

# Exciplex Photophysics. II. Fluorescence Quenching of Substituted Anthracenes by Substituted 1,1-Diphenylethylenes

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**Abstract:** The fluorescence quenching of substituted anthracenes by substituted 1,1-diphenylethylenes in benzene and acetonitrile solvent at room temperature is reported. The quenching efficiency is observed to vary strongly with the donor-acceptor properties of the interacting pair, with no quenching seen ( $k_q < 10^7$ ) in some cases and diffusion-controlled quenching observed in others. In the systems studied, the olefin is generally assumed to be the donor, but in one case probably becomes the acceptor. Both fluorescence lifetime and steady-state quenching measurements are reported and in one case exciplex emission and two-component decay curves are observed and analyzed. The kinetics are discussed in terms of the standard excimer kinetic model.

This paper<sup>2</sup> describes a study of the fluorescence quenching of several anthracene derivatives by a series of substituted 1,1-diphenylethylene derivatives. The anthracenes and olefins were selected to span a considerable range of donor-acceptor properties of the pairs, as deduced by the usual electron donating-withdrawing considerations. The following questions were considered of interest. (a) Is exciplex emission observable? (b) Are there discrepancies between the steady-state and transient quenching rate parameters which would indicate exciplexes of lifetime considerably in excess of the duration of an encounter between noninteracting species? (c) Does the quenching efficiency follow the donor-acceptor properties of the quenching pairs? (d) What is the effect of nonpolar vs. polar solvents on the fluorescence quenching? This information would provide a firm foundation for the interpretation of the photochemical behavior of these systems which is now under investigation.

The following anthracenes were used: anthracene, (A); 9,10-dicyanoanthracene, (DCA); 9,10-dimethoxyanthracene, (DMEOA). As quenchers the following olefins were used: 4,4'-dimethoxy-1,1-diphenylethylene, (DMEODPE); 4,4'-dimethyl-1,1-diphenylethylene, (DMDPE); and 4,4'-dinitro-1,1-diphenylethylene, (DNDPE).

Experiments with unsubstituted 1,1-diphenylethylene proved difficult because of the instability of this olefin during the time required to measure fluorescence lifetimes and steady-state quenching constants. In all cases, the primary excited species was either anthracene or one of its derivatives.

Benzene and acetonitrile were selected as solvents for reasons of solubility and polarity.

## I. Experimental Section

Fluorescence lifetimes were measured with the single photon counting technique<sup>3</sup> which employed a gated nanosecond flash lamp and conventional electronics. The excitation system consisted of a nanosecond lamp and a Spex Minimate monochromator. Filters were used to isolate the fluorescence. The technical details of the single photon counting technique have been described elsewhere.<sup>3,4</sup> Steady-state measurements were made with an intensity ratio instrument described by Ware and Lewis.<sup>5</sup>

The search for exciplex emission was done with a fluorimeter consisting of a Heath monochromator and a Spex Minimate monochromator (excitation), a 150-W xenon high-pressure lamp, and a low-noise 1P28 photomultiplier. The sensitivity of this system was such that fluorescence with a quantum yield  $>10^{-3}$  could be detected for systems absorbing 10-50% of the incident light.

Care was taken to ensure that the measurements were not influenced by thermal or photochemical decomposition of the so-

lutes, by solvent fluorescence, or by fluorescence of impurities in the solutes. The anthracene and substituted anthracenes were obtained commercially. The synthesis and characterization of the olefins will be discussed elsewhere.

## II. Results and Discussion

With one exception, all the anthracenes examined exhibited single exponential decay in both the presence and absence of quencher. The decay kinetics followed simple pseudo-first-order kinetics,<sup>3</sup> *i.e.*

$$1/\tau = (1/\tau)_{t_{Qj}=0} + (k_q)_{tr}[Q] \quad (1)$$

where

$$(k_q)_{tr} = \Delta(1/\tau)/\Delta[Q] \quad (2)$$

The exception was DCA quenched by DMEDPE in benzene which exhibited a double exponential decay. Studies of decay curves as a function of quencher concentration for this system yielded sufficient variation in the components, which were similar in magnitude, so as to permit approximate analysis for the individual rate constants. Values for  $(k_q)_{tr}$  are given in Tables I and II.

In all cases studied, fluorescence spectra at several quencher concentrations were examined for evidence of exciplex emission. The only case where exciplex emission was detected was the DCA-DMEDPE system.

Steady-state quenching experiments gave linear Stern-Volmer plots. Values of  $K_{sv}$ , *i.e.*

$$K_{sv} \equiv \left[ \frac{I_F^0}{I_F} - 1 \right] \frac{1}{[Q]} = (k_q)_{ss}(\tau)_{t_{Qj}=0} \quad (3)$$

are also given in Tables I and II. For all systems examined where quenching was observed to occur, no discrepancy between  $(k_q)_{ss}$  and  $(k_q)_{tr}$  was found within experimental error.

Values for  $(k_q)_{tr}$  were consistently higher when the solvent was acetonitrile as compared to benzene. As can be seen from Tables I and II, in one case the ratio of rate constants in the two solvents is somewhat greater than that explicable in terms of relative diffusion rate ( $\eta(\text{acetonitrile})/\eta(\text{benzene}) = 0.57$ ), implying a solvent effect due to polarity.

The quenching constants in Tables I and II range from  $10^8$  to  $10^{10} M^{-1} \text{ sec}^{-1}$ . Thus for a number of the quencher-fluorophor systems we observe rate constants considerably below that for diffusion-controlled quenching. These data can be rationalized on the basis of the following simple scheme

**Table I.** Quenching Data for Various Aromatic-Olefin Pairs in N<sub>2</sub>-Saturated Benzene at 25°

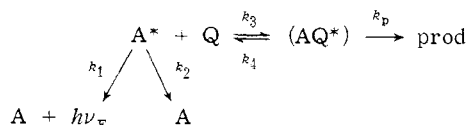
Fluorophor	Quencher	$\tau_0$ , nsec	$(k_q)_{tr} \times 10^{-9}$ , $M^{-1} \text{ sec}^{-1}$	$(k_q)_{ss} \times 10^{-9}$ , $M^{-1} \text{ sec}^{-1}$	$k_p/k_4^a$
9,10-Dicyanoanthracene	Dimethoxydiphenylethylene	12.4	9.8	10	
	Dimethyldiphenylethylene	12.4	<i>a</i>	4.5	
	Dinitrodiphenylethylene	12.4	3.4	4.1	0.70
Anthracene	Dimethoxydiphenylethylene	3.6	1.3	1.4	0.15
	Dimethyldiphenylethylene	3.6	0.33	0.33	0.034
	Dinitrodiphenylethylene	3.6	<i>b</i>	<i>b</i>	<i>b</i>
9,10-Dimethoxyanthracene	Dimethoxydiphenylethylene	13.3	NQ <sup>d</sup>	NQ	NQ
	Dimethyldiphenylethylene	13.3	NQ	NQ	NQ
	Dinitrodiphenylethylene	13.3	17	16	4.0

<sup>a</sup> Two-component decay. <sup>b</sup> Spectral overlap makes measurements impossible. <sup>c</sup> Based on  $k_3 = 1 \times 10^{10} M^{-1} \text{ sec}^{-1}$ . Calculated from  $(k_q)_{ss}$ . <sup>d</sup> NQ = no quenching.

**Table II.** Quenching Data for Various Aromatic-Olefin Pairs in N<sub>2</sub>-Saturated Acetonitrile at 25°

Fluorophor	Quencher	$\tau_0$ , nsec	$(k_q)_{tr} \times 10^{-9}$ , $M^{-1} \text{ sec}^{-1}$	$(k_q)_{ss} \times 10^{-9}$ , $M^{-1} \text{ sec}^{-1}$	$k_p/k_4^a$	$R^c$
9,10-Dicyanoanthracene	Dimethoxydiphenylethylene	15.2	15	17		1.7
	Dimethyldiphenylethylene	15.2	13	14		3.1
	Dinitrodiphenylethylene	15.2				
Anthracene	Dimethoxydiphenylethylene	5.4	3.4	2.2	0.28	1.6
	Dimethyldiphenylethylene	5.4	0.51	0.55	0.058	1.7
	Dinitrodiphenylethylene	5.4	<i>b</i>	<i>b</i>	<i>b</i>	
9,10-Dimethoxyanthracene	Dimethoxydiphenylethylene	11.2	NQ <sup>d</sup>	NQ	NQ	
	Dimethyldiphenylethylene	11.2	NQ	NQ	NQ	
	Dinitrodiphenylethylene	11.2				

<sup>a</sup> Based on  $k_3 = 1 \times 10^{10} M^{-1} \text{ sec}^{-1}$ . Calculated from  $(k_q)_{ss}$ . <sup>b</sup> Spectral overlap made measurements impossible. <sup>c</sup>  $R = (k_q)_{ss}(\text{acetonitrile}) / (k_q)_{ss}(\text{benzene})$ . <sup>d</sup> NQ = no quenching.



Agreement between  $(k_q)_{tr}$  and  $(k_q)_{ss}$  implies<sup>6</sup> that, if  $k_3$  is approximately diffusion limited, the lifetime of  $(\text{AQ}^*)$  is subnanosecond in magnitude, a situation that can arise either because of a very large  $k_4$  (the feedback rate constant), a very large  $k_p$ , or both. If  $k_p \gg k_4$  and if  $k_p \approx 10^{10}$ – $10^{11} \text{ sec}^{-1}$ , then the quenching efficiency will be high and the behavior will approach that of a diffusion-controlled process. The same situation prevails if both  $k_p$  and  $k_4$  are  $10^{10}$ – $10^{11} \text{ sec}^{-1}$ . If  $k_4 \gg k_p$  and if  $k_4 \approx 10^{10}$ – $10^{11} \text{ sec}^{-1}$ , then quenching will be inefficient. Either  $k_4$  or  $k_p$  must be very large compared to  $10^9 \text{ sec}^{-1}$  in order that one not see a discrepancy between the steady-state and transient quenching constants (unless  $k_3$  is considerably below the diffusion-controlled limit).

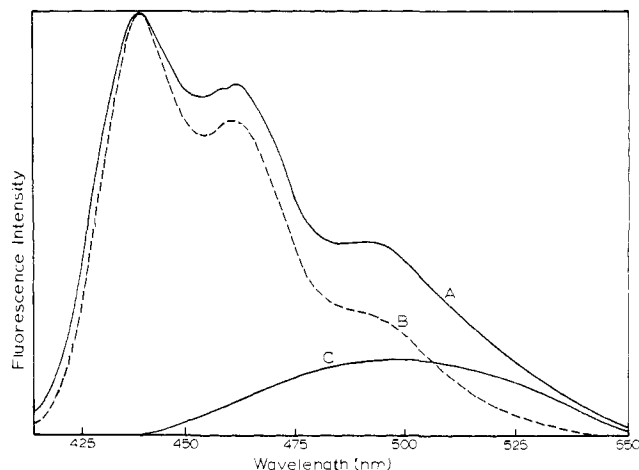
Only in one case do we see a two-component decay. Otherwise, all the combinations examined exhibit the limiting behavior; *i.e.*, the exciplex, if present, probably has a lifetime not greater than 100 psec.<sup>6</sup>

In both Tables I and II the excited molecule-quencher systems are arranged in order of their donor-acceptor properties. Consider first DCA. It is quenched by all three olefins but with decreasing efficiency (as judged by  $k_q$ ) as one goes from the best to the worst donor. If one now decreases the acceptor property of the aromatic hydrocarbon by going to anthracene, the quenching efficiency is less than with DCA and any of the olefins and furthermore appears to again decrease as one goes from the best to the worst donor. Unfortunately, it was not possible to study A and DNDPA because of unfavorable spectral overlap. Finally, a further decrease in the acceptor tendency of the aromatic in the case of DMEOA results in the absence of quenching ( $k_q < 10^7 M^{-1} \text{ sec}^{-1}$ ) by the best donor or by DMEDPE. However, DNDPE quenches DMEOA at a diffusion-controlled rate! A reasonable conclusion is that in this case the aromatic and olefin have changed roles, with the olefin becoming the acceptor. This view is consistent with the observation that no quenching is seen with either A or DCA and DNDPE.

It must be emphasized that the simple scheme given above requires five rate constants, and only two ( $k_1$  and  $k_2$ ) are directly accessible. Also,  $k_p$  may well be the sum of two or more rate constants representing several channels out of the exciplex other than feedback (step represented by  $k_4$ ) to regenerate  $\text{A}^*$ . The single exponential decay in the presence of quencher, the absence of exciplex emission, and the agreement between steady-state and transient measurements limit the information available from fluorescence measurements. The individual constants  $k_3$ ,  $k_4$ , and  $k_p$  cannot be determined without additional assumptions.

The system DCA-DMEDPE was unique in exhibiting emission that we attribute to an exciplex. In Figure 1 are shown two time-resolved spectra for this system in benzene at 25°. These time-resolved spectra were taken with the single photon counting technique.<sup>3,7</sup> The single channel analyzer associated with the ADC of the multichannel pulse height analyzer was used to select a portion of the decay curve which was then subjected to spectral analysis. Curve B represents the spectrum at the maximum of the decay curve and was obtained with a narrow time window of a few nanoseconds. Curve A was taken with a much wider time window which spanned the tail of the decay curve where there should be more exciplex emission present. The difference between these two curves is also shown, and corresponds approximately to the difference spectrum obtained from steady-state emission spectra for this system in the presence and absence of quencher. This time-resolved spectrum provides rather convincing evidence for an exciplex as an intermediate in the fluorescence quenching in this case and in turn strengthens the assumption that in all of the systems studied the intermediate is an exciplex, presumably with charge-transfer character.

As mentioned above, the system DCA-DMEDPE exhibited a two-component decay for the DCA\*. This implies a



**Figure 1.** Nanosecond time-resolved fluorescence spectrum of 9,10-dicyanoanthracene quenched by 4,4'-dimethyl-1,1-diphenylethylene in benzene at room temperature. Curve A: measured with a wide time window with emission occurring in the tail of the fluorescence decay curve. Curve B: measured at the peak of the fluorescence decay curve with a narrow time window. Curve C: difference spectrum attributed to the exciplex.

substantial decrease in the lifetime of the exciplex such that feedback ( $k_4$ ) is now an important process relative to the processes labeled  $k_p$  and  $k_3[Q]$ . An attempt was made to resolve these two-component curves for a series of quencher concentrations using a grid search program for the four parameters in

$$[A^*] = c_1 e^{-\lambda_1 t} + c_2 e^{-\lambda_2 t} \quad (4)$$

The results are shown in Figure 2. A plot of  $\lambda_1 + \lambda_2$  was linear with approximately the scatter shown in Figure 2. Since<sup>2,8</sup>

$$\lambda_1 + \lambda_2 = k_1 + k_2 + k_3[Q] + k_4 + k_p \quad (5)$$

this plot should have a slope of  $k_3$  and an intercept of  $k_1 + k_2 + k_4 + k_p$ . The intercept of the plot of  $\lambda_2$  can be used,<sup>8</sup> along with the known  $k_1 + k_2$ , to obtain a point for the intercept of  $\lambda_1 + \lambda_2$ , a procedure which is helpful in obtaining the best estimate for the slope and thus  $k_3$ . This approach gave  $k_3 = 9 \times 10^9 M^{-1} \text{ sec}^{-1}$ . From  $k_4 + k_p$  and  $k_3$  and the equation

$$\frac{1}{k_q} = \frac{1}{k_3} + \frac{k_4}{k_3 k_p} \quad (6)$$

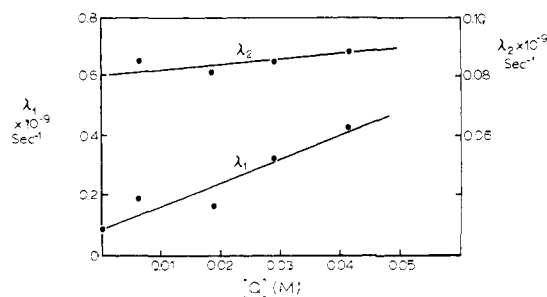
one obtains  $k_4 \approx k_p \approx 4 \times 10^7 \text{ sec}^{-1}$ .

Unfortunately the DCA-DMDPE system was the only one which exhibited exciplex emission and a two-component decay curve. It is of interest with respect to the other systems studied to investigate the implications of two constraints that can be applied: (a) since there is no discrepancy between the steady-state and transient quenching constants, in these systems  $k_4 + k_p$  must be large<sup>6</sup> probably greater than  $10^{10} \text{ sec}^{-1}$ ; (b) assume  $k_3$  to be approximately diffusion controlled. From eq 6 one obtains

$$k_4/k_p = (k_3/k_q) - 1 \quad (7)$$

and one can estimate  $k_4/k_p$  from eq 7 and the assumed value for  $k_3$ , provided  $k_q > k_3$  by a considerable amount. On the other hand, if  $k_q \approx k_{\text{diff}}$ , then it is perhaps not unreasonable to assume that  $k_q$  is in fact approximately equal to  $k_3$ , which implies  $k_4 \ll k_p$  and eq 6 reduces to  $k_q \approx k_3$ .

If we consider DCA quenched in benzene by the three olefins listed in Table I, we have  $k_3$ ,  $k_4$ , and  $k_p$  for



**Figure 2.** Plots of the decay constants associated with  $C_1 \exp(-\lambda_1 t) + C_2 \exp(-\lambda_2 t)$  for 9,10-dicyanoanthracene quenched by 4,4'-dimethyl-1,1-diphenylethylene in benzene at room temperature. Note that the  $\lambda_1$  intercept is a measured quantity (the reciprocal unquenched lifetime).

DMDPE from the two-component decay curve analysis. For DNDPE we observe  $k_q < k_{\text{diff}}$ , but not by a large margin. If we take  $k_3 \approx 10^{10} M^{-1} \text{ sec}^{-1}$ , then  $k_q = 4 \times 10^9 M^{-1} \text{ sec}^{-1}$  yields  $k_4/k_p = 4$  from eq 7. Since  $k_p + k_4$  must be<sup>6</sup> of the order of  $10^{10} \text{ sec}^{-1}$ , the above ratio implies that both  $k_4$  and  $k_p$  are of this order of magnitude with the inefficiency due to  $k_4 > k_p$ . For DMEODPE on the other hand  $k_q \approx 10^{10} M^{-1} \text{ sec}^{-1}$  and one cannot use eq 7 to estimate  $k_4/k_p$ . If, however, one assumes that  $k_q \approx k_3$ , then  $k_4$  must be viewed as considerably less than  $k_p$  and the condition  $k_p > k_4$  is responsible for the high efficiency of quenching. But  $k_p$  must now be of the order of  $10^{10} \text{ sec}^{-1}$  because of the absence of a discrepancy between steady-state and transient measurements<sup>6</sup> and in fact  $k_4$  could be less than that observed for DMDPE, which would give a smooth decrease in  $k_4$  as the donor properties of the olefin are changed from DMEODPE to DNDPE; however, this is speculative.

For the other systems listed in Table I,  $k_q$  decreases further as compared to DCA-DNDPE, and if again one assumes  $k_3 = 10^{10} M^{-1} \text{ sec}^{-1}$ , estimates of  $k_4/k_p$  can be obtained (see Tables I and II).

Since  $k_4 + k_p$  must still be of the order of  $10^{10} \text{ sec}^{-1}$ , then these are also interpreted as cases where  $k_4 \approx 10^{10} - 10^{11} \text{ sec}^{-1}$  and the inefficiency is due to  $k_4 > k_p$ . These last conclusions do not depend upon the exact values of  $k_3$  chosen because of the low value of  $k_q$  relative to  $k_{\text{diff}}$ .

The data in Table II for the solvent acetonitrile can be interpreted in a parallel manner. It is of interest that the only solvent effect that cannot be explained in terms of the relative viscosities of acetonitrile and benzene is observed with the case that gives the double exponential decay. Perhaps the higher dielectric medium increases  $k_p$ , and thus  $k_q$  approaches  $k_3$  more closely as the solvent polarity increases. If this view is correct, the change in  $k_p$  is rather large.

Work continues in this area with three objectives: (1) to relate these studies to the products obtained under these and other conditions; (2) to relate these kinetic studies to polarographic oxidation-reduction potentials of the anthracenes and olefins; (3) to confirm the direction of electron transfer by flash spectroscopic identification of the radical ions in polar solvents.

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## Synthesis of Noble-Gas Dihalides by Laser Photolysis of Matrix-Isolated Halogens

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**Abstract:** Condensed inert gas-halogen mixtures have been subjected to argon-ion laser and mercury-arc photolysis, resulting in the photoproduction of KrF<sub>2</sub>, XeF<sub>2</sub>, XeCl<sub>2</sub>, and XeClF. Raman-active vibrations have been measured for all four species, and infrared bands of XeCl<sub>2</sub> and XeClF have been identified. The limits of noble-gas reactivity under these conditions have been explored.

Since Bartlett<sup>1</sup> synthesized the first rare gas compound in 1962, researchers have reported dozens of new species containing "inert" gases. Shortly thereafter, the matrix-isolation technique was directed to the production of rare gas compounds; Turner and Pimentel<sup>2,3</sup> observed the infrared spectra of matrix-isolated XeF<sub>2</sub> and KrF<sub>2</sub> produced by ultraviolet irradiation of condensed Ar:Xe:F<sub>2</sub> and Ar:Kr:F<sub>2</sub> mixtures. A more recent infrared investigation of the condensed products of a xenon-chlorine glow discharge by Nelson and Pimentel<sup>4</sup> identified XeCl<sub>2</sub> and assigned a band at 313 cm<sup>-1</sup> to  $\nu_3$ . In one of the early Raman matrix-isolation studies, Boal and Ozin<sup>5</sup> produced XeCl<sub>2</sub> using the same synthetic approach and identified  $\nu_1$  at 253 cm<sup>-1</sup>.

Matrix-Raman studies of OF<sub>2</sub> and Cl<sub>2</sub>O in this laboratory<sup>6,7</sup> have shown that laser photodecomposition of the precursor gives rise to new chemical species, namely OF, ClO, and Cl-ClO, which were directly observed by laser Raman spectroscopy. The matrix moderates photodecomposition by the laser and allows the observation of Raman spectra of the precursor and photolysis product.

Accordingly, we attempted a study of inert gas dihalides using laser photolysis of matrix-isolated halogens in the inert gas matrix. For compounds of limited stability, like XeCl<sub>2</sub>, and the new mixed halogen species XeClF, this was a particularly useful approach.

### Experimental Section

The experimental techniques, equipment, and manometric procedures have been described in previous papers from this laboratory.<sup>8,9</sup> Most experiments involved a 2% halogen-rare gas mixture; for one investigation, an Ar:Xe:F<sub>2</sub> ratio of 100:1:1 was used. Halogens were purified as follows: F<sub>2</sub> (Allied) was passed slowly through a stainless-steel U tube precooled with liquid N<sub>2</sub>; Cl<sub>2</sub> (Matheson) was condensed with liquid N<sub>2</sub> and outgassed; OF<sub>2</sub>, ClF, and ClF<sub>3</sub> (Ozark-Mahoning) were used without further purification. Rb<sup>37</sup>Cl (99% enriched) was reacted with concentrated HNO<sub>3</sub> to produce <sup>37</sup>Cl<sub>2</sub>. The gaseous product was passed through Drierite, condensed, and outgassed.

Prior to sample preparation of fluorine-containing species, the stainless-steel vacuum line and sample can were passivated overnight with 30-50 Torr of the appropriate compound. Sample deposition was 3 mmol/hr for the Raman experiments and varied from an initial rate of 1 mmol/hr to a final rate of 2 mmol/hr for infrared studies. Gases were deposited on a tilted copper wedge (Raman) or a CsI window (infrared) maintained at 16°K. In some

of the present experiments, the inert gas-halogen mixture was subjected to microwave discharge prior to deposition. The microwave discharge (Burdick Corp., Milton, Wis., Model MW 200, 2450 MHz, 375 W) was maintained through the flowing gas stream using a standard Evenson-Broida cavity on a quartz spray-on nozzle (2-mm orifice). The cavity was placed 6 in. from the copper block; the glow extended through the orifice to within 1 cm of the copper block.

Raman spectra shifted 100-1200 cm<sup>-1</sup> from the laser source were recorded on a Spex Ramalog obtained by irradiation with the 4579, 4765, 4880, 4965, 5017, and 5145 Å argon ion and 3564 Å krypton ion laser lines using 50 to 150 mW of power at the sample unless otherwise specified.

Dielectric filters were employed to prevent unwanted plasma emission lines from appearing in the spectra, and band calibration was accomplished by superimposing emission lines on the spectrum during the running scan by replacing the dielectric filters with a neutral density filter. Infrared spectra were recorded on a Beckman IR-12, and calibrations were made relative to H<sub>2</sub>O rotational lines present in the scans. Precision of band positions in infrared and Raman spectra is  $\pm 1$  cm<sup>-1</sup> or better (as listed). Slit widths were 500  $\mu$  for Raman surveys and varied from 3 cm<sup>-1</sup> at 300 cm<sup>-1</sup> to 1 cm<sup>-1</sup> at 800 cm<sup>-1</sup> during infrared scans.

### Results

The experimental observations will be presented in turn for the several noble gas-halogen mixtures studied.

**XeF<sub>2</sub> Raman.** Laser irradiation of 2% F<sub>2</sub> in Xe yielded a Raman signal at 512.4  $\pm$  0.5 cm<sup>-1</sup>, which is shown in Figure 1. This signal is in excellent agreement with the gas-phase assignment 514.5 cm<sup>-1</sup> to  $\nu_1$  of XeF<sub>2</sub> which is listed in Table I.<sup>10</sup> Survey scans with blue (4579, 4765, and 4880 Å) excitation showed the XeF<sub>2</sub> band present immediately after sample exposure to the laser beam. Also, the signal intensity exhibited little change with prolonged irradiation from the beam. Green (5145 Å) excitation initially showed no signal in the spectrum, but 10 min of photolysis was sufficient to produce a weak band at the frequency shift appropriate to XeF<sub>2</sub>. No signal was discernible for F<sub>2</sub>, normally found about 890 cm<sup>-1</sup>.

Streng and Streng<sup>11</sup> produced XeF<sub>2</sub> from sunlight irradiation of Xe:OF<sub>2</sub> mixtures, a reaction that was duplicated by laser photolysis of 2% OF<sub>2</sub> in Xe condensed at 16°K. The resultant XeF<sub>2</sub> band (512.5  $\pm$  1.0 cm<sup>-1</sup>) was the strongest observed in this series of experiments and was even