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## Hyperfine interactions in homonuclear diatomic molecules and u-g perturbations. I. Theory

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**Résumé.** — Les interactions hyperfines dans les molécules diatomiques homonucléaires lourdes sont étudiées théoriquement. L'élément de matrice du Hamiltonien est établi dans le cas général et explicité dans le cas d'un ensemble d'états électroniques ayant une limite de dissociation commune. Les effets de perturbation hyperfine en résultant sont illustrés dans l'exemple de l'état B de l'iode. En particulier, un mélange de l'état B  $0_u^+$  avec un état lg est prévu près de la limite de dissociation. Comme les méthodes de calcul s'appliquent à toute molécule diatomique homonucléaire ayant un spin nucléaire non nul, on peut s'attendre à rencontrer de similaires brisures de symétrie u-g dans d'autres molécules.

**Abstract.** — The hyperfine interactions in heavy homonuclear diatomic molecules are studied theoretically. The general matrix element of the related Hamiltonian is derived in the general case and detailed in the case of an ensemble of electronic states sharing the same dissociation limit. The predicted hyperfine perturbation effects are illustrated through the example of the iodine B state. In particular a mixing of the B  $0_u^+$  state with a lg state is to be expected near the dissociation limit. As the calculation methods apply to any non-zero nuclear spin homonuclear diatomic molecule, similar u-g symmetry breakings are likely to be met in other molecules.

### 1. Introduction.

The high resolution available with lasers as excitation sources has opened to the spectroscopic researcher the study of weak interactions in atoms and molecules in the optical domain. Among these weak effects, the hyperfine interactions due to non-zero nuclear spin are amongst the most studied, and the best molecular example is certainly the  $^{127}\text{I}_2$  molecule, in which a lot of work has been devoted to the hyperfine structure of the B  $0_u^+$  excited state ([1-4] and references therein). Specifying that hyperfine interactions are weak means that the related energy is small compared to all the other energies. This is generally the case in a diatomic molecule, for which the hyperfine splittings are much smaller than the rotational, vibrational and electronic energy separations. These hyperfine splittings can then be predicted through a second-order approximation involving different perturbing electronic states which share with the B state the same dissociation limit [5]. By this method, the observed hyperfine structure can be accurately described by four effective parameters:  $eQq'$  (electric quadrupolar),  $C'$  (magnetic dipolar),  $\delta'$  (scalar spin-spin) and  $d'$  (tensorial spin-spin).

However, this approximation, justified for low vibrational levels of the B state, is no longer valid for the high vibrational ones. As the latter are close to the dissociation limit, their hyperfine structure can be of the same order of magnitude as rotational, vibrational and even electronic energy separations, and strong perturbation effects are to be expected. According to the predictions of the general theory given by Vigué, Broyer and Lehmann [5, 6], the hyperfine structure of these levels must exhibit large deviations from that of low ones in the B state, especially when a predicted u-g mixing comes into play. Thus the near-dissociation levels are expected to reflect sensitively all the possible intramolecular interactions.

In order to check these theoretical predictions, we have undertaken the systematic study of the hyperfine structure of rovibrational levels in the range  $28\text{-}0.5\text{ cm}^{-1}$  below the  $^{127}\text{I}_2$  B state  ${}^2\text{P}_{1/2} + {}^2\text{P}_{3/2}$  dissociation limit ( $71 < v' < 82$ ). In a recent paper [7a], preliminary results have been reported, with the first observation of u-g symmetry breaking in a homonuclear diatomic molecule. We present now the complete hyperfine analysis, which is divided into two parts. Part I (this paper) gives the theoreti-

cal framework for the interpretation of the observed spectrum. In part II extensive experimental data and related results will be reported.

In this paper (part I) we first introduce the u-g symmetry breaking through hyperfine interactions, as can be predicted by group theory. As a result, any u or g state (with  $\Omega \leq 2$ ) can perturb the B state, and we have to derive in the second section the general matrix element of the perturbing Hamiltonian between all of the 10 states sharing the same dissociation limit. The third section is devoted to the evaluation of these matrix elements from the known atomic properties, and *a priori* calculations lead us to the prediction of the main hyperfine perturbations in the B  $0_u^+$  state.

## 2. The u-g symmetry.

For a homonuclear diatomic molecule with identical nuclei (true homonuclear diatomic molecule), there exists a symmetry operation  $(ab)^*$ , which is a permutation of the nuclei *a* and *b* (written as  $(ab)$ ), followed by the inversion of the spatial coordinates of all the nuclei and electrons through the molecular centre of mass, written  $E^*$  following Bunker's notation [8].  $E^*$  determines the parity of a state. It is possible to show that the symmetry operation  $(ab)^*$  inverts the vibronic coordinates through the centre of mass (molecular point group inversion operator *i*) and interchanges the nuclear spins ( $p(ab)$ ), so that :

$$(ab)^* = iR^\circ p(ab) . \quad (1)$$

In this relation  $R^\circ$  is the identity operator of the rotation group *K*, the inversion *i* belongs to the point group  $D_{\infty h}$  and  $p(ab)$  belongs to the nuclear spin permutation group (see Fig. 1) ; *i* determines the g or u levels. According to Bunker [8] *i* is not a « true symmetry » operator of the complete Hamiltonian because of the effect of nuclear spin coupling terms. The ungerade (u)-gerade (g) labels given by *i* are « near symmetry » labels that are spoiled by interactions involving the nuclear spins. As a first consequence, only the hyperfine interactions can induce u-g perturbations in a true homonuclear diatomic molecule. The case of isotopic molecules such as HD or  $^{127}\text{I}-^{129}\text{I}$  is different. Since the centre of mass is no longer a centre of symmetry, the relevant point group  $C_{\infty h}$  does not contain the inversion *i*. It follows that all the terms of the rovibronic Hamiltonian related to the vibration or the rotation of the molecule are not invariant under the *i* operation. However, for the electronic Hamiltonian, the identity of the nuclear charges (neglecting the volume effects) gives for this part the symmetry group  $D_{\infty h}$ , so that u and g states can still be defined, but in that case they can be coupled through pure rovibronic interactions. These u-g « near symmetry » breakings have been observed for instance in the HD molecule [9] where electric dipolar transitions have been observed between two rotational or vibrational levels of the same state, or even between two electronic states such as F  $^1\Sigma_g^+$  and X  $^1\Sigma_g^+$ .

The second consequence of the relation (1) is that any u-g perturbation in a true homonuclear diatomic molecule will correspond to a « flip-flop » of one spin with respect to the other, by analogy with the  $\text{H}_2$  case where  $I_a = I_b = 1/2$ .

Indeed the relation (1) can be written :

$$E^* = (ab) i R^\circ p(ab) . \quad (2)$$

For u and g states, say  $|uI\rangle$  and  $|gI'\rangle$  where *I* and *I'* stand for the total nuclear spin, the different operators of (2) act as follows :

$$\begin{aligned} (ab) |uI\rangle &= \varepsilon |uI\rangle \\ (ab) |gI'\rangle &= \varepsilon |gI'\rangle, \quad \varepsilon = \pm 1 \text{ according} \end{aligned}$$

to the boson or fermion nuclear character, respectively,

$$\begin{aligned} i |uI\rangle &= - |uI\rangle \\ i |gI'\rangle &= + |gI'\rangle \\ p(ab) |uI\rangle &= (-1)^{I+1} |uI\rangle \\ p(ab) |gI'\rangle &= (-1)^{I'+1} |gI'\rangle. \end{aligned}$$

The hyperfine Hamiltonian  $H_{\text{hf}}$  is of even parity, so that under  $E^*$  we must have :

$$\langle uI | E^* H_{\text{hf}} E^{*\dagger} | gI' \rangle = \langle uI | H_{\text{hf}} | gI' \rangle$$

and from (2), we have :

$$\begin{aligned} \langle uI | E^* H_{\text{hf}} E^{*\dagger} | gI' \rangle &= \\ &= (-1)^{I+I'+1} \langle uI | H_{\text{hf}} | gI' \rangle \end{aligned}$$

where  $E^{*\dagger}$  is the adjoint operator of  $E^*$ .

Thus, any u-g hyperfine coupling implies an odd nuclear spin change  $\Delta I = \pm 1, \pm 3, \dots$  which corresponds to a reorientation of one nuclear spin with respect to the other.

Now let us consider  $\sigma_v$ , the reflection at a plane passing through the internuclear axis, which determines the +/- character of the electronic eigenfunctions [10]. The operator  $i\sigma_v$  has the same effect as the nuclear permutation  $(ab)$ . Then,  $\chi_i$  and  $\chi_{\sigma_v}$  being the characters associated with the symmetry operations *i* and  $\sigma_v$ , we infer in the case when the nuclei are fermions (see appendix) :

$$\chi_i \chi_{\sigma_v} = (-1)^{I+J}$$

where *J* is the total angular momentum ignoring nuclear spin and  $\chi_{\sigma_v} = +1$  or  $-1$ , depending upon whether the electronic state is + or -.

This rule, together with  $\Delta I$  deduced from (2), leads to the selection rules for *I* and *J* due to the coupling of the B  $0_u^+$  state with all other states (Table I). It should be noted that any B state coupling with a gerade state will affect the nuclear spin but with an even or odd change in *J*, depending on the  $\sigma_v$  character. The effects of a u-g perturbation in the B state can be very different in the two cases,

Table I. — Selection rules for *I* and *J* due to the main hyperfine couplings between a 0<sub>u</sub><sup>+</sup> state (B 0<sub>u</sub><sup>+</sup>) and other Ω electronic states.

States	Δ <i>I</i>	Δ <i>J</i>
Ω <sub>u</sub> <sup>+</sup>	0, ± 2	0, ± 2
Ω <sub>u</sub> <sup>-</sup>	0, ± 2	± 1
Ω <sub>g</sub> <sup>+</sup>	± 1	0, ± 2
Ω <sub>g</sub> <sup>-</sup>	± 1	± 1

as has been observed experimentally [7a]. Moreover, it is easy to see using the relation (2) that any hyperfine coupling between two u or two g states implies an even nuclear spin change Δ*I* = 0, ± 2, ...

### 3. The general matrix element of the hyperfine (and gyroscopic) Hamiltonian for a heavy molecule.

As will be shown later, the hyperfine interactions between states near a dissociation limit can be of the same order as rovibrational or electronic interactions. In these cases, a hyperfine second-order perturbation approach cannot be used for the eigenvalue representation and a direct diagonalization of the full Hamiltonian is required. We derive here a general expression for the hyperfine/gyroscopic Hamiltonian matrix element, which is convenient for computer calculations.

For heavy molecules such as I<sub>2</sub>, only the axial component Ω of the total electronic angular momentum **L** + **S** is defined (Hund's case c). Ω is a good quantum number in the absence of hyperfine or gyroscopic perturbations. Each electronic state belongs to one of the irreducible representations of the D<sub>∞h</sub> symmetry group. All the Ω ≠ 0 states are doubly degenerate in the σ<sub>v</sub> symmetry, and a symmetrized basis set can be defined as :

$$|C_\varepsilon\rangle = \left(\frac{1}{\sqrt{2}}\right)^{|\varepsilon|} \left[ | \Omega v J (I_a I_b) IFM_F \rangle 3 + \varepsilon | - \Omega v J (I_a I_b) IFM_F \rangle \right] \quad (3)$$

where ε = 0 for Ω = 0 and ε = χ<sub>σ<sub>v</sub></sub> = ± 1 for Ω ≠ 0, with **I** = **I**<sub>a</sub> + **I**<sub>b</sub> and **F** = **I** + **J**; *v* is the vibrational quantum number. The electronic part of the wave-functions defined in this way are symmetrical or antisymmetrical with respect to the σ<sub>v</sub> symmetry [7b].

The hyperfine/gyroscopic Hamiltonian *H*<sub>hfg</sub> can be written as :

$$H_{hfg} = V + H_{hf} = V + H_{hf}(a) + H_{hf}(b) + H_{hf}(a, b) \quad (4)$$

where *V* = - (ħ<sup>2</sup>/2 μ *r*<sup>2</sup>) **J** · (**L** + **S**) is the gyroscopic term, *H*<sub>hf</sub>(*a*) is the electronic interaction at the nucleus *a* and *H*<sub>hf</sub>(*a, b*) is the mainly direct [5] interaction between the two nuclei. The latter term, small and essentially diagonal with respect to the electronic wave-functions [5, 6] can be omitted in a first approximation. Then *H*<sub>hf</sub> can be expressed [5] as

$$H_{hf} = \sum_{\alpha=a,b} \sum_k \sum_{q=-k}^{+k} (-1)^q Q_q^k(I_\alpha) V_{-q}^k(e_\alpha) \quad (5)$$

where the tensorial operator *Q*<sup>*k*</sup>(**I**<sub>α</sub>) acts only on the nuclear spin of the atom α and *V*<sup>*k*</sup>(*e*<sub>α</sub>) acts only on the electrons.

From the expression of the symmetrized wavefunctions (3), the matrix elements of *H*<sub>hf</sub>, using the Wigner-Eckart theorem can be written as :

$$\begin{aligned} \langle C_{\varepsilon'} | H_{hf} | C_\varepsilon \rangle &= \delta_{M_F M_{F'}} \delta_{F F'} (-1)^{F+I'+J} \times \left\{ \begin{matrix} J' & k & J \\ I & F & I' \end{matrix} \right\} \times \\ &\times \left[ \langle \overline{C}_{\varepsilon'} | V^k(e_a) | \overline{C}_\varepsilon \rangle \langle (I_a I_b) I' || Q^k(I_a) || (I_a I_b) I \rangle + \right. \\ &\quad \left. + \langle \overline{C}_{\varepsilon'} | V^k(e_b) | \overline{C}_\varepsilon \rangle \langle (I_a I_b) I' || Q^k(I_b) || (I_a I_b) I \rangle \right] \end{aligned}$$

with

$$| \overline{C}_\varepsilon \rangle = \left(\frac{1}{\sqrt{2}}\right)^{|\varepsilon|} ( | \Omega v J \rangle + \varepsilon | - \Omega v J \rangle )$$

where ε (or ε') = 0 for Ω (or Ω') = 0 and ε (or ε') = χ<sub>σ<sub>v</sub></sub> = ± 1 depending on the substate for Ω (or Ω') ≠ 0.

Then taking account that :

$$\begin{aligned} \langle -\Omega' v' \parallel V_{-\Delta\Omega}^k(e_i) \parallel -\Omega v \rangle &= (-1)^k \langle \Omega' v' \parallel V_{\Delta\Omega}^k(e_i) \parallel \Omega v \rangle \\ \langle -\Omega' v' \parallel V_{-\Omega^+}^k(e_i) \parallel +\Omega v \rangle &= (-1)^k \langle \Omega' v' \parallel V_{\Omega^+}^k(e_i) \parallel -\Omega v \rangle, \end{aligned}$$

standard algebra gives the complete derivation of the  $H_{\text{hf}}$  matrix element in the symmetrized  $|C_\epsilon\rangle$  basis set, for a homonuclear diatomic molecule. We obtain (see Ref. [7b]) :

$$\begin{aligned} \langle C_{\epsilon'} \parallel H_{\text{hf}} \parallel C_\epsilon \rangle &= \sum_k \delta_{M_F M_{F'}} \delta_{FF'} (-1)^{F+\Delta I+\Delta J+\Omega'+k} \times \\ &\times \sqrt{(2J'+1)(2J+1)(2I'+1)(2I+1)} \times \begin{Bmatrix} J' & k & J \\ I & F & I' \end{Bmatrix} \\ &\times \begin{Bmatrix} I_a & k & I_a \\ I & I_a & I' \end{Bmatrix} \times C_k \begin{pmatrix} I_a & k & I_a \\ -I_a & 0 & I_a \end{pmatrix}^{-1} \times \begin{pmatrix} J' & k & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix} \\ &\times 2 \left(\frac{1}{\sqrt{2}}\right)^{|\epsilon'|} \left(\frac{1}{\sqrt{2}}\right)^{|\epsilon|} \times \frac{1+\epsilon'\epsilon(-1)^{\Delta J}}{2} \\ &\times \left\{ \langle \Omega' v' \parallel V_{\Delta\Omega}^k(e_a) \parallel \Omega v \rangle + (-1)^{\Delta I} \langle \Omega' v' \parallel V_{\Delta\Omega}^k(e_b) \parallel \Omega v \rangle \right. \\ &\left. + C(\Omega^+) \times \epsilon \times \left[ \langle \Omega' v' \parallel V_{\Omega^+}^k(e_a) \parallel -\Omega v \rangle + (-1)^{\Delta I} \langle \Omega' v' \parallel V_{\Omega^+}^k(e_b) \parallel -\Omega v \rangle \right] \right\} \quad (6) \end{aligned}$$

with

$$\Delta I = I' - I, \Delta J = J' - J, \Delta\Omega = \Omega' - \Omega \quad \text{and} \quad \Omega^+ = \Omega' + \Omega.$$

The  $C_k$  are the atomic reduced matrix elements [11] :  $C_1 = \beta g I_a$  for  $k=1$  (nuclear magnetic dipole moment) and  $C_2 = 1/2 e Q I_a$  for  $k=2$  (nuclear electric quadrupole moment) ; moreover when  $\langle C_{\epsilon'} \parallel H_{\text{hf}} \parallel C_\epsilon \rangle \neq 0$  :

$$C(\Omega^+) = \begin{pmatrix} J' & k & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix} \begin{pmatrix} J' & k & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix}^{-1}.$$

The hyperfine Hamiltonian is limited to tensorial terms of rank 1 and 2 which correspond to the main interactions, namely magnetic dipolar and electric quadrupolar interactions, respectively.

The 3 j symbol  $\begin{pmatrix} J' & k & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix}$  together with the results of table I gives the selection rules for the coupling of the B  $0_u^+$  state with all the states labelled by the irreducible representations of the point group  $D_{\infty h}$ . The selection rules and values of the nondiagonal matrix elements coupling B  $0_u^+$  to the states sharing the same dissociation limit are reported in table II for their electronic part. The operators involved in this coupling are  $V^0$  (gyroscopic),  $V^1$  (hyperfine magnetic dipolar) and  $V^2$  (hyperfine electric quadrupolar). The calculated value of the matrix elements will be discussed in the next section.

The selection rules described in table II lead to several predictions about the hyperfine coupling

effects in a  $0_u^+$  state :

i)  $H_{\text{hf}}$  couples  $\Omega = 0$  as well as  $\Omega \neq 0$  states, so that some  $\Omega \neq 0$  character and magnetic moment can be induced in a  $0_u^+$  state by mixing with a  $\Omega \neq 0$  state with a magnetic moment.

ii) In the  $0_u^+$  state, levels such that  $\Delta J = \pm 2$  can be strongly coupled by  $V^2$ . In that case  $J$  is no longer a good quantum number and this explains the superhyperfine structure observed in some band heads (part II).

iii) The  $0_u^+$  state can be coupled by  $H_{\text{hf}}$  to all the  $\Omega = 0, \pm 1, \pm 2$  states sharing the same dissociation limit  ${}^2P_{3/2} + {}^2P_{1/2}$ . Whilst for the  $\Delta I$  selection rule there is no distinction between the near degenerate substates with  $\Omega \neq 0$ , this degeneracy is lifted by the  $\Delta J$  selection rule where  $c_+$  ( $= C_{\epsilon=+1}$ ) and  $c_-$  ( $= C_{\epsilon=-1}$ ) are distinguished from each other.

iv)  $H_{\text{hf}}$  couples u and g states. This leads to a u-g symmetry breaking in a true homonuclear diatomic molecule. This effect can be seen either by u-g predissociation or, as in this case near a dissociation limit where strong u-g perturbations are to be expected, through line shifts and extra-lines.

#### 4. Evaluation of the hyperfine couplings.

The general expression (6) we have obtained involves in the  $\langle V^k \rangle$  term several reduced matrix

Table II. — Selection rules and values in megahertz of the gyroscopic  $\langle \bar{V}^0 \rangle$ , hyperfine magnetic dipolar  $\langle \bar{V}^1 \rangle$  and hyperfine electric quadrupolar  $\langle \bar{V}^2 \rangle$  matrix elements between  $B 0_u^+$  and all the states sharing the same  ${}^2P_{3/2} - {}^2P_{1/2}$  dissociation limit. The matrix elements  $\langle \bar{V}^0 \rangle$ ,  $\langle \bar{V}^1 \rangle$  and  $\langle \bar{V}^2 \rangle$  correspond to the electronic part of the wave function only.

States	$\langle \bar{V}^0 \rangle$		$\langle \bar{V}^1 \rangle$		$\langle \bar{V}^2 \rangle$		$\langle \bar{V}^0 \rangle / \sqrt{2J'(J'+1)}$	$\beta g I_a \langle \bar{V}^1 \rangle$	$\frac{1}{2} e Q_{5/2} \langle \bar{V}^2 \rangle$
	$\Delta I$	$\Delta J$	$\Delta I$	$\Delta J$	$\Delta I$	$\Delta J$	(MHz) $r_+ = 10 \text{ \AA}$	(MHz)	(MHz)
$0_g^+$					$\pm 1$	$0, \pm 2$	0	0	- 573
$0_u^-$			0	$\pm 1$			0	- 2 882	0
$0_g^-$			$\pm 1$	$\pm 1$			0	3 709	0
(B) $0_u^+$					$0, \pm 2$	$0, \pm 2$	0	0	- 573
$\left\{ \begin{array}{l} 1' g(c_+) \\ 1' g(c_-) \end{array} \right.$			$\pm 1$	0	$\pm 1$	$0, \pm 2$	0	- 3 491	0
$\left\{ \begin{array}{l} 1'' g(c_+) \\ 1'' g(c_-) \end{array} \right.$			$\pm 1$	$\pm 1$	$\pm 1$	$\pm 1$	0	- 3 491	0
$\left\{ \begin{array}{l} 1' u(c_+) \\ 1' u(c_-) \end{array} \right.$	0	0	0	0	$0, \pm 2$	$0, \pm 2$	170	5 830	0
$\left\{ \begin{array}{l} 1'' u(c_+) \\ 1'' u(c_-) \end{array} \right.$	0	0	0	$\pm 1$	$0, \pm 2$	$\pm 1$	170	5 830	0
$\left\{ \begin{array}{l} 2 g(c_+) \\ 2 g(c_-) \end{array} \right.$					$\pm 1$	$0, \pm 2$	0	0	810
$\left\{ \begin{array}{l} 2 u(c_+) \\ 2 u(c_-) \end{array} \right.$					$\pm 1$	$\pm 1$	0	0	810
$\left\{ \begin{array}{l} 2 u(c_+) \\ 2 u(c_-) \end{array} \right.$	0	0	0	0	$0, \pm 2$	$0, \pm 2$	100	1 013	810
$\left\{ \begin{array}{l} 2 u(c_+) \\ 2 u(c_-) \end{array} \right.$	0	0	0	$\pm 1$	$0, \pm 2$	$\pm 1$	100	1 013	810
$\left\{ \begin{array}{l} 2 u(c_+) \\ 2 u(c_-) \end{array} \right.$					$0, \pm 2$	$0, \pm 2$	0	0	810
$\left\{ \begin{array}{l} 2 u(c_+) \\ 2 u(c_-) \end{array} \right.$					$0, \pm 2$	$\pm 1$	0	0	810

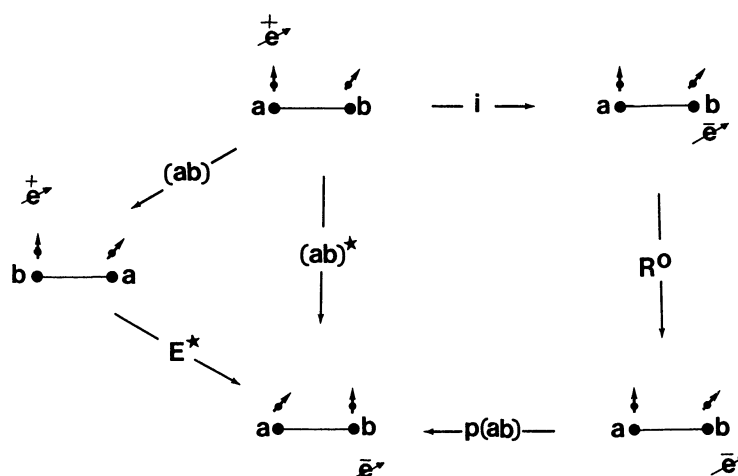


Fig. 1. — Symmetry operations in a homonuclear diatomic molecule.  $\uparrow$  nuclear spin ;  $\uparrow$  electronic spin ;  $\dot{e}$  electron above the plane of the figure ;  $\bar{e}$  electron below the plane of the figure. The operation  $i$  has the same effect as  $(ab)^*$  on the rovibronic coordinates of a homonuclear diatomic molecule.

elements which need to be known for the fits of the experimental data.

To a good approximation, we can write [6b, 12]

$$\langle V^k \rangle = \langle v | v' \rangle \langle \bar{V}^k \rangle f(r_+) \quad (7)$$

where  $\langle v | v' \rangle$  is the vibrational overlap between the interacting states,  $\langle \bar{V}^k \rangle$  involves only the electronic wavefunctions and  $f(r_+)$  is 1 for  $k = 1$  or 2 and  $f(r_+) = -\frac{\hbar^2}{2 \mu r_+^2}$  for  $k = 0$ ,  $r_+$  being the

classical outer turning point of the potential curve.

If large internuclear distances are to be considered, as near a dissociation limit, the evaluation of  $\langle V^k \rangle$  is made easier for two reasons. First, as the molecule in its vibrational movement spends a great part of the time on the outer limb of the potential well, a reasonably good estimate of the  $\langle v | v' \rangle$  overlap can be made from the *ab initio* calculated outer limb of the electronic states concerned. The second simplification arises from the fact that as the exchange terms in the interaction energy become weak, any molecular state can be represented on a

separated-atom basis set for the pure electronic wavefunctions.

4.1  $\langle \bar{V}^k \rangle$  EVALUATION. — The separated-atom basis set for a  ${}^2P_{1/2} + {}^2P_{3/2}$  dissociation limit is built

up from the atomic wavefunctions  $|j = 3/2, m_j\rangle$  and  $|j' = 1/2, m_{j'}\rangle$ . The electronic molecular wavefunction consists of symmetrized products of the atomic wavefunctions [12]:

$$\begin{aligned}
 |u\rangle &= \frac{1}{\sqrt{2}} \left( \left| \frac{3}{2}, m \right\rangle_a \left| \frac{1}{2}, m' \right\rangle_b + \left| \frac{3}{2}, m \right\rangle_b \left| \frac{1}{2}, m' \right\rangle_a \right) \\
 |g\rangle &= \frac{1}{\sqrt{2}} \left( \left| \frac{3}{2}, m \right\rangle_a \left| \frac{1}{2}, m' \right\rangle_b - \left| \frac{3}{2}, m \right\rangle_b \left| \frac{1}{2}, m' \right\rangle_a \right) \text{ for } \Omega \neq 0, \text{ and} \\
 |u\rangle &= \frac{1}{2} \left( \left| \frac{3}{2}, m \right\rangle_a \left| \frac{1}{2}, m' \right\rangle_b + \left| \frac{3}{2}, m \right\rangle_b \left| \frac{1}{2}, m' \right\rangle_a \right. \\
 &\quad \left. \pm \left| \frac{3}{2}, -m \right\rangle_a \left| \frac{1}{2}, -m' \right\rangle_b \pm \left| \frac{3}{2}, -m \right\rangle_b \left| \frac{1}{2}, -m' \right\rangle_a \right) \\
 |g\rangle &= \frac{1}{2} \left( \left| \frac{3}{2}, m \right\rangle_a \left| \frac{1}{2}, m' \right\rangle_b - \left| \frac{3}{2}, m \right\rangle_b \left| \frac{1}{2}, m' \right\rangle_a \right. \\
 &\quad \left. \pm \left| \frac{3}{2}, -m \right\rangle_a \left| \frac{1}{2}, -m' \right\rangle_b \mp \left| \frac{3}{2}, -m \right\rangle_b \left| \frac{1}{2}, m' \right\rangle_a \right)
 \end{aligned} \tag{8}$$

for  $\Omega = 0$ , where the subscripts a and b designate the two atoms.

As in Hund's case (c) we have  $\Omega = |m + m'|$ , the five possible combinations give 10 different states as noted in table III, half of them being gerade (minus sign in (8)), and the other half ungerade (plus sign in (8)).

The variation of  $H_{\text{hf}}$  under the inversion  $i$  can be easily demonstrated in the separated-atom representation. If we introduce

$$\begin{aligned}
 |1\rangle &= \left| \frac{3}{2}, m \right\rangle_a \left| \frac{1}{2}, m' \right\rangle_b \\
 |2\rangle &= \left| \frac{1}{2}, m' \right\rangle_a \left| \frac{3}{2}, m \right\rangle_b,
 \end{aligned}$$

the  $|1\rangle$  and  $|2\rangle$  states are eigenstates of  $H_{\text{hf}}$ , since

$$\langle 1 | \bar{V}^k(e_i) | 2 \rangle = {}_i \left\langle \frac{3}{2}, m \right| \bar{V}^k(e_i) \left| \frac{1}{2}, m' \right\rangle_{i'} \left\langle \frac{1}{2}, m' \right| \frac{3}{2}, m \right\rangle_{i'} = 0$$

with  $i = a$  or  $b$  and  $i' = b$  or  $a$ .

Thus  $|1\rangle$  and  $|2\rangle$  diagonalize the hyperfine Hamiltonian, but  $|1\rangle$  and  $|2\rangle$  do not possess  $i$  symmetry. Only symmetrized products such as in (8) have this symmetry and are wavefunctions of the molecular Hamiltonian. Then there are non-zero matrix elements of  $\bar{V}^k(e_i)$  in this basis set and it follows that the u – g symmetry can be broken by the hyperfine interactions.

All of the 10 states of table III can be written as :

$$\sum_i C_i |j_i m_i\rangle_i |j'_i m'_i\rangle_{i'}$$

Table III. —  $m$  and  $m'$  values for the 10 case c states at the  ${}^2P_{3/2} - {}^2P_{1/2}$  dissociation limit.  $\Omega = |m + m'|$ . The  $\Omega = 1$  and 2 states are doubly degenerate.

$\Omega$	$m$	$m'$	u/g
0	1/2	- 1/2	u and g
0	- 1/2	1/2	u and g
1	1/2	1/2	u and g
1	3/2	- 1/2	u and g
2	3/2	1/2	u and g

and we have to calculate matrix elements of the form :

$$\sum_{ln} \delta_{jln} C_l C_n \alpha \langle J_l m_l | \bar{V}^k(e_i) | J_n m_n \rangle_\alpha$$

where the matrix element relates to the atom  $\alpha$ ,  $\alpha = a$  or  $b$ .

From the Wigner-Eckart theorem, we have :

$$\begin{aligned} \langle jm' | \bar{V}_q^k | jm \rangle &= \\ &= (-1)^{j-m'} \begin{pmatrix} j & k & j \\ -m' & q & m \end{pmatrix} \langle j || \bar{V}^k || j \rangle, \end{aligned}$$

and the reduced matrix element  $\langle j || \bar{V}^k || j \rangle$  can be easily calculated from the known magnetic dipolar and electric quadrupolar hyperfine atomic parameters  $a_j$  and  $eq_j Q_I$  [11]. We have :

$$\begin{aligned} \left\langle \frac{3}{2} \left\| \bar{V}^1 \right\| \frac{3}{2} \right\rangle &= \sqrt{15} a_{3/2} \\ \left\langle \frac{1}{2} \left\| \bar{V}^1 \right\| \frac{1}{2} \right\rangle &= \sqrt{3/2} a_{1/2} \\ \left\langle \frac{3}{2} \left\| \bar{V}^2 \right\| \frac{3}{2} \right\rangle &= \sqrt{5} eq_{3/2} Q_I. \end{aligned}$$

For <sup>127</sup>I<sub>2</sub>, complete evaluation of the matrix elements (6) is possible from the known measured atomic values [13, 14] apart from the vibrational overlap  $\langle v | v' \rangle$ . The results, together with those for  $V^0$ , are given in table II.

**4.2  $\langle v | v' \rangle$  EVALUATION.** — Calculation of the vibrational overlap between two electronic states requires a knowledge of the potential curves. For high vibrational levels, the main contribution to the  $\langle v | v' \rangle$  value comes from the outer turning point  $r_+$ . Since accurate long-range potentials have been calculated by Saute and Aubert-Frécon [15] for internuclear distances larger than 7 Å, the  $\langle v | v' \rangle$  integral can be evaluated. Near the outer turning point  $r_+$ , a good approximation of the wavefunctions is [16] :

$$\psi(r) = CAi_+(-a\zeta),$$

where  $Ai_+$  is a Airy function calculated at  $r_+$ , with

$$a = \frac{\partial U(r)}{\partial r} \bigg|_{r=r_+} \bigg| \frac{\partial U(r)}{\partial r} \bigg|_{r=r_+}$$

and

$$\zeta = (r - r_+) \left[ \frac{2\mu}{\hbar^2} \left| \frac{\partial U(r)}{\partial r} \right|_{r=r_+} \right]^{1/2}.$$

Figure 2 represents the overlap of the  $v' = 78$  level of the B state with several other states of table II. It should be noted that the states labelled in figure 2 are linear combinations of those of table II.

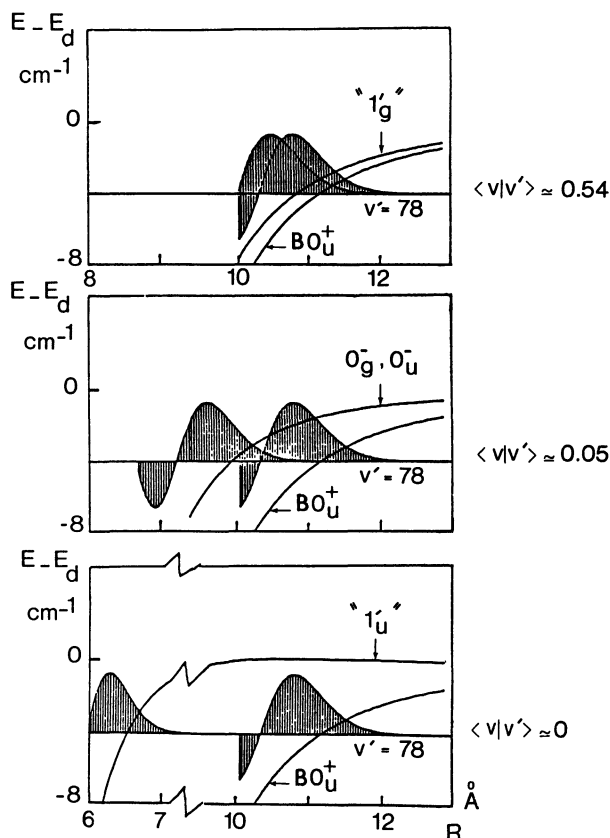


Fig. 2. — Outer lobe of the radial part of the wavefunction of various states at the  ${}^2P_{3/2} - {}^2P_{1/2}$  I<sub>2</sub> dissociation limit. The relevant potential curves are indicated.  $E_d$  is the dissociation limit.

For example, the  $1g$  state closest to the B state is :  $\langle |1'g\rangle \rangle = 0.84 |1'g\rangle + 0.54 |1''g\rangle$  [15], for large internuclear distances ( $r_+ \approx 10 \text{ Å}$ ).

The results of figure 2 show that a strong u - g mixing of the  $v' = 78$  B state level with the  $\langle |1'g\rangle \rangle$  state is to be expected, while  $0g^-$ ,  $0u^-$  as well as  $\langle |1'u\rangle \rangle$  states have negligible or moderate mixing with the B state : these predictions have been experimentally confirmed.

## 5. Conclusion.

The hyperfine perturbations between electronic states in heavy time homonuclear molecules have been studied. The general matrix element of the perturbing Hamiltonian has been derived, together with some predictions of the main effects with emphasis given to the clarification of the u - g perturbation effects. This provides the theoretical basis for the interpretation of the experimental results reported in paper II. The particular case studied here is the iodine B state, but without loss of generality, the calculation methods apply to any non-zero nuclear spin homonuclear diatomic molecule. So the u - g perturbation which is likely to be observed in other molecules can be predicted and calculated using a method similar to that developed for iodine in this paper.



**Appendix.**

Neglecting coupling terms  $H'$  (in general small) in the molecular Hamiltonian  $H$  we can write the essential part of the Hamiltonian,  $H_0$ , as :

$$H_0 = H - H' = H_{\text{elect}} + H_{\text{vib}} + H_{\text{rot}} + H_{II}.$$

$H_{II}$  is the nuclear spin-spin interaction.

The wave-function can then be written in a separable basis as :

$$\phi_0 = \phi_{\text{elec.}} \phi_{\text{vib}} | Jm_J \rangle | Im_I \rangle.$$

The nucleus permutation operation  $(ab)$  gives  $(ab)\phi_0 = -\phi_0$  (when the nuclei are fermions as it is the case for iodine).

From symmetry considerations it is possible to show that under  $(ab)$  the nuclear spin basis function

and the rotational basis function are transformed as :

$$\begin{aligned} (ab) | Im_I \rangle | Jm_J \rangle &= \\ &= (-1)^{I+1+J} | Im_I \rangle | Jm_J \rangle. \end{aligned}$$

Now in a homonuclear diatomic molecule

$$(ab) \phi_{\text{elec.}} = (i\sigma_v) \phi_{\text{elec.}}$$

$$\text{then } (ab) \phi_{\text{elec.}} = \chi_i \chi_{\sigma_v} \phi_{\text{elec.}}$$

and

$$\begin{aligned} (ab) \phi_0 &= -\phi_0 = \\ &= \chi_i \chi_{\sigma_v} \phi_{\text{elec.}} (-1)^{I+J+1} | Im_I \rangle | Jm_J \rangle \phi_{\text{vib}} \end{aligned}$$

as  $(ab)$  does not act on  $\phi_{\text{vib}}$

$$\text{then } \chi_i \chi_{\sigma_v} (-1)^{I+J} = 1.$$

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