STIMULATED RADIATIVE DISSOCIATION AND GAIN MEASUREMENTS OF Xe_2Cl IN SOLID XENON

Mario E. FAJARDO and V.A. APKARIAN
Department of Chemistry, University of California, Irvine, CA 92717, USA

Received 27 October 1986

The molecular charge transfer states of Cl-doped solid xenon form an ideal four-level laser system. UV excitation on the molecular XeCl (B←X) pair potentials leads to the formation of the diatomic exciplex which relaxes with a nearly unity quantum yield to the triatomic $Xe_2^+Cl^-(4\,^2\Gamma)$ state. The radiative dissociation of the triatomic exciplex can be stimulated to provide monoenergetic atoms ≈ 1 eV above ground. While these systems are characterized by large gain coefficients, scattering losses predominate in samples prepared by standard matrix isolation techniques. Scattering losses are due to the inability of the lattice to accommodate the excess kinetic energy released in the bound to repulsive transition of the triatomic exciplex.

1. Introduction

In a previous paper, herein referred to as I, we reported on the spectroscopy of xenon chloride exciplexes in rare gas matrices [1]. Atomic chlorine is photogenerated cooperatively in solid xenon by UV irradiation of matrix-isolated HCl or Cl_2. The diatomic $Xe^+Cl^-(B)$ state can be accessed directly in the atomic solids by UV excitation of the charge transfer transition over pair potentials that could be directly correlated with the gas phase B←X transition. In xenon matrices, the only observed emission is due to the radiative dissociation of $Xe_2^+Cl^-$ $(4\,^2\Gamma)$ centered at 570 nm.

The pertinent energy level diagram of the system is shown in fig. 1. The photodynamics can be described as

$$Xe + Cl + h\nu \rightarrow Xe^+Cl^-(B/C)\,, \qquad (1)$$

followed by charge rearrangement within the lattice cage to yield the triatomic exciplex,

$$Xe^+Cl^-(C) + Xe \rightarrow Xe_2^+Cl^-(4\,^2\Gamma)\,, \qquad (2)$$

the triatomic subsequently dissociates by radiation,

$$Xe_2^+Cl^-(4\,^2\Gamma) \rightarrow Xe + Xe + Cl + h\nu + KE\,. \qquad (3)$$

The kinetic energy released in the radiative dissociation of $Xe_2^+Cl^-$ is due to the fact that the transition

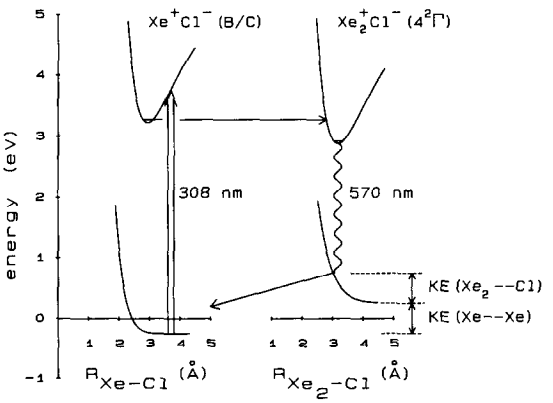

Fig. 1. Solid state energy level diagram showing states involved in four-level laser and disposal of kinetic energy after radiative dissociation (see text for details). Zero of energy is taken as the energy at infinite separation of the Cl atom from the xenon solid.

terminates on a steeply repulsive ground potential. The triatomic emission lineshape was simulated theoretically in I to conclude that the transition terminates 1 eV above ground. This release of kinetic energy is partitioned equally between the two coordinates: Xe–Xe and Xe_2–Cl.

The system clearly corresponds to an ideal four-level laser. The pump transition, XeCl (B←X), has a large oscillator strength due to its charge transfer nature. The triatomic $(4\,^2\Gamma)$ state is populated from

0 009-2614/87/$ 03.50

the pumped level, eq. (2), on a timescale faster than 10 ps, and relaxes radiatively with a lifetime of 225 ns. This state then acts as the metastable upper level of the lasing transition. The transition terminates on the repulsive wall of the ground state, which is depleted on a timescale of 10^{-13} s.

The analogy to the four-level laser is also appropriate for gas phase and liquid phase xenon chloride exciplexes. Gain measurements have previously been reported in gas phase [2] $Xe_2^+ Cl^-$, and laser action has been demonstrated in electron-beam-pumped high-pressure gas cells [3]. We have performed gain measurements in both solid and liquid xenon, the liquid xenon measurements will be reported in the subsequent Letter [4], here we report on our solid state observations. Two types of measurements are reported. The first, pump–dump measurements, consist of monitoring the stimulation of emission by following the depletion of the spontaneous radiation. The second, gain measurements, consist of directly monitoring the small signal amplification of injected radiation resonant with the 4 $^2\Gamma$ emission.

2. Experimental

HCl- or Cl_2-doped xenon solids are prepared by standard matrix isolation techniques. The details can be found in I. The matrices are extensively irradiated with the 308 nm output of an excimer laser – typically for 1 h at a repetition rate of 5 Hz and a fluence of 100 mJ/cm^2. The growth of the $Xe_2Cl(4\,^2\Gamma)$ emission at 570 nm, which is a direct measure of Cl atom concentration, is monitored during the irradiation period. All subsequent measurements are made at reduced excitation fluences to avoid further photogeneration of Cl atoms.

The excitation geometry shown in fig. 2 is the same for both pump–dump and gain measurements. The 308 nm output of the excimer laser is split to pump a dye laser and then recombined with the dye output through a dichroic mirror. Both beams are focused on the sample through the same CaF_2 lens (focal length = 30 cm, ϕ = 2.5 cm). A telescope in the dye beam is used to match the spot sizes of the two lasers on the solid sample.

In the pump–dump experiments, fluorescence perpendicular to the excitation beam is collected with a

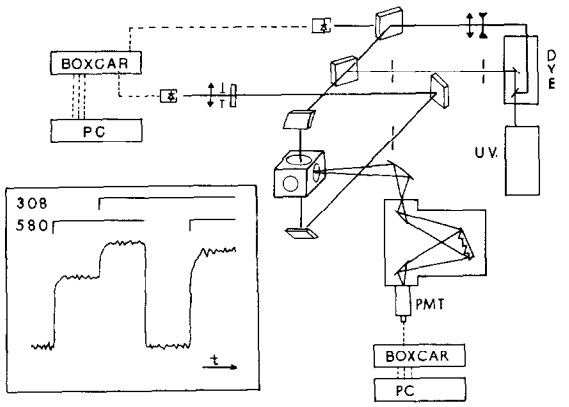

Fig. 2. Experimental diagram showing geometry used for small-signal gain measurements and pump–dump experiments. Inset shows boxcar-averaged intensity levels obtained during gain measurement (see text for explanation).

PMT through a 1/4 m monochromator. In all the experiments to be reported, the 308 nm beam is used as the pump to excite the diatomic B←X transition, while the dye laser is used as the dump to stimulate the $Xe_2^+ Cl^-$ (4 $^2\Gamma$) transition.

The gain measurements are performed at 580 nm. In this case the transmitted dye beam is spatially filtered by several irises and collected with a quartz lens and photodiode at a distance of $\approx$ 1 m from the sample after bending the beam with several mirrors. An acetone cell and a pair of interference filters are used to block any 308 nm light from reaching the photodiode. The detection is gated with zero delay and averaged with a boxcar.

3. Results and discussion

The laser-induced emission profile of $Xe_2^+ Cl^-$ (4 $^2\Gamma$) is shown in fig. 3 in the presence (trace a) and absence (trace b) of the dump beam. While the pump beam scatter can be completely blocked from detection, the dump beam scatter cannot. The monochromator input slit is closed between 570 and 640 nm to prevent the PMT from saturation hence the discontinuity in fig. 3a. The pump beam energy is 12 μJ in both scans while the dump beam energy at 590 nm is 390 μJ. Both beams are focused on a spot of $\approx$0.74 mm^2 as measured by the burn

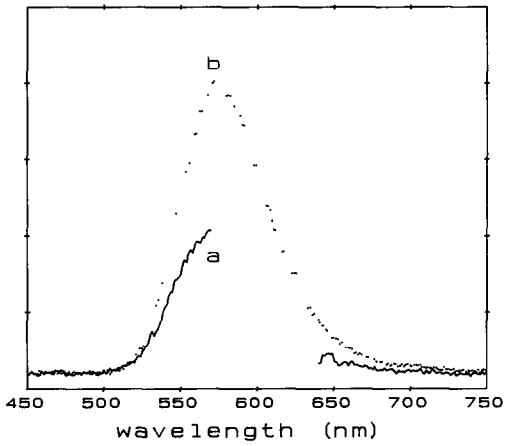

Fig. 3. $Xe_2^+Cl^-(4\,^2\Gamma)$ emission from a 1:1000 HCl:Xe solid at 12 K during 308 nm excitation observed with (a) and without (b) 590 nm dye laser dump beam. Monochromator slits were closed from 570 nm to 640 nm when using dump beam to avoid saturation of photomultiplier. Trace (a) is corrected for scattered 590 nm light and baseline.

pattern on a Pt film deposited on a microscope cover slip. The entire emission is reduced symmetrically, indicating that the emission profile is homogeneous.

In fig. 4a, the fluorescence intensity at 550 nm is shown for a sequence of 1 min boxcar averages of each: pump off, dump off (baseline); pump on, dump off; pump on, dump on; only dump on; followed by a repetition of pump on, dump on; and pump on, dump off. In this example (I(pump) = 12 μJ, I(dump) = 390 μJ) ≈60% of the $4\,^2\Gamma$ population undergoes stimulated radiative dissociation. The fraction of $4\,^2\Gamma$ population that decays by stimulated emission, $\Delta N^*/N^*$, is calculated as the difference between fluorescence signal levels with both pump and dump on, S(P+D), and only pump on, S(P), corrected for baseline and scattered light S(D).

$$\frac{\Delta N^*}{N^*} = -\frac{S(\mathrm{P+D}) - S(\mathrm{P}) - S(\mathrm{D}) + \text{baseline}}{S(\mathrm{P}) - \text{baseline}}. \quad (1)$$

A plot of $\Delta N^*/N^*$ versus intensity of dump beam is shown in fig. 4b. A saturation behavior is observed such that no more than 70% of the population can be stimulated. We believe this is due to a temporal mismatch between the pump and dump beams. The pump beam pulsewidth is 25 ns fwhm, however it has a tail that extends to 50 ns. The dump beam pulsewidth is 15 ns fwhm and is delayed relative to the

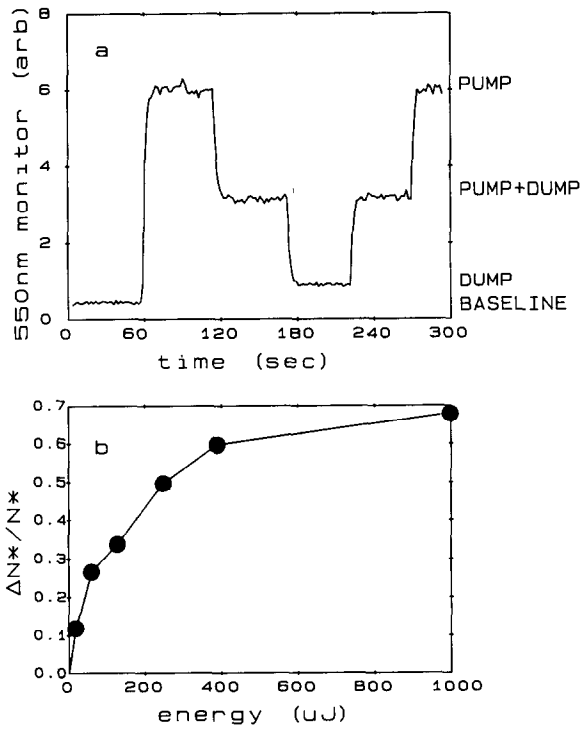

Fig. 4. Pump–dump signal levels from same sample as fig. 3. (a) Boxcar-averaged PMT signals with $\lambda_{monitor} = 550$ nm, $\lambda_{pump} = 308$ nm, $\lambda_{dump} = 590$, pump energy = 12 μJ and dump energy = 390 μJ. The dump only signal for $180 < t < 220$ s does not return to baseline due to scattered 590 nm light reaching the PMT. (b) Fraction of excited state population that undergoes stimulated radiative dissociation versus dump laser energy.

pump beam by 3 ns.

A typical sequence of signal levels in a gain measurement is shown in the inset to fig. 2. The sequence of beams is shown by the bars. The sample in this case was a 1:1000 Cl_2:Xe solid with an estimated thickness of 200 μm. The pump beam intensity was 1.3 mJ focused on a 10 mm^2 spot while the dye beam intensity was 2μJ, focused to a spot smaller than the pump beam ≈2 mm^2. A single pass gain of ≈30% can be seen in the sequence. Assuming a gain path length, l, of 200 μm a gain coefficient, γ, of 13 cm^{-1} is derived according to

$$\gamma = \frac{\ln(I/I_0)}{l}, \quad (2)$$

consistent with the expected value of $\gamma \approx 10$ cm^{-1} estimated from

$$\gamma = \frac{N^* \lambda^4}{8\pi c \Delta\lambda t_{\text{spont}}}, \quad (3)$$

with $N^* = 10^{18}$ cm^{-3}, $\lambda = 580$ nm, $\Delta\lambda = 70$ nm, and $t_{\text{spont}} = 225$ ns. N^* was estimated from the pump beam energy, 1.3 mJ at 308 nm, and the excitation volume of 0.002 cm^3. The pump beam is completely depleted. These values, while approximate, indicate that these systems can be characterized as high gain media, however scattering losses are also high. The loss term depends strongly on the nature and history of the matrix: effects that are poorly understood. In the present method of preparing Cl/Xe solids – photolysis of HCl in a pulsed deposited matrix – the scattering losses often predominate such that gain is not always measurable.

4. Conclusions

Very large gain coefficients are to be expected in solids in contrast with the gas phase, due mainly to their high packing densities[5]. While the $4\,^2\Gamma$ emission can be efficiently stimulated in solid xenon and a large gain coefficient can be verified, these amorphous solids are not very useful as amplifier media because of the scattering losses that predominate. Large rare gas polycrystals of excellent optical quality have previously been prepared for VUV laser applications [6]. Such crystals could in principle be prepared with interstitial halogen dopants and exploited as laser media – a promotion of solid state rare gas halide exciplex lasers from the realm of science fiction [7] to that of science fact. In gas phase media, bound to repulsive type transitions are ideally suited as lasers. In solids, if the excess kinetic energy cannot be accommodated in the immediate trap site, permanent destruction of the lattice results and leads to highly scattering lossy media. This consideration is of little concern in the case of liquid phase exciplexes discussed in the following Letter [4].

Despite the poor performance of these amorphous solids as gain media, emission can be effectively stimulated. This process then provides an effective means for the generation of hot, almost monoenergetic atoms in condensed media and therefore is useful for molecular dynamical studies related to energy transfer, diffusion and photomobility. A theoretical, molecular dynamics, study of Cl_2 photodissociation in rare gas solids was recently reported [8]. Stimulated radiative dissociation should be an ideal scheme for preparing the fast atoms to test the different, predicted modes of energy accommodation.

Acknowledgement

We gratefully acknowledge the support of this research by a grant from the Research Corporation and funds made available through the UCI Committee on Research.

References

[1] M.E. Fajardo and V.A. Apkarian, J. Chem. Phys. (Nov. 1986), to be published.
[2] K.Y. Tang, D.C. Lorents and D.L. Huestis, Appl. Phys. Letters 36 (1980) 347.
[3] F.K. Tittel, W.L. Wilson, R.E. Stickel, G. Marowsky and W.E. Ernst, Appl. Phys. Letters 36 (1980) 405;
F.K. Tittel, G. Marowsky, W.L. Wilson and M.C. Smayling, IEEE J. Quantum Electron. 17 (1981) 1488.
[4] L. Wiedemann, M.E. Fajardo and V.A. Apkarian, Chem. Phys. Letters 133 (1987) 55.
[5] V.A. Apkarian, Chem. Phys. Letters 110 (1984) 168.
[6] N. Schwentner, O. Dossel and A. Nahme, in: Laser techniques for extreme ultraviolet spectroscopy, AIP Conference Proceedings 90, eds. T.J. McIlrath and R.R. Freeman (AIP, New York, 1982).
[7] M. Gundersen, scientific consultant to Real Genius (film, 1985), private communication.
[8] R. Alimi, A. Brokman and R.B. Gerber, in: Stochasticity and intramolecular redistribution of energy, Proceedings of the NATO Conference, eds. R. Lefebvre and R. Mukamel (Reidel, Dordrecht, 1986).