

DYNAMICS OF THE B $^3\Pi(0_u^+)$ AND A $^3\Pi(1_u)$ STATES OF CHLORINE BY LASER INDUCED FLUORESCENCE

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Chlorine B $^3\Pi(0_u^+)$ state lifetimes have been measured by laser-induced fluorescence in several predissociated ($v' = 14-19, 21$) and non-predissociated ($v' = 5-12$) levels. Trial and error Franck-Condon calculations have been performed to check the nature and position of the predissociating state. The results have been used to give a value of R_e for the A $^3\Pi(1_u)$ state responsible for predissociation, $R_e = 2.48 \pm 0.01 \text{ \AA}$. The obtained data show that interference effects due to crossing between B and A states modify the lifetimes of the B state appreciably. The inadequacy of the low-lying vibrational levels region, i.e. $v' < 8$, to measure the radiative lifetime of the B state ($\tau_R(B)$) is shown. Previous values for $\tau_R(B)$ can therefore be affected by considerable errors.

1. INTRODUCTION

The great variety of chemiluminescent and photochemical properties exhibited by the diatomic halogens and interhalogens¹⁻³ has motivated extensive spectroscopic and dynamic studies of their excited electronic states.^{1,4-6} The B $^3\Pi(0_u^+)$ and $^3\Pi(1_u)$ states of chlorine are responsible for the photochemistry of chlorine atoms, initiated through predissociation or optical dissociation of Cl_2 at wavelengths $\lambda < 500 \text{ nm}$, and extensive quantum-resolved dynamics of the B $^3\Pi(0_u^+) - X^1\Sigma_g^+$ and continuum absorption systems have been carried out.^{1,5,6}

The B $^3\Pi(0_u^+)$ excited state is one of the five non-degenerate states of Cl_2 that have the low-lying valence-shell configuration designated 2431 by Mulliken.⁷ Other state is the $^1\Pi(1_u)$, repulsive and correlating with $\text{Cl } ^2P_{3/2} + \text{Cl } ^2P_{3/2}$ atoms, as do the other 2431 states except the B state, which correlates to $\text{Cl } ^2P_{1/2} + \text{Cl } ^2P_{3/2}$. The three remaining states of the 2431 configuration are the A $^3\Pi(1_u)$, $^3\Pi(0_u^-)$ and $^3\Pi(2_u)$, but information about them is scarcer. The left-hand limb of the potential energy curve of the $^1\Pi(1_u)$ state is known from work on the absorption continuum of Cl_2^1 and from the photofragment spectrum of chlorine.⁸ Recently, spectroscopic constants for the lower vibrational levels of the A state have been obtained⁹ for the first time by means of optical-optical double resonance experiments.

The spectrum of the B-X system of chlorine is particularly simple in appearance

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and can be easily resolved. Lifetime measurements by laser induced fluorescence (LIF) in the B state indicate the presence of a strong rotationally dependent heterogeneous predissociation for the $v' > 12$ levels.¹⁰⁻¹² The lifetime data at zero pressure give good agreement to the relationship

$$1/\tau_0 = 1/\tau_\infty + k_v J'(J' + 1), \quad (1)$$

where τ_0 is the collision-free lifetime, k_v the predissociation constant for the v' level, J' the rotational level of the upper state, and τ_∞ the lifetime for $J' = 0$ which, in the absence of any other perturbation, should be equal to the radiative lifetime of the B state. Determinations of the B state radiative lifetime by LIF were carried out by Clyne and McDermid¹³ and Clyne and Martinez,¹⁴ giving a final value of $\tau_R = 305 \mu\text{s}$, measured in the $v' = 5$ level. However, the long lifetimes of Cl_2 present serious diffusion problems, and the former value can be regarded as an estimation.

The selection rules for non-radiative transitions limit the possible states responsible for predissociation of the B state to the $^1\Pi(1_u)$ and $A \ ^3\Pi(1_u)$ states. The values of the measured predissociation constants k_v decrease smoothly with increasing v' ,¹² but calculations for the B- $^1\Pi$ system show that the predissociation probability exhibits a strong oscillating behaviour with v' .¹⁵ This fact is sufficient to exclude the $^1\Pi$ state as responsible for the observed predissociation. Calculations¹⁵ showed that the A state provided the dissociative channel, concluding that the repulsive branches of the A and B states should cross below the dissociation limit to chlorine ground state atoms, which is below the $v' = 13$ level of B. In that case, it would be reasonable that nonradiative processes between both states were very efficient, especially in the crossing zone, not defined with precision yet. This should affect the radiative lifetimes of the B state, showing variations with v' and J' , due to the relatively great differences in lifetimes between both states: the predicted radiative lifetime of the A state is about 15 ms,¹ which is much higher than the estimate of 0.3 ms for the B state.

Very few data can be found in the literature about lifetimes of $\text{Cl}_2(\text{B})$ and their rovibrational dependence for non-predissociated levels. In that way, the study of the $5 \leq v' \leq 12$ region is thought to be of interest, where the crossing with the A state is expected to occur. In this work lifetime measurements of these excited states by LIF are presented, in order to clarify the A-B crossing region; a study of the predissociated levels $v' \geq 13$ has also been carried out, which should permit the obtention of a more consistent group of data, to contrast with those obtained for non-predissociated levels.

2. EXPERIMENTAL

The basic experimental setup has already been described in previous works.¹⁶ Chlorine excitation was first carried out by means of a dye laser (Quantel TDL IV) pumped by the second harmonic (532 nm) of a Nd-YAG laser (Quantel 481C). The dye laser gave pulses of 15 ns duration with a linewidth of 0.08 cm^{-1} . Alternatively, a second more energetic dye laser was used (Lambda Physik FL 3002E) pumped by an excimer laser (Lambda Physik EMG 200E), giving pulses of several mJ of energy (20 ns FWHM, linewidth 0.2 cm^{-1} , which could be narrowed up to 0.04 cm^{-1} by means of a Fabry-Perot etalon). Methanolic solutions of several dyes (Coumarin 500,

Fluorescein 548, and Coumarin 480, from Exciton Co.) covered the studied spectral range (465–570 nm).

Chlorine of natural isotopic abundance was used (Matheson 99.99%), and was deoxygenated and purified by vacuum distillation before use. Pressure in the fluorescence chamber was controlled by a capacitance manometer (MKS Baratron 222B), operating in the $10\text{--}10^{-3}$ Torr range. The excitation-fluorescence cell was made of pyrex glass, with 25 cm long and 12 cm diameter, in order to minimize diffusion problems as much as possible. Nevertheless, these dimensions are still probably insufficient to measure the longest lifetimes of the B state accurately, as will be discussed later.

Laser excitation spectra were recorded by detecting the total induced fluorescence by means of a high-gain, fast photomultiplier (EMI 9816B) and using a boxcar integrator (Stanford Research Systems SR250). Cut-off filters were interposed between the fluorescence cell and the photomultiplier to block scattered laser light. A Tektronix digital oscilloscope acquired the fluorescence decays from the photomultiplier output. Fluorescence lifetimes were obtained after averaging and processing the signals with a microcomputer connected to the system.

3. RESULTS

For the study of non-predissociated levels, excitation spectra of the bands ($v'-v''$) 5-1, 5-2, 6-2, 7-2, 8-2, 8-3 and 12-0 were obtained and assigned. The diatomic isotopic species present in natural chlorine are $^{35}\text{Cl}^{35}\text{Cl}$ (57% abundance), $^{35}\text{Cl}^{37}\text{Cl}$ (37%) and $^{37}\text{Cl}^{37}\text{Cl}$ (6%), and our measures refer only to $^{35}\text{Cl}_2$. The spectra were recorded typically at a total pressure of 50 mTorr of chlorine. Figure 1 shows a laser excitation spectrum of the 6-2 band as an example. Recent spectroscopic data for the B and X states^{17,18} and Franck-Condon factors¹⁹ were used for this purpose. In the predissociated levels, the studied bands were 14-0 to 19-0 and 21-0. Due to the strong predissociation, these bands show very weak intensities in LIF, and chlorine pressures near to 1 Torr were necessary to record the spectra. These bands showed an extremely simple structure: only lines with low J' values could be observed ($J' \leq 12$), the maximum fluorescent intensities corresponding to J' values near the band head. Overlapping between different bands was nearly absent, making assignment rather simple.

Fluorescence lifetimes were measured by tuning the laser wavelength to a ($v'J'$) \leftarrow ($v''J''$) overlap-free absorption line and detecting the fluorescence decay from the excited level. For the non-predissociated levels, each ($v'J'$) level was measured at different chlorine pressures, in order to give zero-pressure lifetimes (τ_0) and self-quenching rate constants (K_{Cl_2}) by means of Stern-Volmer (S-V) plots. The selected pressure interval was typically 0.5–10 mTorr, in order to minimize collisional effects, which are known to cause important energy transfer processes in chlorine, especially upward $V-V$ transfer to predissociated levels for $v' \geq 9$.²⁰ The Stern-Volmer plots were linear in the studied intervals.

Table 1 shows the obtained results for the non-predissociated levels, and also for

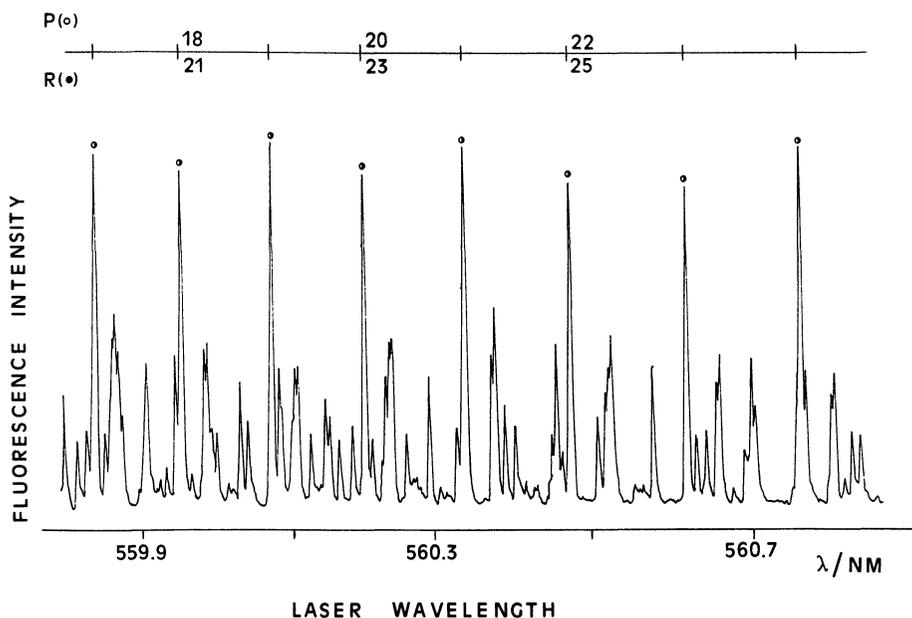


Figure 1 Laser excitation spectrum of the 6-2 band of Cl_2 (B-X), showing the assignment of the 35-35 isotope. Note accidental overlapping of $P(J)$ and $R(J+3)$ lines.

the $J' = 0$ line of $v' = 19$, which is not affected by predissociation. For $v' = 6$, it was not possible to resolve the $P(J) + R(J+3)$ doublets, but the mixed decay was monoexponential, indicating that lifetimes from J' and $J' + 5$ are practically equal. The same kind of features were observed in the $v' = 12$ level. Errors in the lifetimes were estimated by making several measurements in the same line at the same pressure and considering the fluctuations. Looking at the data of *Table 1*, it can be seen that there is no appreciable dependence of τ_0 with J' , the differences falling within the experimental error. A smooth variation of τ_0 with v' can be appreciated, lifetimes going up from $v' = 5$ to $v' = 7$, here showing a maximum and decreasing softly from here on. The higher value for $v' = 19$ has a greater experimental error associated, so it cannot be considered to be in contradiction with the trend of the rest of the levels. This behaviour will be discussed later. Self-quenching rate constants present a very uniform behaviour in the lower levels ($v' = 5-8$), with an average value of $K_{\text{Cl}_2} = (3.38 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. This value is highly increased for $v' \geq 12$, in accordance with the $V-V$ transfer mechanism already mentioned. Our zero-pressure lifetimes are substantially different from the estimated value of Clyne and Martinez of $305 \mu\text{s}$ for $v' = 5$;¹⁴ this can be attributed to the insufficient dimensions of our cell to measure adequately the lifetimes of the B state. Nevertheless, the chamber accounts for relative variations of the lifetimes.

Lifetime measurements were also performed for various J' in the predissociated levels cited above. Due to the extremely low fluorescence intensity, higher pressures had to be employed, making lifetime measurements systematically at $P_{\text{Cl}_2} \approx 50 \text{ mTorr}$.

Table 1 Zero pressure lifetimes and self-quenching constants ($M = \text{Cl}_2(X)$) for different rovibrational levels of $^{35}\text{Cl}_2$ B state

v'	J'	$\tau_0(\mu\text{s})$	$k_M \times 10^{11}$ ($\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$)
5	16	100 ± 12	3.59 ± 0.6
	24	139 ± 15	3.24 ± 0.4
	25	112 ± 14	4.00 ± 0.5
6	12 + 17	141 ± 4	3.41 ± 0.2
	19 + 24	156 ± 10	3.22 ± 0.4
	26 + 31	141 ± 3	3.36 ± 0.1
	32 + 37	140 ± 8	3.03 ± 0.3
7	2	164 ± 8	3.26 ± 0.2
	14	189 ± 6	3.47 ± 0.1
	24	181 ± 4	3.73 ± 0.1
	40	175 ± 25	3.78 ± 0.4
8	18	144 ± 10	3.52 ± 0.2
	26	137 ± 8	2.38 ± 0.3
12	0 + 4	112 ± 7	68.8 ± 1.0
	8 + 12	125 ± 15	63.1 ± 2.0
19	0	170 ± 70	85.0 ± 2.6

For these levels, pressure effects are almost negligible, as predissociation is clearly dominant. Lifetime measurements for different J' levels gave satisfactory fits to Eq. (1). Figure 2 shows the linear plots of τ_0^{-1} vs. $J'(J' + 1)$ for the $v' = 16$ -19 levels, and $k_{v'}$ values were obtained from their slopes. The obtained results are shown graphically in Figure 3. The concordance with Clyne's values¹² is qualitatively good, although slight differences are more evident for the lower v' values.

4. DISCUSSION

The nonradiative predissociation rate A_{nr} of a given bound level can be expressed by:^{21,22}

$$A_{nr} = (2\pi/\hbar) |\langle \Psi_c | H' | \Psi_b \rangle|^2, \quad (2)$$

where Ψ_c and Ψ_b are the wavefunctions of the continuum (predissociating) and bound states, respectively, and H' the operator responsible for the perturbation. It is irrelevant whether the predissociating state is completely repulsive or partly attractive. This last case is the one observed in chlorine. Anyway, here we adopt the usual notation, designing the predissociating state as "continuum". When the potential curves of both states intersect, the Franck-Condon principle can be applied, and Eq. (2) becomes

$$A_{nr} = k_{v'} J'(J' + 1) = k' P_{v'} J'(J' + 1), \quad (3)$$

with $k' = (\hbar^2/4\mu^2 c) |W_e(\bar{R})|^2$; $P_{v'} = |\langle \chi_c | R^{-2} | \chi_b \rangle|^2$, where μ is the reduced mass, c is the velocity of light, R is the internuclear distance, χ_c and χ_b are the vibrational

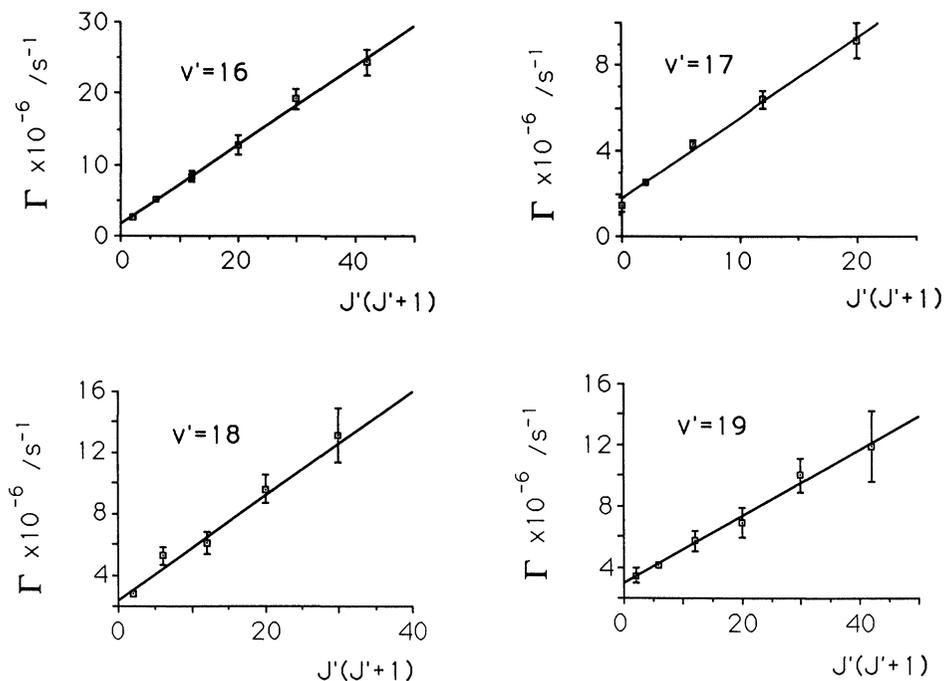


Figure 2 Dependence of $\Gamma (= \tau_0^{-1})$ with $J'(J'+1)$ in $^{35}\text{Cl}_2(\text{B})$ for the vibrational levels shown. The $k_{v'}$ values are as follows (units in s^{-1}): $k_{16} = 5.69 \times 10^5$; $k_{17} = 4.00 \times 10^5$; $k_{18} = 3.77 \times 10^5$; $k_{19} = 2.24 \times 10^5$.

wavefunctions of the continuum and bound states, respectively, $W_e(\bar{R})$ is a dimensionless quantity involving only electronic operators and coordinates, \bar{R} being the transition R -centroid, and $P_{v'}$ is the predissociation probability. Near the crossing point, the R variation is expected to be negligible, and its value can be approximated by R_c , the crossing point value, and $P_{v'}$ can be given by

$$P_{v'} = |\langle \chi_c | R^{-2} | \chi_b \rangle|^2 \simeq R_c^{-4} |\langle \chi_c | \chi_b \rangle|^2, \quad (4)$$

where the overlap integral $|\langle \chi_c | \chi_b \rangle|^2$ is known as the Franck-Condon density (FCD) between both states.

Franck-Condon density calculations were performed for the A-B system. In order to obtain information about the location of the predissociating state: starting from the experimental vibrational dependence of $k_{v'}$ with v' (Figure 3), trial and error calculations are made, assuming different functional forms from the potential of the A state, until experimental and calculated values agree satisfactorily. Two different programs were used for this purpose: the first one, based on purely quantum calculations, solves Schrödinger's equation numerically, making use of Numerov's method²³⁻²⁶ to obtain the wavefunctions. Franck-Condon densities are then simply evaluated by numerical integration. The spectroscopic constants for the B state potential were those given by Coxon.¹⁷ For the A state, the constants were those

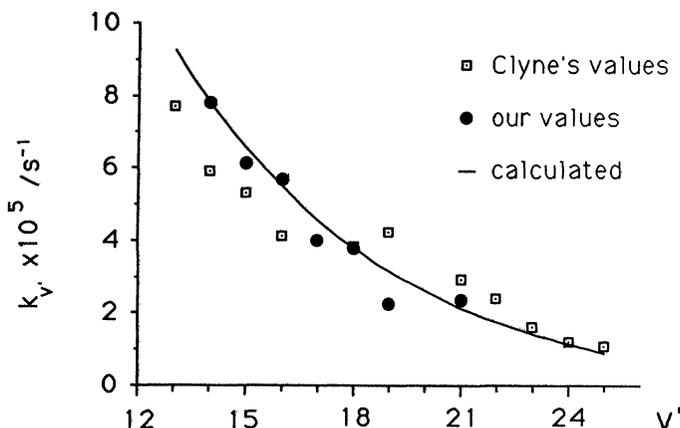


Figure 3 k_v , vs. v' plot for the predissociated levels of $\text{Cl}_2(\text{B})$; Clyne's values are also shown. The full curve corresponds to Franck-Condon density calculations.

from the recent work of Ishiwata *et al.*,⁹ thought to be valid for $3 \leq v' \leq 8$ and $1 \leq J' \leq 15$ of the A state. The optimum integration step and interval were found to be 0.005 and 1.6–9.0 Å respectively. Alternatively, semiclassical calculations were performed, based on the WKB approximation, giving good agreement with quantum calculations. Here the results were extended to the non-predissociated levels. The details of this method and its limitations can be found, for example, in Ref. (27) FCD calculations for the $\text{B}^{-1}\Pi$ system were also performed, and the FCD vs. v' pattern proved to be strongly oscillating, thus confirming that the repulsive curve cannot predissociate the B state.

An RKR curve was calculated for the A state, based on the vibrational constants of Ishiwata *et al.* The parameter in the A state curve more sensitive to changes in FCDs was R_e , the internuclear distance, whose value is not known precisely. Figure 4 shows the results of the vibrational dependence of FCDs, both quantum and semiclassical, for different values of $R_e(\text{A})$. The best fit to the data of Figure 3 corresponds to $R_e(\text{A}) = 2.48 \text{ \AA}$, the values of 2.47 and 2.49 Å being also reasonable. FCD values corresponding to $R_e > 2.49 \text{ \AA}$ show a faster decreasing behaviour, giving a worse adequation to our experimental data. On the other hand, FCDs for $R_e < 2.47 \text{ \AA}$ show a very slow decreasing trend, almost linear. Thus, the best adequation is found to be for $R_e = 2.48 \pm 0.01 \text{ \AA}$. Our value is in good agreement with Heaven and Clyne's former value of 2.46 Å,¹⁵ based simply on a Morse potential for the A state.

This result leads to the conclusion that the repulsive branches of A and B curves must cross in the $v' = 2-8$ region of the B state, with both branches practically parallel. Other authors consider this curve crossing unsatisfactory, proposing values of $R_e(\text{A})$ close to 2.43 Å,^{28,29} for which the B curve is completely "inserted" in the A curve. But this value produces a worse adequation to our FCD values, and our result of 2.48 Å is to be preferred. According to this R_e value and looking at Figure 4, we

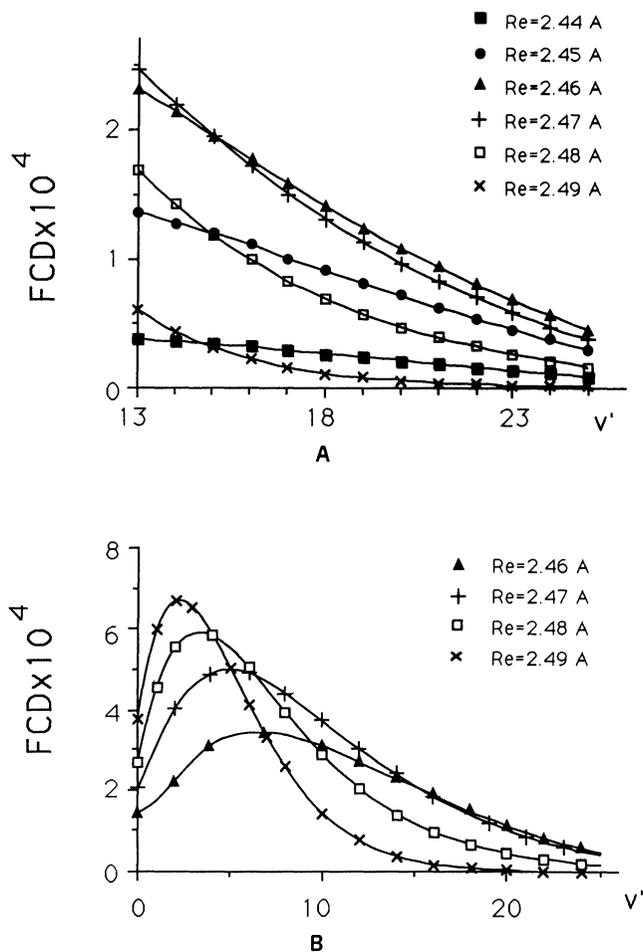


Figure 4 Variation of FCD with v' for the B-A system of Cl_2 : (a) quantum calculations; (b) semiclassical results, extended to non-predissociated levels. Note that different interval of v' levels is shown in (a) and (b).

must admit the fact that Franck-Condon densities show a maximum around $v' = 2-8$ of B state. This should allow the existence of lifetime variations with v' in the B state. From the data of *Table 1*, we can observe the existence of smooth lifetime variations, with a maximum around $v' = 6-7$, and decreasing from here on. The value for $v' = 19$ must be considered carefully, since the error associated to this measure is due to the great K_{Cl_2} value, which leads to uncertainties in the evaluation of τ_0 from the S-V plot, and the fact that the $P(1)$ line has a very weak fluorescence intensity. The value of $170 \pm 70 \mu\text{s}$ is therefore consistent with the general decreasing behaviour. Though the quantification of this effect is not feasible due to uncertainties in the absolute values of lifetimes, a qualitative explanation of how lifetimes correlate with FCDs for non-predissociative levels may be illustrative.

The interaction of the A and B curves can be considered to produce a mixing

between both electronic states, $|A\rangle$ and $|B\rangle$, yielding two new states, one of higher energy, here designated $|+\rangle$, and the other with lower energy, $|-\rangle$. These new states can be expressed as a linear combination of the primitive ones:

$$|+\rangle = C_{B+}|B\rangle + C_{A+}|A\rangle, \quad |-\rangle = C_{A+}|B\rangle + C_{B+}|A\rangle,$$

with the normalization condition

$$C_{A+} = \pm(1 - C_{B+}^2)^{1/2}.$$

In such a case, it can be stated that two “new” lifetimes appear, τ_+ and τ_- , their values being³⁰

$$\tau_+ = \left(\frac{C_{A+}^2}{\tau_A^0} + \frac{C_{B+}^2}{\tau_B^0} \right)^{-1}; \quad \tau_- = \left(\frac{C_{B+}^2}{\tau_A^0} + \frac{C_{A+}^2}{\tau_B^0} \right)^{-1}, \quad (5)$$

where τ_A^0 and τ_B^0 are the lifetimes of the “pure” A and B states. For chlorine, if we assume the estimations of $\tau_R(B) = 0.3$ ms and $\tau_R(A) = 15$ ms¹, we can consider $\tau_A^0 \gg \tau_B^0$ and Eq. (5) can be simplified to give

$$\tau_+ \simeq \tau_B^0 / C_{B+}^2. \quad (6)$$

As the strength of the perturbation is more intense, the value of C_{B+}^2 will go away from 1 (its maximum value, in absence of interaction); thus, Eq. (6) indicates that the zone where the interaction is more intense will lead to longer lifetimes of the “new” B state: the bigger the FCD value is (and also the magnitude of the perturbation) the more the value of C_{B+}^2 will deviate from 1. This can explain the slow variations in lifetimes with v' in *Table 1*.

Consequently, lifetime measurements in the $v' \simeq 5$ zone of the B state leading to establish its radiative lifetime may result in considerably errors in τ_R , as this zone is most intensely affected by the interaction with the A state. Thus, the value of $\tau_R(B) = 305 \mu\text{s}$ by Clyne *et al.* may be an overestimation. Other values in the literature support this affirmation: in the work of Kernashitskii *et al.*³¹ a value of $\tau_R(B) = 50 \mu\text{s}$ is derived for $v' = 0$ from Cl_2 chemiluminescence measurements in a supersonic nozzle. According to our results, the $v' = 0$ level would exhibit less perturbation effects and a measurement for $v' = 0$ would yield a more accurate radiative lifetime, but absorption to this level is negligible to be considered in LIF. More recent values for $\tau_R(B)$ exist in the literature. Billy *et al.*³² have reported the values of 1200, 50 and $150 \mu\text{s}$ for $v' = 12, 13$ and 24, respectively, using a supersonic beam of chlorine. They attributed the variations in lifetimes to hyperfine predissociation, but a more detailed analysis of their data is necessary, as such large variations between adjacent vibrational levels are not expected to occur. Another evidence of lifetime variations within the B state can be found in the values for the $v' = 7$ -12 levels measured by Clyne and McDermid,¹³ giving $\tau_0 \simeq 85 \mu\text{s}$, well below from $300 \mu\text{s}$ (though these values are suspect of being too low, principally due to the insufficient dimensions of the fluorescence chamber).

In accordance with our model, the lifetime measurement for $v' = 19$ must provide a lower limit for the lifetimes of the B state. Though our value of $170 \pm 70 \mu\text{s}$ is probably an overestimation, and the real one should be closer to our values for $v' = 8$ and 12, which are more precise. The value of Clyne and Martinez of $305 \mu\text{s}$ should

be an upper limit, corresponding to the high interaction region with the A state. Anyway, it can be worthwhile to remark that this value is an extrapolation, since the longest measured lifetime was 250 μs at the lowest pressure.¹⁴

In conclusion, lifetime measurements from LIF of the B state of chlorine must be considered with great care: due to the coupling of the B and A states, electronic conversion from the B state to other components of the $^3\Pi$ multiplet must be taken into account. The value of the radiative lifetime of the B state still remains uncertain, but should be below the estimation of 305 μs . The most adequate levels to measure it in LIF would be those far away from the maximum in Figure 4, where the interaction with the A state is expected to be lower.

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