

Oriented geminate recombination of Cl₂ in solid xenon at high pressure

G.J. Hoffman, E. Sekreta and V.A. Apkarian¹

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

Received 18 December 1991; in final form 29 January 1992

Photodissociation studies of Cl₂-doped Xe in a diamond anvil cell are reported. Excitation of the dissociative ¹Π_u←X transition at 308 nm, leads to complete recombination at 100 K, and 4 GPa. The recombinant emission shows a polarization ratio of 0.95, indicating that the molecular orientation is preserved to some extent during the process.

1. Introduction

In this Letter, we report the first polarization measurements of recombinant emission in Cl₂-doped solid xenon under high pressure, in a diamond anvil cell (DAC). The motivation behind the study is entrenched in a background of prior experimental and theoretical studies which we succinctly review before presenting the data.

The photodissociation of Cl₂ in rare gas solids is a model system which may serve as a test of the extent of our understanding of many-body dynamics. The approach in this effort has been one of iteration between experiment and theory. Bondybey and Fletcher reported the first studies on this system [1]. At 4 K, a nearly complete cage effect was observed in solid Ar and Kr when Cl₂ was excited to the repulsive ¹Π_u potential, 1.2 eV above the molecular dissociation limit (337.1 nm). These studies relied on monitoring the recombinant A'→X emission. The absence of dissociation was inferred from the persistence of this emission with irradiation time. Perhaps more tantalizing was the observation that the emission was polarized, since this would imply that during the dissociation/recombination process the molecule retains memory of its initial orientation. Fajardo et al. established that, under similar conditions, although access of the covalent repulsive

surface does not lead to permanent dissociation, access to molecule–host charge transfer states in Xe and Kr leads to very efficient dissociation via ionic potentials [2]. Classical molecular dynamics (MD) simulations were able to reproduce the low-temperature results, and identified the mechanism for efficient caging as due to locking of the molecule in orientations unfavorable to cage exit and efficient momentum transfer between fragment and cage atoms [3]. Accordingly, the theory predicted that at elevated temperatures, a photodissociation threshold should be observed, near 95 K in the case of solid Xe, which would be directly associated with the threshold for molecular free rotation. At these elevated temperatures, diffusion and clustering make measurements on isolated guests difficult. Thus, Katz and Apkarian resorted to measurements under high pressure, in a diamond anvil cell [4]. The technique introduced a powerful tool, since a much larger set of thermodynamic conditions was made available for meaningful comparisons between experiment and theory. The first studies carried out at 2 GPa, indicated that throughout the temperature range of 30–300 K, although dissociation could be observed, it was entirely dominated by the two-photon ionic mechanism. The upper limit on the one-photon direct dissociation as a function of temperature was established to be $\Phi < 10^{-4}$ at 100 K. A new generation of MD simulations in constant NPT (number, pressure, temperature) ensembles was recently com-

¹ Alfred P. Sloan Fellow.

pleted, to carry out simulations under the experimental conditions of the DAC [5]. These established that indeed the application of 2 GPa pressure on the solid arrests dissociation at 100 K, both due to blocking of molecular rotations and due to the increased barrier for cage exit. In the absence of dissociation, the extent of polarization in the recombinant emission was suggested as an observable that could be used to compare experiment with theory. The theory predicted that at 100 K and 10 GPa, rotation is completely blocked and that the recombination should proceed with complete retention of initial orientation, while at 2.5 GPa the retention is $\approx 80\%$. That such measurements are possible, and that the first measurements are consistent with the theory, is the aim of this Letter. In a parallel development, Schwentner and co-workers have carried out extensive wavelength and temperature dependence studies of Cl_2 dissociation in different rare gases at zero pressure [6,7]. Their studies have revealed details previously missed, which are, however, in surprisingly good agreement with the most recent MD simulations [8].

2. Experimental

The experimental details of the DAC technique have been previously reported [4]. A cell of the Merrill-Bassett design, which can be loaded in vacuum at cryogenic temperatures, is used in these measurements. The sample used had a concentration of 1:500 Cl_2 (99%) in Xe (99.9995%). The excitation source was a XeCl excimer laser, $\lambda=308$ nm (Lambda Physik, EMG 201). Emission from the sample was collected and dispersed through a 0.3 m monochromator (McPherson 218), and detected with a thermoelectrically cooled photomultiplier tube (Hamamatsu R943-02) using a photon counter (SRS SR400). Lifetime data were acquired using an averaging digital oscilloscope (Tektronix 2430) with 1 k Ω termination. A calcite Glan-Thompson polarizer selected the input beam polarization. A near-infrared metallic thin film polarizer was used to observe emission polarization. To maximize signal, the grating of the monochromator was placed at zero order. The transmitted 308 nm light was blocked by an acetone filter, and nearly all $\text{Xe}_2^+ \text{Cl}^-$ emission was

blocked by a 780 nm long-pass filter. The polarization properties of the monochromator at zero order were determined using a blackbody source and the same polarizer and long-pass filter. The sample was at a pressure of 4 GPa for all of the measurements presented here; the polarization measurements were conducted at 100 K.

Polarization measurements on a sample in this DAC are complicated by polarization scrambling of the excitation beam for certain orientations of the input polarizer relative to the cell. Why this occurs is not clear, as diamond is not birefringent. However, there are two polarizer orientations, perpendicular to each other, that preserve polarization with a ratio of 10:1 or greater. Emission polarization measurements were made for input light polarized at these angles.

3. Results and discussion

The observed emission spectrum is shown in fig. 1. The features in the spectrum are characteristically broad, as has been previously observed for Cl_2 in solid Xe both at zero pressure [2] and at 2 GPa [4]. The maxima in this spectrum appear to be shifted from those previously reported, by ≈ 15 nm. The source of this shift is not obvious. The $A' \rightarrow X$ transition it-

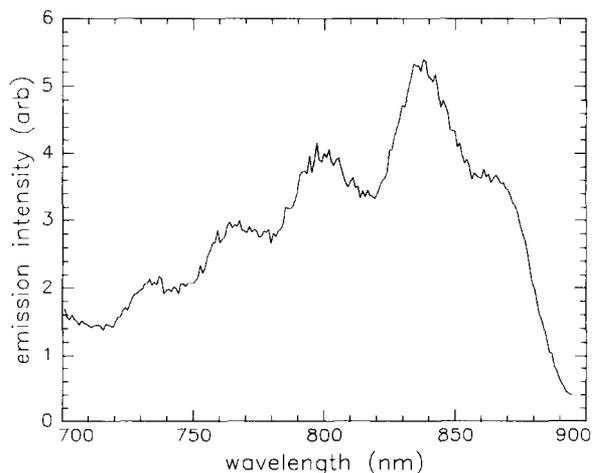


Fig. 1. Emission spectrum of a sample of 1:500 Cl_2 in Xe at a pressure of 4 GPa and at a temperature of 27 K. The decrease in signal to the red end of the spectrum is due to the red cut-off of the photomultiplier tube.

self ought not be pressure sensitive, as it involves only valence, non-charge-transfer states. However, one possible explanation is that emission from $(\text{Cl}_2)_n$ clusters dominates in fig. 1. Luminescence from $(\text{Cl}_2)_2$ in solid Kr at low pressure was seen to differ significantly in both location and width of spectral features [9] ^{#1}.

At pressures greater than 4 GPa, permanent dissociation is not detectable. This is established by both the absence of growth in the Xe_2Cl emission intensity, and the absence of any permanent loss in the recombinant emission intensity.

Table 1 presents the temperature dependence of the Cl_2 luminescence lifetime. Not surprisingly, as temperature increases, the lifetime decreases. Above 120 K, Cl_2 luminescence was not detectable. This provides an upper limit of temperature for performing polarization measurements. Below 60 K, the lifetime of 2 ms appears to be nearly independent of temperature; presumably, in this limit, the relaxation is dominated by radiative decay. The radiative decay of the $A' \rightarrow X$ emission in solid Kr, for both monomer and dimer, were reported as 49 ms [9]. Reduction of radiative lifetime for this formally dipole forbidden transition in Xe is to be expected. This could be ascertained by measurements in zero pressure Xe, for which at present there are no reported data.

A polar plot of emission intensity, normalized to the polarization dependence of the monochromator (minus 20000 counts), versus analyzing polarizer angle is shown in fig. 2. The polarization of the excitation beam is also shown in the figure (at 25° from

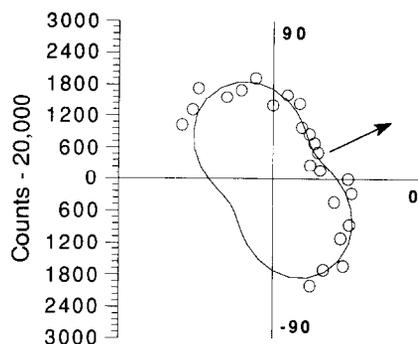


Fig. 2. Polar plot of emission intensity of Cl_2 versus polarizer angle normalized to the polarization sensitivity of the monochromator at zero order and subtracted by 20000 counts. The arrow shows the polarization of the 308 nm excitation beam. The points represent the data; the line is a nonlinear least squares fit of the function $f(\theta) = A - B \cos[2(\theta - C)]$ to the data.

horizontal). The emission is clearly perpendicularly polarized. A nonlinear least-squares best fit to the data, using a function of the form $f(\theta) = A - B \cos[2(\theta + C)]$, is also shown in the figure. The best fit gives $C = 32^\circ \pm 9^\circ$ (99% confidence), giving good agreement within experimental uncertainty to the orientation of the input polarizer. Using the best fit values of A and B , one obtains for the polarization ratio, $I_{\parallel}/I_{\perp} = (A - B + 20000)/(A + B + 20000) = 0.95 \pm 0.02$ (99% confidence). As this ratio is significantly different from one, a lack of reorientation for some fraction of the Cl_2 molecules upon dissociation and recombination can be inferred. However, the quantitative interpretation of this measurement is difficult, given the expected extensive electronic mixing of the states. A polarization ratio of 0.7 had been measured by Bondybey and Fletcher for the same transition in an Ar matrix at 4 K and zero pressure [1]. Thus, the effect is much weaker in the present case. The reduction in net polarization could be in part due to the cluster contribution to the observed emission, for which no polarization is expected. However, it is known that the Cl_2 -Xe system is subject to a strong interaction along the insertion mode which can produce significant mixing of states affecting transition dipoles in both excitation and emission [10]. This is a particularly serious consideration since the observed emission is for a formally forbidden transition. Systematic measurements as a function of temperature and pressure

^{#1} Despite the resemblance between fig. 1 and the emission spectrum of solid Cl_2 reported in ref. [2], the emission observed from the DAC cannot be that of solid Cl_2 . The time dependence of the emission of pure Cl_2 is complex and nonexponential, while the lifetimes observed here were exponential.

Table 1
 Cl_2 luminescence lifetime dependence on temperature

T (K)	τ (ms)
40	1.8
60	1.9
80	0.9
100	0.3
115	0.07

in samples in which the Cl_2 is well isolated would provide self-consistent data which may be more useful for making quantitative comparisons between experiment and theory. Such measurements are presently underway.

In conclusion, we have established that polarization measurements associated with photodissociation dynamics, and as a function of temperature and pressure, are feasible in diamond anvil cells. In the present example, we conclude that: (a) at pressures above 4 GPa, Cl_2 does not undergo permanent dissociation in solid Xe when excited to the $^1\Pi_u$ surface with 1.5 eV of excess energy; (b) at 4 GPa, and 100 K, the recombination proceeds with at least partial retention of initial molecular orientation.

Acknowledgement

Research supported by the US Air Force Phillips

Laboratory under contract S04611-90-K-0035.

References

- [1] V.E. Bondybey and C. Fletcher, *J. Chem. Phys.* 64 (1976) 3615.
- [2] M.E. Fajardo, R. Whithnall, J. Feld, F. Okada, W. Lawrence, L. Wiedeman and V.A. Apkarian, *Laser Chem.* 9 (1988) 1.
- [3] R. Alimi, A. Brokman and R.B. Gerber, *J. Chem. Phys.* 91 (1989) 1611.
- [4] A.I. Katz and V.A. Apkarian, *J. Phys. Chem.* 94 (1990) 6671.
- [5] R. Alimi, R.B. Gerber and V.A. Apkarian, *J. Chem. Phys.*, submitted for publication.
- [6] H. Kunz, J.G. McCaffrey, R. Schrieffer and N. Schwentner, *J. Chem. Phys.* 94 (1991) 1039.
- [7] J.G. McCaffrey, H. Kunz and N. Schwentner, *J. Chem. Phys.* 96 (1992) 155.
- [8] R. Alimi, R.B. Gerber, J.G. McCaffrey, H. Kunz and N. Schwentner, *J. Chem. Phys.*, submitted for publication.
- [9] G.J. Hoffman and V.A. Apkarian, *J. Phys. Chem.* 95 (1991) 5372.
- [10] D.M. Prosperio, R. Hoffmann and K.C. Janda, *J. Am. Chem. Soc.* 113 (1991) 7184.