

COOPERATIVE PHOTOPRODUCTION OF $Xe_2^+ Cl^-$ IN LIQUID Cl_2/Xe SOLUTIONS: STIMULATED EMISSION AND GAIN MEASUREMENTS

Lawrence WIEDEMAN, Mario E. FAJARDO and V.A. APKARIAN

Department of Chemistry, University of California, Irvine, CA 92717, USA

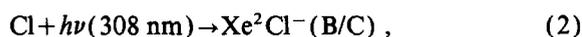
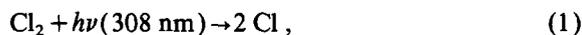
Received 27 October 1986

Cooperative photogeneration of $Xe_2^+ Cl^-$ can be accomplished by near UV laser excitation of Cl_2/Xe solutions with a high quantum efficiency. Gain measurements on the $Xe_2^+ Cl^-$ (4^2T) transition are reported. The liquid phase rare gas halides should be regarded as a family of ideal "dye" lasers.

1. Introduction

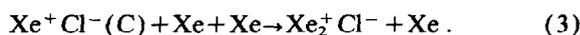
In the preceding Letter [1], herein referred to as II, we discussed the correspondence of the charge transfer states of chlorine-doped solid xenon to an ideal four-level laser. While stimulated emission can effectively be induced, the solids are poor candidates as laser media due to their extensive scattering properties. This concern is inconsequential for the case of the liquid phase exciplexes. The kinetic energy release in the radiative dissociation of the triatomic exciplex can be fully accommodated between excitation pulses.

In the case of solids, the exciplexes are formed by charge transfer to Cl atoms which are photogenerated by permanent dissociation of HCl or Cl_2 dopands. In the case of the Cl_2/Xe gas mixtures or liquid solutions the xenon chloride exciplexes can be efficiently generated by two different cooperative mechanisms. The first mechanism, in which both photodissociation and subsequent charge transfer by photoassociation proceed within each excitation pulse, applies to gas mixtures at relatively low pressures (≈ 1 atm). This process has been well documented in the gas phase [2], viz.



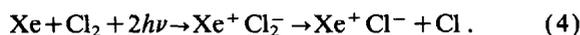
the diatomic exciplex is then reactively quenched to

form the triatomic



In our earlier paper [3] (referred to as I) dealing mainly with solid state photodynamics, we also reported on our gas phase verification of this mechanism. The argument was based on the fact that the wavelength dependence of the exciplex production follows the Cl_2 absorption profile.

In the case of high density Cl_2/Xe systems the second mechanism – cooperative attachment-induced dissociation is the more important channel, viz.



This four-body scattering event was shown to be important in the case of Cl_2 doped solid xenon in I. The same mechanism was recently shown to be operative in the case of $Xe:Cl_2$ van der Waals complexes generated in seeded molecular beams [4]. In both solid and liquid xenon, $Xe^+ Cl^-$ is reactively quenched to form $Xe_2^+ Cl^-$ without ever having the chance to emit. Note that at 308 nm excitation, the Cl atom produced in eq. (4) is also available for photo-association as in eq. (2). Thus both mechanisms are expected to have a power dependence of order 1.5. In the case of Cl_2/Xe solutions, efficient photogeneration of $Xe_2^+ Cl^-$ is observed from 308 to 350 nm, the power dependence both at 340 and 350 nm is second order, moreover the efficiency of the process is higher at 350 than at 330 nm (the peak of

Cl_2 absorption). All of these observations support the second mechanism as the operative one in liquids. A more quantitative account of these measurements will be reported in a full paper. For the present suffice to state that $\text{Xe}_2^+ \text{Cl}^-$ is cooperatively photogenerated in Cl_2/Xe solutions by near UV laser irradiation (308–350 nm is the wavelength range studied to date).

As long as the collisional quenching of $\text{Xe}_2^+ \text{Cl}^-$ ($4^2\Gamma$) by the solvent is inefficient, the four-level laser analogy made in II applies to the case of liquids as well. Very high densities of exciplexes can also be created in the liquids, therefore a large gain coefficient is to be expected. In fact, the radiative dissociation of the triatomic exciplex can be driven to superradiance. In this respect we present gain measurements and discuss the generality of the liquid phase rare gas exciplexes as ideal lasers. The details of the photodynamics, which have some very significant implications with respect to notions of reaction dynamics in liquids, are left to a subsequent publication.

2. Experimental

The experimental scheme is the same as the one discussed in the previous Letter with the exception of replacing the matrix substrate with a high pressure cell. The design of the cell is illustrated in fig. 1. A 7 mm pathlength cell is formed by sandwiching a pair of sapphire windows on a stainless steel ring. The cell is mounted on the tip of a liquid He cryostat, liquid nitrogen is used as refrigerant. Temperature is measured with a diode sensor anchored on the main body of the cell on opposite sides from the cryotip. Temperature control is provided by resistive heating from a nichrome wire wound on the cryotip. A stainless steel fill tube, 1/16" outer diameter, is welded on the cell body. The Cl_2 pressure is measured with a capacitance manometer while the xenon pressure is measured with a Bourdon gauge. Typically, the cell and filling manifold are filled with 100–200 Torr of Cl_2 , then pressurized to 400 psi with xenon, left to equilibrate and subsequently cooled. All three phases are then accessible for study in the same apparatus.

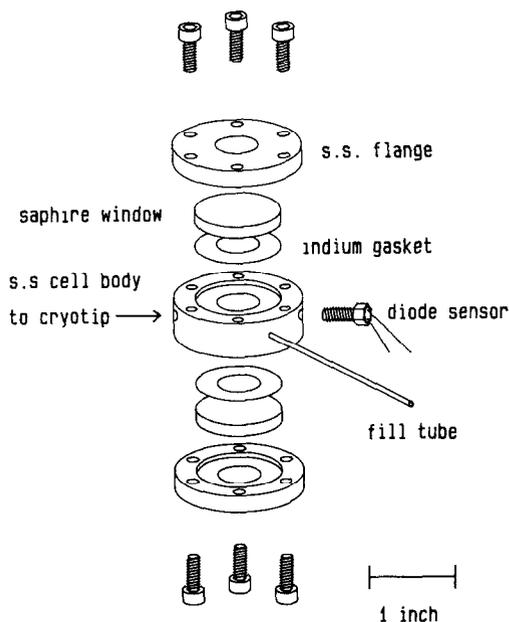


Fig. 1. High pressure xenon cell.

3. Results and discussion

The emission spectra of xenon chloride exciplexes in low pressure gas and solid state media were presented [3] in I. Emission spectra during cooldown of a high pressure mixture (35 atmospheres) is shown in fig. 2a. The only emitter state is the triatomic $\text{Xe}_2^+ \text{Cl}^-$ ($4^2\Gamma$). The most obvious feature is the shift of the linecenter as a function of the density of the medium. The shift is due to the ionic-covalent nature of the transition: the ionic state energy is lowered by dipole-induced polarization of the medium while the covalent repulsive surface remains essentially intact. This aspect was treated in I for the diatomic exciplex emissions in Ar, Kr and Xe. The classical cavity cell model of solvent shift theories is sufficient to account for the observed lineshift [3,5]. According to this model, the spectral shift in energy is given as

$$\Delta E = [8(n^2 - 1)/(2n^2 + 1)]\Delta\mu^2/d^3, \quad (5)$$

in which n is the index of refraction; $\Delta\mu^2$ is the square of the difference in the dipole moments in the upper and lower states of the transition; and d is the cavity diameter. Since the lower state in this case is the repulsive covalent wall we may assume that its dipole

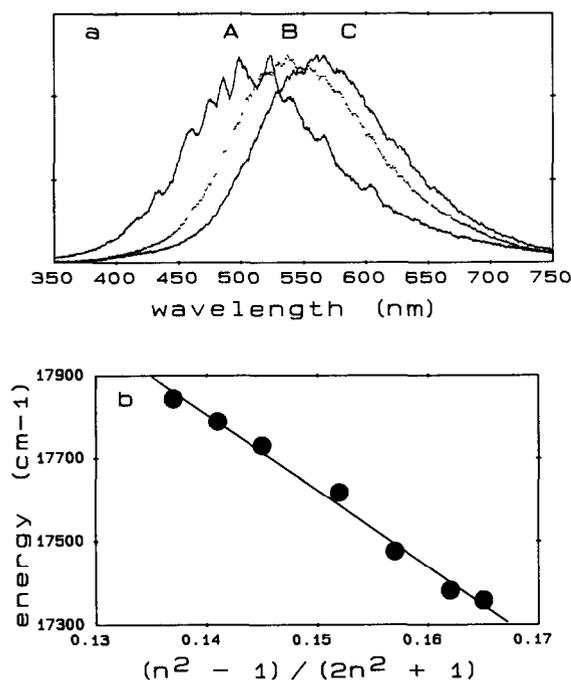


Fig. 2. (a) Emission spectra of 1:200 Cl_2 :Xe sample with $\lambda_{\text{exc}}=308$ nm. Curve (A) is gas phase emission at $T=290$ K, $P=35$ atm, curves (B) and (C) are liquid phase emissions at $T=260$ K and $T=213$ K respectively. Spectra are normalized to same height. (b) Plot of emission linecenter versus dielectric correction factor $(n^2 - 1)/(2n^2 + 1)$ for seven liquid phase spectra spanning temperature range $213 < T < 260$ K. See text for details.

is negligible in comparison to the exciplex state for which a dipole of 12 D has been calculated theoretically [6]. A plot of the emission linecenter versus the polarization of the medium is shown in fig. 2b. Linecenter in this case is defined as the first moment, M , of the emission profile,

$$M = \int_{-\infty}^{\infty} \nu g(\nu) d\nu / \int_{-\infty}^{\infty} g(\nu) d\nu. \quad (6)$$

The index of refraction was evaluated according to

$$(n^2 - 1)/(n^2 + 2) = \frac{4}{3}\pi N\alpha, \quad (7)$$

in which N is the atomic number density of xenon and α is the atomic polarizability. The density of the liquid at different temperatures was obtained from ref. [7]. The data are in good agreement with the model, and if 12 D is replaced for $\Delta\mu$ in eq. (4), from the slope of the linear correlation a cavity diameter

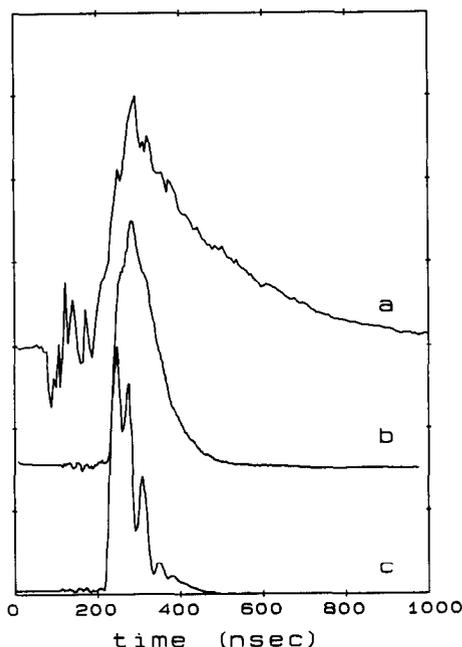


Fig. 3. Time evolution of $\text{Xe}_2^+ \text{Cl}^- (4^2\Gamma)$ emission. (a) Emission from the solid sample at $T=160$ K. (b) Liquid phase emission at $T=184$ K. (c) 308 nm excimer laser pulse profile.

of 6.9 \AA is derived. This is in acceptable agreement with the usual assumption that d is of the order of twice the dipole length: the $\text{Xe}_2^+ - \text{Cl}^-$ distance is 3.00 \AA (see discussion in I).

The time evolution of the $\text{Xe}_2^+ \text{Cl}^- (4^2\Gamma)$ emission near the melting point is shown in fig. 3. In the solid phase, at 160 K, the exciplex relaxes by spontaneous emission. The measured lifetime is 229 ± 20 ns which within experimental error is the radiative lifetime of $4^2\Gamma$ reported in I. Immediately upon melting, the emission intensity increases by a factor of ≈ 50 and its time evolution follows the laser pulse shape. The laser pulse and the $4^2\Gamma$ emissions in liquid xenon at 184 K are shown in figs. 3c and 3b, respectively. The emission is self-stimulated - superradiant. Due to the large index of refraction of the liquid cell, the superradiant beam could be observed off axis from the pump beam direction - the cell acts as a thick parallel plate.

The results of a gain measurement are presented in fig. 4 in the same format as in II. A single pass gain of 11% is observed for a pump fluence of 100 mJ/cm^2 . The expected stimulated emission cross section, σ_s ,

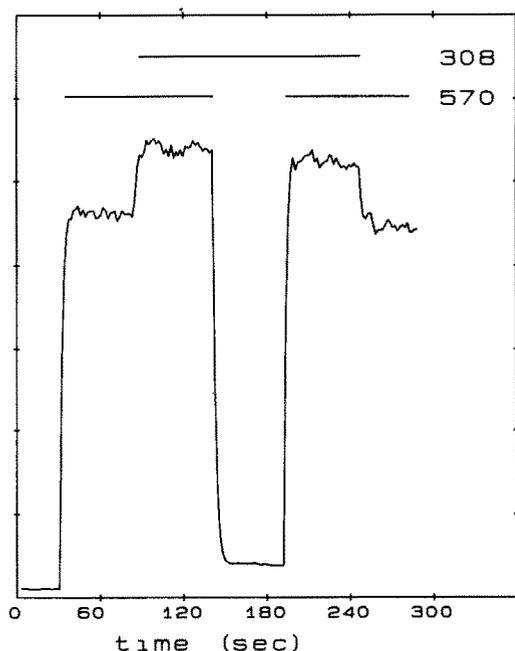


Fig. 4. Boxcar-averaged intensity levels obtained during gain measurement in a 1:600 Cl₂:Xe sample at $T=174$ K, $\lambda_{\text{exc}}=308$ nm, $\lambda_{\text{probe}}=570$ nm. The sequence of laser beams applied is shown by the bars at the top of the figure: background, probe only, pump and probe, pump only, pump and probe, probe only.

is 4.2×10^{-18} cm², a factor of 2 smaller than in the case of solids due to the broader lineshape. Given σ_s , and the path length, $l=0.7$ cm, the Xe₂⁺Cl⁻ number density, N^* , can be calculated,

$$N^* = \frac{\ln(I/I_0)}{\sigma l}$$

For a gain of 11%, $N^*=3.5 \times 10^{16}$ cm⁻³ is calculated. The pump photon density in this case was 2.1×10^{17} photons cm⁻³. Since the pump beam is completely attenuated, it can be inferred that the quantum yield of Xe₂⁺Cl⁻ production is minimally 0.2 (20% window losses assumed). Gain measurements are similar to absorption measurements in that they yield absolute number densities. However, in order to obtain the total excited state number density it is essential that the probe beam duration be longer than the pump beam. This is not the case in the present, the dye laser pulsewidth ≈ 15 ns fwhm, is shorter than the pump. Hence, the quantum yield of 0.2 is a lower bound. Note that the theoretical limit

for this yield is 0.66 for either photogeneration mechanism – eqs. (1) followed by (2) or (4) followed by (2). Additional loss channels are the non-radiative quenching of Xe₂⁺Cl⁻ by the solvent and the recombination induced by the solvent cage. Evidently the cage effect is minor for Cl₂ dissociation in liquid xenon, while the collisional quenching near the freezing point of the liquid is estimated to be ≈ 25 ns.

A further implication of these gain measurements is that Xe₂⁺Cl⁻ is the lowest energy exciplex. The tetratomic Ar₃⁺F⁻ was recently observed leading to the surmise that tetratomic rare gas halides may in general be more stable than their triatomic counterparts [8]. This is clearly not the case for the xenon chlorides. If it were, then Xe₂⁺Cl⁻ would have been reactively quenched both in the solids and liquids. The relaxation of Xe₂⁺Cl⁻ in solid xenon is exclusively radiative. In liquid xenon there is a collisional deactivation component which however cannot be attributed to reactive quenching due to its inefficiency.

4. Conclusions

This Letter constitutes a preliminary report on our studies of liquid phase rare gas exciplexes. Cooperative photoprocesses are ubiquitous in condensed media and present a powerful technique for dynamical studies. Clearly, many details such as mechanisms of energy transfer and non-radiative relaxation will have to be elucidated. However even at this preliminary stage some very significant conclusions can be made.

The xenon chloride charge transfer states form an ideal four-level laser. As such they possess all of the desirable characteristics of an ideal “dye” laser. We have demonstrated gain and superradiance, enclosure of the system in a resonator cavity is a straightforward matter and such a system is presently under construction. The generality of this scheme to all liquid phase rare gas halides is indeed an exciting prospect since it would imply the discovery of the tunable UV dye laser in such systems as liquid argon chlorides. In addition to dispersive tuning of such optically pumped lasers, temperature tuning of the linecenter is possible. In the case of the xenon chlo-

rides these combined tuning mechanisms should provide continuous tunability over the entire visible spectrum. A further advantage of the liquid phase rare gas halides as laser media is the fact that in contrast with organic dye molecules they are essentially indestructible. Electron-beam pumping of these liquids should also be considered. The liquid phase neon exciplexes could then be accessed as possible VUV lasers.

Some of the other implications of this work are (a) the triatomic exciplex is the lowest energy charge transfer complex between xenon and chlorine; (b) the cage escape probability of Cl atoms upon photodissociation of Cl₂ is nearly unity in the liquid phase while a factor of 50 less in solid xenon; (c) the collisional quenching of Xe₂⁺Cl⁻ by xenon is absent in solid xenon while in the liquid, near its freezing point, it proceeds in a timescale comparable with our pump laser pulsewidth ≈ 25 ns.

Acknowledgement

We gratefully acknowledge the support of this

research by a grant from the Research Corporation, funds made available through the UCI Committee on Research, and an award from the Dreyfus Foundation.

References

- [1] M.E. Fajardo and V.A. Apkarian, Chem. Phys. Letters 133 (1987) 51.
- [2] G. Inoue, J.K. Ku and D.W. Setser, J. Chem. Phys. 76 (1982) 733; 80 (1984) 6006; A.W. McCowen and J.G. Eden, J. Chem. Phys. 81 (1984) 2933.
- [3] M.E. Fajardo and V.A. Apkarian, J. Chem. Phys. (Nov. 1986), to be published.
- [4] M. Boivineau, J. le Calvé, M.C. Castex and C. Jouvet, Chem. Phys. Letters 128 (1986) 528.
- [5] D.C. McKean, Spectrochim. Acta 23A (1967) 2405.
- [6] W.J. Stevens and M. Krauss, Appl. Phys. Letters 41 (1981) 308.
- [7] F. Theewes and R. Bearman, J. Chem. Thermodyn. 2 (1970) 507.
- [8] R. Sauerbrey, Y. Zhu, F.K. Tittel and W.L. Wilson Jr., J. Chem. Phys. 85 (1986) 1299.