitudes were determined by extrapolation to the position of the laser pulse indicated by the first point significantly away from the base line. For the faster decays this extrapolation probably represents the largest error. Curves like that in Figure 4 for DPCP were also determined on the same day with the same cavity, laser focusing, incident microwave power, detector diode current, etc. The optical densities of the samples were determined at 337 nm on a Cary 219 spectrophotometer. The signal expected for 100% light absorption and unit quantum yield was then calculated. Then, calibration curves for loss as a function of solute concentration (like Figure 3) were run using the same cavity as for the transient experiments and the same cell. The values, C. of the slopes of these curves were used to calculate values of  $\beta^{-1}$  so that  $\Delta \mu$  could be calculated from eq 13. Values so determined are listed in Table I with auxiliary information.

Discussion of Triplet States. The dipole moments of the triplet states of the aromatic ketones can be discussed by reference to the behavior of formaldehyde. The dipole moment is 2.33 D for the ground state, and Stark-effect



Figure 6. Plot of the decay rate constant for benzil triplet in benzene as a function of the concentration of 2,5-dimethyl-2,4-hexadiene. Data from optical absorption  $(\nabla)$  and dielectric loss  $(\nabla)$ .

measurements give 1.56 D for the  ${}^{1}A_{2}(n\pi^{*})$  state ( $\Delta \mu$  =  $(-0.77)^{23}$  and 1.29 D for the  ${}^{3}A_{2}(n\pi^{*})$  ( $\Delta\mu = -1.04$ )<sup>24</sup> state. The dipole moment for the ground state arises from the fact that the bonding  $\pi$  electrons are shifted toward the oxygen end of the bond as well as any displacement of the nonbonding electrons away from the rest of the molecule so they are no longer centered on the oxygen. Excitation to an  $n\pi^*$  state shifts an n electron toward the carbon and so reduces the moment. The larger decrease in moment for the triplet over the singlet may be rationalized by the argument that the unpaired electrons are farther apart in the triplet state although changes in geometry and other factors may be involved.

The result found here for benzophenone  $\Delta \mu = -0.9$  is similar to that found in Stark-effect measurements on a molecular crystal at low temperature ( $\mu_{\rm T}$  = 1.8 D,  $\Delta \mu$  = -1.2 D).<sup>7,25</sup> The agreement between that value and  $\Delta \mu =$ 0.9 measured here for benzene solution is regarded as good because of the possible influence of differing environments. The lowest triplet state of benzophenone is generally regarded as  $n\pi^*$  and is not significantly mixed with higher triplet states of  $\pi\pi^*$  character. Since the orbitals involved are mainly localized at the carbonyl group, the change in dipole moment is similar to that for formaldehyde.

The states of  $\pi\pi^*$  character encountered here for aromatic carbonyls involve promotion of the ring  $\pi$  electrons so that the electrons on the oxygen are repelled even farther away from the ring increasing the dipole moment. Sheng and El-Sayed<sup>8</sup> have found  $\mu = 4.0 \text{ D} (\Delta \mu = +1.2 \text{ D})$ for the  ${}^{3}\pi\pi^{*}$  state of benzaldehyde at 4.2 K. (But  $\mu = 2.0$ D for the  $3n\pi^*$  state.) Fluorenone represents a case where a  $\pi\pi^*$  state is lowest<sup>26</sup> and the dipole moment change  $\Delta\mu$ = +1.3 is rather similar to that for the low-temperature study on benzaldehyde.

The situation for acetophenone is somewhat different in that the lowest triplet state is  $n\pi^*$  but that a state of  $\pi\pi^*$  character lies close enough that significant mixing occurs.<sup>27</sup> Since the dipole moment for the  $\pi\pi^*$  state is expected to be larger than for the ground state, the value for the mixed state will be in between. The somewhat reduced change  $\Delta \mu = -0.55$  for acetophenone (vs.  $\Delta \mu = -0.9$ for benzophenone) may represent evidence for this mixing. An alternative or additional consideration is partial population of a second triplet state which is close in energy. In this case the value found for the dipole moment rep-

(26) T. Kobayashi and S. Nagakura, Chem. Phys. Lett., 43, 429 (1976). (27) Y. H. Li and E. C. Lim, Chem. Phys. Lett., 7, 15 (1970).

resents the average for the states which are populated. Benzaldehyde, for which we find  $\Delta \mu \sim 0,^{28}$  probably has both effects operating.<sup>29</sup> Xanthone shows a number of unusual aspects in its behavior.<sup>30</sup> (These include a very short triplet lifetime of  $\sim$ 70 ns in benzene, thus necessitating the use of CCl<sub>4</sub> to lengthen the lifetime so that the true amplitude can be measured.) The dipole moment change observed was small,  $\Delta \mu = +0.3$  D, but positive suggesting either a large degree of  $\pi\pi^*$  and  $n\pi^*$  mixing or a small energy gap between two triplet states and population of both.

In molecules of the type D-Ar-A there exist low-lying  $\pi\pi^*$  states where the  $\pi$  and  $\pi^*$  orbitals are not localized in the same region of space so that electronic charge is transferred an appreciable distance in forming the excited state. For example, the transfer of a unit charge from the center of a benzene ring to an adjacent carbonyl would produce a dipole moment of about 18 D.



Large changes in dipole moment have been observed upon formation of singlet states of some aromatic donor-acceptor molecules. Prime examples are amino- and methoxyarylcarbonyls and nitroanilines.<sup>31</sup> The molecules 4-(dimethylamino)benzaldehyde, 2,5-dimethoxybenzaldehyde, and 4,4'-bis(dimethylamino)benzophenone (Michler's ketone) from this study belong to this category and show relatively large increases in dipole moment upon excitation of the lowest triplet state (4.9, 1.5, and 3.1 D, respectively). As was discussed above, these values do not necessarily represent a pure  $\pi\pi^*$  state but may be an average over the actual populations of lowest  $\pi\pi^*$  state and thermally populated  $n\pi^*$  state.

Benzil and the related molecule furil represent a different situation. The decrease in dipole moment for the triplet of benzil (3.75 D) is equal to the value for the ground state so that the value for the triplet state is approximately zero.<sup>32</sup> Photochemical and photophysical studies, however, suggest<sup>33,34</sup> that the state is of  $n\pi^*$  character agreeing with the direction of change but not with the magnitude. A change in geometry to a trans configuration for the carbonyl groups



readily accounts for a zero overall dipole moment for the triplet. This geometry has already been suggested based on luminescence properties.<sup>33</sup> To investigate this behavior further, the rigid homomorph of benzil, 9,10phenanthrenequinone



<sup>(28)</sup> A change in  $\mu$  of 0.1 D would be detectable.

- (31) See, for example, values listed in ref 10.
- (32) Within experimental error the change in  $\mu^2$  is equal to  $\mu_g^2$ . A small moment for the triplet of up to about 1 D would be possible. (33) D. J. Morantz and A. J. C. Wright, J. Chem. Phys., 54, 692 (1971).
- (34) J. F. Arnett and S. P. McGlynn, J. Phys. Chem., 79, 626 (1975).

<sup>(23)</sup> D. E. Freeman and W. Klemperer, J. Chem. Phys., 45, 52 (1966). (24) A. D. Buckingham, D. A. Ramsey, and J. Tyrrel, Can. J. Phys.,

<sup>48, 1242 (1970).</sup> (25) J. W. Barker and L. J. Noe, J. Chem. Phys., 57, 3035 (1972); 58, 5192 (1973).

<sup>(29)</sup> A discussion of two substituted benzaldehydes is given by M. Hossain and D. M. Hanson, Chem. Phys., 30, 155 (1978).

<sup>(30)</sup> See, J. C. Scaiano, J. Am. Chem. Soc., 102, 7747 (1980), for a recent discussion of xanthone.

was studied. The phosphorescence spectrum of this molecule is like that of benzil and is derived from an  $n\pi^*$  state.<sup>35</sup> The observed dipole moment change is -0.6 D, which is small and similar to that for acetophenone or benzophenone. The strong contrast with the behavior of benzil supports the suggested structural change in the latter. Overall, the physical measurement made here strikingly confirms the geometrical change for benzil.

The related molecules 4,4'-dimethoxybenzil and furil show decreases in dipole moment but not all the way to zero as for benzil. In these cases, the dipole moment is determined by more than the relative orientation of the carbonyl groups. For example, furil could have a structure with trans carbonyl groups but with the individual ring dipole moments pointing in the same direction to give a moment approximately twice that of furan. These two examples illustrate a possible problem in interpreting data on nonrigid molecules.

A final example, which is not a ketone, is quinoxaline (1,4-diazanaphthalene). The ground-state moment is 0.5 D along the axis between the two rings. The dipole moment of the lowest triplet state is found here to be 2.3 D. It cannot be determined whether the moment increased in the original direction or changed direction as well. A study of quinoxaline in durene crystals<sup>36</sup> is best interpreted if  $\mu(T_1) > 1.41$  D in a direction opposite to that of the ground state. The present result is in agreement with this result. (It should be noted that the value determined here may be influenced by the formation of an excimer<sup>37</sup> although only a small amount is expected at the concentration 1.5 mM used here.)

Results and Discussion for Radicals. Several radical systems were also investigated. One of these was the neutral durosemiquinone, the subject of the initial report.<sup>1</sup> A reinvestigation of this system is in order to show that the two types of experiments agree and to verify the large value of the dipole moment found previously (3.9-4.2 D). Solutions of various concentrations of duroquinone and durohydroquinone in benzene were studied. A solution of 1 mM durohydroquinone in benzene showed only a slow growth (7- $\mu$ s half-time) to a low-amplitude peak of about 90-units height. Solutions containing 0.5, 1.0, and 2.0 mM durohydroquinone in addition to the duroquinone showed peak amplitudes (extrapolated to the time of the pulse) of 370, 1200, and 1400 units, respectively. The rise time (half-period) with 0.5 mM was about 2  $\mu$ s while that for the two higher concentrations was  $0.5 \ \mu s$  (the response time of the amplifier and RC filter used). The decay of the signal  $(t_{1/2} \sim 10 \ \mu s)$  was considerably longer than the rise and probably represented bimolecular radical reactions. In this case, a model compound had to be used in determining the dipole moment since the reactants have little or no moment. The compounds 2,2,6-trimethylcyclohexanone and 3,3,5,5-tetramethylcyclohexanone seem well suited to serve as models for determining the rotational correlation times. The moments<sup>22</sup> and values of  $g(\tau)$  relative to diphenylcyclopropenone are 2.85 D, 1.12 and 3.18 D, 1.27, respectively. The amplitude for the solution with 2 mM durohydroquinone was used for the calculation, and the absorbance at 337 nm was used to calculate the fraction of light absorbed (i.e., it was assumed that all absorption was by the quinone for which the triplet quantum yield is 1.0).<sup>38</sup> From the results for the differing concentrations



**Figure 7.** Time dependence of apparatus output for a solution of 10 mM  $\alpha, \alpha, \alpha$ -trifluoroacetophenone in decane (**①**). The insert shows the triplet decay measured optically. The negative-going step represents formation of radicals whose dielectric loss is less than for the initial ketone. In the presence of a small amount of oxygen these radicals then react to form two peroxyl radicals which together cause more loss than the ketone.

of hydroquinone mentioned above, it is likely that nearly all of the excited quinone was quenched by reaction with the hydroquinone. If some of the light is not absorbed by the duroquinone to lead to radicals, then the dipole moment to be calculated will be a lower limit. Taking account of the fact that two semiquinone radicals are produced from one quantum, the calculated moments are 3.6 and 3.4 D, respectively, based on the two reference compounds. The value previously obtained using 2,2,6-trimethylcyclohexanone as a reference was 3.9 D. A recalculation of that data using an up-to-date value of the dipole moment gives 3.6 D for the semiguinone. Thus, the two experiments using somewhat different approaches for calibration are in excellent agreement. The higher value of 4.2 D using cyclohexanone as reference is probably not correct because the rotational relaxation time for that molecule is probably shorter than that for the semiquinone. (The relative value of  $g(\tau)$  is 0.68.)

Radicals produced by reaction of excited acetophenones with hydrocarbon solvents were also studied. A specific example is  $\alpha, \alpha, \alpha$ -trifluoroacetophenone in decane. The lifetime of the excited trifluoroacetophenone with respect to abstraction from the solvent is less than 1  $\mu$ s. The reactions are

$$CF_{3}COC_{6}H_{5} \xrightarrow{h\nu} {}^{3}(CF_{3}COC_{6}H_{5})$$

$$(CF_{2}COC_{6}H_{5}) + C_{10}H_{22} \rightarrow CF_{2}\dot{C}(OH)C_{6}H_{5} + C_{10}H_{22}$$

Figure 7 shows the signal observed (solid points). The two reactions above (which are not resolved in time) lead to the initial drop in dielectric absorption. In welldeoxygenated solutions only this downward step of about 100 units is seen. This initial decrease represents the change in loss when one trifluoroacetophenone and one decane molecule are replaced by the two radicals. To a first approximation, the radical from the decane solvent (actually several isomers) should not be polar so that the main change in loss comes from the conversion of the trifluoroacetophenone into the ketyl radical. There is a small, slow, subsequent increase on about a  $30-\mu$ s time scale

<sup>(35)</sup> A. Kuboyama and S. Yabe, Bull. Chem. Soc. Jpn., 40, 2475 (1967).
(36) Y. Udagawa and D. M. Hanson, J. Chem. Phys., 65, 5367 (1976).
(37) K. Yamamoto, T. Takemura, and H. Baba, Bull. Chem. Soc. Jpn.,

<sup>51, 724 (1978).
(38)</sup> D. R. Kemp and G. Porter, Proc. R. Soc. London, Ser. A, 326, 117 (1971).

representing the radical-radical reactions. That the initial loss is not fully recovered shows that the products produce less loss than the trifluoroacetophenone. If the solution also contained a small concentration of oxygen (open circles), the radicals reacted with it to produce peroxyl radicals (the rising portion). The two peroxyl radicals<sup>39</sup> together produce more loss than the trifluoroacetophenone.

$$CF_{3}\dot{C}(OH)C_{6}H_{5} + O_{2} \rightarrow CF_{3}C(\dot{O}_{2})(OH)C_{6}H_{5}$$
$$\cdot C_{10}H_{21} + O_{2} \rightarrow \cdot O_{2}C_{10}H_{21}$$

A long-term decay on the 100- $\mu$ s time scale (not illustrated) represents the disappearance of the peroxyl radicals. The presence of two types of radicals in this system complicates any quantitative analysis. The reaction with oxygen forms two types of peroxyl radicals each with potentially a different formation rate and loss. However, the corresponding growth curve can be fitted reasonably well with a single exponential implying approximately equal reaction rates for the two types of radicals. Two different oxygen concentrations were obtained by bubbling with different O<sub>2</sub>-N<sub>2</sub> mixtures. The second-order rate constants for the two O<sub>2</sub> concentrations were 4.8  $\times$  10<sup>9</sup> for 52  $\mu$ M O<sub>2</sub> and 5.3  $\times$  10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> for 117  $\mu$ M O<sub>2</sub>. The agreement indicates that the analysis is correct. The rate observed is reasonable for a diffusion-controlled reaction in this solvent.

## Conclusions

The present work demonstrates very convincingly that measurement of changes in dielectric loss are practical and that data can readily be interpreted in terms of changes in dipole moment (at least for rigid molecules). The data so obtained are of considerable value in understanding the structure of the states in question. In general, the changes in dipole moment of triplet states seem to correlate with

their character:  $n\pi^*$  states showing a decrease from the ground state and  $\pi\pi^*$  states showing an increase. A number of cases which are believed to have significant mixing between two different triplet states or to have thermal population of a second triplet state show somewhat smaller changes in dipole moment. Experiments at other than room temperature should allow these alternatives to be distinguished. Several cases with rather large increases in dipole moment (such as, (dimethylamino)benzaldehyde) demonstrate the charge-transfer nature of those triplet states. The suggested rearrangement of benzil triplet to a trans configuration has been strikingly confirmed by a decrease in dipole moment to near zero. The practicality of studying dipole moments of radicals has also been shown. It has been found that peroxyl radicals have rather large dipole moments and so can be studied in a direct fashion by this method.

It should be emphasized that this technique is not intended as a replacement for other conventional methods of study of transients such as optical absorption. Microwave dielectric absorption should be regarded as a valuable supplement to these usual methods. Unfortunately, the method is limited to nearly nonpolar solvents. As is well-known in many fields, the existence of data from a rather different technique can often completely eliminate certain alternative explanations of a process which are otherwise difficult to distinguish.

A number of rather polar states have been invoked in various photochemical reactions, and a subsequent application of this technique will be toward establishing the properties of these states. Further improvement of the time resolution is desired so that singlet states with 10-ns lifetime can be observed. With the present apparatus, a reduction in cavity Q will be necessary as well as the use of a faster amplifier. These changes must decrease the signal-to-noise ratio. To compensate, more laser energy and more signal averaging will be necessary.

Acknowledgment. This research was supported by the Office of Basic Energy Sciences of the Department of Energy.

<sup>(39)</sup> The reaction of ketyl radicals with oxygen is often written to yield  $HO_2$  rather than the peroxyl radical as shown here. (See A. Garner and F. Wilkinson, J. Chem. Soc., Faraday Trans. 2, 72, 1010 (1976) for a recent example.) The present data cannot readily distinguish between these alternatives as long as no conversion of the ketyl peroxyl radical to  $HO_2$  takes place on the time scale of these experiments.