

## Theoretical calculation of pressure dependence of spontaneous emission spectrum from XeCl *B-X* transition

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### Abstract

By using a quasi-equilibrium model which indicates that all the rotational lines are emitting independently and are collision-broadened to the same Lorentzian width, the numerical simulation of the spontaneous emission spectrum originated from XeCl *B-X* transition is given to interpret the reversal of the spectral narrowing observed at high gas pressure. The technique employed in this paper is supposed to be suitable to other diatomic excimers as well.

**Key words:** excimers; spectrum.

### Introduction

Analysis of spontaneous emission spectrum has opened up a powerful way to study the potential curves of the electronic states in the Franck-Condon region as well, as the vibrational and rotational structure of the excimer molecules. Observations of the spectra under different gas pressures have generated a lot of interest. The one which was first carried out by Brau and Ewing<sup>[1]</sup> reveals wider spectral line width at low pressure discharges. This broadening occurs mostly on the short wavelength side, and has been interpreted as the ineffective vibrational relaxation in comparison with the excimer formation and radiation processes. In our recent experiments at pressures ranging from 0.6 to 14 atm., and current densities from 0.25 kA/cm<sup>2</sup> to 2 kA/cm<sup>2</sup> in dilute Ne/Xe/HCl and He/Xe/HCl mixtures<sup>[2]</sup>, we observed that the decreasing trend of the spectral line width stopped at a particular pressure  $P_r$ , at higher gas pressures, the fluorescence spectra tended to rebroaden. The reversal pressure  $P_r$ , defined as the

gas pressure where the spectral width of the fluorescence intensity envelope reaches its minimum value, is found to be relatively insensitive to the current density but quite sensitive to the gas mixture composition.

It is our purpose in this paper to numerically simulate the spontaneous emission spectrum originated from XeCl  $B-X$  transition and to interpret the observed characteristics of the spectral line width with the operating conditions, by using a quasi-equilibrium model which indicates that all the rotational lines are emitting independently and are collision broadened to the same Lorentzian width, the full width at half maximum of the XeCl  $B-X$  spontaneous emission as a function of the total gas pressure observed in Ref. [2] has been interpreted.

## §1. The Quasi-Equilibrium Model

In this section we confine ourselves to the XeCl  $B-X$  fluorescence spectrum with the strongest emission from the  $v'=0$  level and  $v'=1$  level in the XeCl  $B^2\Sigma_{1/2}$  state. As shown in Fig. 5 of Ref. [2], these traces show the spectral image density distribution of the strongest emission bands around  $\lambda=308$  nm. The bandhead locations for the various vibrational transitions  $v'$  to  $v''$  corresponding to the  $v'=0$  and 1 sequences are marked by vertical arrows above the traces. At high gas pressures, the emission states appear to be rotationally relaxed into a Boltzmann or near Boltzmann distribution, this assumption stands at least when no lasing occurs.

For a bound-bound transition, the spontaneous emission intensity from the rotational level  $J'$  with thermal equilibrium distribution and vibrational level  $v'$  to the rotational level  $J''$  with vibrational level  $v''$  can be evaluated as follows<sup>[3]</sup>:

$$I_{v'J'v''J''(e,f)} = \Omega V \frac{h^2 c^3 B'}{4\pi k T [T_{B(e,f)}^{v'J'} - T_{X(e,f)}^{v''J''}]} F_{v'J'v''J''}, \quad (1)$$

$$S_{J'J''} n_{Bv'} \exp\left(-\frac{B'K'_{(e,f)} - D' |K'_{(e,f)}|^2}{kT} hc\right),$$

where the subscript  $(e, f)$  are the results of the coupling of  $O$  and  $B$  states which gives four distinct branches  $R_e, R_f, P_e$  and  $P_f$  with the recommended notation of Brown et al<sup>[4]</sup>;  $F_{v'J'v''J''}$  is the Franck-Condon density for the transition  $(v'J')$  to  $(v''J'')$  which, as the function of the wavelength, was given in Table 1<sup>[5]</sup>. The symbol  $n_{Bv'}$  indicates the population of the vibrational level  $v'$  in the  $B$  state per cubic centimetre,

and

$$S_{J'J''} = \begin{cases} J'+1, & (P \text{ branch}) \\ J', & (R \text{ branch}) \end{cases} \quad (2)$$

$\Omega$  is the solid angle of the measurement of the spontaneous emission intensity.  $V$  is the discharge volume. According to Ref. [6], the term values of XeCl in the  $B$  and  $X$

Table 1 Franck-Condon Factors ( $\times 10^3$ ) for B-X system of XeCl. First entry is for  $N'=N''=0$ . Second is for  $N'=N''=50$

$v''$	$v'=0$	$v'=1$	$v'=2$	$v''$	$v'=0$	$v'=1$	$v'=2$
0	121 16	84 20	105 30	5	57 133	114 0	12 1
1	218 63	65 54	60 66	6	21 100	140 6	2 5
2	234 119	10 61	6 58	7	5 79	131 18	2 5
3	186 153	7 37	4 25	8	0 44	103 25	14 7
4	115 155	58 10	16 3				

states may be approximated as:

$$T_{B(e,f)}^{v''J'} = T_{eB}' + \omega_e(v'+1/2) - \omega_e x_e(v'+1/2)^2 + B'K'_{(e,f)} - D'|K'_{(e,f)}|^2 \quad (3)$$

and

$$T_{X(e,f)}^{v''N''} = T_{eX}' + \sum_{i=1}^4 C_{vi}''(v''+1/2)^i + B''K''_{(e,f)} - D''|K''_{(e,f)}|^2 + H''|K''_{(e,f)}|^3, \quad (4)$$

where  $T'_{eB}$  and  $T'_{eX}$  are electronic parameters, for XeCl,  $T'_{eB} = 3240.8 \text{ cm}^{-1}$  and  $T'_{eX} = 0$ .  $\omega_e$  and  $\omega_e x_e$  are the vibrational parameters, for B state,  $\omega_e = 195.17 \text{ cm}^{-1}$ , and  $\omega_e x_e = 0.543 \text{ cm}^{-1}$ , and

$$K'_{(e,f)} = J'(J'+1) \pm \frac{1}{2} \delta \left( J' + \frac{1}{2} \right), \quad (5)$$

the rotational constant  $B' = 0.0669 \text{ cm}^{-1}$ , the centrifugal distortion constant  $D' = 3.2 \times 10^{-8} \text{ cm}^{-1}$ , and the splitting constant  $\delta = 2.0$ . For XeCl X state we have

$$\left. \begin{aligned} K''_e &= N''(N''+1) - 0.4N'', \\ K''_g &= N''(N''+1) + 0.4(N''+1), \end{aligned} \right\} \quad (6)$$

the vibrational parameters of X state  $C_{vi}''$  for  $i=1$  to 4 are  $26.22 \text{ cm}^{-1}$ ,  $0.321 \text{ cm}^{-1}$ ,  $-0.0853 \text{ cm}^{-1}$  and  $0.00191 \text{ cm}^{-1}$ , respectively. Since the X state of XeCl is a weak bounded level, the internuclear distance and consequently the moment of inertia of the nonrigid rotator are changing during the vibration, the interaction of vibration and rotation must be taken into consideration. This effect was discussed by Pauling and Wilson<sup>[7]</sup> using wave-mechanical calculations to a first approximation. Designating the quantities corresponding to energy levels measured from the point of equilibrium internuclear by the subscript  $e$ , the rotational constant  $B''$ , the first centrifugal distortion constant  $D''$  and the second centrifugal distortion constant  $H''$  in the vibrational level  $N''$  can be given by:

$$B'' = B_e - \alpha_e \left( v + \frac{1}{2} \right) + \alpha_e'' \left( v + \frac{1}{2} \right)^{1/2} + \dots,$$

$$\left. \begin{aligned} D'' &= D_0 + \beta'_e \left( v + \frac{1}{2} \right) + \dots, \\ H'' &= H_0 + \gamma'_e \left( v + \frac{1}{2} \right) + \dots, \end{aligned} \right\} \quad (7)$$

where

$$\left. \begin{aligned} \alpha'_e &= \frac{6\sqrt{\omega_e \gamma_e} B_0^3}{\omega_e} - \frac{2B_0^2}{\omega_e}, \\ \beta'_e &= D_0 \left( \frac{8\omega_e \gamma_e}{\omega_e} - \frac{5\alpha'_e}{B_0} - \frac{\alpha'^2_e \omega_e}{24B_0^2} \right), \end{aligned} \right\} \quad (8)$$

The value of  $\alpha'$  and  $\gamma'_e$  for XeCl  $X$  state can be obtained by interpolating the measured values corresponding to zeroth and twelfth vibrational levels.

Where  $\omega_e = 26.27 \text{ cm}^{-1}$ ,  $\omega_e \gamma_e = 0.278 \text{ cm}^{-1}$ ,  $B_0 = 0.056 \text{ cm}^{-1}$ ,  $B_{12} = 0.0274 \text{ cm}^{-1}$ ,  $D_0 = 9.7 \times 10^{-7} \text{ cm}^{-1}$ ,  $D_{12} = 1.9 \times 10^{-6} \text{ cm}^{-1}$ ,  $H_0 = -2.0 \times 10^{-11} \text{ cm}^{-1}$  and  $H_{12} = -1.8 \times 10^{-10} \text{ cm}^{-1}$  for XeCl  $X$  state in following calculation.

Within the random phase approximation, these spectral lines from the different vibrational and rotational levels are additives and overlap each other. According to our quasi-equilibrium model which indicate that all the rotational lines are emitting independently and are collision-broadened to the same Lorentzian width. Thus the spontaneous emission intensity at a given wavelength near 308 nm is a superposition of the contributions from all possible rotational transitions if there is no correlation among them at all. The spontaneous intensity at wavelength within  $d\lambda$  can be expressed by a fivefold summation.

$$I(\lambda) d\lambda = \frac{V h^2 \nu^3 B' \Omega}{2\pi^2 k T \Delta\nu_c} \sum_{v''=0}^{v''_{\max}} n_{Bv''} \sum_{v''=0}^{v''_{\max}} \sum_{J'=1}^{J'_{\max}(v'')} \left[ \sum_{N''=J'-1}^{N''=J'+1} \sum_{(e,f)} F_{e'J'v''N''} \frac{S_{J'N''} \exp\left[-\frac{B'K'_{(e,f)} - D' |K'_{(e,f)}|^2}{kT}\right]}{1 + (2c/\Delta\nu_c)^2 \left(\frac{1}{\lambda} - T'_{B(e,f)} + T'_{X(e,f)}\right)^2} \right], \quad (9)$$

where the maximum rotational quantum number

$$J'_{\max}(v'') = N''_{\max}(v'') \pm 1 \quad (10)$$

being a function of the vibrational quantum number  $v''$  of the  $X$  state.  $\Sigma'$  means the summation except  $N'' = J'$ .  $\Delta\nu_c$  is the line width, we use impact approximation for low gas pressure<sup>[9]</sup> and statistical approximation<sup>[10]</sup> for high gas pressure in our calculation.

## § 2. Computational Results and Discussion

The computational results of the fluorescence intensity versus the emission wavelength at various gas pressures are plotted in Fig. 1. The discharge current density is fixed at 500 A/cm<sup>2</sup>, and the gas mixture used is Ne/Xe/HCl = 989/10/1.

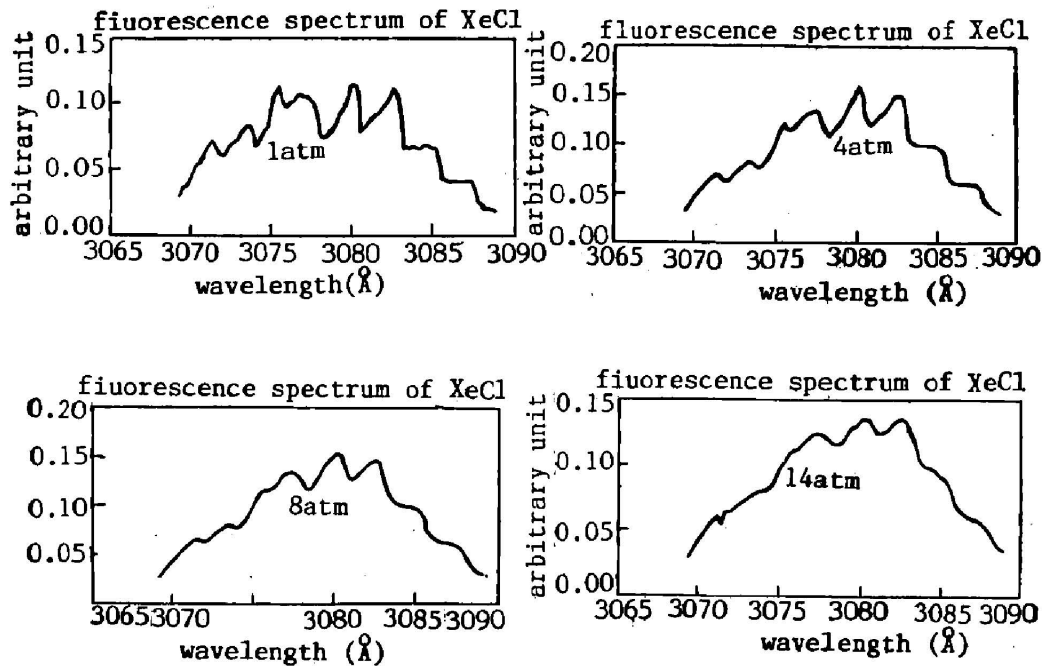


Fig. 1 Computer simulations of the spontaneous emission spectra of XeCl at different gas pressures. The discharge current density  $j$  is fix at  $500 \text{ A/cm}^2$ , and the mixture used here is Ne:Xe:HCl=989:10:1

A pressure dependence of the full width at half maximum (FWHM) of the XeCl excimer  $B^2\Sigma_{1/2} - X^2\Sigma_{1/2}$  spontaneous emission intensity which was directly calculated from the simulated spectrum calculation is shown in Fig. 2. For comparison, the experimental data observed in our recent experiment<sup>[2]</sup> are also designated here.

The experimental arrangement for generating the emission spectrum is a homogeneous pulsed avalanche/self-sustained discharge of approximately 200 ns duration. The discharge is produced inside an X-ray preionized high pressure chamber of about 8 cm inside diameter and 7 cm maximum interior height. The aluminum anode and cathode are of relatively large outer diameter but the geometry and cross-sectional area of the discharge are precisely controlled within the central uniform-field region by the aperture opening of the X-ray preionization source. In the present experiment, the cross-sectional area of the discharge column is about  $1 \text{ cm}^2$  and the total discharge volume is fixed at 0.5

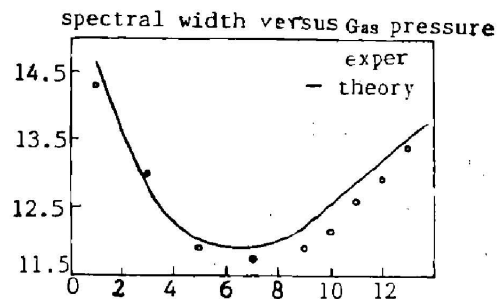


Fig. 2 Full width at half-maximum intensity of the XeCl B-X spontaneous emission as a function of the total gas pressure observed in the small-volume discharge with  $j$   $500 \text{ A/cm}^2$ . The gas mixture is of initial mol ratio Ne:Xe:HCl=989:10:1

cm<sup>3</sup>. The time-integrated spectra are recorded on Polaroid type 665 films using the sampling camera provided by the Spex Model 1401 spectrometer. The details for determination of spectral width from the time-integrated spectrum can be found in Ref. [2].

The computational and experimental results in Fig. 2 represent the same trend of the functional relationship which shows the band shifting toward the blue at low gas pressure. This is the consequence of the finite vibrational relaxation rates which reduce the relative population of the  $v'=0$  level and subsequently the contributions from 0 to  $v''$  sequence.

In addition, Fig. 2 shows a re-broadening of the spectra at gas pressures higher than  $P_r$ . This phenomenon is interpreted as the result of collisional broadening including a red shift of all the rotational lines.

At low gas pressure, the impact approximation is valid, either the Lorentzian width or the shift of the spectral lines displays a linear function of  $P$ . The dominate factor of determining the spectral breadth should be the vibrational relaxation process. Conversely, when gas pressures are sufficiently high, the statistical broadening mechanics becomes considerable. Both the width and the shift enhance rapidly with gas pressure according to a square-law. This does not affect the intensity distribution at any wavelength homogeneously. In fact, at the region where the rotational lines are more densely distributed, the effect of gas pressure broadening appears stronger. The macroscopic consequence is that the emission spectrum shows a re-broadening of the intensity envelop.

Recognizing the fact that the mean thermal speed of the dilute gas  $\bar{V}_{He} > \bar{V}_{Ne}$  at the same translational temperature, it is not difficult to see that the reversal pressure  $P_r$  would be reduced if Helium is used in place of Neon as the diluent gas at otherwise identical condition. This phenomenon is also indicated by the experimental observations as was shown in Ref. [2].

There are a couple of causes that produce broadening of the spectral line associated with the discharge current density. First of all, the rate of changes the translational temperature at a fixed gas pressure increase with the electron number density almost linearly. The higher temperature, in turn, favors wide spectrum because of more frequency collisions with the perturbers, faster dissociation of the lower energy level, and elevated population in vibrationally and rotationally excited levels. The breadth of the spectrum also comes from electron broadening. In principle, the impact approximation is always applicable in the treatment of electron perturbers<sup>[11]</sup>.

However, a number of complications such as inelastic collisions as well as overlapping lines would be involved if any kind of accuracy is demanded of the theory. Here we merely consider two limiting cases: The one which assumes every collision is

inelastic, and another one which assumes all collisions are elastic. The difference between these two limits is essentially negligible. In regard to a Ne/Xe/HCl gas mixture of 10 atm., the calculated results are shown in Fig. 3. For comparison, the experimental data corresponding to current densities of 0.25 kA/cm<sup>2</sup>, 0.5 kA/cm<sup>2</sup> and 2 kA/cm<sup>2</sup> (after Ref. [2]) are also plotted. The result shows that our calculated curve is in good agreement with that of the experiment.

In conclusion, numerical simulation of the spontaneous emission originated from XeCl B-X transition is given to interpret the observed characteristics of the spectral linewidth from 0.6 to 14 atm. The technique employed in this paper is supposed to be suitable to other diatomic excimer systems as well.

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### XeCl B-X 跃迁自发辐射谱压力关系的理论计算

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### 提 要

采用假定所有旋转能级独立辐射和碰撞加宽劳伦茨线宽的准平衡模型, 对 XeCl B-X 跃迁自发辐射谱进行了数值模拟计算, 从而解释了高压下谱线的加宽现象。本文采用的方法还可适用于其它双原子准分子。

关键词: 准分子; 光谱。

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spectral width versus current density

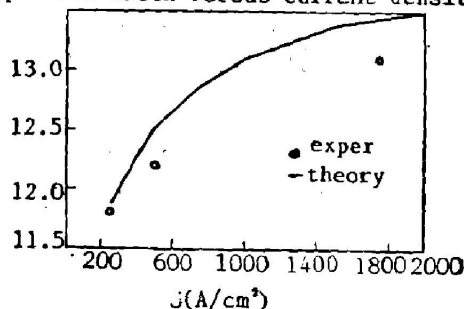


Fig. 3 FWHM of the XeCl B-X spontaneous emission as a function of the discharge current density