

recommendation,<sup>2</sup> based only upon our preliminary room temperature value for  $k_1$ , is attributable to the fact that  $k_1/k_2 \gg 10$  over the complete temperature range.

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## Comparison of the Optoacoustic and Hg Tracer Methods for the Study of Energy-Transfer Processes in Gas Mixtures

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Rates of energy transfer from vibrationally excited SF<sub>6</sub> and pentafluorobenzene to argon in the gas phase have been studied by using the Hg tracer technique and time-resolved optoacoustics. These two techniques which rely on fundamentally different physical principles were found to give equivalent results. The implications for the study of energy-transfer processes in gas mixtures are discussed.

### I. Introduction

The rate at which energy is transferred between vibrational, rotational, and translational degrees of freedom in gaseous systems is of fundamental importance in understanding the fate of species excited as a result of chemical or physical processes. A variety of different techniques have been applied to the study of energy transfer from vibrationally excited molecules. These include ultraviolet absorption,<sup>1,2</sup> infrared absorption,<sup>3</sup> infrared fluorescence,<sup>4</sup> optoacoustics,<sup>5,6</sup> thermal lensing,<sup>7</sup> and most recently the Hg tracer technique.<sup>8</sup> However, at present it is difficult to compare the results from studies using these different techniques as, in general, these methods have been applied to measure relaxation rates of different gas mixtures, using different excitation methods and excitation energies. Furthermore, the above methods do not all monitor the same specific relaxation processes. For example, the ultraviolet absorption method measures changes in vibrational excitation whereas the Hg tracer and optoacoustic techniques monitor changes in the translational excitation of the mixtures.

Recently in our two laboratories we have applied the optoacoustic and Hg tracer methods to the study of the rates of energy transfer in a wide variety of gas mixtures. The former technique measures the development of a pressure wave, propagating from

the origin of excitation, at some distant (initially undisturbed) point in the fluid medium. The latter technique measures the temporal change in absorption at 254 nm by a trace of Hg vapor caused by Doppler and Lorentz line broadening due to the heating of a gas mixture. Both techniques measure the rate at which energy is transferred from the initial vibrational excitation to translational excitation of the gas.

In order to compare the results obtained from these two different methods we have conducted relaxation experiments in mixtures of SF<sub>6</sub> and argon and of pentafluorobenzene (PFB) and argon in our two laboratories. Both methods depend to a greater or lesser degree on various physical processes which occur during relaxation (e.g., the specific relaxation mechanism and occurrence of fluid flow) which will be discussed.

### II. Experimental Section

The apparatus and experimental techniques used in the optoacoustic (OA)<sup>6</sup> and Hg tracer<sup>9-11</sup> methods have been described previously and hence only a brief description is given here. In both experimental systems a CO<sub>2</sub> TEA laser tuned to the P20, 10.6- $\mu$ m CO<sub>2</sub> laser line was used to excite the SF<sub>6</sub> and PFB mixtures. Excitation energies were in the range 3000-6000 cm<sup>-1</sup> in the Hg tracer technique and 3000-20 000 cm<sup>-1</sup> in the optoacoustic study. This energy range was dictated by our previous observations that at such energies relaxation rate constants for SF<sub>6</sub>/Ar and PFB/Ar mixtures are independent of energy,<sup>12,13</sup> thus facilitating a direct comparison of the results from the two different methods.

**II.A. Optoacoustic Method.** In the OA experiments, mixtures were irradiated in a large cylindrical static cell (30 cm long, 31 cm i.d.). A fast piezoelectric transducer placed 8.6 cm normal

(1) Hippler, H.; Troe, J.; Wendelken, H. *J. J. Chem. Phys.* **1983**, *78*, 5351.  
(2) Ichimura, T.; Mori, Y.; Nakashima, N.; Yoshihara, K. *J. Chem. Phys.* **1985**, *83*, 117.

(3) Jalenak, W.; Weston, Jr., R. E.; Sears, T. J.; Flynn, G. W. *J. Chem. Phys.* **1985**, *83*, 6049.

(4) Rossi, M. J.; Pladzievecz, J. R.; Barker, J. R. *J. Chem. Phys.* **1983**, *78*, 6695.

(5) Smith, N. J. G.; Davis, C. C.; Smith, I. W. M. *J. Chem. Phys.* **1984**, *80*, 6122.

(6) Beck, K. M.; Ringwelski, A.; Gordon, R. J. *J. Chem. Phys. Lett.* **1985**, *12*, 529.

(7) Siebert, O. R.; Grabiner, F. R.; Flynn, G. W. *J. Chem. Phys.* **1974**, *60*, 1504.

(8) Braun, W.; Scheer, M. D.; Kaufman, V. *J. Res. Natl. Bur. Stand.* **1986**, *91*, 313.

(9) Braun, W.; Scheer, M. D.; Cvetanovic, R. J. *J. Chem. Phys.* **1987**, *88*, 3715.

(10) Wallington, T. J.; Scheer, M. D.; Braun, W. *J. Chem. Phys. Lett.* **1987**, *138*, 538.

(11) Dagaut, P.; Wallington, T. J.; Braun, W. *J. Photochem.*, in press.

(12) Beck, K. M.; Gordon, R. J. *J. Chem. Phys.* **1987**, *87*, 5681.

(13) Braun, W.; Wallington, T. J. *J. Chem. Phys. Lett.* **1987**, *140*, 441.

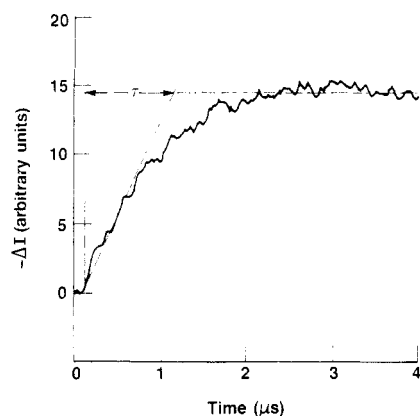


Figure 1. Change in absorption at 254 nm following the irradiation of a 1.3 Torr sample of a mixture of PFB and Ar (Ar mole fraction = 0.81).

to the laser beam was used to measure the temporal shape of the acoustic pulse generated by the relaxing gas. The cell dimensions were large enough to guarantee that there was no interference with reflected waves on the time scale of the measurement. The output of the transducer was amplified from  $10^3$  to  $5 \times 10^3$  times with a dc coupled amplifier, digitized with a 100-MHz transient recorder using a 80-ns channel width, and averaged over 1000 shots in a microcomputer.

The acoustic wave produced by the relaxing molecules consists of a positive condensation pulse of amplitude  $I_+$  followed by a negative rarefaction pulse of amplitude  $I_-$ . The ratio  $I_-/I_+$  is a monotonically increasing function of the dimensionless quantity  $\epsilon$ , defined as

$$\epsilon = r/c\tau \quad (1)$$

where  $r$  is the radius of the excited volume,  $c$  is the speed of sound, and  $\tau$  is the relaxation time. For fast relaxation ( $\epsilon \gg 1$ ),  $I_-/I_+$  approaches unity, while for slow relaxation ( $\epsilon \ll 1$ )  $I_-/I_+$  approaches zero. The quantitative relation between  $I_-/I_+$  and  $\epsilon$  depends on the geometry of the excited volume and on the rate law for the relaxation process. In our original study<sup>6</sup> the predicted relation between  $I_-/I_+$  and  $\epsilon$  did not agree quantitatively with the data, and we had to rely on an experimental calibration. We have since tracked this problem down to a saturation effect due to multiphoton excitation, with varying amounts of energy absorbed in different regions of the laser beam. By using a "top hat" laser geometry we overcame this problem and obtained quantitative agreement between the observed waveform and the solution of the acoustic wave equation. The accuracy of the calculations for top hat excitation with exponential decay of the excited molecules was verified experimentally for OCS in He and Ar baths.<sup>14</sup>

**II.B. Hg Absorption Method.** Gas mixtures for the Hg tracer experiment were manometrically prepared in a 150-cm<sup>3</sup> bulb. Samples of the gas mixture were then admitted into a small cylindrical cell (18 mm  $\times$  9 mm o.d.) containing a trace of Hg vapor. A condenser attached to the cell maintained a constant pressure of Hg vapor at a value determined by the temperature of the circulating water. The IR beam was partially focused so that it uniformly irradiated the central region of the cell. A focused Hg resonance lamp was positioned coaxially to the laser beam and was used to monitor light absorption at 254 nm along the cell axis.

A typical experiment consisted of irradiating a sample, using 100–600 laser pulses. The temporal change in the absorption by the small amount of Hg in the cell ( $\approx 1.8$  mTorr) monitored the changing translational temperature of the gas mixture. Absolute changes in temperature, ranging from 10 to 500 K, were calculated by using previous calibrations which relate the change in absorption at 254 nm to the temperature-induced change of the Doppler and Lorentz absorption line widths of the Hg atoms in the cell. Absorption data were recorded with a 1P28 photomultiplier

TABLE I: Values of  $(1/P\tau)^a$  Obtained for Various SF<sub>6</sub>-Ar Mixtures by Using the Hg Tracer Method

mole frac of SF <sub>6</sub>	$(1/P\tau) \times 10^2$ , (Torr $\mu$ s) <sup>-1</sup>	mole frac of SF <sub>6</sub>	$(1/P\tau) \times 10^2$ , (Torr $\mu$ s) <sup>-1</sup>
0.00	$0.63 \pm 0.06^b$	0.28	$3.09 \pm 0.82$
0.02	$0.81 \pm 0.12$	0.50	$4.85 \pm 0.33$
0.10	$1.29 \pm 0.15$	0.73	$6.33 \pm 0.21$
0.19	$2.24 \pm 0.16$	1.00	$8.55 \pm 1.55$

<sup>a</sup>Quoted errors represent  $\sigma$  from a linear heat-squares analysis.

<sup>b</sup>Calculated from the linear least-squares equation  $(1/P\tau) = A + BX_M$ , where  $X_M$  = mole fraction of M = SF<sub>6</sub>;  $A = (0.63 \pm 0.06) \times 10^{-2}$ ,  $B = (7.92 \pm 0.20) \times 10^{-2}$ .

TABLE II: Values of  $(1/P\tau)^a$  Obtained for Various PFB-Ar Mixtures by Using the Hg Tracer and Optoacoustic Methods

mole frac of PFB	$(1/P\tau)$ , (Torr $\mu$ s) <sup>-1</sup>	mole frac of PFB	$(1/P\tau)$ , (Torr $\mu$ s) <sup>-1</sup>
Hg Tracer Method <sup>b</sup>			
0.00	$0.053 \pm 0.014^c$	0.31	$0.84 \pm 0.16$
0.02	$0.17 \pm 0.05$	0.48	$1.12 \pm 0.05$
0.04	$0.17 \pm 0.02$	0.75	$1.39 \pm 0.11$
0.10	$0.45 \pm 0.15$	1.00	$1.32 \pm 0.10$
0.19	$0.64 \pm 0.07$		
Optoacoustic Method			
0.00044	$0.0726 \pm 0.0008$	0.0158	0.0891
0.0136	$0.0734 \pm 0.0025$	0.0179	0.1067
0.0158	$0.0744 \pm 0.0027$		

<sup>a</sup>Errors represent one standard deviation. <sup>b</sup>Data taken from ref 13.

<sup>c</sup>Calculated from the equation  $(1/P\tau) = A + BX_M + C(X_M)^2$ , where  $X_M$  is mole fraction of M = PFB and  $A = 0.053 \pm 0.014$ ,  $B = 3.18 \pm 0.18$ ,  $C = -1.92 \pm 0.21$ .

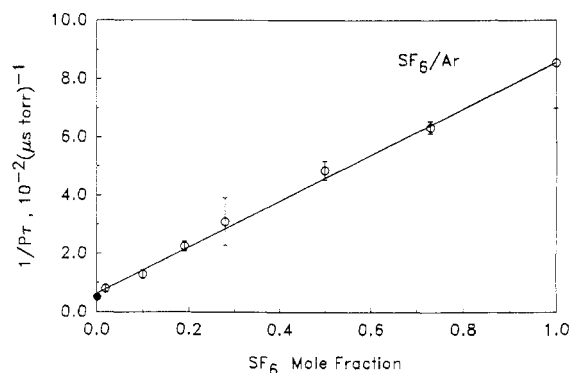


Figure 2. Plot of  $1/(P\tau)$  as a function of the mole fraction of SF<sub>6</sub> in mixtures of SF<sub>6</sub> with Ar, using the Hg tracer technique (O) and the optoacoustic technique (●).

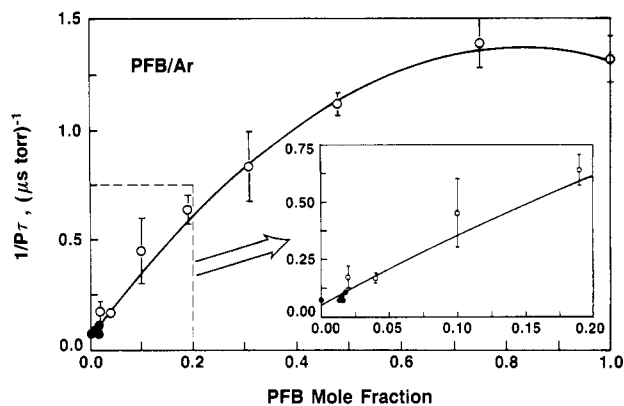
mounted at the exit of a monochromator. The signals generated were stored for each laser pulse in a transient digitizer triggered at the start of each pulse. The data were subsequently transferred to an on-line computer for signal averaging.

### III. Results and Analysis

**III.A. Hg Method.** Figure 1 shows the observed temporal behavior of the Hg absorption at 254 nm following the irradiation of 1.3 Torr of a mixture of PFB and Ar (mole fraction of Ar = 0.81). The increase in absorption reflects the release of translational excitation in the mixture, as sensed by the trace of Hg vapor. The "time constant",  $\tau$ , was measured by extrapolating the initial slope up to the maximum (equilibrium) absorption, as shown in Figure 1. As discussed previously  $\tau$  represents the time the system would take to achieve equilibration if the rate of energy transfer into translation were to continue at its initial rate. For a first-order process  $\tau$  is simply the time constant, while for nonexponential processes it represents a measure of the initial rate of energy transfer into translational excitation.

During the present work  $\tau$  was observed to be inversely proportional to the total pressure (the product  $P\tau$  was a constant) for each of the mixtures studied. At the lowest pressures and for

(14) Beck, K. M.; Gordon, R. J., submitted for publication.



**Figure 3.** Plot of  $1/(P\tau)$  as a function of the mole fraction of PFB in mixtures of PFB with Ar, using the Hg tracer technique (O) and the optoacoustic technique (●).

the most dilute mixtures the measured time constants were relatively long (4–5  $\mu$ s). As we have discussed previously,<sup>9</sup> during this time interval, some gas can expand from the laser irradiated zone as a result of fluid flow. Since the absorption due to Hg is sensitive to both temperature and density, the maximum in the absorption–time curve is less than it would be if there were no slight reduction in the gas density. Using a computer model describing the fluid flow within the cell,<sup>15</sup> corrections for this expansion effect were calculated. These corrections were small (10–25%) and were applied to data with time constants longer than about 3.5  $\mu$ s. Values of  $1/P\tau$  obtained for a variety of PFB–Ar and SF<sub>6</sub>–Ar mixtures are tabulated in Tables I and II. The errors quoted represent one standard deviation,  $\sigma$ , obtained from a least-squares analysis.

Values of  $1/P\tau$  measured for SF<sub>6</sub>–Ar mixtures are plotted as a function of mole fraction of SF<sub>6</sub> in Figure 2, and similarly measured values of  $1/P\tau$  for PFB–Ar mixtures are shown as a function of the mole fraction of PFB in Figure 3. It is clear from both of these figures that values of  $1/P\tau$  measured at the highest mole fraction of argon do not properly reflect the infinite dilution condition and that this limit must be arrived at through an extrapolation procedure. The data shown in Figure 2 can be represented by the linear function

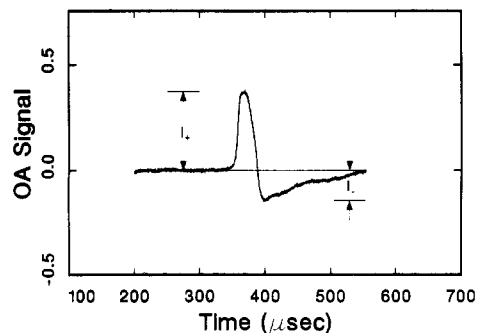
$$(1/P\tau) = A + BX_M \quad (2)$$

where  $X_M$  is the mole fraction of the excited molecule M, in this case M = SF<sub>6</sub>, and A, the intercept, represents the infinite dilution value. Linear least-squares analysis of the data given in Figure 2 yields an intercept of  $A = 0.0063 \pm 0.0006$  (Torr  $\mu$ s)<sup>−1</sup> where the error represents one  $\sigma$ . We have found that the following functional form fits the  $1/P\tau$  data of Figure 3

$$(1/P\tau) = A + BX_M + C(X_M)^2 \quad (3)$$

where M = PFB. The smooth curve in Figure 3 represents the nonlinear least-squares fit of the data to expression 3, which yields a value of  $A = 0.053 \pm 0.014$  (Torr  $\mu$ s)<sup>−1</sup>, where the error again represents one  $\sigma$ . In earlier work, Braun and Wallington<sup>13</sup> were able to explain this behavior with a three-tier model involving transfer of energy between vibrational, rotational, and translational degrees of freedom. This model predicts an overall rate constant which varies nonlinearly with  $X_M$  and can be fit by eq 3.

**III.B. Optoacoustic Experiments.** The Hg tracer technique is best suited for studying gas mixtures that are rich in the excited molecule M (SF<sub>6</sub> or PFB). In order to determine the rate constant for relaxation of M by the Ar bath it was necessary as just shown to measure the relaxation rate as a function of  $X_M$ , the mole fraction of M, at a fixed average excitation energy  $\langle E \rangle$  and then extrapolate to derive a value for infinite dilution. In contrast, the OA method is best used in very dilute mixtures where the maximum temperature jump is small (<25 K). The mode of operation



**Figure 4.** Typical optoacoustic waveform for SF<sub>6</sub> + Ar. Experimental conditions were 18.1 Torr containing 0.26% SF<sub>6</sub>, a laser fluence of 0.194 J cm<sup>−2</sup> with a beam radius of 0.54 cm, and an average absorbed energy of 5020 cm<sup>−1</sup>. The signal was averaged over 1000 shots.

here was to work with a fixed mole fraction while varying  $\langle E \rangle$ .

A typical OA waveform is shown in Figure 4. The values of  $I_-$  and  $I_+$  can be taken directly from data such as shown in this figure. The relaxation time can then be deduced from the relation between  $I_-/I_+$  and  $\epsilon$ . An important concern using this procedure is the exact rate law for V–T,R relaxation. Previously<sup>11</sup> we found for SF<sub>6</sub> + Ar that at a fixed pressure  $I_-/I_+$ , and hence  $\tau$ , was independent of energy over the range 3000 <  $\langle E \rangle$  < 19 000 cm<sup>−1</sup>. The energy independence of  $\tau$  implies an exponential decay of  $\langle E \rangle$  over this energy range; i.e.

$$\langle E(t) \rangle - E_\infty = (E_0 - E_\infty) \exp(-t/\tau) \quad (4)$$

where  $E_0$  and  $E_\infty$  are the initial and asymptotic values of  $\langle E(t) \rangle$ . The Hg detector method, which allows observation of the detailed relaxation waveform, provides corroborating evidence for exponential behavior (for example, see Figure 1 for a PFB–Ar mix). A less extensive study of the energy dependence of the PFB + Ar relaxation using the OA method showed  $\tau$  to be independent of the excitation energy between 2650 and 14 000 cm<sup>−1</sup>, while an earlier Hg tracer study<sup>13</sup> showed that  $\tau$  is constant between 550 and 5500 cm<sup>−1</sup>. For SF<sub>6</sub> + Ar below 3000 cm<sup>−1</sup>  $\tau$  decreases and approaches the larger value observed in fluorescence<sup>16,17</sup> and thermal lens<sup>18</sup> experiments. The studies of these two molecules suggest that in the discrete part of the vibrational manifold the relaxation rate increases with the density of states and approaches a limiting value in the quasi-continuum.

The mole fraction of SF<sub>6</sub> used in the OA study ranged from 0.02% to 0.4% and was typically <0.25%. Even at the highest concentration, the contribution of SF<sub>6</sub>\* + SF<sub>6</sub> collisions to the total decay rate was negligible. The average value of  $(P\tau)^{-1}$  for these mixtures with 3000 <  $\langle E \rangle$  < 6000 cm<sup>−1</sup> was  $0.0051 \pm 0.0009$  (Torr  $\mu$ s)<sup>−1</sup> with 1 $\sigma$  uncertainty.

In the case of PFB + Ar the VT rate constant is an order of magnitude larger than for SF<sub>6</sub> + Ar. This necessitated using an order of magnitude lower total pressure, and to achieve a usable signal  $X_m$  had to be made accordingly larger. The values of  $X_m$  used ranged from 0.048% to 1.8%, not quite overlapping the Hg tracer data. Since self-relaxation cannot be ignored in this case, care must be taken in comparing the two experiments. The results of the OA experiment are shown in Figure 3b. Since the OA data were too limited to extract the  $X_m$  dependence directly, they had to be corrected for self-relaxation in some other way. Two extreme possibilities are (i) that  $(P\tau)^{-1}$  is independent of mole fraction for  $X_m < 2\%$  or (ii) that the least-squares fit of the Hg tracer result can be extrapolated to  $X_m = 0$ , yielding

$$(P\tau)_0^{-1} = (P\tau)^{-1} - 3.18X_m (\mu\text{s Torr})^{-1} \quad (5)$$

which can be used to adjust the OA data. In the first analysis,

(16) Steinfeld, J. I.; Burak, I.; Sutton, D. G.; Novak, A. W. *J. Chem. Phys.* **1970**, *52*, 5421.

(17) Bates, Jr., R. O.; Knudtson, J. T.; Flynn, G. W.; Ronn, A. M. *Chem. Phys. Lett.* **1971**, *8*, 103.

(18) Bailey, R. T.; Cruickshank, F. R.; Guthrie, R.; Pugh, D.; Weir, I. J. M. *Chem. Phys.* **1987**, *114*, 411.

(15) Braun, W.; Wallington, T. J.; Cvetanovic, R. J. *J. Photochem.*, in press.

the OA results were averaged together, ignoring any  $X_m$  effect. The result is  $0.0832 \pm 0.0148$  (Torr  $\mu$ s) $^{-1}$ , which lies between the  $X_m = 0.00$  and  $X_m = 0.02$  values in Table II. In the second analysis we calculated  $(P\tau)_0^{-1}$  from the experimentally measured values of  $(P\tau)^{-1}$  using eq (5), and obtained an average value of  $0.0428 \pm 0.0092$ , which is within  $1\sigma$  of the Hg tracer values.

#### IV. Discussion

The results obtained by using the optoacoustic method are compared with those measured by using the Hg tracer technique in Figures 2 and 3. It can be seen from these figures that the results obtained by the optoacoustic method for SF<sub>6</sub>-Ar and PFB-Ar mixtures are in good agreement with those obtained by extrapolation of the data obtained by using the Hg tracer technique for less dilute mixtures. This agreement between two techniques which rely on fundamentally different physical principles serves to validate both experimental methods. The data shown in Figures 2 and 3 also emphasize the complementary nature of the two techniques. Thus while the Hg tracer technique can be applied to mixtures with widely varying dilutions it cannot be used with very dilute mixtures (mole fractions of argon greater than 0.98) as the temperature rise in such dilute mixtures is insufficient to cause a measurable signal. In contrast the optoacoustic method works best for dilute mixtures where the temperature jump is small, allowing the relation between  $I_-/I_+$  and  $\epsilon$  to be calculated from the linearized wave equation. The order of magnitude difference between the rate constants for PFB + Ar and SF<sub>6</sub> + Ar demonstrates the dynamic ranges of both techniques.

Measurements of the rates of energy transfer made in very dilute mixtures yield information on the rates of transfer of energy from the excited species (in our case either PFB or SF<sub>6</sub>) to the bath gas (Ar). As we have discussed above, the optoacoustic

method is better suited to make such measurements. Measurements of the dependence of rates of energy transfer on the composition of the gas mixture yield information on the specific mechanism of energy transfer in these mixtures.<sup>12</sup> The Hg tracer technique is better suited to such measurements. An example of this is the quadratic energy dependence of the rate constant on mole fraction which, as mentioned earlier, suggests a mechanism involving both rotational and vibrational degrees of freedom. For a complete understanding of energy-transfer processes in gas mixtures it is desirable to measure rates of energy transfer over as wide a range of dilution as possible. Hence the Hg tracer and the optoacoustic techniques described in the present work represent two complementary methods for determining the rate at which energy is transferred into translational excitation of gas mixtures. Future work is planned in our laboratories to further compare the results from these two techniques for a variety of different gas mixtures.

*Note Added in Proof.* More extensive optoacoustics measurements with PFB + Ar at a mole fraction of 0.00041 yielded a rate constant of  $0.045 \pm 0.003$  (Torr  $\mu$ s) $^{-1}$ . Applying the correction of eq 5 reduces this value to  $0.044$  (Torr  $\mu$ s) $^{-1}$ , which is in excellent agreement with our original value.

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## Temperature Dependence of the Rates of Photophysical Processes of Fluorenone

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Fluorescence lifetimes, fluorescence quantum yields, and triplet yields have been measured as a function of temperature in five solvents of different polarity. The rate coefficients for the dominant photophysical processes depopulating the fluorescent state have been found to depend on the solvent and temperature. The solvent dependence is attributed to the different extent of energy shift for the various excited states involved in these processes. The experimental results require the assumption of temperature-dependent and -independent singlet-triplet intersystem crossing rates. The temperature-dependent process is identified as a thermoneutral or endothermic transition from the lowest excited singlet to a higher triplet state.

#### Introduction

The study of radiationless deactivation of the fluorescent state of aromatic compounds has received considerable attention. Most of these studies attempted to elucidate the effect of the solvent and temperature on the rates of photophysical processes<sup>1</sup> and to reveal the role played by higher triplet states in the nonradiative deactivation of the first excited singlet state.<sup>2</sup>

The photophysics of fluorenone in solution exhibits some unique features as a consequence of the location of excited states and their dependence on the solvent. Using picosecond time-resolved spectroscopy, Kobayashi and Nagakura<sup>3</sup> succeeded in outlining a consistent picture of the energy level diagram for fluorenone in polar and nonpolar solvents (Figure 1). The major feature apparent from this diagram is that S<sub>1</sub> is a  $\pi\pi^*$  state in a polar solvent while it is of  $n\pi^*$  character in nonpolar media. On this

basis one expects solvent dependence for the rates and the mechanism of the photophysical processes occurring from the first excited singlet state. The room-temperature flash-photolytic measurements of the photophysical parameters of fluorenone by Linschitz and co-workers<sup>4</sup> confirmed indeed the expectations.

In order to reveal the nature of the solvent effect in the photophysics of fluorenone, we have determined the basic photophysical parameters as a function of temperature between 180 and 340 K in five different solvents. Fluorescence lifetimes, fluorescence quantum yields, and triplet yields were measured, and from these, rate coefficients for the elementary processes depopulating the first excited singlet state were derived.

#### Experimental Section

Fluorescence spectra were taken with a photon-counting spectrofluorimeter constructed in our laboratory. The instrument,

(1) Wu, K. C.; Ware, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 5906.

(2) Tanaka, M.; Tanaka, I.; Tai, S.; Hamanoue, K.; Sumitani, M.; Yoshihara, K. *J. Phys. Chem.* **1983**, *87*, 813.

(3) Kobayashi, T.; Nagakura, S. *Chem. Phys. Lett.* **1976**, *43*, 429.

(4) Andrews, L. J.; Derouede, A.; Linschitz, H. *J. Phys. Chem.* **1978**, *82*, 2304.