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► To cite this version:

N. Billy, G. Gouédard, B. Girard, Jacques Vigué. Lifetimes and predissociations in the Cl₂ B-state. Journal de Physique II, 1991, 1 (3), pp.323-342. 10.1051/jp2:1991171 . jpa-00247521

HAL Id: jpa-00247521

<https://hal.science/jpa-00247521>

Submitted on 1 Jan 1991

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Classification

Physics Abstracts

33 70F — 33 80G

Lifetimes and predissociations in the Cl₂ B-state

N. Billy, G. Gouédard, B. Girard and J. Vigué

Laboratoire de Spectroscopie Hertzienne (*), Département de Physique de l'ENS, 24 rue Lhomond, 75231 Paris Cedex 05, France

(Received 6 August 1990, accepted in final form 16 November 1990)

Résumé. — Nous présentons un ensemble d'études expérimentales et de calculs concernant les durées de vie et les prédissociations de l'état B de la molécule Cl₂. On montre que la durée de vie radiative de cet état est très longue ($\tau_{v=12} \approx 1,2$ ms), en accord avec la valeur du moment dipolaire de transition B-X précédemment déterminée, et confirmée. Nos mesures de durée de vie des états ($J = 0, v \geq 13$) montrent l'existence d'une prédissociation hyperfine pour ces états. Finalement un modèle simple des premiers états $\Omega = 1_u$ de Cl₂ est donné, qui explique, à un facteur 2 près, la prédissociation gyroscopique de l'état B $^3\Pi_{0u}^+$ par les états A $^3\Pi_{1u}$ et $^1\Pi_{1u}$.

Abstract. — We present an ensemble of experimental studies and calculations about the lifetimes and predissociations in the B state of the Cl₂ molecule. The radiative lifetime is shown to be very long ($\tau_{v=12} \approx 1.2$ ms), in accordance with the previously determined and confirmed value of the B-X transition dipole moment. Our measurements of lifetimes for ($J = 0, v \geq 13$) show the existence of a hyperfine predissociation of these states. Finally a simple model of the first $\Omega = 1_u$ states of Cl₂ is given which explains, within a factor of 2, the gyroscopic predissociation of the B $^3\Pi_{0u}^+$ state by the A $^3\Pi_{1u}$ and $^1\Pi_{1u}$ states.

1. Introduction.

In this paper, we present new experimental results concerning the decay processes of the Cl₂ B state as well as a theoretical interpretation of these results, and a thorough discussion of the previous knowledge of these processes. We give a detailed description of the experiment which has given evidence of the hyperfine predissociation of this state [1]. We also present new information concerning the radiative decay rate and we discuss the vibrational dependence of the gyroscopic predissociation and the electronic states responsible for it.

The B states of halogen and interhalogen molecules have been the subject of a large number of experimental studies. However the works on the Cl₂ B state are comparatively rare, probably because laser excitation is considerably less efficient than for I₂ and

(*) Unité de Recherche de l'Ecole Normale Supérieure et de l'Université Paris 6, associé au C.N.R.S., U.R.A. 18

Br_2 . This is due to the weakness of the B-X transition moment and to unfavorable Franck Condon factors for the transitions starting from well populated levels of the ground state. The decay processes of the I_2 B state have revealed many interesting features [2], the predissociation is due to a combination of the Coriolis, hyperfine and also magnetic couplings (in the presence of an external magnetic field) and these three coupling terms interfere. The existence of a similar predissociation in the Br_2 B state is now well established [3, 4, 5], but with considerably less detail. In Cl_2 , till recently only the gyroscopic predissociation due to the Coriolis coupling was known [6, 7, 8, 9]. We think that it is interesting to follow this predissociation through a chemical family. Moreover, the radiative decay rate of the Cl_2 B state is also quite interesting for several reasons :

- several previous determinations are not in agreement [6, 10-12],
- the measurement of the corresponding very long lifetime represents some kind of an experimental challenge,
- the B-X transition has been considered for a laser chemically pumped by atom recombination [12, 13] and its feasibility depends strongly on the value of this lifetime

The paper is organized as follows : section 2 describes the experimental setup used for decay measurements ; section 3 discusses the results concerning the radiative decay rate , section 4 presents our results on the hyperfine predissociation and a discussion of the predissociation mechanism.

2. Experimental setup.

We have excited the Cl_2 B-state fluorescence on an unskimmed supersonic expansion of pure Cl_2 (Matheson : stated purity 99.0 %) Cl_2 was expanded in vacuum through a glass nozzle (nozzle diameter $\approx 30 \mu\text{m}$) with a typical pressure of 400 mbar. This beam source was located directly in the main chamber of our beam machine which is described in reference [14]. The laser beam crosses the Chlorine beam 10 mm from the nozzle (see Fig 1)

The laser is a cw single frequency dye laser. With Coumarin 102 pumped by the 406-413 nm lines of a Krypton ion laser the spectral range 470-520 nm was covered with a typical power of 0.4 W.

The fluorescence light is detected by two photomultipliers. PM1 looks only at the fluorescence emitted near the excitation region while PM2, located downstream the molecular beam and facing the nozzle can see the fluorescence emitted along the path followed by the molecules of the beam. This arrangement is well adapted for long lifetime

Fig 1 — Schematic drawing of the experimental set-up used for lifetime measurements N = glass nozzle , F = filters , L = Laser Beam (perpendicular to the plane)

measurements [15]. Stray light rejection is obtained by a set of light baffles along the laser beam and long pass filters (Schott OG550 or MTO J5) on both photomultipliers. Fast photon counting electronics are used on both photomultipliers.

The signals from PM1 were recorded as a function of laser wavelength (which was accurately measured by a home made lambdameter [16]) so that an unambiguous identification of the excitation transitions was possible. In order to record the fluorescence decay following pulsed excitation, the laser intensity was modulated by an acousto-optic modulator (Isomet IMD80) with a rise time ~ 150 ns and the signals from PM2 were sent to a multichannel analyser (with 1 μ s per channel maximum time resolution). The various results thus obtained are discussed below.

3. The radiative decay rate.

3.1 THE TIME-RESOLVED FLUORESCENCE SIGNAL — If the molecules are excited by a short pulse at $t = 0$, the excited state population $n(t)$ is given by

$$n(t) = n(0) e^{-\Gamma t} \quad (1)$$

where $\Gamma = \tau^{-1}$ is the decay rate of the excited state. During their decay, the molecules fly towards the photomultiplier, with a velocity v and the fluorescence detection efficiency increases with time as the solid angle $\Delta\Omega(t)$ of the photocathode seen by the molecules at time t . Accordingly the fluorescence intensity as a function of time t is given by

$$J(t) \propto e^{-\Gamma t} \langle \Delta\Omega(t) \rangle \quad (2)$$

where the brackets represent the average over the distribution of molecular velocities v . Neglecting the effects of the molecular beam divergence:

$$\Delta\Omega(t) = 2\pi \left(1 - \sqrt{\frac{(d - vt)^2}{r^2 + (d - vt)^2}} \right) \quad (3)$$

Here r is the radius of the photocathode and d is the distance between the photocathode and the excitation region. In the limit of a small photocathode ($r \ll d$) and time t much shorter than the average flight time $\langle t_f \rangle = d/\langle v \rangle$, we get

$$J(t) \propto e^{-\Gamma t} \left(1 + 2 \frac{t}{\langle t_f \rangle} \right) \quad (4)$$

These equations exhibit well the interests of this experimental setup: the fluorescence decay can be studied over long times with a well understood collection efficiency. Moreover, the short time behaviour of $J(t)$ gives a direct information on the relative values of Γ and $2/\langle t_f \rangle$: if $\Gamma \langle t_f \rangle < 2$, $J(t)$ increases and it decreases in the opposite case.

In practice, we have used distances $d = 95, 145, 295$, and 595 mm. For the first three distances the area covered by the beam of excited molecules impinging on the PM surface is smaller than the photocathode and the approximation of neglecting the beam divergence is good. Then formula (2)-(3) hold for all times and, taking into account the velocity distribution in the beam, a complete modelisation of the signal $J(t)$ can be obtained. In particular, if the lifetime τ is longer than the mean time of flight $\langle t_f \rangle$ one observes a maximum of signal corresponding to the arrival of excited molecules on the PM surface, the long time behaviour ($t > \langle t_f \rangle$) being then essentially governed by the distribution of slow velocities in the beam.

On the contrary, for the experiments using the longest ($d = 595$ mm) distance the divergence of the beam can no longer be neglected for $t \simeq \langle t_f \rangle$; only the short time signal can be fitted using equations (2)-(3), i.e. without a delicate modeling of the beam structure.

3.2 THE EXPERIMENTAL RESULTS — In the Cl_2 B state, the predissociation thresholds are well established [6]: for $^{35}\text{Cl}_2$, predissociation begins at $v = 12$, $J = 21$ and $v = 13$, $J = 0$. In order to study a predissociation-free level, we have chosen the levels $v = 12$, $J = 0$ and 4: these two levels are simultaneously excited by the P(1) and R(3) transitions at $19\,942.90\text{ cm}^{-1}$. The fluorescence signal is quite strong (typically $2\text{--}3 \times 10^5$ counts/second on PM1 with continuous excitation). Reference [17] describes our work on the isotopic shift in the Cl_2 B-X system and proves the accuracy of our wavenumber measurement and our good analysis of the excitation spectra.

In order to record the fluorescence time dependence $J(t)$, we have used 10- or 50- μs long laser pulses separated by a time interval longer than the longest time of flight t_f . These pulse lengths are adequate as they are short with respect to the lifetime τ and the time of flight. We have recorded the signal $J(t)$ with the laser at resonance and slightly out of resonance, for the same number of laser pulses (typically 10^5 or 2×10^5) and these two signals were subtracted. In this way laser stray light and a fluorescence with a short ($\sim 20\text{ }\mu\text{s}$) lifetime which is excited without any resonant character were partly eliminated, this signal is probably due to a background gas or vapor in the experimental chamber. The distances d used were 95, 145, 295 and 595 mm. With the lowest two values, we get almost no information on the lifetime except that it is long; but we can fit the whole curve to equations (2) and (3). We deduce in this way a value of the average velocity:

$$\langle v \rangle = 418 \pm 20\text{ m/s}.$$

The average velocity is slightly smaller than what is predicted by the theory of supersonic expansions [18]: $\langle v \rangle = 490\text{ m/s}$. Figure 2 presents a typical curve $J(t)$ recorded with $d = 595$ mm. As the signal increases with time at short time, the lifetime τ is longer than half the average flight time. $\tau > 650\text{ }\mu\text{s}$. A direct fit to the initial part ($t < 300\text{ }\mu\text{s}$) of the curve $J(t)$ gives the following value:

$$\begin{aligned} \tau &= 1\,200 \pm 400\text{ }\mu\text{s} \\ \text{or} \quad \Gamma &= 830 \pm 280\text{ s}^{-1}. \end{aligned}$$

This fit is illustrated in figure 2a, figure 2b shows the complete $J(t)$ variation, whose long time part has not been fitted. This value of the lifetime τ is considerably longer than all the previously published values [10-12].

Before making a detailed comparison, we are going to discuss the B-X absorption strength: this is the classical way of measuring a transition dipole moment and it can be used to deduce radiative lifetimes. Coxon [11] has thus predicted a value of the radiative lifetime of the level $v = 0$:

$$\tau(v = 0) \simeq 600\text{ }\mu\text{s}$$

3.3 THE B-X ABSORPTION SPECTRUM AND ITS IMPLICATIONS ON THE B STATE RADIATIVE LIFETIME. — The visible and near UV absorption coefficient of Cl_2 was measured in 1933 and 1937 by Gibson and Bayliss [19a] and Aikin and Bayliss [19b] using plate photometry. They took care to record the absorption spectrum at various temperatures, permitting them to distinguish the absorption coefficients of the first two vibrational levels ($v = 0$ and 1). Several works interpreted these data and specifically the temperature dependence of the absorption coefficient [20-22].

Fig. 2 — The fluorescence signal I recorded on PM2 as a function of time t after pulsed excitation. The levels $v = 12$ $J = 0$ and 4 were simultaneously excited. In the present recording, the distance d (from the excitation region to photocathode) is 595 mm a and b present similar recordings with different time resolution. The full curve on recording a is the best fit to the data points. From this fit and several similar ones, we have deduced the radiative lifetime reported in the text

We present in figure 3 this absorption coefficient as it has been recorded photoelectrically by Seery and Britton [23]. This spectrum is due to three contributions: absorption from $X^1\Sigma_g^+$ to the $^1\Pi_{1u}$, $B^3\Pi_{0u}^+$ and $A^3\Pi_{1u}$ states. We have measured a few points in the low frequency tail using standard methods (the cell was 46 mm long and the pressure varied between 0 and 1 bar) as data were absent in this region

The most complete analysis of the spectrum is due to Coxon [11]. the intense peak ($\epsilon_{\max}^0 = 71.6 \pm 0.7 \text{ l.mole}^{-1} \text{ cm}^{-1}$, centered at $30\,456 \pm 24 \text{ cm}^{-1}$ [24]) is due to the $^1\Pi$ -X transition. The weak shoulder on the low frequency side is due to the B-X absorption and Coxon [11] estimates the following parameters for this absorption: $\epsilon_{\max}^0 = 3 \text{ l.mole}^{-1} \text{ cm}^{-1}$ centered at $25\,500 \text{ cm}^{-1}$. Finally, following Mulliken [24], it is easy to relate the $A^3\Pi_{1u}$ -X and $^1\Pi_{1u}$ -X absorption coefficients and to deduce that the contribution of the $A^3\Pi_{1u}$ -X absorption should be almost negligible ($\epsilon_{\max}^0 \approx 0.25 \text{ l.mole}^{-1} \text{ cm}^{-1}$ centered near $25\,150 \text{ cm}^{-1}$).

Fig 3 — The extinction coefficient ϵ of Chlorine vapor measured at low resolution as a function of wavelength ϵ is the decadic extinction coefficient in liter mole⁻¹ cm⁻¹ (i.e. ϵ is defined by $\log_{10}(I_0/I) = -\epsilon c l$ where l is the absorption length and c the concentration in mole/l) The vertical scale is logarithmic in order to give a better visualization of the data ; + reference [23] data , • our measurements Upper scale (wavenumber) unit 10⁴ cm⁻¹

From this estimate of the B-X absorption coefficient, Coxon [11] deduced the following value of the dipole transition strength .

$$D_{BX}^2(r \sim 2.0 \text{ \AA}) = 0.0059 \text{ Debye}^2$$

and we have verified this calculation [25].

Kernatshitskii *et al.* [12] have proposed a considerably larger value

$$D_{BX}^2 \approx 0.06 \text{ Debye}^2.$$

This value is deduced from absolute intensity measurements of the light emitted by the B-X transition in a shock wave heated supersonic expansion . this procedure does not seem very reliable mainly because of the uncertainty concerning the density of Cl₂ B state. If this value was right, the absorption coefficient for the B-X transition should peak at $\epsilon \approx 30 \text{ l.mole}^{-1} \text{ cm}^{-1}$ near $25\,500 \text{ cm}^{-1}$ in obvious contradiction with experiment (see Fig. 3)

In order to complete our knowledge of the B-X transition dipole moment, we recorded some absorption lines and measured the integrated line strengths. Such a measurement is very easy with a single-frequency dye laser. We have eliminated a large fraction of the laser

intensity noise by a difference technique, recording the intensities of the transmitted and reference beams as well as the electronic difference of these two intensities. The experiment was made in a low-pressure absorption cell (pressure 153 mbar, length 499 mm). From the integrated line strength, we have deduced the dipole transition moment, using standard formulae [26]. The existence of several isotopic species and the nuclear spin statistical weights have been taken into account in the evaluation of the populations of the absorbing levels. The Franck Condon factors and r -centroids have been taken from Coxon's calculations [27] and interpolated to the exact J value. The main uncertainty comes from the imperfect knowledge of the Chlorine density in the cell (error in the pressure measurement, real purity): this error should not exceed $\pm 20\%$. The values thus obtained (see Tab. 1) are in very good agreement with Coxon's value; they are slightly smaller, but correspond to a larger value of the internuclear distance ($r \sim 2.1 \text{ \AA}$).

Table I — For the observed transitions, we give the quantity $\tilde{\alpha}_1$ directly related to the integrated absorption coefficient [26], the Franck Condon factor and r centroid interpolated from Coxon's calculation [27] to the present J value. The transition dipole moment is deduced from $\tilde{\alpha}_1$, after evaluation of the population of the absorbing level, and using the calculated Franck Condon factor

Transition	15-0 P(33)	20-1 R(11)	13-0 R(8)
$10^7 \tilde{\alpha}_1$	1.57	1.26	0.67
$10^4 \langle v' v'' \rangle ^2$	2.07	22.1	1.73
$r_{v'v''}(\text{\AA})$	2.112	2.100	2.114
$10^3 D_{\text{BX}}^2(r_{v'v''})$ (Debye ²)	5.1	5.5	5.0

This last point raises the question of the B-X transition dipole moment variation with internuclear distance. This r -variation is not a simple problem. It has been rather extensively studied for the same B-X transition in the case of Iodine [28-31]. A theoretical discussion of the value near the X state equilibrium distance has been made by Mulliken [32], but it seems difficult to deduce from this discussion the r -dependence. In I_2 , experiments show that $D_{\text{BX}}^2(r)$ is maximum near $r = 3 \text{ \AA}$ (the exact location of the peak as well as its value are still not clear) and $D_{\text{BX}}^2(r)$ decreases rapidly at large r . This last point is not surprising: at large r , $D_{\text{BX}}^2(r)$ must vanish as the transition becomes an electric dipole forbidden $^2\text{P}_{3/2} \rightarrow ^2\text{P}_{1/2}$ transition. The long range behaviour is given by

$$D_{\text{BX}}^2 \propto r^{-8}.$$

This result is a simple generalisation to the case of transition dipole moment of the result established by Goodisman [33] for diagonal dipole moment.

We expect a similar behaviour in Chlorine as in Iodine. The most uncertain point is the r -value at which starts the decrease of the dipole transition moment. We have made several hypothesis:

a) $D_{\text{BX}}^2(r)$ is independent of r in all the region of interest and its value has been taken equal to Coxon's estimate $D_{\text{BX}}^2 = 0.0059 D^2$.

b) $D_{\text{BX}}^2(r)$ is constant and equal to $0.005 D^2$ for $r < 2.2 \text{ \AA}$ and decreases like r^{-8} for $r > 2.2 \text{ \AA}$, being continuous at this point

c) $D_{\text{BX}}^2(r)$ behaves as r^{-8} over the whole range of internuclear distance (i.e. $D_{\text{BX}}^2 = 1.51 r^{-8}$ with r in $\text{\AA}$ and D_{BX}^2 in D^2).

We have calculated the radiative decay rate of the B state in these three cases. Only the B-X transition is expected to contribute, as all the other possible emissions are in the far infra-red and have therefore very small Einstein coefficients. We have used the approximate formulation which has been shown to be a very good approximation by Tellinghuisen and Julienne [34]:

$$\Gamma_{\text{rad}}(v) = \langle v | \Gamma_{\text{rad}}(r) | v \rangle \quad (5)$$

with .

$$\Gamma_{\text{rad}}(r) = \frac{64 \pi^4}{12 \pi \epsilon_0 h^4 c^3} (U_{\text{B}}(r) - U_{\text{X}}(r))^3 D_{\text{BX}}(r)^2 \quad (6)$$

in S.I. units.

The vibrational wavefunctions have been calculated by standard methods (RKR calculation of the B-state potential curve using the spectroscopic analysis of reference [27] and numerical integration of the Schrödinger equation).

Because of the $[U_{\text{B}}(r) - U_{\text{X}}(r)]^3$ factor, $\Gamma_{\text{rad}}(r)$ decreases very rapidly with increasing r in the three cases considered above. The resulting values of $\Gamma_{\text{rad}}(v)$ are plotted as a function of v in figure 4. Several comments can be made .

— for $v \leq 15$, the vibrational dependence is not strong, but is noticeably different for the three cases ,

— for high v ($v > 15$) $\Gamma_{\text{rad}}(v)$ behaves like $\omega_v = \frac{\partial E}{\partial v}$. This is a consequence of the ω_v scaling law near a dissociation limit [35],

— our measurement of the radiative decay rate is in good agreement with these calculations, favoring slightly the b or c hypothesis.

Fig 4 — Calculated values of the radiative decay rate Γ_{rad} as a function of the vibrational quantum number v . The three curves a, b, c correspond to the three different functions used for the transition dipole moment (see text). The point represents our experimental result for this quantity (all previous measurements would be out of scale).

We are now going to compare our present measurement of $\Gamma_{\text{rad}} = (830 \pm 280) \text{ s}^{-1}$ for $v = 12$ with the previous determination of Γ_{rad} , done by Clyne and Martinez [10] for $v = 5$: $\tau = 305 \pm 15 \text{ } \mu\text{s}$, i.e. $\Gamma_{\text{rad}} = (3.28 \pm 0.16) 10^3 \text{ s}^{-1}$. This has been measured in a low-pressure gas cell, recording the direct decay. The problem in the cell experiments comes from the diffusion of molecules out of the field of view of the detector, which decreases the apparent lifetimes. This has been clearly illustrated by the result of a previous experiment by Clyne and McDermid [6] where this effect led to a considerably shorter lifetime: $\tau(v = 8) = 83 \pm 5 \text{ } \mu\text{s}$. We do not know at the moment the reason explaining the difference between Clyne and Martinez value [10] and ours. It is not quite sure that this diffusion effect is truly negligible in Clyne and Martinez experiment: in the 1-10 mTorr pressure range, the measurement cannot be represented by a linear Stern Volmer plot. On the other hand, the vibrational dependence of Γ_{rad} does not seem strong enough to explain this difference (see Fig. 4).

4. B state rotational and hyperfine predissociations.

4.1 SUMMARY OF PREVIOUS KNOWLEDGE. — The first evidence [6] of predissociation in the Cl_2 B state was obtained from the disappearance of fluorescence for the levels $v > 12$. Lifetime measurements as a function of the rotational quantum number J were then made and proved that the predissociation is due to heterogeneous Coriolis coupling [7, 8]. The predissociation rate is well represented by

$$\Gamma_{\text{pred}} = k_v J(J + 1) \quad (7)$$

and accurate values of k_v (C_v^2 in the relations of Ref [2]) have been measured for most of the vibrational levels between $v = 13$ and 25. If this description is exact, the predissociation rate should vanish for $J = 0$, but this was not verified by the results of reference [7]. This error was explained and corrected in reference [8]: rotational relaxation from $J = 0$ towards $J = 2$ is equivalent to quenching because of the low quantum yield of the latter level and, to get correct lifetime values for $J = 0$, the measurements must be made at very low pressure. In reference [8], it is stated that the level ($v = 13$, $J = 0$) has a purely radiative lifetime. However, the experimental demonstration is not so convincing. From a global fit of their data, the authors deduced a zero pressure lifetime longer than $140 \text{ } \mu\text{s}$. We have reanalyzed their data in a different way, using the lifetime measured at the lowest pressure, $\tau = 14.3 \text{ } \mu\text{s}$ at $p = 4.8 \text{ mTorr}$ and the slope of the Stern Volmer plot $\partial\Gamma/\partial p = (9 \pm 0.3) 10^3 \text{ s}^{-1} \text{ mTorr}^{-1}$: i.e. $\Gamma(p = 0) = \Gamma(p) - p \times \partial\Gamma/\partial p$. The calculated zero pressure lifetime we deduced is

$$\tau(v = 13, J = 0) = 37.4 \pm 2.1 \text{ } \mu\text{s}.$$

This value is considerably shorter than the radiative lifetime, as discussed in section 3, and is not far from our value ($\tau = (50 \pm 10) \text{ } \mu\text{s}$, see Tab II).

4.2 OUR MEASUREMENTS ON THE $J = 0$ LEVELS. — We have studied the decay curves of the $J = 0$ levels with $v > 12$ for the $^{35}\text{Cl}_2$ isotopic species only. The curves were recorded in a way completely similar to the experiment with $v = 12$. As the lifetimes appeared to be shorter, we have used shorter flight distances ($d = 95, 145$ and 295 mm). Figure 5 presents the experimental curves recorded for a series of levels with the largest of these flight distances. The fitted decay rates are given in table II, which recalls also the k_v values of reference [8], both results also appear in figure 6.

Table II — *Gyroscopic predissociation parameters k_v [8], and decay rates of $J = 0$ levels $\Gamma(v, J = 0)$ for $12 \leq v \leq 29$ measured in this work.*

v	$k_v/10^5 \text{ s}^{-1}$	$\Gamma(v, J = 0)/10^3 \text{ s}^{-1}$
—	—	—
12		0.83 ± 0.28
13	7.7 ± 0.4	20 ± 4
14	5.9 ± 0.4	15 ± 3
15	5.3 ± 0.4	13.5 ± 3
16	4.1 ± 0.5	11.5 ± 2
17	—	11.3 ± 2
18	3.8 ± 0.5	10.8 ± 2
19	4.2 ± 0.7	10.7 ± 2
20	—	9.6 ± 2
21	2.9 ± 0.5	—
22	2.4 ± 0.4	8.2 ± 2
23	1.6 ± 0.5	7.0 ± 2
24	1.2 ± 0.3	7.3 ± 2
25	1.1 ± 0.3	6.9 ± 2
26	—	5.7 ± 1
27	—	—
28	—	—
29	—	5.5 ± 4

Several comments can be made.

— The $v \geq 13$, $J = 0$ decay rates are much larger than expected from any possible extrapolation of the $v < 12$ values.

— These $J = 0$ decay rates decrease when v increases but this vibrational dependence is slower than the vibrational dependence of the gyroscopic predissociation rate.

— The molecular beam density is calculated to be low enough to prevent any noticeable effect of rotational relaxation. Using standard formulae for supersonic expansions [36], one estimates the density as given by :

$$n_{\text{Cl}_2} = 8 \times 10^{12} z^{-2} \text{ cm}^{-3}$$

where z (cm) is the distance from the nozzle. Even in the excitation region ($z = 1$ cm), the calculated apparent quenching rate (8) is of the order of 2.200 s^{-1} , and this quantity decreases very rapidly along the molecular beam (the density being already reduced by a factor 4 for $z = 2$ cm after a time of flight $t_f \approx 25 \mu\text{s}$).

— We have not been able to extract two lifetimes from the fit of these decay curves. Simple theoretical arguments predict that the two hyperfine sublevels of the $J = 0$ levels ($F = 1$ and 3) have different lifetimes. This point will be discussed below.

4.3 THEORETICAL DISCUSSION OF THE HYPERFINE PREDISSOCIATION. — The first point is that the observation of a predissociation at $J = 0$ is necessarily in this case a hyperfine predissociation. For all the molecular coupling terms except the hyperfine Hamiltonian, and in the absence of external fields, the selection rules for predissociation are :

$$\Delta J = 0, \quad u \leftarrow | \rightarrow g, \quad + \leftarrow | \rightarrow - \quad (\text{total parity})$$

Fig 5 — The fluorescence signal I as a function of time t . In each case, the $J = 0$ level has been excited and the vibrational quantum number is given for each curve. The time scale is the same for all the graphs. The distance d is now 295 mm, and the full curve is the best fit of the data.

Fig 6 — Plots of k_v values from reference [8] ($\bullet$), and $\Gamma(v, J = 0)$ values from this work ($\times$). Note the different scales.

The electronic states which can be responsible for this predissociation dissociate into two ground state $^2P_{3/2}$ Chlorine atoms. There is no O_u^+ state coming from this limit and the other electronic states have either no $J = 0$ state (this is the case for the $\Omega \neq 0$ states) or their $J = 0$ state has the wrong parity (this the case for O_g^+ or O_u^- states). Hence, the predissociation is necessarily due to a coupling to a $J \neq 0$ level and such a coupling, in the absence of external fields, is necessarily due to the hyperfine Hamiltonian.

The $J = 0$ states of $^{35}\text{Cl}_2$ have two hyperfine sublevels. As the nuclear spin of ^{35}Cl is $3/2$ (and the same for ^{37}Cl) and as the even J levels of the $B^3\Pi_{O_u^+}$ states are ortho-states, the total spin I takes the value 1 and 3 for the $J = 0$ level. Because of the hyperfine structure, these two levels are not degenerate. It seems that there are no measurements of the Cl_2 B-state hyperfine structure, but the hyperfine structure of the Iodine B state has been measured accurately (see Ref. [37] and Refs. therein) and is well understood theoretically [38]. Moreover the molecular hyperfine constants can be related to atomic hyperfine constants [39-41] and these atomic constants are known for Chlorine [42]. The $J = 0$ hyperfine structure is due to the quadrupolar term (taken at the 2nd order of perturbation theory, i.e. coupling to the $J = 2$ level), and to spin-spin terms. For levels not too close to the dissociation limit (for the level $v = 13$ for instance) the eq Q_B constants can be estimated to be close to -27 MHz and the spin-spin constants d and δ should not exceed a few kHz. The resulting hyperfine splitting of the $J = 0$ level can be estimated to be of the order of a few tens of kHz. If the hyperfine coupling which creates the predissociation is dominated in Chlorine as in Iodine [2] and in Bromine [4, 5] by the magnetic dipolar term, the $J = 0$ predissociation rate is given by :

$$\Gamma_{\text{pred}}(J = 0, F = I) = \frac{a_v^2}{3} I(I + 1) \quad (8)$$

leading to the following predissociation rate $\frac{2}{3} a_v^2$ and $4 a_v^2$ for $F = 1$ and 3 respectively. As the radiative decay rate Γ_{rad} is almost negligible with respect to the observed decay rates (Tab. II and Fig. 4), the ratio of the decay rates of these two sublevels should be close to 6. As this ratio is large, it seems probable that our measurement is close to one of these decay rates (and not an average value), but we do not know which one. Because of statistical weight, the larger signal, at short time, should come from the level $I = 3$, and we will assume that we have measured the larger of these two decay rates. Therefore the values of a_v^2 are simply the measured $\Gamma_{\text{pred}}(J = 0)$ divided by 4.

Another point which is worth discussing is that the predissociation is due to a direct hyperfine coupling to the continuum. An alternative explanation is that it could be due to the admixture of $J = 2$ level in the $J = 0$ level (mixing due to the hyperfine quadrupolar term). This effect, acting alone, should give the following predissociation rate :

$$\Gamma'_{\text{pred}} = \left[\frac{\langle J = 0, I | \mathcal{H}_{\text{HFS}} | J = 2, I \rangle}{E_{J=0} - E_{J=2}} \right]^2 \times 6 k_v \quad (9)$$

Taking for the order of magnitude of the hyperfine matrix element eq Q , and remembering that $(E_{J=2} - E_{J=0} = 6 B_v)$, we get the order of magnitude of the effect :

$$\Gamma'_{\text{pred}} \approx \left(\frac{\text{eq } Q}{B_v} \right)^2 \times \frac{k_v}{6} \quad (10)$$

For $v = 13$, we get the following value $\Gamma'_{\text{pred}} \approx 7 \text{ s}^{-1}$, which seems quite negligible when compared to our observations

A final question is that, as soon as $J \neq 0$, the hyperfine predissociation should interfere with the gyroscopic predissociation [2]. The interference term $-a_v C_v \mathbf{I} \mathbf{J} \sqrt{2}$ is linear in J while the main predissociation term $C_v^2 J(J+1)$ (where $C_v^2 = k_v$) is quadratic. As a_v^2 is considerably smaller ($a_{13}^2 \approx 5 \times 10^3 \text{ s}^{-1}$ while $C_{13}^2 \approx 7.7 \times 10^5 \text{ s}^{-1}$) one could think that this interference term would be negligible. At least for $J = 1$, the interference term may be large. But, as discussed in the next paragraph, the electronic states $^3\Pi_{1u}$ and $^1\Pi_{1u}$ contribute to the Coriolis and also to the hyperfine predissociations, so that the evaluation of the interference term is not simple.

4.4 VIBRATIONAL DEPENDENCE OF THE PREDISSOCIATION — This problem has already been studied by Clyne and Heaven [9]. Their conclusion was that this vibrational dependence can be reproduced only if the predissociation is due to the A $^3\Pi_{1u}$ state, and not to $^1\Pi_{1u}$. This makes a large difference with the case of Bromine and Iodine where the B-A $^3\Pi_{1u}$ Franck Condon density is negligible when compared to the B- $^1\Pi_{1u}$ one. The ratio of these two densities is below 10^{-6} in the case of Iodine [43] and about 5×10^{-6} in the case of Bromine [3].

However, we do not think that the potential energy curve proposed by Clyne and Heaven for the A $^3\Pi_{1u}$ state is quite correct for the following reasons:

i) Mulliken's theoretical treatment [44] of the relative positions of the B $^3\Pi_{0u}^+$ and A $^3\Pi_{1u}$ states in the halogen molecules strongly supports the idea that the B $^3\Pi_{0u}^+$ potential energy curve is nested in the A $^3\Pi_{1u}$ curve. This conclusion is clearly verified by the available spectroscopic information for Iodine [50] and Bromine [3].

ii) We are going to show that the B $^3\Pi_{0u}^+$ -A $^3\Pi_{1u}$ Franck-Condon density would be too large in a configuration where the B and A potential curves cross each other on the repulsive limb.

iii) The A $^3\Pi_{1u}$ RKR potential energy curve deduced from the spectroscopic work of Ishiwata *et al* [45] is noticeably different from the Morse curve used by Clyne and Heaven (in particular the r_e value is lower by about 0.02 Å). Reference [45] contains, to our knowledge, the first high resolution study of the Cl₂ A $^3\Pi_{1u}$ -X $^1\Sigma_g^+$ system.

In fact reference [9] gives only the *relative* variations of the Franck-Condon density, but not *absolute* values. We have recalculated these, using numerical integration of the Schrödinger equation, using for the B state the RKR curve from [27], and for the A state the Morse curve defined in [9]. For the level B $^3\Pi_{0u}^+$ ($v = 13$), we get:

$$|\langle B, v = 13 | A, E = E(B, v = 13) \rangle|^2 = 2.7 \times 10^{-4} \text{ cm}.$$

The F.C. density is related to the gyroscopic predissociation coefficient $k_v = C_v^2$ by the relation [2]

$$k_v = \frac{2\pi}{\hbar} |\langle B, v | A, E \rangle|^2 \left(\frac{\hbar^2}{\sqrt{2\mu} r_c^2} \right)^2 |\langle B | \mathcal{H}_c^{\text{el}} | A \rangle|^2. \quad (11)$$

Here r_c is the internuclear distance at the crossing point of the two potential energy curves ($r_c = 2.24 \text{ Å}$) and μ is the molecular reduced mass, $\langle B | \mathcal{H}_c^{\text{el}} | A \rangle$ is the electronic matrix element of the Coriolis coupling operator:

$$\langle B | \mathcal{H}_c^{\text{el}} | A \rangle = \sum_{q=\pm 1} \langle B | (T_q^1(L) + T_q^1(S)) | A \rangle. \quad (12)$$

The ratio $k_v/|\langle B, v | A, E = E_v \rangle|^2$ does not vary very much with v , remaining in the range $2,3 \times 10^9 - 3,4 \times 10^9 \text{ s}^{-1} \text{ cm}^{-1}$ for $13 \leq v \leq 25$, with an average value $2,77 \times 10^9 \text{ s}^{-1} \text{ cm}^{-1}$. From this mean, we can deduce the electronic matrix element :

$$|\langle B | \mathcal{H}_c^{\text{el}} | A \rangle|^2 \approx 3.2 \times 10^{-2}.$$

This value is too small to be understood, if we assume that the A and B states are reasonably well described as two fine-structure components of one and the same $^3\Pi$ state. In this approximation, the electronic matrix element is due only to the spin part of the operator and should theoretically be

$$|\langle B | \mathcal{H}_c^{\text{el}} | A \rangle|^2 = 2$$

(we have included a factor $\sqrt{2}$ in the matrix element corresponding to the $\Omega = \pm 1$ symmetrization of the A state wavefunction).

The only way to understand this large difference between the « experimental » and theoretical values is to assume that the B-A Franck-Condon density is too large, by a factor of the order of 60. We have tried to build a more realistic representation of the A $^3\Pi_{1u}$ and $^1\Pi_{1u}$ states, by using the *ab initio* calculations of Peyerimhoff and Buenker [47], which do not include fine structure effects, and following Mulliken's [44] ideas to incorporate them. Our procedure is described in the appendix. In this way we have calculated the potential energy curves represented in figure 7, where the B $^3\Pi_{0u}^+$ curve is the RKR one. The A $^3\Pi_{1u}$ and $^1\Pi_{1u}$ curves are, as explained in the appendix, the results of *ab initio* calculations slightly fitted to incorporate at best the available experimental data.

Adjustments of the parameters described in the appendix do not change essentially our results : in this configuration the main contribution to the B state predissociation comes from the A $^3\Pi_{1u}$ state ; this contribution to k_v is a smoothly decreasing function of v . On the

Fig 7 — Potential energy curves for the Cl_2 states considered, full curve B $^3\Pi_{0u}^+$ (from Ref [27]), (— — —) A $^3\Pi_{1u}$ (from Ishiwata *et al.* [45]), (— · — · —) 1u curves obtained by diagonalization (this work). Energy origin $T_e(\text{B } ^3\Pi_{0u}^+)$, the X $^1\Sigma_g^+$ minimum would appear $17\,818 \text{ cm}^{-1}$ downwards

contrary the position and shape, and therefore the importance of the $^1\Pi_{1u}$ state contribution vary widely with the details of the potentials

We have plotted in figure 8 the experimental and calculated absolute k_v values. For the calculated results we have also drawn the contribution of the $A^3\Pi_{1u}$ state alone. Our results indeed reproduce, within a factor 2 or 3, the observed k_v values. The remaining discrepancy could certainly be accounted for by the simplicity of the model; the lack of precise experimental data about the $^1\Pi_{1u}$, $^3\Sigma_u^+$ and $^3\Delta_u$ states makes unuseful any attempt to further improve the agreement. We think however that our model giving reasonable, if not precise, values for the predissociation rate of the $B^3\Pi_{0u}^+$ state of Cl_2 is a first step in the description of the positions and wavefunctions of the first excited configuration of Cl_2 . Even if the agreement between the experimental and calculated values of k_v is not perfect, our results indicate clearly that the two states $A^3\Pi_{1u}$ and $^1\Pi_{1u}$ both contribute to the predissociation. This feature is completely different from the case of the heavier halogen molecules, where the $A^3\Pi_{1u}$ contribution is negligible.

Fig 8 — Experimental ($\circ$) (Ref [8]) and calculated k_v values, ($\bullet$) results of our calculations, (+): contribution of the $A^3\Pi_{1u}$ state alone

Conclusion.

Concerning the radiative lifetime of the Cl_2 B state, and the transition dipole moment for the B-X transitions, our experimental results show clearly that this lifetime is very long, and longer than any previously determined value. We have confirmed the value of the B-X dipole

moment by direct absorption measurements, and showed that our experimental value of the B state radiative lifetime is in good agreement with the dipole value.

We have presented and discussed thoroughly our measurements of the hyperfine predissociations, information on this predissociation is still limited, and its full understanding will require more experimental data. In trying to bridge the gap with the heavier halogens, we have made a theoretical analysis of the vibrational dependence of the gyroscopic predissociation coefficient. This analysis has led us to build a simple model in which the potential energy curves and electronic wavefunctions have been calculated for the two $1u$ states involved. These calculations give a nice account of the $B^3\Pi_{O_u^+}$ predissociation and show in particular that the $^3\Pi_{1u}$ and $^1\Pi_{1u}$ states' contributions are of comparable orders of magnitude. On the whole, we think that the understanding of the various decay processes (radiative, gyroscopic and hyperfine) of the Cl_2 B state is now considerably improved, though a large amount of experimental work remains to be done.

Appendix.

In the absence of fine-structure effects, twelve molecular states arise from the $^2P + ^2P$ limit of separated chlorine atoms. These states are easily established by use of the Wigner-Witmer rules [46]

$$\begin{array}{cccccc} ^1\Sigma_g^+(2), & ^1\Sigma_u^-, & ^1\Pi_g, & ^1\Pi_u, & ^1\Delta_g \\ ^3\Sigma_g^+(2), & ^3\Sigma_g^-, & ^3\Pi_g, & ^3\Pi_u, & ^3\Delta_u. \end{array}$$

Most of the corresponding potential energy curves have been calculated in an *ab initio* study by Peyerimhoff and Buenker [47]. Because of the fine structure, the $^2P + ^2P$ dissociation limit splits into three different limits ($^2P_{3/2} + ^2P_{3/2}$, $^2P_{3/2} + ^2P_{1/2}$, $^2P_{1/2} + ^2P_{1/2}$ of relative energies 0, 882 and 1 765 cm^{-1}), and the 12 molecular states split into 23 different case a components. Introduction of fine structure effects is of major importance here: the $B^3\Pi_{O_u^+}$ state dissociation limit is the second ($^2P_{3/2} + ^3P_{1/2}$) one, while the $A^3\Pi_{1u}$ and $^1\Pi_{1u}$ states share the lower limit. In other words the B-state predissociation exists only because the fine-structure Hamiltonian gives different dissociation limits to these states.

A valence description of these molecular states seems a good approximation and fine structure effects, which are small for Chlorine (atomic f.s. constant $a = 588.2\text{ cm}^{-1}$) [48] can be introduced as a perturbation.

We start from molecular states represented as symmetrized products of atomic wavefunctions. For example:

$$\begin{aligned} |^3\Pi_u, O_u^+\rangle = \frac{1}{2} [& |1, 0, -1/2, -1/2\rangle + |0, 1, -1/2, -1/2\rangle \\ & - |-1, 0, 1/2, 1/2\rangle - |0, -1, 1/2, 1/2\rangle] \end{aligned}$$

The ket is here to be read $|m_{\ell 1}, m_{\ell 2}, m_{s1}, m_{s2}\rangle$ m_{ℓ} and m_s being the projections on the molecular axis of the orbital and spin angular momenta of the atoms 1 and 2. ($\ell = 1$ and $s = 1/2$ being omitted for brevity).

The total Hamiltonian is the sum of the electrostatic Hamiltonian $\mathcal{H}_1$ plus the fine structure contribution:

$$\mathcal{H}_{FS} = \sum_{i=1}^2 a_i \cdot s_i \quad (a_i)$$

The ${}^3\Pi_{O_u^+}$ state is the only O_u^+ state of the configuration, and is an eigenvector of the total Hamiltonian, of energy

$$E({}^3\Pi, O_u^+) = V_{\Pi} - \frac{a}{2} - \frac{X}{2} \quad (a_2)$$

where we have used Mulliken's notation [24].

In the following we are going to use this relation to define the diagonal V_{Π} term, starting from the known RKR curve of the B ${}^3\Pi_{O_u^+}$. In the configuration there are five 1 u states coming from ${}^3\Pi_u$, ${}^1\Pi_u$, ${}^3\Sigma_u^+(2)$ and ${}^3\Delta_u$.

For these 1 u states the Hamiltonian Matrix is, (the eigenstates being taken in the order ${}^3\Pi_{1u}$, ${}^1\Pi_{1u}$, ${}^3\Sigma_u^+(1)$, ${}^3\Sigma_u^+(2)$ and ${}^3\Delta_{1u}$

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_{FS} \quad (a_3)$$

$$\mathcal{H}_1 = \begin{bmatrix} V_{\Pi} - \frac{X}{2} & & & & \\ & V_{\Pi} + \frac{X}{2} & & & 0 \\ & & V_{3\Sigma_u^+(1)} & & \\ 0 & & & V_{3\Sigma_u^+(2)} & \\ & & & & V_{3\Delta_u} \end{bmatrix} \quad (a_4)$$

and

$$\mathcal{H}_{FS} = \frac{a}{2} \begin{bmatrix} 0 & 1 & 1 & \sqrt{2} & \sqrt{2} \\ 1 & 0 & 1 & -\sqrt{2} & -\sqrt{2} \\ 1 & 1 & 0 & 0 & 0 \\ \sqrt{2} & -\sqrt{2} & 0 & 0 & 0 \\ \sqrt{2} & -\sqrt{2} & 0 & 0 & -1 \end{bmatrix}. \quad (a_5)$$

A similar treatment has already been given by Mulliken [24] but, in the F.S. matrix the ${}^3\Delta_{1u}$ diagonal term was erroneously taken equal to 0. Thus the Hamiltonian has to be diagonalized at each internuclear distance to get the proper (adiabatic) potential energy curves. To proceed we need numerical values for the V_i terms. They could be taken from the *ab initio* calculations of Peyerimhoff and Buenker [47], but several problems arise: the ${}^3\Delta_u$ curve has not been calculated, and there is no obvious relation between our arbitrary choice for the two ${}^3\Sigma_u^+$ states and the eigenstates of the *ab initio* calculation. We have used the approximation that these three states degenerate:

$$V_{3\Sigma_u^+(1)} = V_{3\Sigma_u^+(2)} = V_{3\Delta_u} = \left(\frac{V_{3\Pi} + V_{1\Pi}}{2} \right) + Y(r) \quad (a_6)$$

For the $Y(r)$ variation we started from the Peyerimhoff and Buenker data, copied from their figure 9. We then fitted the $Y(r)$ variation by a product of a polynomial and a decreasing exponential:

$$Y(r) = (5.125 - 25.016 r + 10.557 r^2) 10^6 e^{-\beta r} \quad (a_7)$$

with Y in cm^{-1} , r in a_0 units. The exponential coefficient has been fixed at the theoretical value of Gordeev [49]: $\beta = 1.96 a_0^{-1}$. This variation fits rather nicely the P.B. results.

The second unknown quantity is the ${}^3\Pi-{}^1\Pi$ distance $X(r)$; we have tried the form :

$$X(r) = \frac{5\,500}{1 + \exp(\beta(r - 50))} \quad (a_8)$$

At long ($r > 5\,a_0$) distances $X(r)$ behaves like $Y(r)$ and decreases exponentially. However for $r < 5\,a_0$ $X(r)$ saturates at a value close to $5\,500\text{ cm}^{-1}$. In this way we have that at $r = 2\,\text{\AA} \approx r_e(X)$ the ${}^1\Pi-{}^3\Pi_{O_u^+}$ distance is $4\,750\text{ cm}^{-1}$. This is in reasonable agreement with the separation found in the continuous absorption spectrum [11] $30\,456 - 25\,500 = 4\,956\text{ cm}^{-1}$.

As may be seen by a perturbation calculation, the position of the $A\,{}^3\Pi_{1u}$ potential energy curve, relative to $B\,{}^3\Pi_{O_u^+}$, is sensitive only at 2nd order to $X(r)$, and so varies very little with the parameters values. The ${}^3\Pi_{1u}$ minimum is shifted to about 360 cm^{-1} beneath the $B\,{}^3\Pi_{O_u^+}$ minimum, without any important radial shift :

$$r_e(A\,{}^3\Pi_{1u}) \approx r_e(B\,{}^3\Pi_{O_u^+})$$

We have compared this $A\,{}^3\Pi_{1u}$ potential energy curve obtained by diagonalization with the one deduced from the precise experimental data of Ishiwata *et al* [45]. Those two curves appear in figure 7 to be extremely close to each other near the bottom of the well. This gives us a rather good confidence in the validity of our model (in this r -region). On the contrary the curves diverge above $v_A \approx 8$ at this point there are no experimental values and we are in a zone of extrapolation of the RKR data. With this geometry the calculations show that the ${}^3\Pi_{1u} \rightarrow {}^3\Pi_{O_u^+}$ interaction is mainly concentrated at short internuclear distances, i.e. on the repulsive limb of the $B\,{}^3\Pi_{O_u^+}$ state. By construction here the ${}^3\Pi_{1u}$ and ${}^3\Pi_{O_u^+}$ potential energy curves cannot cross each other, nevertheless the interaction between them is mainly concentrated in this $r \approx 2.4\,\text{\AA}$ region. The F.C.D. calculations show then weak values, which are moreover very sensitive to the potential energy curves distance in this region : this is probably the origin of our difficulties in obtaining precise absolute values for the predissociation rates.

The calculation gives also a position and an electronic nature to the ${}^1\Pi_{1u}$ state. Unfortunately the position cannot be compared (except at $r \approx r_e(X)$) with any experimentally determined value. It is therefore unreasonable to hope for a precise determination of the parameters involved. The best looking results are however obtained with a ${}^1\Pi_{1u}$ state rising steeply for $r \leq 2.5\,\text{\AA}$, and more or less flat for higher r values, with a possibility of a very shallow potential well around $3\,\text{\AA}$, i.e. near the crossing of the outer limb of the $B\,{}^3\Pi_{O_u^+}$ state. As a consequence the ${}^1\Pi_{1u} \leftrightarrow B\,{}^3\Pi_{O_u^+}$ interaction is mainly concentrated in this region, and could result in the small oscillations experimentally observed [9] in the $k(v)$ variations.

More importantly, our diagonalization gives a description of the various states involved, in a basis of pure case a) states :

$$|\tilde{i}\rangle = \sum_{j=1}^5 \alpha_{ij}(r) |j\rangle \quad (a_9)$$

where the $|\tilde{i}\rangle$ are the perturbed states and $|j\rangle$ the pure case a) states of the preceedingly defined basis ($i = 1 \dots 5$ for ${}^3\Pi_{1u}$, ${}^1\Pi_{1u}$, ${}^3\Sigma^+(1u, 1)$, ${}^3\Sigma^+(1u, 2)$, ${}^3\Delta_{1u}$)

On the other hand the Coriolis interaction between the $B\,{}^3\Pi_{O_u^+}$ state (supposed to be a pure $S = 1$, $\Omega = 0^+$ case a) state) and the $1u$ states of the configuration is strictly limited by the

$\Delta S = 0$ selection rule. The ${}^3\Pi_{O_u^+} \leftrightarrow {}^1\Pi_{1u}$ Coriolis interaction exist only because of the partially triplet nature of ${}^1\tilde{\Pi}_{1u}$.

The matrix elements for predissociation involve only the ${}^3\tilde{\Pi}_{1u}(|\tilde{1}\rangle)$ and ${}^1\tilde{\Pi}_{1u}(|\tilde{2}\rangle)$ states and are

$$\langle B {}^3\Pi_{O_u^+} | \mathcal{H}_c | \tilde{1} \rangle = \sum_{j=1}^5 \left\langle B, v \left| \alpha_{vj}(r) \frac{\hbar^2}{2\mu} \frac{1}{r^2} \right| j, E = E_B(v) \right\rangle \times \langle B {}^3\Pi_{O_u^+} | \mathcal{H}_c^{\text{el}} | j \rangle.$$

The electronic factors $\langle B {}^3\Pi_{O_u^+} | \mathcal{H}_c^{\text{el}} | j \rangle$ are, in our model, easily shown to be equal respectively to: 1, 0, -1, $-\sqrt{2}$, $\sqrt{2}$ for $j = 1$ to 5. The full matrix element calculation requires however the use of properly symmetrized $\Omega = 1$ wavefunctions, which introduces a supplementary $\sqrt{2}$ factor in the matrix elements.

In particular the ${}^3\Pi_{O_u^+} \leftrightarrow {}^1\tilde{\Pi}_{1u}$ interaction cannot be intense unless there is an important mixing between the $S = 0$ and $S = 1$ states; this implies that the $Y(r)/a$ and $X(r)/a$ ratios be low enough, which happens, in our model, at rather large internuclear distances ($r \geq 3 \text{ \AA}$).

More precisely, in our model, the ${}^1\tilde{\Pi}_{1u}$ state is written, in terms of case a) wavefunctions, and near its crossing with the $B {}^3\Pi_{O_u^+}$, at $r_c = 3,25 \text{ \AA}$.

$$\begin{aligned} {}^1\tilde{\Pi}_{1u}(r \approx 3.25 \text{ \AA}) = & -0.226 |1\rangle + 0.886 |2\rangle \\ & -0.131 |3\rangle - 0.311 |4\rangle - 0.223 |5\rangle \end{aligned}$$

This example shows the rather important admixture of triplet functions (1, 3, 4, 5) within the ${}^1\tilde{\Pi}_{1u}$ state.

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