

Energy splitting between the B and C states of xenon chloride

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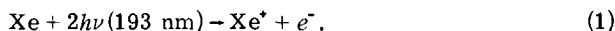
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The energy splitting between $B(1/2)$ and $C(3/2)$ excimer states in xenon chloride has been determined by comparing the thermal equilibrium intensity ratio of the broadband $C(3/2) \rightarrow A(3/2)$ fluorescence emission at 340 nm to that of the narrowband $B(1/2) \rightarrow X(1/2)$ fluorescence emission at 308 nm. The formation of the excimers is initiated via two-photon ionization of Xe atoms in the presence of Cl_2 and an Ar buffer. The room temperature equilibrium intensity ratio I_{C-A}/I_{B-X} is found to be 0.15 ± 0.01 . Using the Einstein A coefficients calculated by Hay and Dunning for these transitions, the energy splitting $E_C - E_B$ is determined as $(5.4 \pm 25) \text{ cm}^{-1}$. Strong emission from the triatomic species Xe_2Cl was also observed.

A great deal of attention has recently been focused on the $C(\frac{3}{2})$ state in xenon fluoride due to the discovery¹⁻³ that this state actually lies about 700 cm^{-1} lower in energy than the $B(\frac{1}{2})$ state, which is the upper laser level in the XeF 351 nm laser. This discovery has important consequences to XeF uv laser efficiency and scalability. In addition, it has led to the dramatic development of a new visible laser system⁴ operating on the $C(\frac{3}{2})-A(\frac{3}{2})$ transition in XeF at around 470 nm. In this work, experimental results on the splitting between the $B(\frac{1}{2})$ and $C(\frac{3}{2})$ states in the xenon chloride molecule are reported. This study was motivated by the fact that if the $C(\frac{3}{2})$ state were to lie sufficiently below the $B(\frac{1}{2})$ state in XeCl, then a new laser operating on the $C(\frac{3}{2})-A(\frac{3}{2})$ in XeCl at 340 nm would be possible.

The experimental technique used was similar to that used in Ref. 1 to measure the $B-C$ state splitting in XeF. An argon fluoride laser, operating at 193 nm, was used to excite mixtures of Xe and Cl_2 in an Ar buffer. Fluorescent emissions from excited XeCl molecules were observed using a 0.3 m spectrometer which could be equipped with either an optical multichannel analyzer (OMA) for recording time-integrated spectra, or with the normal slit and photomultiplier tube arrangement for recording time-resolved signals.

The kinetic chain leading to these emissions was initiated via two-photon ionization of the Xe atoms

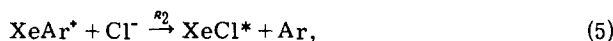
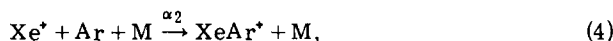
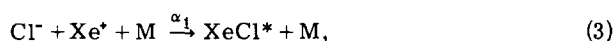


Typical experimental conditions with an xenon density of $5 \times 10^{17} \text{ cm}^{-3}$ and a focused laser intensity of 10^{10} W/cm^2 resulted in an estimated ion density of $5 \times 10^{13} \text{ cm}^{-3}$ using the two-photon ionization cross section derived earlier.^{1,5}

Absorption of the laser radiation by the argon and chlorine constituents of the mixture was insignificant. The lowest order absorption process in Ar at 193 nm would be nonresonant three-photon ionization,⁶ which may be neglected. From the data of Seery and Britton,⁷ we may estimate that the cross section for single-photon absorption in Cl_2 at 193 nm is less than 10^{-21} cm^2 . Thus, for the typical Cl_2 densities used in these experiments

of $\sim 3 \times 10^{16} \text{ cm}^{-3}$, attenuation of the laser beam by Cl_2 absorption was not significant. However, the absorption process in Cl_2 leads to dissociation,⁷ and at laser intensities of 10^{10} W/cm^2 , several percent of the Cl_2 molecules in the laser focus region are expected to be converted into atoms. This fact would have to be considered in rigorous kinetic studies, but has negligible influence on the results obtained here.

The XeCl^* excimers were subsequently formed in the presence of an argon buffer in the reactions



Contrary to the results of Kligler *et al.*¹ for XeF, the temporal behavior of the XeCl emissions did not follow a simple ion-ion recombination law. For this reason, it is felt that most, if not all of the reactions [(2)-(7)] were operative in this experiment. The rate constants k_1-k_4 are either known, or may be estimated: $k_1 = 3.1 \times 10^{-10} \text{ cm}^3/\text{sec}$ for electron and gas temperatures of 300 K,⁸ $\alpha_1 \sim 1.0 \times 10^{-25} \text{ cm}^6/\text{sec}$ by analogy with theoretical calculations⁹ for $\text{Xe}^+ + \text{F}^- + \text{Xe}$, $\alpha_2 \sim 10^{-31} \text{ cm}^6/\text{sec}$ by analogy with several similar reactions,¹⁰ $k_2 \sim 10^{-6} \text{ cm}^3/\text{sec}$ by analogy¹¹ with $\text{Ar}_2^+ + \text{F}^-$, $k_3 \sim 10^{-6} \text{ cm}^3/\text{sec}$ by analogy¹² with $\text{Xe}_2^+ + e^-$, and $k_4 = 7.2 \times 10^{-10} \text{ cm}^3/\text{sec}$.¹³ A simple analysis using these rates, Ar pressures in the range 10-1000 Torr, Cl_2 pressures in the range 0.1-2 Torr, and Xe pressures in the range 10-200 Torr, shows that, in general, none of reactions (2)-(7) may be neglected.

In spite of the somewhat complicated formation kinetics, it was possible to make a measurement of the $B-C$ state energy separation in XeCl. The basic assumption we make is that once they are formed, for a sufficient buffer gas pressure (greater than $\sim 1 \text{ atm}$), the electronic distribution in the excimer states relaxes to a 300 K Boltzman distribution before they radiate. From

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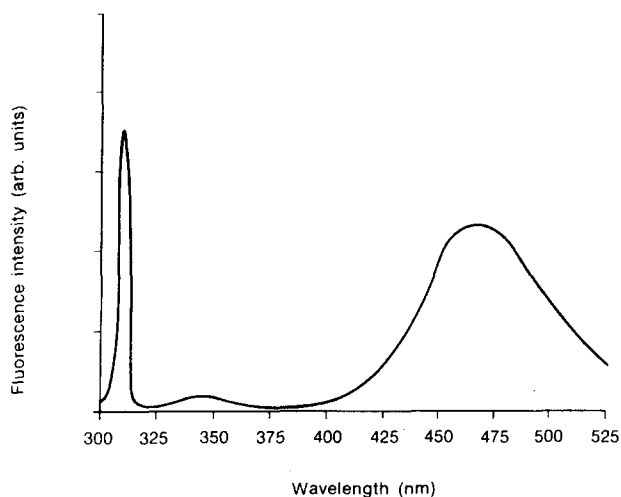


FIG. 1. Fluorescence spectrum from ArF* lasers excited Xe/Cl₂ mixture. Xe pressure is 200 Torr. Cl₂ pressure is 0.050 Torr. Three emission bands are observed: XeCl (*B*-*X*) at ~308 nm, XeCl (*C*-*A*) at ~340 nm, and Xe₂Cl* at ~470 nm.

the ratio of fluorescence intensities in the narrow *B*-*X* band to that of the *C*-*A* band, the energy splitting may then be obtained. It has been pointed out by Julienne and Krauss¹⁴ that the *C*-*A* and *B*-*A* emission bands in the RGH excimers overlap, and this fact must be included in the analysis. We therefore write¹⁴

$$I_b/I_n = (A_{CA}/A_{BX})\theta + A_{BA}/A_{BX}, \quad (8)$$

$$\theta = \exp[-(E_C - E_B)/kT]. \quad (9)$$

In these experiments, I_b and I_n represent the equilibrium fluorescence intensities for the *C*-*A* (plus *B*-*A*) and *B*-*X* emission bands, respectively; A_{CA} , A_{BX} , and A_{BA} represent the Einstein *A* coefficients for the *C*-*A*, *B*-*X*, and *B*-*A* transitions, respectively; E_C and E_B represent the electronic energies for the *C* and *B* states, respectively; and kT is the thermal energy.

Figure 1 shows a typical OMA fluorescence spectrum from a laser excited Ar/Xe/Cl₂ mixture. Three emission bands are prominent in this spectrum. The narrow emission band at 308 nm is from the XeCl *B*-*X* transition, the weak broader band centered at ~340 nm is from the overlapping XeCl *B*-*A* and *C*-*A* transitions, while the very broad band at ~470 nm is from the triatomic species Xe₂Cl*. Fluorescence spectra were taken for fixed Cl₂ and Xe pressure, with varying Ar pressure. Because the quantum efficiency of the OMA detector varies significantly in the 300-400 nm spectral region, it was essential to calibrate the relative spectral sensitivity of the detection system using a tungsten-halogen standard lamp. Prior to further analysis, the laser excited spectra were first adjusted to account for the sensitivity variation.

The 340 and 308 nm emission bands were then each integrated over their full spectral widths. The resulting intensity ratios I_b/I_n are plotted versus argon pressure in Fig. 2 for several partial pressures of chlorine. The asymptotic ratio is found to be 0.15 ± 0.01 . Using the Einstein *A* coefficients calculated by Hay and Dunning¹⁶ of $A_{BX} = 9.3 \times 10^7 \text{ sec}^{-1}$, $A_{CA} = 8.1 \times 10^6 \text{ sec}^{-1}$,

and $A_{BA} = 6 \times 10^6 \text{ sec}^{-1}$, we obtain the energy splitting between the *B* and *C* states, $E_C - E_B = (5.4 \pm 25) \text{ cm}^{-1}$. Thus, this experiment places the *C* and *B* states in XeCl at essentially the same energy, within approximately 25 cm^{-1} . Tellinghuisen¹⁷ has observed that this intensity ratio in XeCl increases with temperature, conclusively demonstrating that the *C* state lies higher in energy than *B*. His preliminary estimate is $E_C - E_B < 100 \text{ cm}^{-1}$. Both of these results disagree somewhat with the results of Brashears and Setser,¹⁸ which if combined with the Julienne and Krauss¹⁴ analysis give $E_C - E_B = (-170 \pm 30) \text{ cm}^{-1}$. However, the functional form of the behavior of the fluorescence intensity ratio versus $P(\text{Ar})^{-1}$ found by Brashears and Setser¹⁸ is quite similar to the results shown in Fig. 2. They were able to interpret the minimum in this plot in terms of competition between vibrational relaxation in both the *B* and *C* states and *B*-*C* state transfer.

Thus, the energy splitting between the $B(\frac{1}{2})$ and $C(\frac{3}{2})$ states in xenon chloride is not such that stimulated emission may be readily produced on the $C(\frac{3}{2})$ - $A(\frac{3}{2})$ transition at 340 nm. Collisional coupling of the two close levels will lead to efficient extraction of the $C(\frac{3}{2})$ state population on the high gain $B(\frac{1}{2})$ - $X(\frac{1}{2})$ transition.

These results on the $B(\frac{1}{2})$ - $C(\frac{3}{2})$ state splitting in XeCl are consistent with a configuration interaction interpretation¹⁹ of the discrepancy between theoretical¹⁶ and experimental¹⁻³ results on the energy ordering of the excited states of XeF. In this model, configuration mixing between the $B(\frac{1}{2})$ and $X(\frac{1}{2})$ states leads to the relative increase in the $B(\frac{1}{2})$ state electronic energy, as well as the binding ($\sim 1200 \text{ cm}^{-1}$) in the $X(\frac{1}{2})$ state. Configuration mixing between the $C(\frac{3}{2})$ and $A(\frac{3}{2})$ states is weaker, with the net result that the $B(\frac{1}{2})$ state lies about 700 cm^{-1} above the $C(\frac{3}{2})$ state in XeF. These same configuration mixing effects appear to play a somewhat smaller role in the structure of XeCl. The binding energy of the $X(\frac{1}{2})$ state in XeCl is²⁰ only $\sim 280 \text{ cm}^{-1}$, and,

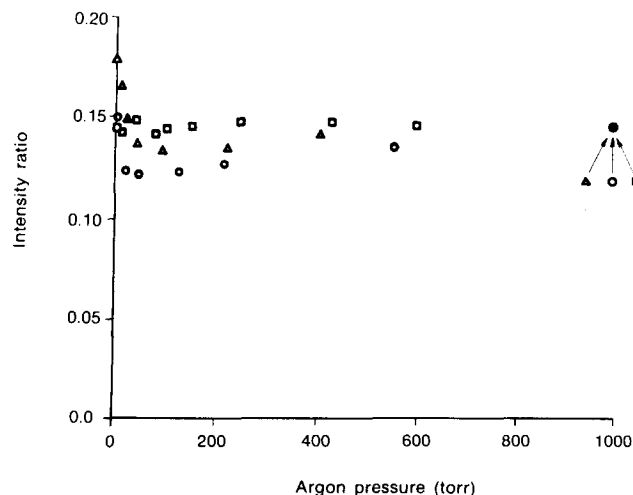


FIG. 2. Ratio of 340 nm band to 308 nm band fluorescence intensities in ArF* laser excited XeCl* plotted vs argon buffer gas pressure. Xenon pressure is 15 Torr. Boxes are data for 1 Torr Cl₂, triangles are data for 0.5 Torr Cl₂, and circles are data for 0.1 Torr Cl₂.

as has been demonstrated here, the $B(\frac{1}{2})$ and $C(\frac{3}{2})$ state energy ordering is in agreement with theory,¹⁶ but is of a much smaller magnitude ($\sim 25 \text{ cm}^{-1}$ experimentally as opposed to $\sim 560 \text{ cm}^{-1}$ theoretically).

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¹D. J. Kligler, H. H. Nakano, D. L. Huestis, W. K. Bischel, R. M. Hill, and C. K. Rhodes, *Appl. Phys. Lett.* **33**, 39 (1978).

²H. C. Brashears and D. W. Setser, *Appl. Phys. Lett.* **33**, 821 (1978).

³J. H. Kolts and D. W. Setser, *J. Phys. Chem.* **82**, 1766 (1978).

⁴W. K. Bischel, H. H. Nakano, D. J. Eckstrom, R. M. Hill, D. L. Huestis, and D. C. Lorents, *Appl. Phys. Lett.* **34**, 565 (1979); C. H. Fisher, R. E. Center, G. J. Mullaney, and J. P. McDaniel, *ibid.* **35**, 26 (1979); W. E. Ernst and F. K. Tittel, *ibid.* **35**, 36 (1979); R. Burnham, *ibid.* **35**, 48 (1979); N. G. Basov, V. S. Zuev, A. V. Kanaev, L. D. Mikheev, and D. B. Stavrovskii, *Sov. J. Quantum Electron.* **9**, 629 (1979).

⁵D. J. Kligler, D. Pritchard, W. K. Bischel, and C. K. Rhodes, *J. Appl. Phys.* **49**, 2219 (1978).

⁶C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. Circ. No. 467, Vol. 1 (U. S. G. P. O., Washington, D. C., 1949).

⁷D. J. Seery and D. Britton, *J. Phys. Chem.* **68**, 2263 (1964).

⁸A. A. Christodoulides, R. Schumacher, and R. N. Schindler, *J. Chem. Phys.* **79**, 1904 (1975); M. Rokni, J. H. Jacob, and J. A. Mangano, *Appl. Phys. Lett.* **34**, 187 (1979).

⁹M. R. Flannery and T. P. Yang, *Appl. Phys. Lett.* **32**, 327 (1978).

¹⁰C. A. Brau, in *Excimer Lasers*, edited by C. K. Rhodes (Springer, Berlin, 1979).

¹¹M. Rokni, J. H. Jacob, and J. A. Mangano, *Phys. Rev. A* **16**, 2216 (1977).

¹²J. N. Bardsley and M. A. Biondi, *Adv. At. Mol. Phys.* **6**, 2 (1970).

¹³J. E. Velazco, J. H. Kolts, and D. W. Setser, *J. Chem. Phys.* **65**, 3468 (1976).

¹⁴P. S. Julienne and M. Krauss, *Appl. Phys. Lett.* **35**, 55 (1979).

¹⁵D. C. Lorents, D. L. Huestis, M. V. McCusker, H. H. Nakano, and R. M. Hill, *J. Chem. Phys.* **68**, 4657 (1978).

¹⁶P. J. Hay and T. H. Dunning, Jr., *J. Chem. Phys.* **69**, 2209 (1978).

¹⁷J. Tellinghuisen, *Topical Meeting on Excimer Lasers* (Optical Society of America, Washington, D. C., 1979).

¹⁸H. C. Brashears and D. W. Setser (unpublished).

¹⁹M. Krauss, in Ref. 10.

²⁰A. Sur, A. K. Hui, and J. Tellinghuisen, *J. Mol. Spectrosc.* **74**, 465 (1979).