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ANALYSIS OF STRUCTURED FLUORESCENCE SPECTRA OF Cl_2 MOLECULE
EXCITED SELECTIVELY WITH SYNCHROTRON RADIATION

by

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Introduction

The electronic structure of halogen molecules has attracted considerable interest these last few years both from a theoretical and experimental point of view. Halogens play a significant role in rare gas monohalide laser systems and may even be important laser molecules by their own (1,2,3).

But in spite of a large number of experimental studies, the interpretation of absorption spectra and UV fluorescence is by far not completely clear. It appears that complex absorption spectra require high resolution and also isotopic molecules for an unambiguous identification of molecular systems. Moreover, even in the case of recent experiments with laser excitation, both in the presence or in the absence of a buffer gas, the assignment of some UV molecular fluorescences remains speculative.

The interpretation is complicated by multiple difficulties partly due to the complexity of upper states reached by excitation, partly due to the multiplicity of the possible lower states (23 electronic states correlating with $^2P_{3/2} + ^2P_{3/2}$, $^2P_{3/2} + ^2P_{1/2}$ and $^2P_{1/2} + ^2P_{1/2}$ atoms) (4). Additional difficulties

result from the different types of fluorescence expected. As it has been shown in various publications after the first interpretation of the I_2 structured continuum by Mulliken (5), characteristic features for transitions between ion-pair potential and valence states are expected when the difference potential displays a minimum (6,7). In that case the structured fluorescence spectrum exhibits large undulations resulting from a quantum interference effect with a strong peak at the long wavelength limit.

Finally it should be noted that the unsatisfactory situation was increased by an insufficient knowledge of potential curves. The recent ab-initio calculations of Peyerimhoff and Buenker (8) are the first which take into account the Rydberg states, but they don't include spin-orbit effect. In contrast, if this interaction is taken into account by Jaffe (9), his unpublished calculations concern only the ionic valence states.

Among halogens, Cl_2 , object of only fragmentary and controversial studies (10,11) was perhaps the less known, until 1979. In close connection with the first ab-initio calculations of excited potential curve (8), we have undertaken a detailed study of Cl_2 in the VUV region combining absorption measurements between 1040 Å (LiF cutoff) and 1500 Å, with fluorescence measurements between 1300 and 4000 Å under selective excitation.

Following absorption studies (12,13,14), the results presented here are focused on an analysis of structured fluorescence bands observed when pure Cl_2 is excited between 1200 and 1400 Å (Fig.(1)). This spectral range appears particularly interesting since it corresponds to an avoided crossing region between Rydberg and Valence states, as revealed both by the theoretical calculation of Peyerimhoff (8) and by the high resolution absorption spectroscopy (12,13,14).

The simplified diagram of the calculated adiabatic potential curves (Fig.2) in the energy region investigated by us, makes evident the difficulties of analysis for either absorption or fluorescence. Between 7 eV and 10 eV, Cl_2 excited electronic states consist of a closely spaced manifold of distinct bound states with different electronic configuration.

- Rydberg states bound by 2-3 eV have their minimum near the value $R_e = 1.99 \text{ \AA}$ of the $X \ ^1\Sigma_g^+$ ground state.

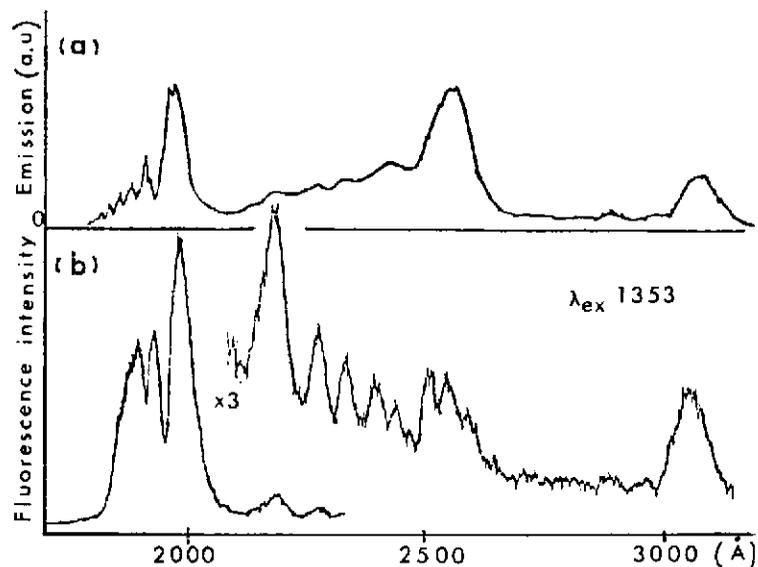


Fig. 1 - a) Microwave discharge of pure Cl₂ (from G. Kühnberger's thesis, Hamburg (1979)) - b) Fluorescence spectrum corresponding to an excitation wavelength λ_{ex} = 1353 Å. The intensity decrease below 1800 Å is due to the transmission characteristics.

- Ionic states exhibit an attractive 1/R interaction for large R with wide and deep minima around 2.7 - 2.9 Å.

At shorter distances, the numerous ionic states which lie below the first Rydberg states, lead to series of avoided crossing between states of same symmetry and hence to double minimum potential wells. Furthermore, due to the change in character from ionic to Rydberg type in excited states, drastic variations in electronic transition moments are expected at internuclear distances corresponding to the crossing region (15,16). The subsequent perturbations give rise to strong irregularities in spectra, irregularities in vibrational spacing, rotational structures and also intensities. Finally, mixing of singlet and triplet excited states by spin-orbit interaction introduces additional complications (9).

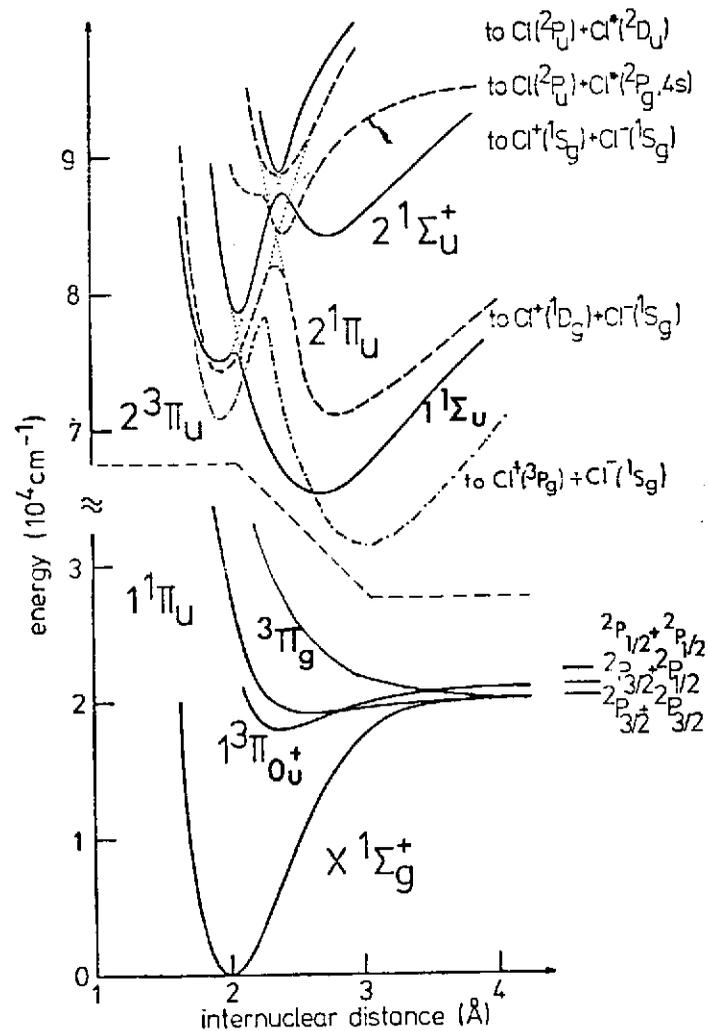


Fig. 2. Simplified Cl₂ potential energy diagram from ab initio calculations (8). X ¹Σ_g⁺, 1³Π_{0u}⁺ and 1¹Π_u are experimental curves (see ref.4)

Experimental arrangement and fluorescence observation

After preliminary investigations with synchrotron radiation at LURE ORSAY (3,17), the experiments have been carried out in the synchrotron radiation Laboratory Hasylab (Hamburg) with two beam lines. On the Hicity line, fluorescence measurements, resolved or integrated in time, have been done at medium resolution. The exciting wavelength is tuned with a first monochromator between 1050 Å and 2000 Å (band pass 2-5 Å). The fluorescence light is analyzed between 1050 Å and 4000 Å by a second monochromator integrated with the sample chamber (band pass \approx 13 Å) (18). For fixed combinations of excitation and fluorescence wavelengths, decay times were measured by making use of the pulse structure of synchrotron radiation. Matheson high purity Cl₂ was used.

In second series of experiments, our investigation was continued at the new high intensity beam line fitted with a VUV 2 m normal incidence monochromator. The band pass in absorption was improved to 0.07 Å. Fluorescence was excited with a band pass of 0.5 Å and analysed with 5 Å resolution (19).

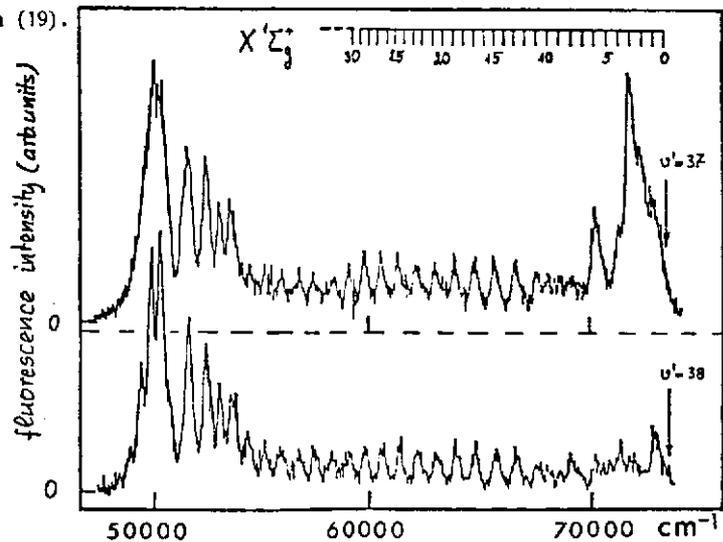


Fig. 3. Two typical fluorescence spectra obtained with the Superlumi line (19) for two different excitation energies (arrows).

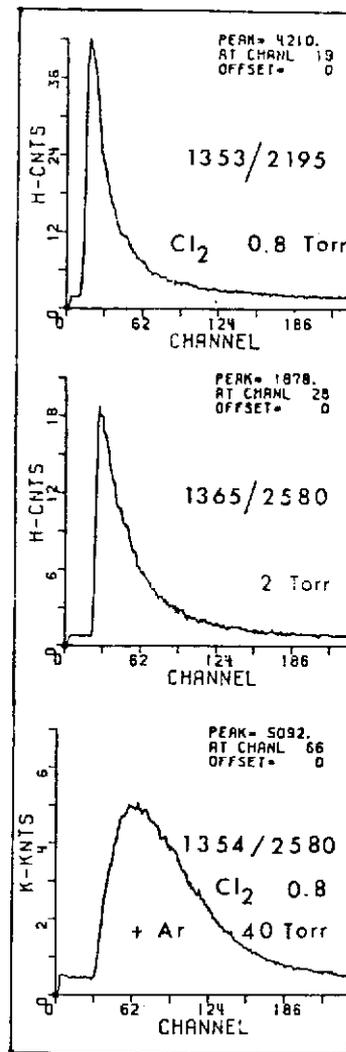


Fig. 4. Time resolved fluorescence signals.

When exciting Cl₂ around 1350 Å (Fig. 1.b), at low pressure conditions where relaxation and collisional mixing of states can be neglected, the fluorescence spectrum analysed between 1350 and 3100 Å shows structured and complex features. The strongest bands, as shown by Fig. 3, extend from resonance emission down to 1990 Å. At lower energy, numerous weaker bands, mostly with a diffuse aspect, seem to present some analogy with series of bands (Fig. 1.a), imprecisely assigned, which have been observed previously in discharges (20,21).

The group of bands observed in discharge between 2140 Å and 2600 Å was attributed to the $^3\Pi_{og} + ^3\Pi_{ob}$ transitions. $T_e = 3 \cdot 816 \text{ cm}^{-1}$ for $^3\Pi_{og}$ by Wieland et al. (20). The weak band system in the region 2365 - 2239 Å was assigned by Khanna to transitions from a gerade upper states with $T_e = 61 \text{ 290 cm}^{-1}$ down to $^3\Pi_{ob}$ state ($T_e = 17658 \text{ cm}^{-1}$) (21) while the 2580 Å correspond to $^3\Pi_{2g} + ^3\Pi_{2u}$ transition from the lowest ion-pair state (22).

In contrast with discharge experiments, the fluorescence bands observed in the present work, for selective excitation of pure Cl₂, may be steadily assigned to transitions from "ungerade" upper states to "gerade" lower states. This assignment is confirmed by the temporal behaviour of the pure Cl₂ fluorescence characterized by a prompt onset which clearly demonstrates that the upper emitting states are reached by primary excitation (Fig. 4). No time

delay is observed ruling out some vibrational relaxation, collisional reaction or cascade effect from the initially "u" excited states to any hypothetical "g" emitting state.

Furthermore, as already discussed in a previous paper (17), it is interesting to recall that a strong enhancement of emission around 2580 Å is observed when Ar (or Kr) is added to Cl₂ excited at 1350 Å, while the other fluorescence bands are quenched. In that case, the 2580 Å time resolved signal which has a typical cascade behaviour (Fig. 4), is ascribed to the ${}^3\Pi_{2g} \rightarrow {}^3\Pi_{2u}$ "laser transition" with a measured radiative lifetime of 16 ns for the upper state.

A different and shorter lifetime, 8 ns, was obtained for the "u" upper state responsible for the emission around 2550 Å in pure Cl₂, while 3 ns and 5.5 ns were measured respectively for the 1990 Å and 2200 Å emissions.

Further consideration may help to characterize the "u" upper states responsible for fluorescence bands observed between 1400 Å and 3100 Å :

- (i) Comparison between absorption and excitation spectra
- (ii) Examination of the characteristic features due to bound free transitions.

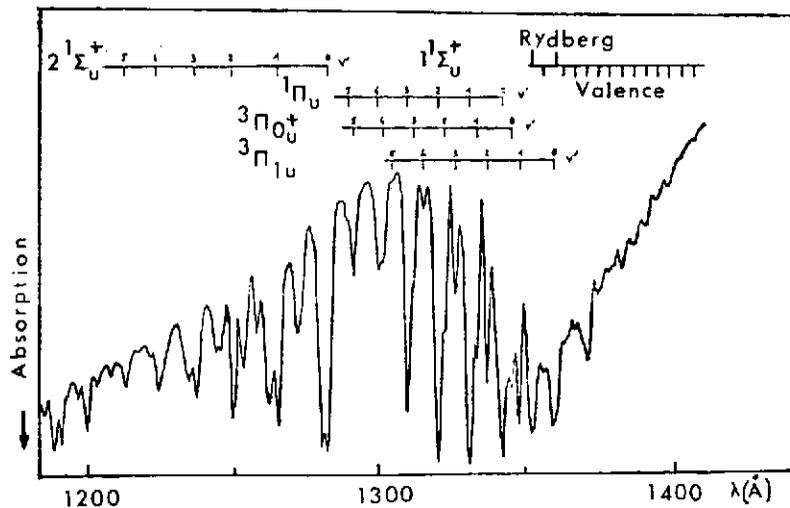


Fig. 5. Absorption spectrum of pure Cl₂ at medium resolution (0.5 Å).

Comparison between absorption and excitation spectra.

In the region 1300 - 1360 Å, three progressions of the absorption spectrum (Fig. 5) are assigned to transitions from the ground state towards Rydberg states ${}^1\Pi_u$, ${}^3\Pi_{0u}^+$ and ${}^3\Pi_{1u}$. The identification of these different systems, the numbering of vibrational levels and the determination of molecular parameters (T_e , ω_e , $\omega_e x_e$) are supported both by the recent absorption analysis at high resolution of natural and isotopic Cl₂ (12, 13, 14), and by our quantitative investigation which may be combined with calculation of FC factors for bound - bound transitions (14). The experimental electronic terms (T_e) are consistent with the theoretical calculation : an excellent agreement is obtained for the ${}^1\Pi_u$ state ($T_e = 74\,408\text{ cm}^{-1}$), but higher values are deduced for the triplet states ($T_e = 74\,237\text{ cm}^{-1}$ ${}^3(\Pi_{0u}^+)$ and $T_e = 73\,501\text{ cm}^{-1}$ ${}^3(\Pi_{1u})$).

Between 1360 and 1400 Å, a crowded region is more difficult to analyse. It consists mainly of red shaded bands arising from transitions between $X\,{}^1\Sigma_u^+$ ($v'' = 0$) to the ionic part of the lowest ${}^1\Sigma_u^+$ state dissociating in $Cl^+({}^1Dg) + Cl^-({}^1Sg)$.

When comparing the high resolution excitation spectra of the total fluorescence with absorption spectra, significant difference is observed. The most prominent progression of absorption (${}^1\Pi_u + {}^1\Sigma_g^+$) and the fainter progression (${}^3\Pi_{1u} + {}^1\Sigma_g^+$) are practically absent suggesting strong predissociation (probably by the 1u component of the repulsive ${}^3\Sigma_u^+$ state).

In that case, the possible emitting states, reached selectively between 1200 and 1500 Å, would be limited to the O_u^+ spin orbit components of only three states : ${}^1\Sigma_u^+$, ${}^3\Sigma_u^-$ and ${}^3\Sigma_u^+$, this last state being not yet calculated by Peyerimhoff, but being expected in this region.

Examination of the characteristic features due to bound-free transitions

Bound-free spectra display characteristic features which can be used to obtain information on the potential curves, as illustrated by different examples (rare gas halides (23, 24), rare gas excimers (25), metal dimers (6,26), halogen molecules (5,27), treated in literature. Recent papers (6,7) give a clear insight into the different approaches used for analy-

sing such spectra either by trial and error method through quantum mechanical calculations or by a semi-classical treatment.

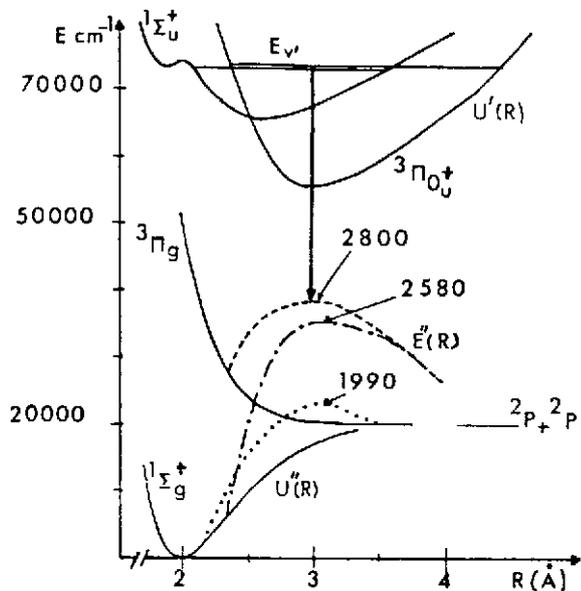


Fig. 6. Potential curves used for simulating bound-free emissions from a vibrational level with $E_{v'}$ energy. Difference potentials $E''(R)$ are indicated for different transitions $1\Sigma_u^+ \rightarrow 1\Sigma_g^+$, $3\Pi_u^+ \rightarrow 1\Sigma_g^+$, $3\Pi_u^+ \rightarrow 3\Pi_g$

Before starting with computation, it appears useful to use first the semi-classical approach with the stationary phase approximation as a guide for understanding and predicting the intensity distribution of the bound-free spectrum.

Following the semi-classical treatment introduced by Mulliken to interpret the structured spectrum of I_2 (Mc Lennan bands), two possibilities for transitions into the continuum have to be considered, depending on the shape of the difference potential curve $E''(R)$ defined by

$$E''(R) = E_{v'} - U'(R) + U''(R)$$

The classical application of the FC principle predicts that the emission from a vibrational level of energy $E_{v'}$ terminates on the dashed curve $E''(R)$, Fig.(6), which is the locus of points where kinetic energy is conserved (points of stationary phase).

For a monotonic difference potential (a single point of stationary phase) the semi classical model predicts structures reflecting the node of the upper vibrational wavefunction.

For an extremum in the difference potential (two points of stationary phase) three classical transitions are expected to give intensity maxima, the right and left turning points and also the transition to the Mulliken's difference potential extremum. Furthermore the contributions to the overlap integral from the two points can add constructively or destructively. In that case, the spectrum displays a characteristic modulated interference pattern with the appearance of broad oscillations which envelop fine structures (Fig. 7).

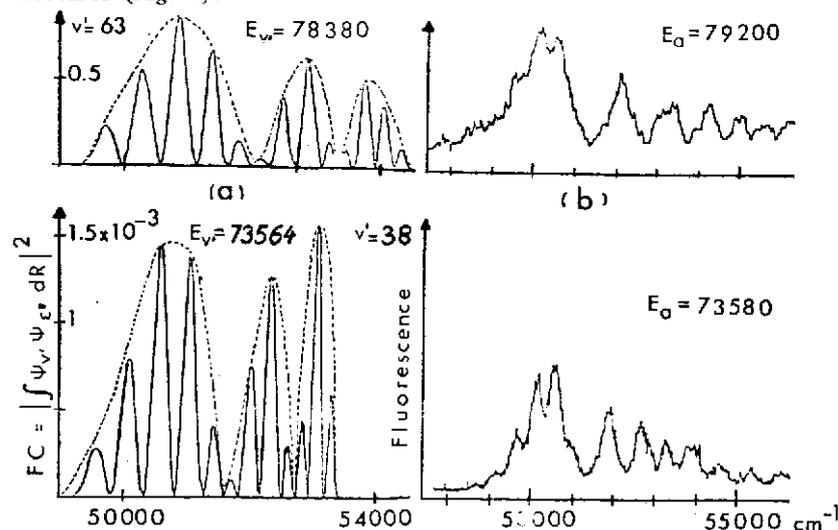


Fig. 7. Interference structures calculated (a) for $1\Sigma_u^+ \rightarrow 1\Sigma_g^+$ transitions. The energy value ($E_{v'}$) of the upper levels (v') are chosen in accordance with E_g excitation energies of the experimental spectra (b).

The semi classical treatment of the integrals detailed in several papers (6,24) clearly demonstrates the origin of the interference effect. It is shown that the narrow oscillations depend on the location of $E''(R)$ relative to the repulsive wall of the lower potential, while the broad oscillations depend on the shape of $E''(R)$. The spacing between the k th broad oscillation and the classical longwavelength limit ν_0 can be used to estimate some molecular parameters of the upper state (T_e , ω_e , v'). For a harmonic upper curve and a totally flat lower state, the following relation has been derived by Golde (24), where $E_{v'}$ is the vibrational energy.

$$\nu_k = \nu_0 + \left(\frac{3\pi}{2}\right)^{2/3} \left(k - \frac{3}{4}\right)^{2/3} \omega_e^{2/3} E_{v'}^{1/3}$$

Simulation of spectra

The goal of our computation is a quantitative description of fluorescence spectra with positions rather than intensities. Therefore it was not tried to optimize the potential functions, nor to take into account the variation of transition moments. Furthermore the effects of rotational energy and subsequent averaging were not introduced in our calculation. Franck-Condon overlap integral $\langle v' | e'' \rangle^2$ was calculated with numerical solution of the radial Schrodinger equation for the wavefunctions and numerical integration of the integral.

The $X^1\Sigma_g^+$ ground state was approximated by a Hulbert-Hirschfelder potential (28):

$$V(R) = D_e \left\{ (1 - e^{-\alpha R})^2 + c x^3 e^{-2x} (1 + bx) \right\} \text{ where } x = 2\beta \left(\frac{R - R_0}{R_0} \right)$$

with the following parameters $D_e = 20277 \text{ cm}^{-1}$, $\beta = 1.989$, $R_0 = 1.988 \text{ \AA}$, $c = 0.2126$ and $b = 1.2121$.

The theoretical repulsive lower states dissociating in $2P + 2P$ atoms (8) were estimated by the form $A \exp(-\alpha R)$. The adiabatic upper states, with a double well resulting of an avoided crossing, are more difficult to fit. On the grounds of our preceding work (14) a complex function was proposed for the $1\Sigma_u^+$ state dissociating in $Cl^+(1D_g) + Cl^-(1S_g)$ while for other ion-

pair states Morse functions have been used.

First we have examined the group of bands between 1400 and 2000. It is clear that the behavior of the fluorescence reflects the specific nature of the emitting $1\Sigma_u^+$ state which, in the adiabatic limit, is described by a double well structure. From our absorption analysis, corroborated by bound-bound F.C. calculation, we were able to assign the discrete features at high energy to bound-bound transitions between the $1\Sigma_u^+$ inner well (Rydberg type) towards the low vibrational levels of the $X^1\Sigma_g^+$ ground state.

Around 2000 \AA the broad bands are associated with bound-free transitions from the outer well (ionic type) to the continuum ground state. Explained by an extremum in the difference potential, the position of the long wavelength peak (1990 \AA) is independent of the excitation energy E_a , while successive spacing between broad maxima depends on $E_a^{1/3}$, in agreement with the semiclassical treatment recalled above. Fine structures, spaced by 15 - 20 \AA , are observed beneath the 1990 \AA band (Fig. 7).

To describe the double well structure of the $1\Sigma_u^+$ adiabatic state we used a complex analytical expression resulting from the combination of Morse and Coulombic potentials. This function has been defined in our preceding paper (14) with an adjustment of parameters such that a good agreement is achieved between high resolution absorption and excitation spectra, bound-bound calculations of F.C. factors and the semi-classical description of fluorescence spectra. It was found that our improved potential ($T_e = 65659 \text{ cm}^{-1}$) for the ionic part) was in good agreement with the $1\Sigma_u^+$ ab initio curve (Fig. 2).

Moreover the present quantum mechanical bound-free calculations constitutes an additional check of the potential curve in particular at large inter-nuclear distances. Thus, the bound-free calculations, for two different excitation energy ($v' = 34$ and $v' = 63$) reproduce well the experimental spectra with a good agreement for the broad oscillations as well as for the fine structures, confirming the reliability of our $1\Sigma_u^+$ curve (Fig. (7)).

The assignment of bands between 2000 and 3100 Å is more speculative.

In looking for the unknown upper potential, we supposed first that the group of bands observed around 2600 Å (Fig. 7) might be associated with the difference potential ${}^3\Pi_{ou}^+ - X {}^1\Sigma_g^+$. With the following parameters for the Morse curve, $T_e = 55\,900\text{ cm}^{-1}$, $D_e = 40\,000\text{ cm}^{-1}$, $R_e = 3.0\text{ Å}$, $\omega_e = 300\text{ cm}^{-1}$, $\tilde{\nu} = 0.764\text{ Å}^{-1}$, we calculated bound-free Franck-Condon factors for $v' = 68$ ($E_{v'} = 73816\text{ cm}^{-1}$). The simulated spectrum reproduces well (Fig. 8) the successive bands observed experimentally between 2200 and 2600 Å, with a fine structure interval ($\Delta\lambda \approx 35\text{-}40\text{ Å}$) in agreement with the experimental spacing in the 2550 Å region.

However, according to the experimental results published for Br_2 and I_2 about the respective positions of the ${}^3\Pi_{ou}^+$ and ${}^3\Pi_{og}^+$ states, the term value used for our simulation seems about 4000 cm^{-1} too low compared to the known ${}^3\Pi_{og}^+$ experimental value $T_e = 57816\text{ cm}^{-1}$ (20).

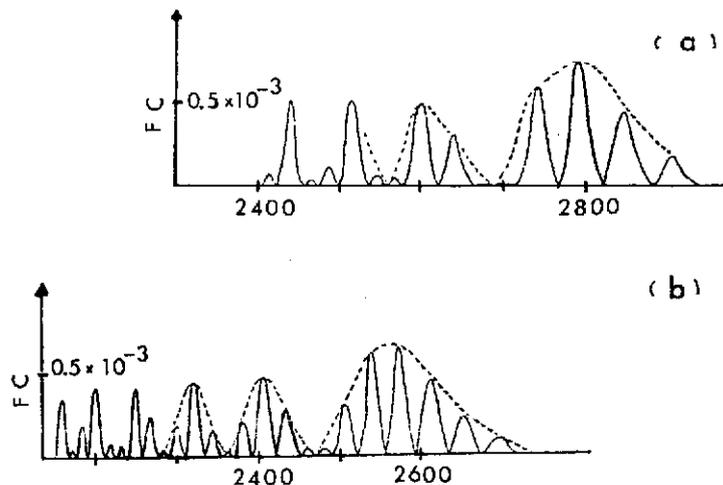


Fig. 8. Interference structures calculated for ${}^3\Pi_{ou}^+ + {}^3\Pi_{og}^+$ (a) and ${}^3\Pi_{ou}^+ + {}^1\Sigma_g^+$ transitions (b). The upper ion-pair state is approximated by a Morse function with parameters defined in the text.

In a second step we investigated which contribution would result from ${}^3\Pi_{ou}^+ + {}^3\Pi_{og}^+$ transitions with the ${}^3\Pi_{ou}^+$ state defined above. To characterize the lower ${}^3\Pi_{og}^+$ repulsive curve, dissociating in ${}^2P_{3/2} + {}^2P_{3/2}$ atoms, we used the Peyerimhoff's curve for the ${}^3\Pi_g$ state, assuming a simple exponential fit of the form $A \exp(-\alpha R)$ with $A = 44.96 \times 10^6\text{ cm}^{-1}$ and $\alpha = 5.68\text{ Å}^{-1}$.

For the same excitation energy ($v' = 68$, $E_{v'} = 73816\text{ cm}^{-1}$) series of bands were computed giving a long wavelength peak limit at 2800 Å (Fig. 8a). This result is by far very different from the experimental spectrum which shows, beyond 2500 Å, a single broad band at 3050 Å (Fig. 1). The most likely reason of this discrepancy seems to be due to the small term value of the ${}^3\Pi_{ou}^+$ state. Just before this meeting, we became aware of the

recent work of Ishiwata et al (29) which seems to give an answer to our questions. Following a 3 photon excitation of pure Cl_2 (via $B {}^3\Pi_{ou}^+$ state), it is shown that the spectrum, originating from the $v' = 0$ level of an upper o_u^+ state (most probably ${}^3\Pi_{ou}^+$ dissociating in $\text{Cl}_2^+({}^3P_1) + \text{Cl}^-({}^1S_0)$), consists of two types of transitions between 2700 Å and 2200 Å. The discrete part (around 2350) is attributed to $o_u^+ \rightarrow {}^1\Sigma_g^+$ ground state, while a broad band system around 2590 Å is assigned to $o_u^+ \rightarrow {}^3\Pi_{og}^+$ repulsive state. This result makes clear that we have to take into account both contributions in our simulation. With new bound-free calculations, we plan, for a near future, to examine the solution proposed by Ishiwata (29) ($T_e = 59927\text{ cm}^{-1}$). We shall also investigate the possibility that the isolated diffuse band at 3050 Å results from a transition between the double well ${}^1\Sigma_u^+$ state towards the ${}^1\Sigma_g^+$ repulsive state dissociating in ${}^2P_{1/2} + {}^2P_{1/2}$ atoms.

Conclusion.

Following a quantitative investigation of absorption spectra of Cl_2 , the present paper gives an analysis of fluorescence bands of Cl_2 between 1400 Å and 3100 Å in order to obtain additional information about upper states.

Series of broad bands, in the region 1900-2000 Å, are interpreted in terms of quantum interference associated with bound-free transitions from the outer well (ionic type) of the $^1\Sigma_u^+$ upper state towards the continuum of the ground state. Bound-free calculation corroborates this assignment and verifies the reliability of the double well $^1\Sigma_u^+$ potential curve proposed in our precedent article. It appears that only slight modifications of the ab initio potential calculated by Peyerimhoff were necessary to reach optimal agreement between experimental and simulated spectra.

Origin of the other fluorescence bands observed between 2000 and 3100 Å is more speculative. In view of our simulated spectra and the recent work of Ishiwata et al (29), the bands between 2000 and 2600 Å might be attributed to $^3\Pi_{ou}^+$ ($T_e = 59927 \text{ cm}^{-1}$) \rightarrow $^3\Pi_{og}^+$ and $^3\Pi_{ou}^+ \rightarrow ^1\Sigma_u^+$ transitions, whereas the isolated band at 3050 Å might be assigned to $^1\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ repulsive state dissociating in $^2P_{1/2} + ^2P_{1/2}$ atoms. Additional work is necessary to make more conclusive statements on their origin.

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