Natural hyperfine and magnetic predissociation of the I2 B state I. - Theory

Jacques Vigué, M. Broyer, J.C. Lehmann

► To cite this version:

Jacques Vigué, M. Broyer, J.C. Lehmann. Natural hyperfine and magnetic predissociation of the I2 B state I. - Theory. Journal de Physique, 1981, 42 (7), pp.937-947. 10.1051/jphys:01981004207093700 . jpa-00209086

HAL Id: jpa-00209086

<https://hal.science/jpa-00209086>

Submitted on 1 Jan 1981

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification

Physics Abstracts

33.60 — 33.80B — 33.80E — 82.50E

Natural hyperfine and magnetic predissociation of the I_2 B state

I. — Theory

J. Vigué, M. Broyer and J. C. Lehmann

Laboratoire de Spectroscopie Hertzienne de l'E.N.S. (*), 24, rue Lhomond, 75231 Paris Cedex 05, France

(Reçu le 19 novembre 1980, accepté le 25 mars 1981)

Résumé. — Cet article analyse en détail le phénomène de prédissociation gyroscopique, hyperfine et magnétique et calcule la dépendance de la probabilité de prédissociation en fonction des divers nombres quantiques dans le cas de l'état B de la molécule d'iode. Les particularités des très faibles prédissociations et des effets d'interférence entre prédissociations sont analysées et les techniques expérimentales applicables sont rapidement présentées. Cet article constitue enfin la base théorique des études expérimentales de la prédissociation de l'état B de l'iode décrites dans les deux articles suivants.

Abstract. — This paper analyses in detail the gyroscopic, hyperfine and magnetic predissociation phenomenon, and calculates the predissociation rate of molecular iodine. The peculiarities of very weak predissociations and of interference effects between predissociation are presented, and the experimental techniques available for that type of predissociation are discussed. This paper is the theoretical basis of the experimental studies of iodine B state predissociations which are described in the following two papers.

1. **Introduction.** — The study of molecular predissociation began half a century ago by the observation of a broadening of the lines in absorption spectra [1] (see also references quoted by Herzberg [2]). This technique is only sensitive to strong predissociation effects. Later on, several other techniques were developed which were much more sensitive : breaking-off in fluorescence bands, fluorescence quantum yield, lifetime measurements, atomic fragment detection... It has even been possible in the case of I_2 B state to measure predissociation rates smaller by several orders of magnitude than the radiative decay rate. This was possible thanks to an interference effect between a magnetic and a natural predissociation [3]. This led to the discovery in the I_2 B state of a predissociation due to hyperfine coupling [4].

To understand these very weak predissociations and their measurement techniques, it is necessary to complete the usual predissociation theory [1, 2]. The purpose of this publication is to present the theoretical calculations which are necessary for evaluating the predissociation rate of I_2 in the B state ; some generality will be kept throughout the calculations so that the results could be easily modified to apply to any other case. This paper is the first of a series of three : the following two papers [5] will present detailed

experimental studies of the hyperfine and magnetic predissociation of the I_2 B state.

2. **General theory of predissociation.** — Usually one considers as a starting point the discrete levels and the continua which appear in a Born-Oppenheimer treatment of the molecular Hamiltonian. We follow this presentation here. Moreover we exclude immediately two types of predissociation from the scope of this paper :

i) rotational predissociation : i.e. the predissociation of the quasi bound states which appear at the top of a potential well, with an energy larger than the dissociation limit but smaller than the rotational barrier. This predissociation is due to a tunnelling effect and cannot be represented by the following formalism ;

ii) indirect predissociation : i.e. the predissociation of a discrete level coupled by a perturbation to discrete levels of another electronic state, which in turn is coupled to a continuum. That type of predissociation presents some special features that we do not consider here.

Therefore we describe here only the predissociation of a discrete excited level m coupled to a continuum level n (i.e. a two state predissociation as opposed to a one (i) or three (ii) state predissociation).

(*) Associé au C.N.R.S.

The coupling Hamiltonian is V . The predissociation rate Γ_p is given by the Fermi Golden rule :

$$\Gamma_p = \frac{2\pi}{\hbar} |\langle \psi_m | V | \psi_n \rangle|^2 \quad (1)$$

where $|\psi_m\rangle$ is the wavefunction of the level m and $|\psi_n\rangle$ the wavefunction of the level n of the continuum having the same energy than the level m ($E_m = E_n$). We suppose that the wavefunctions of the continua are normalized so that

$$\langle \psi_m E_n | \psi'_m E'_n \rangle = \delta(E_n - E'_n). \quad (2)$$

This normalization condition implies that the density of states does not appear in the Fermi Golden rule (1). If several continua are coupled to m , a summation must be performed in equation (1).

This treatment is valid under two assumptions (given here, without demonstration since they appear in various references [6]) :

i) if we define the function $\gamma(E_n)$ by the following equation

$$\gamma(E_n) = \langle \psi_m E_m | V | \psi_n E_n \rangle$$

the variations of this function have a characteristic scale ΔE_n . Then the first condition is

$$\Gamma_p \ll \frac{\Delta E_n}{\hbar}. \quad (3)$$

Usually the variation of $\gamma(E_n)$ is mainly due to the variation of the Franck-Condon integral. Therefore the characteristic scale is given, in order of magnitude, by the quantum of vibration of the molecule :

$$\Delta E_n \approx \hbar \omega_v.$$

Then inequality (3) is equivalent to

$$\Gamma_p \ll \omega_v. \quad (4)$$

This is usually true ; otherwise, it means that the predissociation width of consecutive vibrational levels is comparable to their separation and the state merges into a quasi-continuum. However, the present treatment is then not valid and usually a strong coupling between two electronic states induces an anticrossing in the potential curves. A special treatment of this case has been made by Child [7].

ii) The second condition is the following : if two discrete states m and m' are coupled by V to the same level of the continuum, then the energy difference $\delta E = E_m - E_{m'}$ must be much larger than $\hbar \Gamma_p$:

$$\hbar \Gamma_p \ll \delta E. \quad (5)$$

This condition may not be always fulfilled ; it will therefore be necessary to discuss this point in each case.

If inequalities (3) and (5) are both fulfilled, one can then show [6] that the rate of predissociation is given by (1) and that the decay of the level m is exponential with a rate Γ given by :

$$\Gamma = \Gamma_{\text{rad}} + \Gamma_p + \Gamma_{\text{coll}} \quad (6)$$

where Γ_{rad} represents the radiative decay rate and Γ_{coll} the collisional decay rate. The rate of decay of a coherence between the levels m and m' is the average of the rates of decay of these two levels (at least in the absence of collisions).

The main problem now is to define the nature of the Hamiltonian V . This will be discussed in the next section. We want to stress immediately a very important point : if two Hamiltonians V_1 and V_2 couple a level m to the same level n , the predissociation rate is given by :

$$\begin{aligned} \Gamma_p &= \frac{2\pi}{\hbar} |\langle \psi_m | (V_1 + V_2) | \psi_n \rangle|^2 \\ &= \frac{2\pi}{\hbar} (|\langle \psi_m | V_1 | \psi_n \rangle|^2 + |\langle \psi_m | V_2 | \psi_n \rangle|^2 + \\ &\quad + 2 \operatorname{Re} (\langle \psi_m | V_1 | \psi_n \rangle \langle \psi_n | V_2 | \psi_m \rangle)). \end{aligned} \quad (7)$$

It appears clearly in equation (7) that the predissociation rate is then not the sum of the predissociation rates due to V_1 and V_2 but that an interference term arises which may be very important. In particular, if $V_1 \gg V_2$, the interference term is much larger than the square term in V_2 . Moreover, the existence of the interference term is direct evidence that two perturbation mechanisms couple the level m to the same level n . The observation of an effect due to an interference term is therefore a test of this last property ; it was used for the first time in the study of the iodine B state [3] and enabled us to prove that magnetic predissociation and natural predissociation are both due to the same 1u state.

3. Nature of the coupling Hamiltonian V . — From our standpoint, it is easy to see that V is made up of all the terms in the total molecular Hamiltonian which are not diagonal in the Born-Oppenheimer basis set. The following list contains all terms, including those due to an external field :

i) the vibrational Hamiltonian $\mathcal{H}_v$

$$\mathcal{H}_v = -\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \quad (8)$$

where r is the internuclear distance and μ the nuclear reduced mass. The effects of this term have been studied by Van Vleck [8] and many other authors [9].

ii) *The fine structure Hamiltonian* $\mathcal{H}_{F.S.}$

This Hamiltonian consists of four terms :

$$\mathcal{H}_{F.S.} = \mathcal{H}_{S.O.} + \mathcal{H}_{S.S.} + \mathcal{H}_{S.R.} + \mathcal{H}_{O.R.} \quad (9)$$

$\mathcal{H}_{S.O.}$ is the spin-orbit Hamiltonian, and $\mathcal{H}_{S.S.}$ is the spin-spin Hamiltonian. $\mathcal{H}_{S.R.}$ and $\mathcal{H}_{O.R.}$ are the spin-rotation and orbit-rotation Hamiltonian studied in detail by Van Vleck [10].

iii) *The rotational Hamiltonian* $\mathcal{H}_R$

$$\mathcal{H}_R = \frac{\hbar^2}{2\mu r^2} (\mathbf{J} - \mathbf{L} - \mathbf{S})^2 \quad (10)$$

$\mathbf{J}$ is the total angular momentum, $\mathbf{L}$ and $\mathbf{S}$ the total electronic orbital and spin angular momenta.

Following Freed [11], we can separate out various terms. The only terms that are non-diagonal are the $\mathbf{L.S}$, $\mathbf{J.L}$ and $\mathbf{J.S}$ terms. The $\mathbf{L.S}$ term, although of different origin, can be incorporated into the spin-orbit Hamiltonian. We therefore retain here only the second and third terms that we shall call the gyroscopic Hamiltonian :

$$\mathcal{H}_G = -\frac{\hbar^2}{2\mu r^2} (J_+(L_- + S_-) + J_-(L_+ + S_+)) \quad (11)$$

The quantization axis is the internuclear axis.

iv) *The hyperfine Hamiltonian*

It contains all tensorial electric or magnetic interactions of the nuclei with the electrons, or with the other nuclei. It can be written

$$\mathcal{H}_{HFS} = \mathcal{H}_{HFS}(a) + \mathcal{H}_{HFS}(b) + \mathcal{H}_{HFS}(a, b)$$

where a and b designate the two nuclei.

As the order of magnitude of $\mathcal{H}_{HFS}$ is rather small, we keep here only the two major terms :

— the nuclear magnetic-dipole interaction with the electrons (tensorial order $k = 1$);

— the nuclear electric-quadrupole interaction with the electrons (tensorial order $k = 2$).

We may therefore write

$$\mathcal{H}_{HFS} = \sum_{x=a,b} \sum_{k=1,2} \mathcal{H}_k(x) \quad (12a)$$

with

$$\mathcal{H}_k(x) = \sum_e \sum_q (-1)^q Q_q^k(\mathbf{I}_x) V_{-q}^k(x, e) \quad (12b)$$

In (12b) the summation goes over all electrons of the molecule, $Q_q^k(\mathbf{I}_x)$ is a tensorial operator of rank k acting on the nuclear spin $\mathbf{I}_x$, $V_{-q}^k(x, e)$ is a tensorial operator of rank k acting on the electron coordinates.

A detailed analysis of $\mathcal{H}_{HFS}$ is given in various references [12, 13].

v) *The Zeeman Hamiltonian* $\mathcal{H}_Z$

It also contains many terms [14, 15], but here we keep only the leading linear electronic terms :

$$\mathcal{H}_Z = -\mu_B \mathbf{B}(g_L \mathbf{L} + g_S \mathbf{S}) \quad (13)$$

where $\mathbf{B}$ is the magnetic field. Although the values of g_L and g_S differ slightly from 1 and 2 respectively, these values are a sufficient approximation here.

vi) *The Stark Hamiltonian* $\mathcal{H}_S$

It is given by

$$\mathcal{H}_S = -\mathbf{D.E} \quad (14)$$

where $\mathbf{D}$ is the electric dipole of the molecule and $\mathbf{E}$ the electric field.

4. Selection rules for the various terms of V . —

4.1 BORN-OPPENHEIMER BASIS SET. — In order to give selection rules, first we must introduce a basis set. We use a Hund's case a or c basis which is appropriate to the case of iodine (mostly case c). The molecular wavefunction can be denoted by the ket

$$|v, S\Lambda\Sigma\Omega, v, J, M_J\rangle$$

in case a. v stands for all omitted electronic quantum numbers; $S, \Lambda, \Sigma, \Omega, J, M_J$ are the usual notations for the angular momenta. v is the vibrational quantum number, which must be replaced by the energy of the level in the case of a continuum.

For a case c basis set, $S\Lambda\Sigma$ are no longer defined and the ket reduces to $|v, \Omega, v, J, M_J\rangle$.

Finally, if the nuclear spins are non-zero, we assume that the molecule is homonuclear (as is the case for $^{127}\text{I}_2$) and we use the symmetrical coupling scheme, $|J(I_a, I_b) IFM_F\rangle$. As has been pointed out [16], the eigenstates of the molecule are linear combinations of basis functions with various values of the total spin I . These combinations may be written :

$$|J\epsilon FM_F\rangle = \sum_I \alpha(I\epsilon JF) |J(I_a, I_b) IFM_F\rangle \quad (15)$$

(ϵ is a label).

4.2 SELECTION RULES. — We have summarized the selection rules in two tables. Table I gives the selection rules related to angular momenta. We also give for each term its dependence on J, μ , and the nuclear charge Z ; this dependence is calculated by assuming hydrogenic wavefunctions which may be a poor approximation [17]. Finally, an order of magnitude is estimated for each term in the Hamiltonian for the case of iodine.

Table II lists the parity selection rules. Three types of parity are considered :

- the total parity, denoted $+$ or $-$;
- the electronic parity for homonuclear diatomic molecules denoted $g - u$;
- the Krönig parity for $\Omega = 0$ states; this parity corresponding to the symmetry σ_v is also denoted $+$ or $-$.

The fact that the $u - g$ parity is violated by the

Table I. — *Angular momentum selection rules and orders of magnitude. For each term we give the selection rules for angular momenta, the dependence on Z , μ and J , and finally a rough estimate of the order of magnitude for iodine. (The magnetic field was taken as 1 tesla, the electric field as 10^6 V/m and the dipole as of 1 Debye.)*

Hamiltonian	$ \Delta A $	$ \Delta S $	$ \Delta \Sigma $	$ \Delta \Omega $	$ \Delta J $	Z, μ, J variation	Order of magnitude (cm^{-1})
$\mathcal{H}_V$	0	0	0	0	0	$\mu^{-0.75}$	100
$\mathcal{H}_{S.O.}$	≤ 1	≤ 1	≤ 1	0	0	Z^4	7 000
$\mathcal{H}_{S.S.}$	≤ 2	≤ 2	≤ 2	0	0		≤ 1
$\mathcal{H}_{O.R.}$	≤ 1	0	0	≤ 1	0	J	$10^{-4} J$
$\mathcal{H}_{S.R.}$	≤ 1	≤ 1	≤ 1	≤ 1	0	J	$10^{-4} J$
$\mathcal{H}_G$	≤ 1	0	≤ 1	$= 1$	0	$\mu^{-1} J$	0.06 J
$\mathcal{H}_{HFS} \left\{ \begin{array}{l} \mathcal{H}_{M.D.}(k=1) \\ \mathcal{H}_{E.Q.}(k=2) \end{array} \right.$	≤ 1 ≤ 2	≤ 1 0	≤ 1 0	≤ 1 ≤ 2	≤ 1 ≤ 2	Z^3 Z^3	0.3 0.1
$\mathcal{H}_Z$	≤ 1	0	≤ 1	≤ 1	≤ 1		0.5
$\mathcal{H}_S$	≤ 1	0	0	≤ 1	≤ 1		1

Table II. — *Parity selection rules : $A + (-)$ indicates that the Hamiltonian is even (odd).*

Hamiltonians	Parities		
	Total parity	u - g parity	Krönig parity ($\Omega = 0$)
$\mathcal{H}_V$	+	+	+
$\mathcal{H}_{F.S.}$	+	+	+
$\mathcal{H}_G$	+	+	+
$\mathcal{H}_{HFS}$	+	no rule	no rule
$\mathcal{H}_Z$	+	+	-
$\mathcal{H}_S$	-	-	+

hyperfine Hamiltonian has been pointed out by Herzberg in his book [2] (page 138).

An important remark arising from the discussion of table II is that, as the Stark Hamiltonian is the only one that couples states of opposite total parity, it cannot interfere with any other Hamiltonian. Therefore, its contribution to a predissociation will always be quadratic in the electric field; to our knowledge, the first evidence for such a predissociation has been given very recently in the I_2 B state [21].

Finally, although not considered here, a predissociation can be induced by collisions [2]. This process has in fact no precise selection rule as is clear if one

considers the low symmetry of a collision between two molecules.

5. Tensorial expressions for the various Hamiltonians. — The evaluation of equation (7) is quite difficult when one of the Hamiltonians is the hyperfine or Zeeman Hamiltonian. In order to make this evaluation simple and automatic, we use a tensorial operator method which enables the use of well known results of Racah algebra. This method appears in our previous paper on hyperfine structure [13] particularly in its appendix. We refer the reader to this paper, and we summarize in the following lines only some fundamental definitions.

We give an equivalent tensorial form for each of the five Hamiltonians. We introduce a projection operator $P_{\Omega v J}$ (or $P_{\Omega v J I}$) which restricts the action of the operator to the sublevels of the level $|\Omega v J\rangle$ (or $|\Omega v J I\rangle$). We define two irreducible tensor operator basis sets ${}^{\Omega \Omega'}_{JJ'} T_q^k$ and ${}_I T_q^k$ where the first operates on all coordinates except nuclear spins and the second on the nuclear spins only. ${}^{\Omega \Omega'}_{JJ'} T_q^k$ has non-vanishing matrix elements only between the levels $\langle \Omega J |$ and $|\Omega' J'\rangle$, and ${}_I T_q^k$ only between states of total nuclear spin I and I' . Three subcases appear, depending on whether the operator has an explicit J and I dependence.

i) The terms having no explicit J or I dependence are $\mathcal{H}_V$, $\mathcal{H}_{S.O.}$, $\mathcal{H}_{S.S.}$.

$$P_{\Omega v J}(\mathcal{H}_V + \mathcal{H}_{S.O.} + \mathcal{H}_{S.S.}) P_{\Omega' v' J'} = \langle \Omega v | \mathcal{H}_V + \mathcal{H}_{S.O.} + \mathcal{H}_{S.S.} | \Omega' v' \rangle \sqrt{2J+1} \delta_{JJ'} \delta_{\Omega \Omega'} {}^{\Omega \Omega'}_{JJ'} T_0^0. \quad (16)$$

ii) The terms having a J but no I dependence are $\mathcal{H}_{S.R.}$, $\mathcal{H}_{O.R.}$, $\mathcal{H}_G$, $\mathcal{H}_Z$ and $\mathcal{H}_S$

$$P_{\Omega v J} \mathcal{H}_G P_{\Omega' v' J'} = v(\Omega, \Omega', v, v', J) \delta_{JJ'} {}^{\Omega \Omega'}_{JJ'} T_0^0 \quad (17a)$$

with

$$v(\Omega, \Omega', v, v', J) = (2J+1) \sqrt{J(J+1)} (-1)^{J-\Omega+1} \begin{pmatrix} J & 1 & J \\ -\Omega & -\Delta\Omega & \Omega' \end{pmatrix} \times \left\langle \Omega v \left| \frac{\hbar^2}{\mu r^2} (T_{-\Delta\Omega}^1(\mathbf{L}) + T_{-\Delta\Omega}^1(\mathbf{S})) \right| \Omega' v' \right\rangle \quad (17b)$$

and $\Delta\Omega = \Omega' - \Omega$.

Equations similar to (17a) can be written for $\mathcal{H}_{S,R}$ and $\mathcal{H}_{O,R}$ but the general definition of v for these Hamiltonians is quite lengthy. A detailed evaluation of their order of magnitude is given for the case of iodine in the thesis of one of us [18]. It appears that these two terms will be masked by $\mathcal{H}_G$ for $\Delta\Omega = \pm 1$ coupling and by other fine structure terms for a $\Delta\Omega = 0$ coupling. However, it is clear that the spin-rotation term can couple two states with $\Delta S = 1$ which $\mathcal{H}_G$ cannot. Therefore, neglecting $\mathcal{H}_{S,R}$ and $\mathcal{H}_{O,R}$ will be more a matter of convenience than a general property

$$P_{\Omega v J} \mathcal{H}_Z P_{\Omega' v' J'} = w_Z(\Omega, \Omega', v, v', J, J') B_{JJ'}^{\Omega\Omega'} T_0^1 \quad (18a)$$

with

$$w_Z(\Omega, \Omega', v, v', J, J') = \frac{\mu_B}{\sqrt{3}} (-1)^{J'-\Omega+1} \begin{pmatrix} J & 1 & J' \\ -\Omega & -\Delta\Omega & \Omega' \end{pmatrix} \times \\ \times \sqrt{(2J+1)(2J'+1)} \langle \Omega v | (T_{-\Delta\Omega}^1(\mathbf{L}) + 2 T_{-\Delta\Omega}^1(\mathbf{S})) | \Omega' v' \rangle \quad (18b)$$

$$P_{\Omega v J} \mathcal{H}_S P_{\Omega' v' J'} = w_S(\Omega, \Omega', v, v', J, J') E_{JJ'}^{\Omega\Omega'} T_0^1 \quad (19a)$$

with

$$w_S(\Omega, \Omega', v, v', J, J') = \frac{1}{\sqrt{3}} (-1)^{J'-\Omega+1} \begin{pmatrix} J & 1 & J' \\ -\Omega & -\Delta\Omega & \Omega' \end{pmatrix} \times \\ \times \sqrt{(2J+1)(2J'+1)} \langle \Omega v | T_{-\Delta\Omega}^1(\mathbf{D}) | \Omega' v' \rangle. \quad (19b)$$

Equations (17), (18), (19) are deduced from the paper of Freed [11]. It has been assumed that the electric or magnetic field is parallel to the quantization axis of the laboratory frame.

iii) Finally only the hyperfine terms have a direct I and J dependence. They are examined in detail in reference [13] and we recall only the main results, valid only for a neutral homonuclear diatomic molecule :

$$P_{\Omega v J I} \mathcal{H}_{HFS} P_{\Omega' v' J' I'} = \sum_{k=1,2} \sum_{x=a,b} w_k(x, \Omega, \Omega', v, v', J, J', I, I') \times \sum_q (-1)^q E_{JJ'}^{\Omega\Omega'} T_q^k I I' T_{-q}^k \quad (20a)$$

with the definition of w_k :

$$w_k(x, \Omega, \Omega', v, v', J, J', I, I') = \frac{(-1)^{k+2I_x+I'+J'}}{2k+1} f_k(x, \Omega, v, \Omega', v') \times \\ \times [(2I+1)(2I'+1)(2J+1)(2J'+1)]^{1/2} \begin{pmatrix} J & k & J' \\ -\Omega & -\Delta\Omega & \Omega' \end{pmatrix} \left\{ \begin{matrix} k & I & I' \\ I_x & I_x & I_x \end{matrix} \right\}. \quad (20b)$$

The coefficients f_k are defined as follows :

$$f_k(x, \Omega, v, \Omega', v') = (-1)^\Omega \langle \Omega v | V_{-\Delta\Omega}^k(x, e) | \Omega' v' \rangle \langle I_x || Q^k(I_x) || I_x \rangle. \quad (20c)$$

They satisfy the symmetry rule [13, 18] :

$$f_k(a, \Omega, v, \Omega', v') = \pm f_k(b, \Omega, v, \Omega', v') \quad (21)$$

+ if the states Ω and Ω' have the same u - g parity, - in the opposite case.

Finally it is important to recall the result of reference [13] concerning the reduced matrix element of the tensorial operators $E_{JJ'}^{\Omega\Omega'} T_q^k$ and $I I' T_q^k$:

$$\langle \Omega J || E_{JJ'}^{\Omega\Omega'} T^k || \Omega' J' \rangle = \sqrt{2k+1} \\ \langle I || I I' T^k || I' \rangle = \sqrt{2k+1}.$$

Moreover, we must note that a small implicit J dependence remains in all the matrix elements involving the vibrational quantum numbers v and v' , because the vibrational wavefunctions and therefore their overlap integrals are always J -dependent.

6. Predissociation rates as a function of the various quantum numbers. Influence of the Zeeman and hyperfine Hamiltonians. — We want to evaluate equation (1) in which V represents the sum of all the Hamiltonians studied

previously. We suppose that the state is coupled to only one continuum n . This evaluation presents new features only if the Zeeman and (or) the hyperfine Hamiltonian play a role in the final results. In all other cases, the result is quite simple and well known. Therefore we limit this calculation to two cases :

- the case of iodine B state ;
- a rapid survey of all other cases in which it will be possible to observe easily Zeeman and hyperfine predissociations.

6.1 HYPERFINE AND MAGNETIC PREDISSOCIATION OF IODINE B STATE. — The $B^3\Pi_{0^+u}$ state of I_2 is predissociated by the $^1\Pi_{1u}$ state. From the various selection rules, it is easy to see that only $\mathcal{H}_G$, $\mathcal{H}_{S.R.}$, $\mathcal{H}_{O.R.}$, $\mathcal{H}_{HFS}$ and $\mathcal{H}_Z$ can couple these two states (iodine is mostly case c and therefore the selection rules on S , A and Σ have little value). We neglect $\mathcal{H}_{S.R.}$ and $\mathcal{H}_{O.R.}$ for reasons stated above. The predissociation rate of the sublevel $|B^3\Pi_{0^+u}, v, J, \varepsilon, F, M_F\rangle$ is given by

$$\Gamma_p(v, J, \varepsilon, F, M_F) = \frac{2\pi}{\hbar} \sum_{J'I'F'} |\langle B^3\Pi_{0^+u}, v, J, \varepsilon, F, M_F | (\mathcal{H}_G + \mathcal{H}_Z + \mathcal{H}_{HFS}) | ^1\Pi_{1u}, E, J', I', F', M_F \rangle|^2. \quad (22)$$

This expression appears very impressive and leads indeed to a large number of terms. We are going to simplify it by a three step approach. At first we suppose that there are no nuclear spins, and we study only the effect of $\mathcal{H}_G$ and $\mathcal{H}_Z$. In a second step we suppose that the magnetic field is zero but that the nuclear spins are present. Finally we consider the general case.

6.1.1 No nuclear spins. — The nuclear spins and consequently the hyperfine Hamiltonian disappear from equation (22) which becomes :

$$\Gamma_p(v, J, M_J) = \frac{2\pi}{\hbar} \sum_{J'} |\langle B^3\Pi_{0^+u}, v, J, M_J | \mathcal{H}_G + \mathcal{H}_Z | ^1\Pi_{1u}, E, J', M_J \rangle|^2. \quad (23)$$

The validity of this expression requires satisfaction of condition (5). Considering the selection rules on J' and the total parity selection rules, it appears that consecutive discrete levels coupled to the same level of the continuum are : v, J and $v, J + 2$ in non-zero magnetic field, and v, J and $v + 1, J$ in zero field. The energy difference δE is then given by :

$$\begin{aligned} \delta E &= \hbar\omega_v & \text{if } B &= 0 \\ \delta E &= 4 B_v J & \text{if } B &\neq 0. \end{aligned}$$

Condition (5) is $\delta E \gg \hbar\Gamma_p$; this is always true in I_2 as Γ_p remains of the order of magnitude of the radiative width.

Equation (23) has already been derived in our previous work [3], and it was evaluated directly. It is, however, a good example of how to use the T_q^k formalism. Let us give, for instance, an evaluation of the square term in $\mathcal{H}_Z$ that we denote $Y(\mathcal{H}_Z - \mathcal{H}_Z)$. As the calculation is general we keep Ω and Ω' in the formulae.

$$Y(\mathcal{H}_Z - \mathcal{H}_Z) = \frac{2\pi}{\hbar} \sum_{J'} |\langle \Omega, v, J, M_J | \mathcal{H}_Z P_{\Omega'EJ'} \mathcal{H}_Z | \Omega, v, J, M_J \rangle|^2 \quad (24)$$

$$P_{\Omega v J} \mathcal{H}_Z P_{\Omega' EJ'} \mathcal{H}_Z P_{\Omega v J} = w_Z(\Omega, \Omega', v, E, J, J') w_Z(\Omega', \Omega, E, v, J', J) B^2 \frac{\Omega \Omega'}{JJ'} T_0^1 \frac{\Omega' \Omega}{J' J} T_0^1. \quad (25)$$

The recoupling of the two T_0^1 is made by the use of a formula from the Appendix of reference [13].

$$\frac{\Omega \Omega'}{JJ'} T_0^1 \frac{\Omega' \Omega}{J' J} T_0^1 = \sum_{K=0,2} (-1)^{2J'} 3\sqrt{2K+1} \begin{pmatrix} 1 & 1 & K \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} 1 & 1 & K \\ J & J & J' \end{matrix} \right\} \frac{\Omega \Omega'}{JJ'} T_0^K.$$

The summation on J' occurring in formula (24) is also easy if one uses the definition of w_Z (equation 18b) and the appendix of reference [13]. This summation is possible in closed form only if one assumes that the variation with J of the continuum vibrational wavefunction is slow enough so that

$$\langle v, (J) | E, (J) \rangle = \langle v, (J) | E, (J \pm 1) \rangle \quad (26)$$

holds. This assumption is quite good in most cases. Then the result is in the general case :

$$Y(\mathcal{H}_Z - \mathcal{H}_Z) = |\alpha_v|^2 B^2 \sum_{K=0,2} (2K+1)(2J+1) \begin{pmatrix} 1 & 1 & K \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & K \\ \Delta\Omega & -\Delta\Omega & 0 \end{pmatrix} \times \\ \times (-1)^{J-\Omega'} \begin{pmatrix} J & J & K \\ \Omega & -\Omega & 0 \end{pmatrix} (-1)^{J-M_J} \begin{pmatrix} J & K & J \\ -M_J & 0 & M_J \end{pmatrix}, \quad (27)$$

with α_v defined by

$$\alpha_v = \sqrt{\frac{2\pi}{\hbar}} \mu_B \langle \Omega v | (T_{-\Delta\Omega}^1(\mathbf{L}) + 2 T_{-\Delta\Omega}^1(\mathbf{S})) | \Omega', E \rangle. \quad (28)$$

Having given this part of the calculation in detail, we can now proceed to the final result for the evaluation of equation (22), in the case of the iodine B state ($\Omega = 0, \Omega' = 1$).

$$\Gamma_p(v, J, M_J) = C_v^2 J(J+1) + \alpha_v C_v \sqrt{2} B M_J + \frac{1}{3} (\alpha_v B)^2 \left[1 + \frac{3 M_J^2 - J(J+1)}{(2J-1)(2J+3)} \right], \quad (29)$$

with

$$C_v = \sqrt{\frac{2\pi}{\hbar}} \left\langle B^3\Pi_{0^+u} v \left| \frac{\hbar^2}{\sqrt{2} \mu r^2} (T_{-1}^1(\mathbf{L}) + T_{-1}^1(\mathbf{S})) \right| {}^1\Pi_{1u} E \right\rangle \quad (30)$$

$$\alpha_v = \sqrt{\frac{2\pi}{\hbar}} \mu_B \langle B^3\Pi_{0^+u} v | (T_{-1}^1(\mathbf{L}) + 2 T_{-1}^1(\mathbf{S})) | {}^1\Pi_{1u} E \rangle. \quad (31)$$

The relative phases of the wavefunctions of the two states 0_u^+ and 1_u are chosen so that α_v and C_v are real. It is easy to verify that equation (29) is equivalent to equation (5) of reference [3b]. It is clear that the C_v^2 term is the pure gyroscopic term, the α_v^2 term the pure magnetic term, and the $\alpha_v C_v$ term is the interference term between the magnetic and natural predissociation.

6.1.2 *No magnetic field but with nuclear spins.* — We must then evaluate

$$\Gamma_p(v, J, \varepsilon, F) = \frac{2\pi}{\hbar} \sum_{J'I'} |\langle B^3\Pi_{0^+u} v J \varepsilon F | \mathcal{H}_G + \mathcal{H}_{\text{HFS}} | {}^1\Pi_{1u} E, J' I' F \rangle|^2. \quad (32)$$

This probability is obviously independent of M_F (therefore omitted in equation (32)). Condition (5) must be fulfilled. Consecutive energy levels coupled to the same level of the continuum are hyperfine sublevels of the level $B^3\Pi_{0^+u} v, J$; their energy separation δE is of the order of the hyperfine splitting δE_{HFS} . The validity of equation (32) requires that :

$$\Gamma_p \ll \delta E_{\text{HFS}}/\hbar.$$

This condition is well verified in the case of I_2 but it might not always be so. Using the definition of the hyperfine eigenstates (15), we get :

$$\Gamma_p(v, J, \varepsilon, F) = \sum_{I'I''} \alpha(I \varepsilon J F)^* \alpha(I'' \varepsilon J F) \times \Gamma(v, J, I, I'', F) \quad (33a)$$

with the definition

$$\Gamma(v, J, I, I'', F) = \frac{2\pi}{\hbar} \sum_{J'I'} \langle B^3\Pi_{0^+u} v, J, I, F | (\mathcal{H}_G + \mathcal{H}_{\text{HFS}}) | \times \\ | {}^1\Pi_{1u} E, J', I', F \rangle \langle {}^1\Pi_{1u} E, J', I', F | (\mathcal{H}_G + \mathcal{H}_{\text{HFS}}) | B^3\Pi_{0^+u} v, J, I'', F \rangle. \quad (33b)$$

The evaluation of (33b) is certainly tedious. The use of the formalism of reference [13] enables us to make the summation over I' and J' , provided that equation (26) is a good approximation. The results of evaluation of (33b) give several terms which are either quadratic in one Hamiltonian or due to interference. We denote these terms formally :

$$\Gamma = \Gamma_{\text{GG}} + \Gamma_{\text{G1}} + \Gamma_{\text{G2}} + \Gamma_{\text{1G}} + \Gamma_{\text{2G}} + \Gamma_{\text{11}} + \Gamma_{\text{22}} + \Gamma_{\text{12}} + \Gamma_{\text{21}}, \quad (34a)$$

where G , 1, 2 designate respectively the gyroscopic Hamiltonian and the tensorial orders 1 and 2 of the hyperfine Hamiltonian. These terms are given by the following equations :

$$\Gamma_{GG} = C_v^2 J(J+1) \quad (34b)$$

$$\begin{aligned} \Gamma_{kk}(v, J, I, I'', F) &= \frac{4\pi}{\hbar} f_k(a, 1u, E, 0^+u, v) f_{k'}(a, 1u, E, 0^+u, v) (-1)^{I+F+1} \times \\ &\times (2J+1) [(2I+1)(2I''+1)]^{1/2} \sum_K (2K+1) \begin{pmatrix} k & k' & K \\ 1 & -1 & 0 \end{pmatrix} \begin{pmatrix} J & J & K \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} F & I & J \\ K & J & I'' \end{matrix} \right\} \\ &\times \left[(-1)^{k+k'+I} \left\{ \begin{matrix} K & k & k' \\ I_a & I_a & I_a \end{matrix} \right\} \left\{ \begin{matrix} K & I & I'' \\ I_a & I_a & I_a \end{matrix} \right\} + (-1)^K \left\{ \begin{matrix} I_a & I_a & I'' \\ I_a & I_a & I \\ k & k' & K \end{matrix} \right\} \right] \end{aligned} \quad (34c)$$

$$\begin{aligned} \Gamma_{Gk} &= 4 C_v \sqrt{\frac{\pi}{\hbar}} f_k(a, 1u, E, 0^+u, v) (-1)^{k+I+I''+2I_a+F+J+1} (2J+1)^{3/2} [J(J+1)]^{1/2} \times \\ &\times [(2I+1)(2I''+1)]^{1/2} \begin{pmatrix} J & J & 1 \\ 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} J & J & k \\ 0 & -1 & 1 \end{pmatrix} \left\{ \begin{matrix} k & I & I'' \\ I_a & I_a & I_a \end{matrix} \right\} \left\{ \begin{matrix} F & I & J \\ k & J & I'' \end{matrix} \right\} \end{aligned} \quad (34d)$$

$$\Gamma_{Gk} = \Gamma_{kG} \quad (34e)$$

This expression is very complex, even when it is written in this compact form. It is easy to verify that as the $3J \begin{pmatrix} J & J & K \\ 0 & 0 & 0 \end{pmatrix}$ is equal to zero if K is odd, only even values of K contribute to Γ_{kk} . Similarly when Γ_{12} is added to Γ_{21} , the terms involving the $9J$ symbols cancel.

In the case of the iodine B state, it has appeared that a simplified version of the present theory is in good agreement with all the available experimental results [15, 18, 5]. The simplification consists in neglecting the contribution of the electric quadrupole term ($k=2$) of the hyperfine Hamiltonian. Then, a new selection rule $I=I''$ appears in equation (33) and the predissociation rate takes a much simpler form :

$$\Gamma_p(v, J, \varepsilon, F) = \sum_I |\alpha(I, \varepsilon, J, F)|^2 \Gamma(v, J, I, F) \quad (35a)$$

with

$$\begin{aligned} \Gamma(v, J, I, F) &= C_v J^2 - a_v C_v \sqrt{2} \mathbf{I} \cdot \mathbf{J} + \\ &+ \frac{a_v^2}{3} \left[\mathbf{I}^2 + \frac{3(\mathbf{I} \cdot \mathbf{J})^2 + \frac{3}{2} \mathbf{I} \cdot \mathbf{J} - \mathbf{I}^2 \mathbf{J}^2}{(2J-1)(2J+3)} \right] \end{aligned} \quad (35b)$$

with the following notation

$$a_v = \sqrt{\frac{2\pi}{\hbar}} f_1(a, 1u, E, 0^+u, v) / (I_a(I_a+1)(2I_a+1))^{1/2} \quad (35c)$$

and

$$\mathbf{I} \cdot \mathbf{J} = \frac{1}{2} (\mathbf{F}^2 - \mathbf{J}^2 - \mathbf{I}^2) \quad \text{and} \quad \mathbf{A}^2 = A(A+1).$$

The validity of this particular form of the predissociation rate expression has no general theoretical

basis. A discussion of its validity in the case of I_2 will be given in the following papers [5].

6.1.3 *General case.* — We must first discuss the validity condition (5). The level

$$|{}^1\Pi_{1u}, E', J', I', F', M_F\rangle$$

is coupled to all the levels $|B^3\Pi_{0^+u}, v, J, I, F, M_F\rangle$ as long as $|J-J'| \leq 2$, $|I-I'| \leq 2$, $|F-F'| \leq 1$. It is therefore probable that the energy difference between two Zeeman hyperfine sublevels having the same value of v, J and M_F can be smaller than their predissociation widths for some values of the magnetic field. Then, for this pair of levels, condition (5) is not fulfilled and the predissociation effects are not described by equation (22). However, for each value of the magnetic field, only a very small fraction of all the Zeeman sublevels are affected by this problem, at least if the average predissociation rate $\langle \Gamma_p \rangle$ is much smaller than the typical zero field hyperfine splitting δE_{HFS} . This is the case in the I_2 B state, thus we will assume the validity of equation (22).

However, in order to calculate the predissociation rates, we need a second assumption : we assume that the wavefunctions are well approximated by their low field limit :

$$|J\varepsilon FM_F\rangle = \sum_I \alpha(I\varepsilon JF) |JIFM_F\rangle.$$

It must be pointed out that, if these two assumptions prove to be unsatisfactory, a complete diagonalization of the hyperfine and Zeeman Hamiltonians should be made for each value of the magnetic field. This will require an enormous amount of

computer time as the number of Zeeman hyperfine sublevels is large, about 4 000 if $J = 100$ for $^{127}\text{I}_2$.

The evaluation of equation (22) is quite easy. We may write :

$$\Gamma_p(v, J, \varepsilon, F, M_F) = \Gamma_p(B = 0) + \Gamma_{ZZ} + \Gamma_{GZ} + \Gamma_{ZG} + \Gamma_{Z,\text{HFS}} + \Gamma_{\text{HFS},Z} \quad (36)$$

The term $\Gamma_p(B = 0)$ is the predissociation rate in

zero field, it is given by equation (34) or (35). The other terms are evaluated always with the same tensorial formalism. In the Zeeman hyperfine interference term $\Gamma_{Z,\text{HFS}}$ and $\Gamma_{\text{HFS},Z}$, we have shown [15, 18] that the term involving the electric quadrupole ($k=2$) term of the hyperfine Hamiltonian vanishes; this is a special circumstance due to the fact that the B state is an $\Omega = 0$ state. As a consequence of this property, for all the magnetic terms, the selection rule $I = I''$ holds :

$$\Gamma_p(v, J, \varepsilon, F, M_F) = \Gamma_p(v, J, \varepsilon, F, M_F)_{(B=0)} + \sum_I |\alpha(I\varepsilon JF)|^2 (\Gamma_{ZG} + \Gamma_{GZ} + \Gamma_{Z,\text{HFS}} + \Gamma_{\text{HFS},Z} + \Gamma_{ZZ}) (vJIFM_F) \quad (37a)$$

with the values

$$(\Gamma_{ZG} + \Gamma_{GZ})(v, J, I, F, M_F) = \sqrt{2} \alpha_v B C_v M_F \frac{\mathbf{F} \cdot \mathbf{J}}{F^2} \quad (37b)$$

$$(\Gamma_{Z,\text{HFS}} + \Gamma_{\text{HFS},Z})(v, J, I, F, M_F) = -\alpha_v B a_v \frac{M_F}{F(F+1)} \times \frac{2}{3} \times \left[\mathbf{I} \cdot \mathbf{F} + \frac{3(\mathbf{F} \cdot \mathbf{J})(\mathbf{J} \cdot \mathbf{I}) - \mathbf{J}^2(\mathbf{I} \cdot \mathbf{F})}{(2J-1)(2J+3)} \right] \quad (37c)$$

$$\Gamma_{ZZ}(v, J, I, F, M_F) = (\alpha_v B)^2 \times \frac{1}{3} \times \left[1 + \frac{2(3M_F^2 - F(F+1))}{F(F+1)} \times \frac{3(\mathbf{J} \cdot \mathbf{F})^2 - \frac{3}{2}\mathbf{J} \cdot \mathbf{F} - \mathbf{F}^2 \mathbf{J}^2}{(2F-1)(2F+3)(2J-1)(2J+3)} \right] \quad (37d)$$

We have given explicit forms to the $3J$ and $6J$ symbols; the values of $\mathbf{I} \cdot \mathbf{F}$ and $\mathbf{J} \cdot \mathbf{F}$ are given by :

$$\mathbf{I} \cdot \mathbf{F} = \frac{1}{2} (\mathbf{F}^2 - \mathbf{J}^2 + \mathbf{I}^2)$$

$$\mathbf{J} \cdot \mathbf{F} = \frac{1}{2} (\mathbf{F}^2 + \mathbf{J}^2 - \mathbf{I}^2),$$

C_v , a_v and α_v are given by equations (30), (31) and (35c).

It is important to note that the predissociation rate and therefore the lifetime depends now on all the quantum numbers $v, J, \varepsilon, F, M_F$. This completely describes the very unusual properties of the predissociation of the iodine B state [3, 4, 15, 18].

6.2 OTHER FAVOURABLE CASES FOR OBSERVATION OF AN HYPERFINE AND/OR MAGNETIC PREDISSOCIATION. — We have just considered in detail the case of the B state of iodine. It is the first and still unique observation of a gyroscopic, hyperfine and magnetic predissociation. The goal of this section is to consider the other cases in which the magnetic or hyperfine coupling can create observable effects on predissociation rates. In all cases, the masking effect by a stronger predissociation should be kept in mind and the eventual interference effects considered. (This last point was overlooked by Huo [19] in her magnetic predissociation study.)

We may distinguish three cases depending on the values of $\Delta\Omega = \Omega' - \Omega$: $\Delta\Omega = 0, \pm 1, \pm 2$.

6.2.1 Case $\Delta\Omega = \pm 1$. — This case has been considered for the iodine B state, with the special values

$$\Omega = 0, \quad \Omega' = 1.$$

We could have calculated the general case in the same way. The points that we must stress are the following :

i) Usually, the predissociation effects due to the gyroscopic Hamiltonian will be much larger than effects due to the hyperfine Hamiltonian or the Zeeman Hamiltonian (for B of order of 1 tesla). The case of iodine is very favourable for two reasons :

— the molecule is heavy and C_v is inversely proportional to the reduced mass;

— a very good cancellation between the L and S terms occurs in C_v [18, 5]. Therefore the case of iodine is a rather special one; however, we hope to find an analogous situation in the case of the B state of bromine;

ii) if the state subjected to predissociation has an Ω value different from zero, usually this state has a non-zero magnetism and therefore the study of magnetic predissociation can be more difficult because of magnetic tuning effects.

6.2.2 Case $\Delta\Omega = 0$. — In this case, $\mathcal{H}_v$, $\mathcal{H}_{\text{F.S.}}$, $\mathcal{H}_{\text{HFS}}$ and $\mathcal{H}_Z$ can couple the two states. Evidently, except if a selection rule forbids the coupling by $\mathcal{H}_v$ and $\mathcal{H}_{\text{F.S.}}$, the effects of $\mathcal{H}_{\text{HFS}}$ and $\mathcal{H}_Z$ should be negligible because of their very large difference of orders

of magnitude. The predissociation rate, essentially due to $\mathcal{H}_V$ and $\mathcal{H}_{F.S.}$, is therefore independent of I , F , M_F . However, as has been pointed out in the discussion of equation (7), the interference terms between the large Hamiltonians $\mathcal{H}_V$, $\mathcal{H}_{F.S.}$ and the small ones $\mathcal{H}_Z$, $\mathcal{H}_{HFS}$ are much larger than the direct quadratic terms due to the small Hamiltonians. It may happen that these interference terms could be detected in favourable cases.

We may search now for cases where coupling between the two states is forbidden for $\mathcal{H}_V$ and $\mathcal{H}_{F.S.}$ but not for $\mathcal{H}_Z$ and/or $\mathcal{H}_{HFS}$. We see two such cases :

i) $\Omega = \Omega' = 0$ and the states are of opposite Krönig parity — then only the Zeeman and the hyperfine Hamiltonian can couple the two states (the fact that the Zeeman Hamiltonian and no other large term can couple 0^+ to 0^- was recognized by Van Vleck [20] and used to explain what he thought to be a pure magnetic predissociation in the iodine B state). The two Hamiltonians can interfere.

ii) The molecule is a homonuclear one and the two states are of opposite g/u symmetry.

Then the hyperfine Hamiltonian can couple the two states, if $|\Delta\Omega| \leq 2$. We recall also that the Stark Hamiltonian can couple the two states, if $|\Delta\Omega| \leq 1$, but no interference is possible between these two effects.

6.2.3 Case $\Delta\Omega = 2$. — Then, only the electric quadrupole term of the hyperfine Hamiltonian can couple the two states.

We will not give the calculations of the predissociation rates for all the particular cases considered here, as although they can be obtained rather easily by the tensorial formalism, the results are lengthy.

7. Some special properties of hyperfine and magnetic predissociations. — After giving some general considerations on the strength of a predissociation, we study the characteristic features of hyperfine and magnetic predissociation.

7.1 STRENGTH SCALE FOR PREDISSOCIATIONS. — This scale is based on experimental considerations :

— *Strong predissociations.* — The predissociation rate Γ_p is larger than the Doppler width $\Delta\omega_D$ of the absorption transition. The predissociation is detectable in absorption spectroscopy by measuring line-widths [2]. Evidently, as usually $\Gamma_{rad} \ll \Delta\omega_D$, in this case the fluorescence quantum yield

$$\rho_f = \Gamma_{rad}/(\Gamma_{rad} + \Gamma_p)$$

is very small. This usually precludes fluorescence studies; however the breaking-off of fluorescence bands is a usual feature of such predissociations [2].

The detection of atoms created as products of predissociation is a sensitive technique. However, in order to distinguish the atoms produced by pre-

dissociation from atoms produced by direct continuum excitation, various techniques must be used : study of the dependence of the atomic density on excitation wavelength, time of flight, or angular distribution of the products.

— *Weak predissociations.* — We mean here a predissociation rate Γ_p comparable or larger than Γ_{rad} , but small enough so that the fluorescence yield ρ_f is not small. Fluorescence studies, including lifetime measurements can now be developed. Linewidth measurements can also be used, but require a Doppler-free technique. However, lifetime measurements, which are insensitive to the cause of the variation of the lifetime, cannot completely characterize the predissociation. Fluorescence quantum yield measurements are possible, but an absolute measurement may be difficult to perform, as this yield is often close to 1. Studies of atomic products are also useful.

— *Very weak predissociations.* — We suppose that Γ_p is much smaller than Γ_{rad} . Then, measurements of lifetime or of fluorescence yield are inadequate because of lack of precision. Detection of atomic products is always possible, but as the product yield is small, the sensitivity of the apparatus must be great.

The only precise technique seems to be the interference of the very weak predissociation with a stronger one. In the I_2 B state, the interference between a very weak gyroscopic predissociation and the magnetic predissociation has permitted us to measure this very weak gyroscopic predissociation [3]. Similarly, the interference between the gyroscopic and the hyperfine predissociation mechanisms gives a measurement of the very weak hyperfine predissociation [4].

7.2 SPECIAL FEATURES OF HYPERFINE AND MAGNETIC PREDISSOCIATION. — The main features result directly from the expressions of the predissociation rate given in § 6.

For hyperfine predissociation, the lifetime and the quantum yield are different for each hyperfine sublevel. It is therefore possible to detect such a predissociation by measuring lifetimes or by comparing the fluorescence quantum yields of these various sublevels. The only experimental difficulty lies in resolving the hyperfine structure. A trick to get rid of this difficulty was found [4, 18] : it is evident that the average predissociation rate is different for ortho and para states, as the accessible values of the total spin are different. This leads to an alternation of the average lifetime which is easy to measure; but at the same time, the decay of all hyperfine sublevels of a rovibrational level is no longer an exponential function of time, but a superposition of exponential decays with a different lifetime for each sublevel. The appearance of non-exponential decay may therefore also be evidence of hyperfine predissociation.

For magnetic predissociation, the predissociation

rate Γ_p and the lifetime are functions of all quantum numbers $v, J, \varepsilon, F, M_F$, and, in the presence of an interference effect, the lifetime is not the same for the two levels having opposite signs of M_F . The consequence is that from the population of the excited state, this unusual relaxation builds up longitudinal quantities of all order of which only orientation and alignment are easily detectable. Evidently, the most striking consequence of the magnetic predissociation is a variation of the fluorescence quantum yield and therefore of the fluorescence intensity as a function of the magnetic field. Although this variation is usually a decrease, in the presence of an interference effect this variation may start as an increase with the magnetic field [3, 15]. The study of the variation of the population, orientation and alignment as a function of the magnetic field gives a precise insight into the predissociation rate. Care must be taken to distinguish the predissociation effects from Hanle or magnetic tuning effects.

8. Conclusion. — In this paper we have presented a detailed theory of the predissociation rates in the case of gyroscopic, hyperfine and magnetic predissociation of iodine. These results are the theoretical basis for the following two articles which treat the experimental results concerning this predissociation and give numerical values of the predissociation parameters.

Other results concern a general survey of the cases in which an hyperfine and/or magnetic predissociation could be observed. Although no specific molecule has been considered, the obvious analogues of iodine are the other halogens. We think that a detailed study of bromine should be fruitful and that, generally speaking, many molecular states presently considered as free of predissociation actually are subject to weak or very weak predissociation effects. Such effects should be observable by some of the techniques briefly mentioned here and which are developed in the two following papers.

References

- [1] KRÖNIG, R. de L., *Z. Phys.* **50** (1928) 347.
- [2] HERZBERG, G., *Spectra of Diatomic Molecules* (Van Nostrand Editor) 1950.
- [3] VIGUÉ, J., BROYER, M. and LEHMANN, J. C., a) *J. Phys. B* **7** (1974) L 158; b) *J. Chem. Phys.* **62** (1975) 4941.
- [4] BROYER, M., VIGUÉ, J. and LEHMANN, J. C., *J. Chem. Phys.* **64** (1976) 4794.
VIGUÉ, J., BROYER, M. and LEHMANN, J. C., *J. Phys. B* **10** (1977) L 379.
- [5] VIGUÉ, J., BROYER, M. and LEHMANN, J. C., *J. Physique* (2 articles of this series).
- [6] FANO, U., *Phys. Rev.* **124** (1961) 1866.
COHEN TANNOUDJI, C. and AVAN, P., *Colloque International du CNRS n° 273* (Editions du CNRS, Paris) 1977, p. 93.
- [7] CHILD, M. S., *Molec. Phys.* **32** (1976) 1495.
- [8] VAN VLECK, J. H., *J. Chem. Phys.* **4** (1936) 327.
- [9] TELLINGHUISEN, J. and ALBRITTON, D. L., *Chem. Phys. Lett.* **31** (1975) 91.
- [10] VAN VLECK, J. H., *Rev. Mod. Phys.* **23** (1951) 213.
- [11] FREED, K. F., *J. Chem. Phys.* **45** (1966) 4214.
- [12] COOK, R. L. and DE LUCIA, F. C., *Am. J. Phys.* **39** (1971) 1433.
- [13] BROYER, M., VIGUÉ, J. and LEHMANN, J. C., *J. Physique* **39** (1978) 591.
- [14] MIZUSHIMA, M., *Rotating diatomic molecules* (Wiley-Interscience) 1975.
- [15] VIGUÉ, J., Thèse, Paris (1978), unpublished.
- [16] LEVENSON, M. D. and SCHAWLOW, A. L., *Phys. Rev. A* **6** (1972) 10.
- [17] RAMSEY, N. F., *Nuclear Moments* (Wiley) 1953, p. 25.
- [18] BROYER, M., Thesis, Paris (1977), unpublished.
- [19] HUO, W. M., *J. Chem. Phys.* **52** (1970) 3110.
- [20] VAN VLECK, J. H., *Phys. Rev.* **40** (1932) 544.
- [21] SULLIVAN, B. J. and DOWS, D. A., *Chem. Phys.* **46** (1980) 231.