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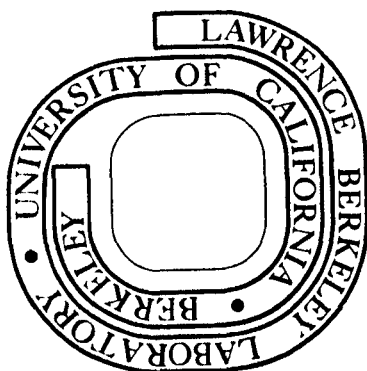
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Zero pressure lifetimes and fluorescence quenching of $\text{ICl}(A^3\Pi_1)$

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(Received)

Lifetimes of $\text{ICl}(A^3\Pi_1)$ are measured by laser-induced fluorescence. Zero pressure lifetimes for excitation between 589 and 669 nm range from 405 ± 40 to 460 ± 40 μsec . Quenching cross sections measured at 293 K near 603 nm vary between 110 \AA^2 for ICl itself and 0.7 \AA^2 for Ne. A radiative lifetime of about 650 μsec was estimated from the integrated absorption spectrum.

I. INTRODUCTION

Laser photochemistry of ICl has lately received considerable attention.^{1 - 4} This attention comes largely because ICl has a fortunate combination of properties. It is fairly stable with respect to disproportionation;⁵ it has a thoroughly analyzed excited electronic state,⁶ the A state, which is easily accessible with a Rhodamine 6-G dye laser; the spectra of the two isotopes are resolvable, permitting isotope selective photochemistry;^{1 - 3} and the A state cannot isoenergetically predissociate to atoms. In order to interpret the photochemistry of ICl*, it is necessary to know the cross sections for quenching of the A state by reactant and diluent molecules.

Laser-induced fluorescence provides a straightforward technique for measuring lifetimes and quenching cross sections. Holleman and Steinfeld⁷ have measured lifetimes in pure ICl and reported a self-quenching cross section and an estimated low pressure lifetime. Recently Havey and Wright⁸ have reported zero pressure lifetimes as a function of wavelength. In this paper the influence of diffusion at low pressures has been eliminated and significantly longer zero pressure lifetimes are reported. Quenching cross sections are measured for a variety of foreign gases as well as for ICl itself.

II. EXPERIMENTAL

ICl disproportionates according to⁵

$$K^2 = \frac{(Cl_2)(I_2)}{(ICl)^2} = 4.9 \times 10^{-6}.$$

However, since I_2 is quite soluble in solid ICl, while Cl_2 is not, the vapor above ICl is Cl_2 -rich, while the solid is I_2 -rich: at 303.6 K, "pure" ICl vapor is about 5% Cl_2 .⁵ ICl, therefore, does not evaporate at constant composition, and it cannot be purified by distillation⁹ or by any other technique which involves pumping on it, since Cl_2 is preferentially pumped away. ICl is also very reactive (e.g., $10 ICl + 5H_2O \rightarrow I_2O_5 + 10HCl + 4I_2$)⁹ and is, therefore, easily contaminated.

ICl is synthesized^{5, 9} under vacuum and is never exposed to air. A 500 ml bulb with 89 gms of I_2 (Mallinkrodt) is evacuated and then cooled to 195 K. The final pressure is $< 10^{-4}$ Torr. Approximately 27 gms of liquid Cl_2 (Matheson Research Purity) is added and the stoichiometric excess determined by weight. The reaction $I_2 + Cl_2 \rightarrow 2 ICl$ is facile at this temperature. The exact stoichiometric amount of I_2 is then sublimed into the cell, and the ICl is purified by several fractional recrystallizations.

The laser used to excite fluorescence is a Chromatix CMX-4 flash lamp pumped dye laser. Depending on the age of the dye, the laser energy is between 1.5 and 6 mJ per one

microsecond pulse in a 0.2 cm^2 beam. For the foreign gas quenching measurements the laser wavelength is between 600 and 605 nm with a 0.3 cm^{-1} spectral linewidth controlled by an intracavity etalon. For the zero pressure lifetime determinations, the laser is operated without an etalon to give 3 cm^{-1} linewidth.

The fluorescence cell is a 35 cm diameter black-painted pyrex sphere with a teflon stopcock. A five cm diameter viewing window which is mounted on a sidearm allows an EMI 9558 QB photomultiplier (with extended S-20 cathode) whose face is covered with a 630 or 695 nm long pass filter to view fluorescence perpendicular to the laser beam. The laser beam passes through a pair of one inch diameter windows. The geometry is such that molecules in a cone approximately 10 cm in diameter at the laser beam and 18 cm in diameter at the back of the cell are within the viewing region of the photomultiplier. With this arrangement, scattered laser light does not interfere with fluorescence measurements. Signal-to-noise ratios are typically 5:1 for a single oscilloscope trace. Signal averaging is performed mostly with a Tektronix 7912 transient digitizer and a PDP 11/30 computer, but some traces are recorded using a Biomation 8100 transient digitizer and a Northern 575 signal averager. Generally, 200 - 250 traces are averaged. I_2 fluorescence is inevitably present,⁷ but its lifetime is much shorter than that of ICl^* at the pressures used. Also, the relative intensity of the I_2 fluorescence may

be reduced by tuning the spectral output of the laser with the etalon. A double exponential decay curve is recorded; I_2 fluorescence generally dominates for the first 10 μ sec. If it is desired to reduce I_2 fluorescence still further, some Cl_2 may be added, as in Fig. 1.

All pressures are measured directly with a calibrated Validyne DP7 manometer with a 0 - 5 Torr range. The calibration is accurate to within 2% and fluctuations in the reading contribute ± 1 mTorr to the uncertainty of the pressure. Fluorescence bulb pressures of 25 μ Torr are required for the zero pressure lifetime experiment. For these measurements, a small volume is used to measure the pressure of the gas which is then expanded into the evacuated fluorescence cell. Using this method, absolute pressures are known to within 5% for bulb pressures above 100 μ Torr and to within 50% for bulb pressures under 100 μ Torr. Comparison with pressures determined from peak fluorescence intensity ratios (as in Ref. 8) shows agreement within the $\pm 25\%$ uncertainty of the intensity measurement. Data were taken at 293 ± 2 K.

III. RESULTS AND DISCUSSION

Fluorescence measurements

Stern-Volmer plots, Fig. 2, of fluorescence decay rate versus ICl pressure for excitation at 604 and 669 nm were made for ICl pressures ranging from 25 μ Torr to 1.4 mTorr. At the lowest pressures the mean free path of ICl is much greater than the dimensions of the volume viewed by the photomultiplier. Thus 4 - 6 mTorr of Xe was added to the cell in order to decrease the mean free path to 0.7 cm and thus prevent lifetime shortening by diffusion. The Stern-Volmer intercepts at zero ICl pressure are corrected ($\sim 20\%$) by subtracting the Xe quenching rate. The resulting zero pressure ICl($A^3\Pi_1$) lifetimes are 410 ± 40 and 460 ± 40 μ sec at 604 and 669 nm respectively. The Stern-Volmer slopes give ICl self-quenching rates of $(3.1 \pm 0.5) \times 10^{-10}$ $\text{cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ (10.0 ± 1.5 Torr $^{-1}$ μ sec $^{-1}$) at 604 nm and $(2.5 \pm 0.4) \times 10^{-10}$ $\text{cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ (8.1 ± 1.2 Torr $^{-1}$ μ sec $^{-1}$) at 669 nm (Fig. 2).

Lifetimes were measured as a function of wavelength for a single Xe - ICl mixture. The results and zero pressure ICl lifetimes deduced are shown in Table I.

The lifetimes in Table I are longer than those reported previously. Since Holleman and Steinfeld⁷ made pressure measurements to an accuracy of only ± 2 mTorr their extrapolation to zero was quite uncertain. The lifetimes of Havey and Wright⁸ appear to have been shortened by diffusion.¹⁰

The substantial dependence of lifetime on wavelength which they report is not reproduced here. The increase of lifetime with increasing wavelength shown in Table I is not much larger than the 10% uncertainties in measurement. Since only radiative decay is possible in the absence of collisions, no rapid variations of lifetime with wavelength should be expected.

Fluorescence quenching rate constants for several foreign gases are determined from Stern-Volmer plots, Fig. 3. In these experiments the ICl pressure is 2 ± 1 mTorr, and the pressure of the quenching gas ranges from zero to whatever pressure gives a fluorescence decay time of approximately 5 - 10 μ sec. At higher pressures, I_2^* fluorescence masks that of ICl*. The rate constants and effective cross sections are shown in Table II.

No variation in quenching cross section with excitation wavelength is detected within the limits of uncertainty ($\sim 10\%$) for $590 \leq \lambda \leq 620$ nm. Chutjian et al.¹² found a similar result for I_2^* self-quenching. For I_2^* , which quenches by predissociating, Steinfeld¹³ noted an almost linear relationship between foreign gas quenching cross section and $\frac{\mu^{1/2} I}{R_c^3}$. where μ is the reduced mass, I is the ionization potential of the quenching molecule, α is the polarizability of the quenching molecule and R_c is the mean distance of closest approach of the collision pair (approximated by the Lennard-Jones σ). No such relationship holds for ICl*.

Integrated absorption

The radiative lifetime may be calculated from the Einstein B coefficient as determined from the integrated absorption of ICl.¹⁴ If the entire absorption spectrum is integrated, the Einstein B coefficient is given by

$$B_{mn} = \int k_{\nu} \frac{d\nu}{\nu} / d_m N_m h, \quad (1)$$

where N_m represents the number density of molecules in lower state m with degeneracy d_m , h is Planck's constant, ν is the frequency in cm^{-1} , B_{mn} is the Einstein coefficient for induced absorption, and k_{ν} is the absorption coefficient defined by $I_{\nu} = I_{\nu}^0 \exp[-k \Delta X]$ where I_{ν}^0 and I_{ν} are the light intensities before and after transmission through a column of gas of length ΔX .

If only a portion of the absorption spectrum is integrated, the expression becomes

$$B_{mn} = \frac{\int k_{\nu} \frac{d\nu}{\nu}}{d_m N_m h \sum_{\nu, v, J} F_{\nu, v, J} \left| R_{\text{vib}}^{\nu, v} \right|^2} \quad (2)$$

where $F_{\nu, v, J}$ = the fraction of ground state molecules in initial state ν, v, J and $\left| R_{\text{vib}}^{\nu, v} \right|^2$ is the Franck-Condon factor. The sum is over the transitions observed in the region integrated. Converting from absorption coefficient as a function of frequency, k_{ν} , to base 10 absorbance units as a function of wavelength, $\text{Abs}(\lambda)$, and neglecting the variation of ν_{nm} or λ_{nm} over the small integration range yields

$$B_{mn} = \frac{2303 RT \int \text{Abs}(\lambda) d\lambda}{d_m h N \Delta X P \sum_{\nu, v, J} F_{\nu, v, J} \left| R_{\text{vib}}^{\nu, v} \right|^2 \lambda_{\text{average}}} \quad (3)$$

where R is the gas constant, N is Avogadro's number, T is the temperature, and P is the sample pressure.

The ICl absorption spectrum was taken on a Cary 17 spectrophotometer with a resolution of 0.35 \AA . In order to obtain accurate absorbance measurements the spectrophotometer must resolve the structure in the absorption profile. The 0.02 \AA linewidth of room temperature ICl requires addition of a broadening gas. ICl spectra were taken with 0 Torr, 380 Torr, and 740 Torr of added CO_2 in order to determine the CO_2 pressure needed to broaden the ICl absorption spectrum. The measured absorbance of the 380 Torr CO_2 + 19 Torr ICl sample was $7 \pm 2\%$ greater than for 19 Torr of pure ICl. Increasing the CO_2 pressure to 740 Torr produced no further increase in absorbance. The spectral structure was directly measured using a Spectra Physics 580A cw dye laser. An increase in ICl linewidth was observed upon addition of 380 Torr of CO_2 from 0.02 \AA to $\geq 0.06 \text{ \AA}$, the approximate distance between ICl lines. A final absorption spectrum was taken of a sample containing 16.5 Torr ICl, 3.0 Torr Cl_2 and 753 Torr CO_2 in a 10 cm cell at 298 K. Added Cl_2 eliminates I_2 absorption. The spectral range is from 591.4 nm to 600.1 nm where neither CO_2 nor Cl_2 absorbs. Integration over this range yields

$$\int \text{Abs}(\lambda) d\lambda = (5.2 \pm 0.3) \times 10^{-8} \text{ cm.}$$

Fractional populations from a Boltzmann weighting of ground

state energy levels⁶ and calculated Franck-Condon factors yield

$$\sum_{v''} \sum_{v'} \sum_J F_{v''J} \left| R_{\text{vib}}^{v'v''} \right|^2 = (5.3 \pm 1.0) \times 10^{-2}.$$

Both $I^{35}\text{Cl}$ and $I^{37}\text{Cl}$ contribute to the absorbance with transitions from $v'' = 0$ to $v' = 20 - 28$ contributing 93% and from $v'' = 1$ to $v' = 25 - 35$ contributing 7% to the sum. Transitions from $v'' = 2$ contribute negligible intensity due to a small (< 2.5%) population and because of unfavorable Franck-Condon factors. When the values above are replaced in equation (3),

$$B_{mn} = (1.08 \pm 0.2) \times 10^6 \frac{\text{sec}}{\text{gm}}.$$

The Einstein A coefficient for spontaneous emission is given by

$$A_{nm} = B_{mn} \frac{d_m}{d_n} 8\pi h c \langle \nu_{nm}^3 \rangle.$$

The $^1\Sigma^+$ ground state is not degenerate and the degeneracy of the $A^3\Pi_1$ state, d_n , is two. A value for the Franck-Condon weighted fluorescence frequency cubed, $\langle \nu_{nm}^3 \rangle$, is also needed to calculate a value for A_{nm} . Franck-Condon factors can only be crudely calculated since there is no information on the X state potential above $v'' = 9$.¹⁰ However, a numerical potential was constructed as follows. For $r < 3 \text{ \AA}$ a Morse function is used,¹¹

$$V(r) = D_e (1 - \exp[-\beta(r - r_e)])^2$$

with $\beta = 1.5624 \text{ \AA}^{-1}$, $r_e = 2.32069 \text{ \AA}$, and $D_e = 24,597 \text{ cm}^{-1}$. This function accurately reproduces the energy level values which are known but dissociates well above the actual value of $17557.575 \pm 0.150 \text{ cm}^{-1}$ for $I^{35}\text{Cl}$.¹⁵ For $r > 3 \text{ \AA}$ the potential is drawn "freehand" to join smoothly with the Morse potential and to dissociate at 17558 cm^{-1} . Calculated Franck-Condon factors for a number of the $v' = 18$ transitions are given in Table III. Most (69%) of the Franck-Condon intensity is accounted for. Assuming a uniform distribution of Franck-Condon intensity in the frequency interval not calculated, $9800 \leq \nu \leq 3300 \text{ cm}^{-1}$, then $\langle \nu_{nm}^3 \rangle = \sum_{\nu} \nu^3 (18, \nu'') \left| R_{\text{vib}}^{\nu' \nu''} \right|^2 = 5.75 \times 10^{11} \text{ cm}^{-3}$. Since this sum strongly weights the highest frequency terms, which are accurately known, the uncertainty in this value of $\langle \nu_{nm}^3 \rangle$ should not be more than 20%. Finally, then $A_{nm} = 1.55 \times 10^3 \text{ sec}^{-1}$, $\tau_{\text{rad}} = 650 \text{ \mu sec}$. The approximations in evaluating Franck-Condon factors and in neglecting the variation of electronic transition moment with internuclear distance limit the accuracy of this calculation. That the measured and calculated lifetimes agree within a factor of two shows true radiative lifetimes are not very much longer than the observed ones. In fact, the observed lifetimes extrapolated to zero pressure are most likely the true radiative lifetimes.

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TABLE I. ICl( $A^3\Pi_1$ ) fluorescence lifetimes.<sup>a</sup>

| $\lambda$<br>(nm) | $\tau_{\text{obs}}^{-1}$<br>(msec <sup>-1</sup> ) | Quenching rate<br>(msec <sup>-1</sup> ) | $\tau_0$<br>( $\mu$ sec) |
|-------------------|---------------------------------------------------|-----------------------------------------|--------------------------|
| 589               | 3.39 $\pm$ 0.15                                   | 0.92 $\pm$ 0.15                         | 405 $\pm$ 40             |
| 604               | 3.36 $\pm$ 0.15                                   | 0.92 $\pm$ 0.15                         | 410 $\pm$ 40             |
| 607               | 3.34 $\pm$ 0.15                                   | 0.92 $\pm$ 0.15                         | 415 $\pm$ 40             |
| 661.5             | 3.04 $\pm$ 0.15                                   | 0.87 $\pm$ 0.15                         | 460 $\pm$ 40             |
| 669               | 3.15 $\pm$ 0.15                                   | 0.87 $\pm$ 0.15                         | 440 $\pm$ 40             |

a. mixture of (25  $\pm$  12)  $\mu$ Torr ICl and (4.78  $\pm$  0.24) mTorr Xe at 293  $\pm$  2 K.

TABLE II. Fluorescence quenching cross sections  
(293 ± 2 K).<sup>a</sup>

| Molecule        | $k(\text{cm}^3 \text{ molec}^{-1} \text{ sec}^{-1})$ | $\sigma(\text{Å}^2)$ | $\frac{\mu^{1/2} I_{\alpha}^b}{R_c^3}$ |
|-----------------|------------------------------------------------------|----------------------|----------------------------------------|
| ICl             | $3.0 \times 10^{-10}$                                | 110                  | 1.00                                   |
| HCl             | $4.6 \times 10^{-11}$                                | 10.2                 | 0.44                                   |
| CO <sub>2</sub> | $3.0 \times 10^{-11}$                                | 7.2                  | 0.41                                   |
| Cl <sub>2</sub> | $2.2 \times 10^{-11}$                                | 6.1                  | 0.67                                   |
| SF <sub>6</sub> | $1.51 \times 10^{-11}$                               | 5.3                  | 0.27 <sup>c</sup>                      |
| Xe              | $4.2 \times 10^{-12}$                                | 1.44                 | 0.74                                   |
| D <sub>2</sub>  | $1.46 \times 10^{-11}$                               | 1.16                 | 0.07                                   |
| Ar              | $4.7 \times 10^{-12}$                                | 1.07                 | 0.33                                   |
| H <sub>2</sub>  | $1.52 \times 10^{-11}$                               | 0.86                 | 0.05                                   |
| Ne              | $4.5 \times 10^{-12}$                                | 0.76                 | 0.10                                   |

Footnotes to Table II.

- a. Rate constants and cross sections have an uncertainty of  $\pm 15\%$  for ICl and  $\pm 10\%$  for all other gases.
- b. Polarizabilities taken from Landolt-Bornstein, Zahlenwerte und Functionen, Springer (1951) Vol. I, Part 3, p. 510. Ionization potentials are taken from J.L. Franklin et al., "Ionization Potentials, Appearance Potentials and Heats of Formation of Positive Ions," (NSRDS-NBS 26, 1969).  $R_e$  is taken as the average of the Lennard-Jones  $\sigma$  for ICl and for the quenching gas as given in J.O. Hirschfelder, C.F. Curtis, and R.B. Bird, Molecular Theory of Gases and Liquids (Wiley, New York, 1954). Appendix I-A, pp. 1110 - 1113. Values for  $\frac{\mu^2 I \alpha}{R_c^3}$  are normalized to the ICl value.
- c. Polarizability taken from A.B. Tipton, A.P. Deam, and J.E. Boggs, J. Chem. Phys. 40, 1144 (1964).

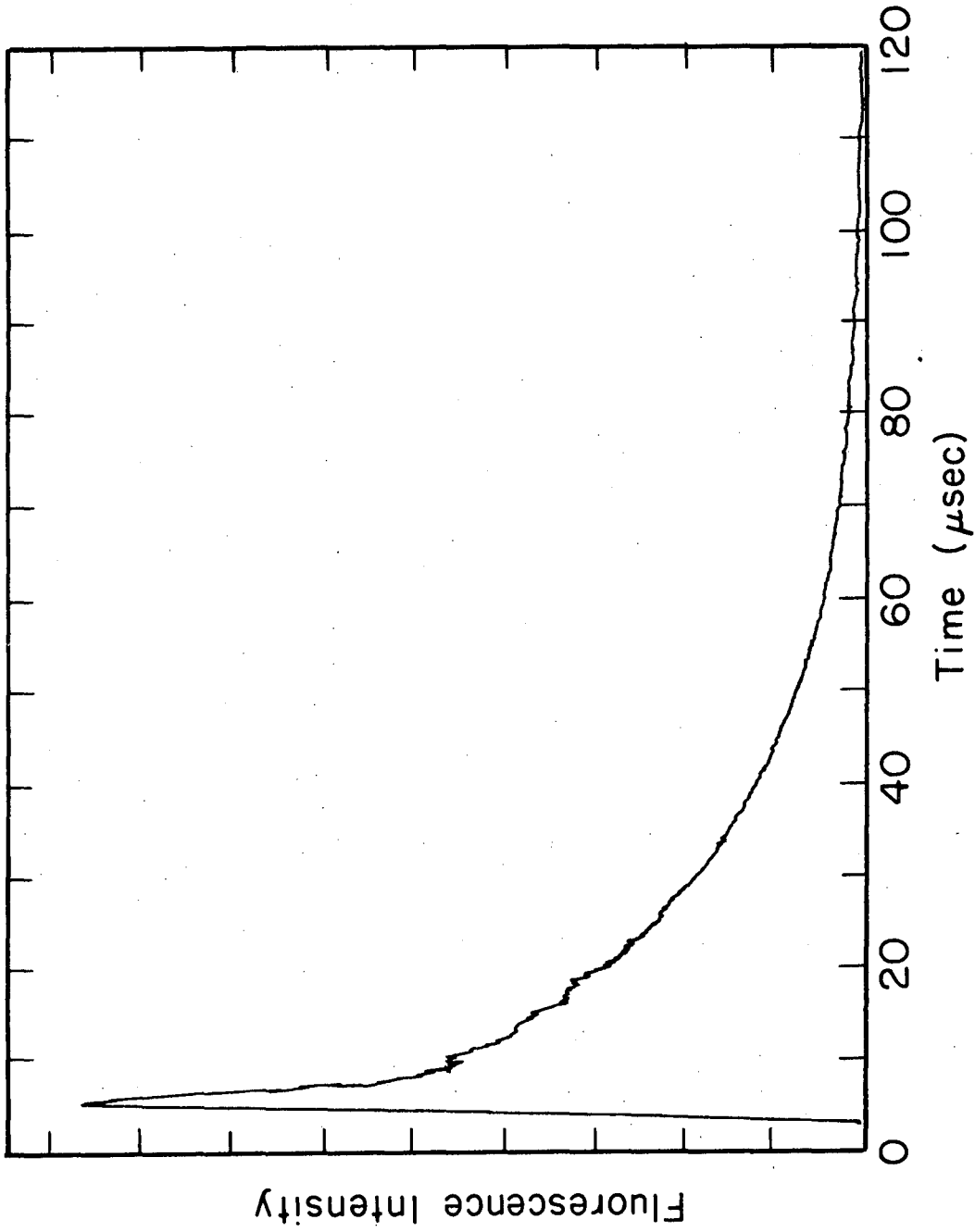
TABLE III. Franck-Condon factors for  $v' = 18$ .

| $v''$ | $\left  R_{\text{vib}}^{v' v''} \right ^2$ | $\nu$<br>( $\text{cm}^{-1}$ ) |
|-------|--------------------------------------------|-------------------------------|
| 0     | 0.0175                                     | 16513                         |
| 1     | 0.0268                                     | 16133                         |
| 2     | 0.0033                                     | 15755                         |
| 3     | 0.0088                                     | 15379                         |
| 4     | 0.0150                                     | 15005                         |
| 5     | 0.0000                                     | 14635                         |
| 6     | 0.0130                                     | 14268                         |
| 7     | 0.0062                                     | 13904                         |
| 8     | 0.0031                                     | 13544                         |
| 9     | 0.0130                                     | 13187                         |
| 10    | 0.0005                                     | 12833                         |
| 11    | 0.0091                                     | 12483                         |
| 12    | 0.0078                                     | 12136                         |
| 13    | 0.0010                                     | 11791                         |
| 14    | 0.0122                                     | 11450                         |
| 15    | 0.0023                                     | 11111                         |
| 16    | 0.0056                                     | 10775                         |
| 17    | 0.0108                                     | 10443                         |
| 18    | 0.0000                                     | 10113                         |
| 19    | 0.0103                                     | 9788                          |
| 45    | 0.0644                                     | 3326                          |
| 46    | 0.0087                                     | 3150                          |
| 47    | 0.0171                                     | 2979                          |
| 48    | 0.0874                                     | 2811                          |
| 49    | 0.1267                                     | 2647                          |
| 50    | 0.1081                                     | 2486                          |
| 51    | 0.0653                                     | 2330                          |
| 52    | 0.0301                                     | 2176                          |
| 53    | 0.0114                                     | 2026                          |
| 54    | 0.0037                                     | 1880                          |
| 55    | 0.0010                                     | 1737                          |
| 56    | 0.0002                                     | 1598                          |

Figure 1. Time resolved ICl\* fluorescence decay. The mixture is 1.5 mTorr ICl, 4 mTorr Cl<sub>2</sub>, and 50 mTorr H<sub>2</sub>. I<sub>2</sub>\* fluorescence becomes negligible in less than 5 μsec because the added Cl<sub>2</sub> reduces its concentration so that  $(I_2)/(ICl) = 2 \times 10^{-6}$ .

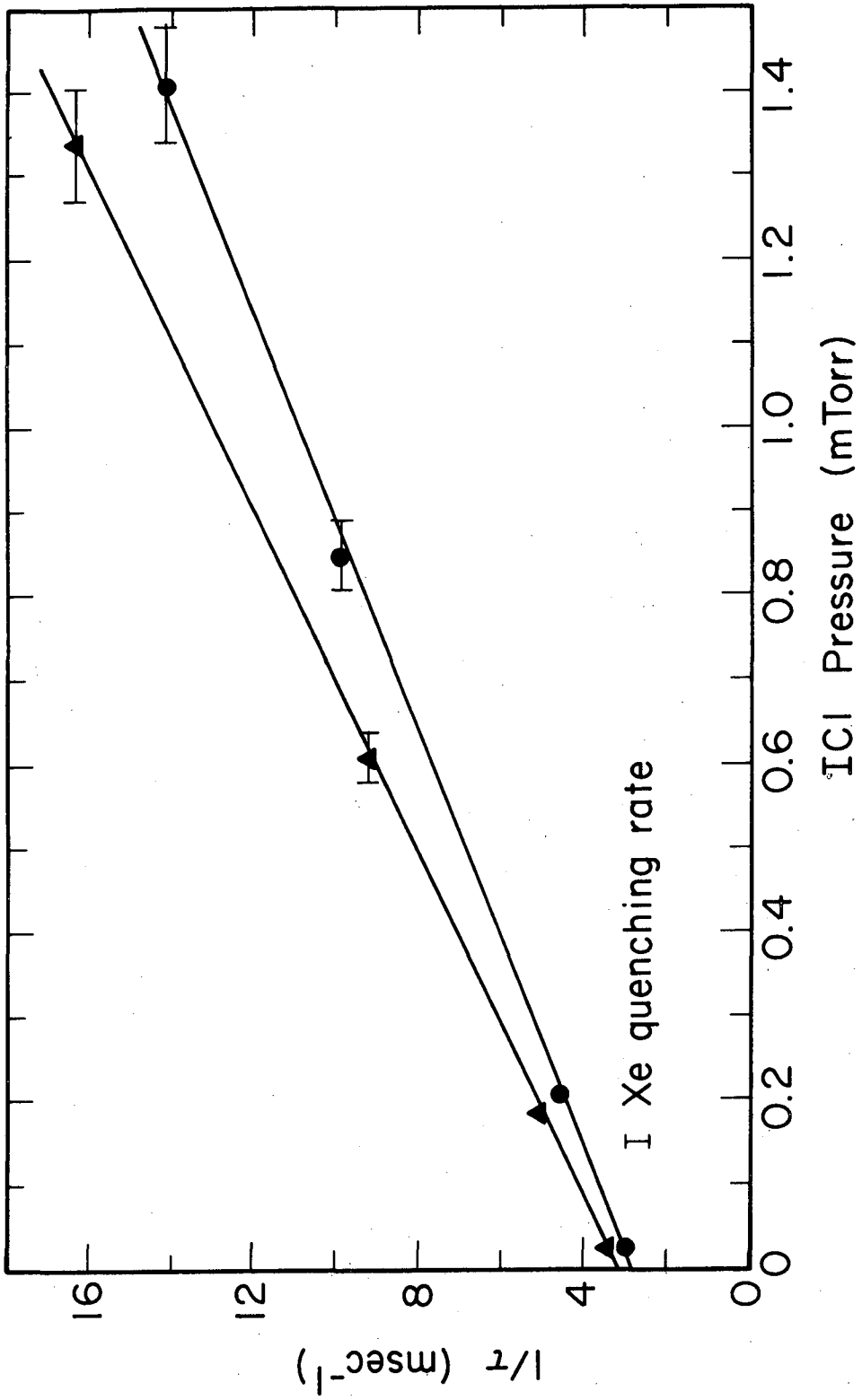
Figure 2. Stern-Volmer plot of the inverse of the ICl\* fluorescence lifetime vs ICl pressure. ● - excitation at 669 nm with  $5.1 \pm 0.3$  mTorr added Xe; ▲ - excitation at 604 nm with  $4.5 \pm 0.3$  mTorr added Xe. The approximate Xe quenching rate is shown.

Figure 3. Stern-Volmer plot of the inverse of the ICl\* fluorescence lifetime vs H<sub>2</sub> pressure. Excitation wavelength is 600 nm.



XBL 789-11165

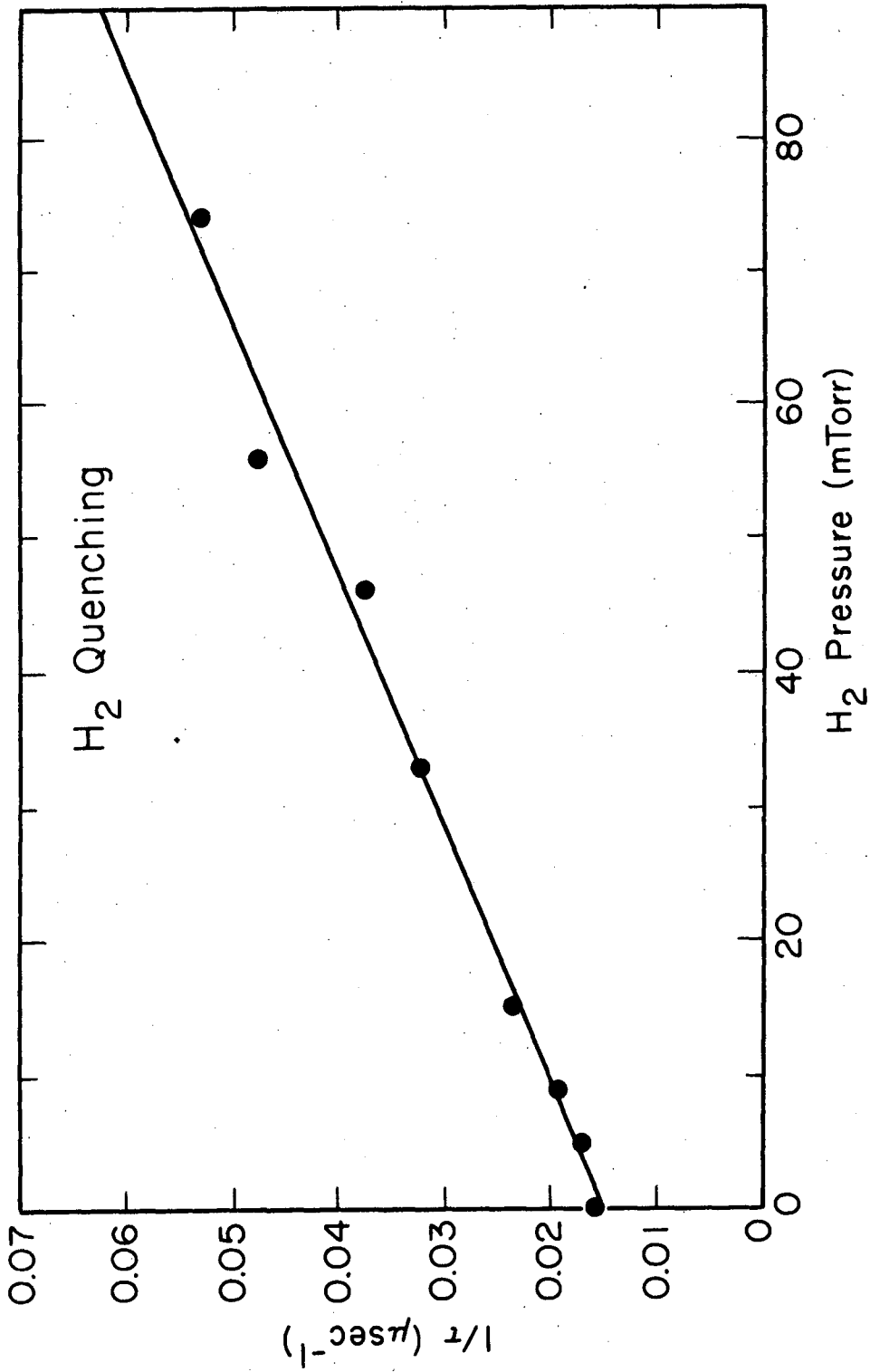
Figure 1



XBL 789-11166

Figure 2





XBL 789-11164

Figure 3

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