

QUENCHING KINETICS OF ELECTRON BEAM PUMPED XeCl

G.P. GLASS, F.K. TITTEL, W.L. WILSON, M.S. SMAYLING

Department of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77001, USA

and

G. MAROWSKY

Max-Planck-Institut für biophysikalische Chemie, D-3400 Göttingen, Federal Republic of Germany

Received 26 June 1981

The rates of several processes removing XeCl* subsequent to its formation by short duration electron beam excitation of Ar/Xe/CCl₄ mixtures have been investigated. A dominant third-order reaction with Xe and Ar has been identified. The effective radiative lifetime of XeCl* has been measured as 41 ± 3 ns.

1. Introduction

There has been considerable interest in understanding the kinetic processes that determine the operating characteristics of diatomic and triatomic excimer lasers [1-3]. In particular, efficient scaling of inert-gas halide lasers to high average powers requires a detailed knowledge of the mechanisms responsible for the formulation and quenching of the up-

per laser level. In a previous paper, the role of XeCl* as a precursor in a reaction chain leading to the formation of Xe₂Cl* by three-body collisions has been discussed [4]. In this work we report the identification of another important channel of XeCl*. This decay channel, which is illustrated in fig. 1, probably involves the production of ArXeCl* as an intermediate species. The rates of various other collisional processes that result in the quenching of XeCl* are also reported, together with an estimate of the effective radiative lifetime of XeCl*.

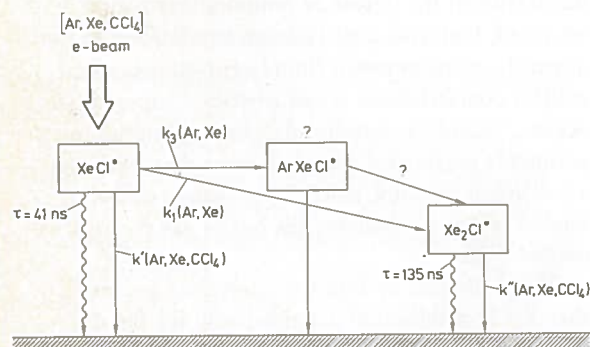


Fig. 1. Schematic diagram depicting main energy flow pathways of electron beam excited Ar/Xe/CCl₄ mixtures. k' and k'' denote two-body quenching by CCl₄, Xe and Ar of XeCl* and Xe₂Cl* respectively. k_1 and k_3 represent three-body quenching of XeCl* via channels leading directly to Xe₂Cl* [4] and XeArCl* respectively.

2. Experimental

The experiments were carried out in a stainless steel cell attached to the field emission diode of an electron beam accelerator (Physics International Pulserad 110). A beam of 1 MeV electrons with a pulse duration of 8 ns (fwhm) was injected transversely into the reaction cell through a 50 μm thick titanium anode foil over an area of 1 × 10 cm, with a current density of $\approx 100 \text{ A/cm}^2$ at the optical axis. Details of the apparatus and operating techniques have been reported previously [4].

All of the measurements were made with computer-aided instrumentation. Temporal behavior of the fluo-

rescence was monitored with a fast photodiode (ITT F4000-S5), and recorded with a transient digitizer (Tektronix R7912). Interference/color glass filters defined the spectral region of interest. Simultaneously, time-integrated, spectrally resolved data were recorded with a calibrated optical multichannel analyzer (PAR OMA1). Both the OMA and the transient digitizer were interfaced to a DEC PDP 11/23 mini-computer system. Subsequent data reduction and feature extraction were accomplished with computer routines developed for these studies.

In order to extract exponential decay constants from the temporal data, a weighted least-squares program [5] was written to determine the best linear relationship between the logarithm of the fluorescent intensity and time. The program was written in such a way that the decay constant could be determined over any arbitrary time interval. Therefore the dependence of the time constant on reaction time could be investigated.

3. Results and discussion

The temporal behavior of the fluorescence, emitted by $\text{XeCl}(\text{B} \rightarrow \text{X})$ at 308 nm, following short duration electron beam irradiation of Ar/Xe/CCl_4 mixtures containing 2 atm Ar and 2 Torr CCl_4 , was found to be invariant whenever the partial pressure of Xe in the mixture was greater than 50 Torr. The intensity of fluorescence emitted by such mixtures rose rapidly to a maximum value, which was attained in 12–14 ns, and then decayed exponentially with a time constant, τ , of ≈ 4 ns. The fluorescent profile thus obtained was found to be very similar to the profile of the current density in the reaction cell, which could be observed using a Faraday probe. When mixtures containing less than 50 Torr Xe were studied, a somewhat different fluorescent profile was obtained. The fluorescence emitted by such mixtures rose to maximum intensity at a rate similar to that observed when using mixtures richer in Xe, but then it decayed more slowly, with an exponential time constant that increased as the partial pressure of Xe in the mixture was lowered. This behaviour is illustrated in fig. 2, which shows how the decay frequency, τ^{-1} , varied as the partial pressure of Xe was changed. For comparison, some results obtained when using mixtures

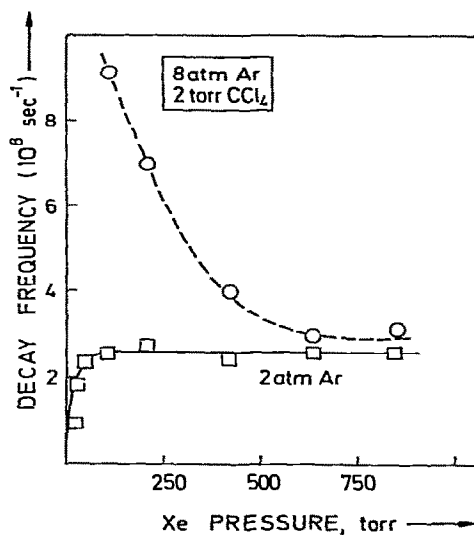


Fig. 2. Decay frequency (τ^{-1}) of $\text{XeCl}(\text{B}-\text{X})$ fluorescence plotted as a function of Xe partial pressure for mixtures containing a fixed pressure of 2 Torr CCl_4 . Data represented by \square were taken using 2 atm Ar. Data represented by \circ were taken using 8 atm Ar. Amplified spontaneous emission effects are evident in these latter mixtures.

containing 8 atm Ar and 2 Torr CCl_4 are also included. Super-radiant emission was observed when using some of these mixtures. This phenomenon could be clearly recognized by the appearance of spectral and temporal narrowing. The high decay frequency recorded for the mixture containing 100 Torr Xe is illustrative of the degree of temporal narrowing that occurred. Unfortunately, the linear relationship that normally exists between fluorescent intensity and emitter concentration is lost whenever super-radiance occurs. Therefore, kinetic analysis was limited to experiments performed using mixtures that contained a low argon pressure, since super-radiant emission tended to occur whenever the buffer gas pressure exceeded 3 atm.

The fluorescence data was analyzed assuming that XeCl^* production occurred only for the duration of the electron beam pulse. At Xe pressures greater than 50 Torr, quenching is sufficiently fast that the fluorescence profile mirrors the XeCl^* production rate. At lower Xe pressures, the fluorescent decay that occurs *after* the current density has decayed effectively to zero is controlled by radiative

and collisional quenching processes. Under these conditions, the decay frequency, τ^{-1} , is given by

$$\tau^{-1} = \tau_{\text{rad}}^{-1} + \sum_{\text{all } Q} k_Q [Q] + \sum_{\text{all } Q} k_{Q,M} [Q] [M], \quad (1)$$

where τ_{rad} is the effective radiative lifetime of XeCl^* , k_Q are the set of second-order rate constants for collisional quenching by the components Q (Ar, Xe, or CCl_4) of concentration $[Q]$, and $k_{Q,M}$ are the set of third-order rate constants for three-body quenching by Q in the presence of M , which in these experiments consists principally of argon.

This interpretation is supported by the following observations:

(a) The risetime of the fluorescence, arbitrarily defined as the time taken for the intensity to rise from 15 to 85% of its maximum value, was found to be relatively insensitive to the partial pressure of xenon, rising from 8 ns for mixtures containing 50 Torr Xe, 2 atm Ar and 2 Torr CCl_4 , to only 9 ns for mixtures containing 1 Torr Xe, 2 atm Ar and 2 Torr CCl_4 .

(b) The current density profile was insensitive to a change in Xe pressure from 1 to 50 Torr in mixtures containing 2 atm Ar.

(c) The fluorescent decay that occurred after the current density had effectively decayed to zero could be well represented by a single-exponential decay constant. If $\text{XeCl}(B \rightarrow X)$ had been generated by an intermediate which itself decayed slowly with a time constant τ' , then the form of the fluorescent decay profile would have been as given by the expression

$$I = C[\exp(-t/\tau') - \exp(-t/\tau)], \quad (2)$$

where I is the intensity measured at time t , C is a constant, and τ is defined in eq. (1).

A detailed study of the quenching kinetics of $\text{XeCl}(B \rightarrow X)$ was made using a number of different mixtures all containing less than 25 Torr of Xe. Results obtained from many different experiments, each performed using mixtures containing a fixed amount of CCl_4 (2 Torr), are shown in fig. 3. In fig. 3, the decay frequency, τ^{-1} , is plotted as a function of xenon partial pressure. The data points are grouped according to the pressure of argon buffer gas present in the mixture: experiments were performed using mixtures containing, (a) 1 atm Ar, (b) 1.5 atm Ar, (c) 2 atm Ar, (d) 2.5 atm Ar, and (e) 3 atm Ar.

All of the data shown in fig. 3 can be fitted by the

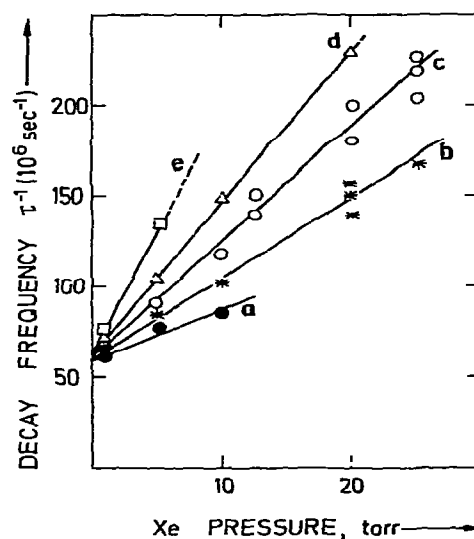


Fig. 3. Plot of the decay frequency (τ^{-1}) of $\text{XeCl}(B-X)$ fluorescence as a function of xenon partial pressure for various mixtures containing different pressure of argon buffer gas. The argon pressures were: (a) 1 atm, \bullet ; (b) 1.5 atm, \times ; (c) 2 atm, \circ ; (d) 2.5 atm, Δ ; (e) 3 atm, \square . All mixtures contained 2 Torr CCl_4 .

equation

$$\tau^{-1} = \tau_0^{-1} + k_{\text{Xe,Ar}} [\text{Ar}] [\text{Xe}], \quad (3)$$

with $\tau_0 = (62 \pm 4) \times 10^6 \text{ s}^{-1}$, and $k_{\text{Xe,Ar}} = (3.8 \pm 0.8) \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$. Comparing eq. (1) with eq. (3), we see that $k_{\text{Xe,Ar}}$ can be identified with the third-order rate constant for three-body quenching of XeCl^* by Xe, and that τ_0^{-1} can be identified with the sum, $\tau_{\text{rad}}^{-1} + k_{\text{CCl}_4} [\text{CCl}_4]$.

It is useful to consider how the other quenching terms in eq. (1) could be identified from data displayed in the form shown in fig. 3. Significant contributions from two- and/or three-body quenching by Ar would result in the zero-pressure intercepts of lines (a)–(e) being displayed from one another by amounts determined by k_{Ar} and $k_{\text{Ar,Ar}}$. Upper limits to the rate constants k_{Ar} and $k_{\text{Ar,Ar}}$ of $2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ and $3 \times 10^{-33} \text{ cm}^6 \text{ s}^{-1}$, respectively, could be set by assigning an upper bound of $\pm 5 \times 10^6 \text{ s}^{-1}$ to the spacings observed in fig. 3. The effect on the displayed data of a contribution from two-body quenching by Xe would be more subtle. In principle, k_{Xe} could be estimated from the intercept on the

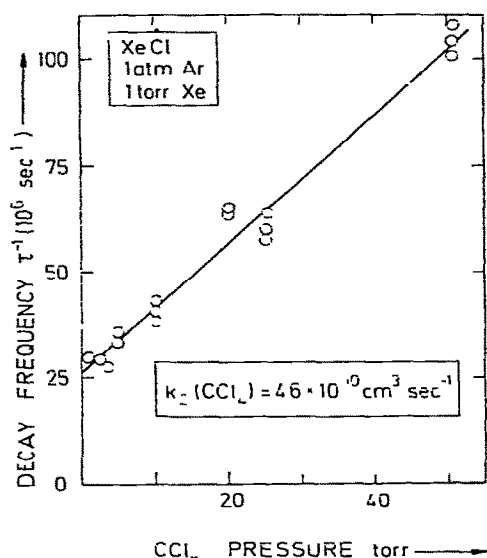


Fig. 4. Decay frequency (τ^{-1}) of XeCl(B-X) fluorescence plotted as a function of CCl₄ partial pressure for mixtures containing a fixed pressure of 1 Torr Xe and 1 atm Ar

zero-pressure axis of the graph obtained by plotting the slope of each of the lines shown in figs 3a-3e versus the argon pressure. Unfortunately no such intercept was observed. However, scatter in the data would have prevented a contribution from $k_{\text{Xe}} = 1.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, the value recently determined in ref [6], from being detected. It should be noted that even at the lowest pressures studied the contribution to quenching from such a two-body process would be only one-tenth of that from the three-body process.

Table 1
Summary of rate constants for reactions quenching XeCl*

Reaction	Measured rate constants	Other work
XeCl* + Ar + Xe → products	$(3.8 \pm 0.2) \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$	—
XeCl* + Ar + Xe → Xe ₂ Cl* + Ar	—	$1.5 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ [4]
XeCl* + Ar + Ar → products	$< 3 \times 10^{-33} \text{ cm}^6 \text{ s}^{-1}$	—
XeCl* + Xe + Xe → products	—	$7.3 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ [7]
XeCl* + CCl ₄ → products	$(4.6 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$	$8.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for Cl ₂ [6] $5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for Cl ₂ [7]
XeCl* + Ar → products	$< 2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$	—
XeCl* + Xe → products	—	$1.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [6]
XeCl* → Xe + Cl + hν	$\tau = 41 \pm 3 \text{ ns}$	$\tau = 11 \text{ ns}$ [10], 40 ns [7] $\tau = 27 \text{ ns}$ for B state [6] $\tau = 53 \text{ ns}$ for C state [6]

The rate of collisional quenching of XeCl* by CCl₄ was established by measuring the decay constant τ for a number of mixtures containing constant amounts of Xe and Ar, but different amounts of CCl₄. Some of the experimental data are shown in fig. 4. In fig. 4, the XeCl decay frequency, τ^{-1} , is plotted as a function of the CCl₄ pressure for mixtures containing 1 Torr xenon and 1 atm argon. From the slope of fig. 4, k_{CCl_4} was calculated as $(4.6 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

The effective radiative lifetime of XeCl* can be estimated from the zero-pressure intercept in fig. 4. This intercept contains a contribution due to collisional quenching of XeCl* by Xe in the presence of Ar. However, this contribution is small, amounting to only $2.5 \times 10^6 \text{ s}^{-1}$ at 1 Torr Xe, and 1 atm Ar. When this contribution was subtracted, τ_{rad}^{-1} was computed as $(24.3 \pm 1.6) \times 10^6 \text{ s}^{-1}$. This corresponds to an effective radiative lifetime of $41 \pm 3 \text{ ns}$.

Rate constants that were determined for the various processes quenching XeCl* are summarized in table 1. The radiative lifetime of XeCl* measured in this work is an effective value for B and C states mixed by collision. The rate constant for the mixing of these states by collisions with argon has been measured as $1.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [8,9]. Therefore, even at 1 atm pressure, the states are efficiently mixed in a time that is much shorter than the radiative lifetime of either state. The value of the effective radiative lifetime compares well with other measurements [6,7] but is much greater than the theoretical prediction [10] used in many modeling studies.

Numerous similarities exist between the pattern of three-body quenching exhibited by XeCl* and that observed previously for XeF* [11,12]. Both excimers

are quenched somewhat more strongly by Xe when Ar is present as a third body than by Xe when it is present alone, and both excimers are quenched much more strongly by Xe in the presence of Ar than by Ar alone [7,11,12]. Using a form of phase-space theory, Shui and Duzy [13] have estimated rate constants for the three-body quenching of XeF* by a variety of inert-gas atoms. These estimates show that XeArF* is formed in preference to Xe₂F* when XeF* is quenched by Xe in the presence of Ar. A similar situation may exist for XeCl*. The total rate constant for three-body quenching of XeCl* by Xe in the presence of Ar, measured in this study, is 20 times greater than that for the production of Xe₂Cl* in this reaction [4]. Obviously, channels leading to products other than Xe₂Cl* must exist. It is probable that one of these involves the molecule XeArCl* as an intermediate species. This molecule has not been observed previously, and may not even exist as a stable long-lived species [14]. However, the complex may exist for the $\approx 10^{-10}$ s required in order for it to play an important role in three-body quenching.

It is clear, based on the results displayed in table 1, that three-body quenching is the dominant loss process in the XeCl laser system. Several reports have appeared in the literature [15], suggesting that higher laser efficiencies can be obtained using neon in place of argon as a diluent in these systems. The increased efficiency has usually been attributed [16] to the production of transient absorbing species that contain argon. However, the extremely fast three-body quenching reaction, discussed above, may be partly responsible for the lower efficiency observed when using argon.

Acknowledgement

The authors would like to acknowledge the experimental assistance of G. Zehuna. This research is

supported jointly by the Office of Naval Research, the National Science Foundation, and the Robert A. Welch Foundation.

References

- [1] C.K. Rhodes, *Excimer lasers* (Springer, Berlin, 1979).
- [2] K.Y. Tang, D.C. Lorents and D.L. Huestis, 32nd Gaseous Electronics Conference, Pittsburgh, Oct. 9-12 (1979).
- [3] D.L. Huestis, *Proc. Lasers* 80 (1980) 143.
- [4] G. Marowsky, G.P. Glass, M. Smayling, F.K. Tittel and W.L. Wilson, *J. Chem. Phys.* 75 (1981), to be published.
- [5] R.P. Bevington, *Data reduction and error analysis for the physical sciences* (McGraw-Hill, New York, 1969) p. 180.
- [6] H.P. Grieneisen, H. Xue-Ting and K.L. Kompa, *Chem. Phys. Letters* 82 (1981) 421.
- [7] K.Y. Tang and D.C. Lorents, *Lasers 80 Conference*, New Orleans, Dec. 15-17 (1980); K.Y. Tang, D.C. Lorents, R.L. Sharpless, D.L. Huestis, D. Helms, M. Durrett and G.K. Walters, 33rd Gaseous Electronics Conference, Norman, Oklahoma, Oct. 8 (1980).
- [8] J. Bokor and C.K. Rhodes, *J. Chem. Phys.* 73 (1980) 2626.
- [9] H.C. Brashears Jr. and D.W. Setser, *J. Phys. Chem.* 84 (1980) 225.
- [10] P.J. Hay and T.H. Dunning Jr., *J. Chem. Phys.* 69 (1978) 2099.
- [11] M. Rokni, J.H. Jacob, J.A. Mangano and R. Brochu, *Appl. Phys. Letters* 30 (1977) 458.
- [12] D.W. Traunor, J.H. Jacob and M. Rokni, *J. Chem. Phys.* 72 (1980) 3646.
- [13] V.H. Shui and C. Duzy, *Appl. Phys. Letters* 36 (1980) 135.
- [14] H.C. Brashears Jr., D.W. Setser and Y.C. Yu, *J. Chem. Phys.* 74 (1981) 10.
- [15] B. Fontaine and B. Forestier, *Appl. Phys. Letters* 36 (1980) 185.
- [16] L.F. Champagne, *Appl. Phys. Letters* 33 (1978) 523.