Hyperfine-Induced *Ungerade-Gerade* Symmetry Breaking in a Homonuclear Diatomic Molecule near a Dissociation Limit: $^{127}I_2$ at the $^2P_{3/2}$-$^2P_{1/2}$ Limit

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A symmetry breaking of the *ungerade-gerade* character through hyperfine perturbation has been directly observed for the first time in a homonuclear diatomic molecule ($^{127}I_2$). An important consequence of this symmetry breaking is the mixing of ortho and para modifications. Evidenced by anomalies in the observed hfs of high-lying rovibrational levels in the $B\,0_u^+$ state and extra lines, it is due to a hyperfine perturbation of this state by a 1g state sharing the same dissociation limit. Such a situation should be met in other molecules.

The labels u-g (*ungerade-gerade*) are used to characterize the inversion symmetry i of the point group $D_{\infty h}$. Because i is a symmetry of the total rovibronic Hamiltonian H_{rve}[1] of a homonuclear diatomic molecule, it cannot be broken down by non-Born-Oppenheimer terms as is the case for the molecule HD.[2] For a nonzero-nuclear-spin homonuclear diatomic molecule, among all internal molecular interactions only the hyperfine (hf) ones can lead to a u-g perturbation.[1,3,4] The related effects are predicted to be very small and had not been directly observed until now; but the probable existence of u-g perturbations in the B state of I_2 had been suspected for some time.[4-7] We report here preliminary results giving the first experimental direct evidence of such effects in the $^{127}I_2$ molecule (nuclear spin $\frac{5}{2}$) through a hf perturbation of the $B\,0_u^+$ electronic state by a 1g state close to their common dissociation limit. We show that some hf ortho-para sublevels of different rovibrational levels are strongly mixed and therefore lose their u-g character. This phenomenon can be thought of as the flip-flop of the nuclear spins. We expect this to be a general behavior of such levels near a dissociation limit in homonuclear molecules with nonvanishing hf interactions.

Many studies have been performed on the hfs of rovibrational levels in the $^{127}I_2$ $B\,0_u^+$ state (Refs. 5, 6, and 8, and references therein). This structure, even for the most precise experiments, was interpreted by introducing four effective hf parameters: eQq' (electric quadrupolar), C' (magnetic dipolar), δ' (scalar spin-spin), d' (ten-

sor spin-spin). Theoretical studies, particularly the very comprehensive one by Broyer, Vigué, and Lehmann,[4] give the effective Hamiltonian and expressions for these constants, through a second-order approximation involving different perturbing electronic states which share with the B state the same dissociation limit. In accordance with these studies, C' was observed to increase with the vibrational number v' of the observed levels,[8a,8b] corresponding to a decrease in the energy separation between the observed and the perturbing levels. Up to now, however, investigations had been limited to $v' \leq 73$, still far from the dissociation limit ($v'=87$); on the other hand, the contribution of the different perturbing levels to the effective constants had not been separated except for C'[8a,8b] which is only induced by the 1u states.

From the recent *ab initio* calculations of the potential curves ($r_{max} \geq 7$ Å) of the bound states at the $^2P_{3/2}$-$^2P_{1/2}$ dissociation limit,[9] we could infer that strong hf interactions are to be expected only on high vibrational levels of $B\,0_u^+$. So we have performed a collisionless sub-Doppler hfs study of the $X \to B$ transition with the help of a supersonic I_2 beam. Its high luminous efficiency and high resolution (~2 MHz) were important assets in this region of faint, crowded lines. We have recorded more than ten thousand hf components in the region between 28 and 0.5 cm^{-1} below the dissociation limit ($70 \leq v' \leq 82$). The excitation spectrum was directly calibrated with a lambdameter giving the distance between main lines to within 1 MHz and an absolute accuracy

of 30 MHz. All measurements were performed with the help of a microcomputer-controlled acquisition setup. Experimental details will be given elsewhere.[10]

The analysis of several rotational levels (J' <30) in a given vibrational level enabled us to determine, through a least-squares fit, the effective parameters eQq', C', δ' and d' for $70 \leqslant v'$ $\leqslant 76$ ($J' < 15$) and $79 \leqslant v' \leqslant 82$. We have plotted in Fig. 1 the parameters C' and δ' which are the most characteristic for the present study. Within the second-order theory, C' has the expected behavior and anomalies appear for δ' mainly at $v' = 76$ as J' increases. Smaller anomalies can also be observed at the same v' in eQq' and d'. For $v' = 76$, $J' > 15$ and for $v' = 77$ and 78 levels, it turns out to be impossible to fit the hfs of a rotational line by the second-order approximation.

In order to interpret these features, we started from the general theory given by Broyer, Vigué, and Lehmann.[4] It shows that the perturbing Hamiltonian can be written to a good approxima-
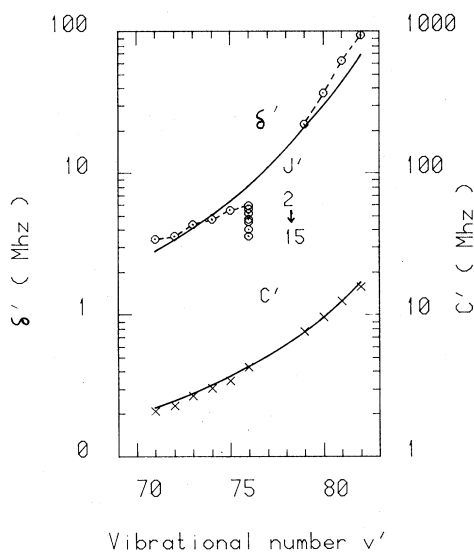

FIG. 1. Variation, with v', of the fitted C' (crosses) and δ' (circles) second-order effective parameters. The former depend on $\langle \mathcal{U} \rangle \langle \mathcal{H}_{MD} \rangle$ whereas the latter depends on $\langle \mathcal{H}_{MD} \rangle \langle \mathcal{H}_{MD} \rangle$ (see text); as $\mathcal{U}$ connects only the 1u states to the studied $B\,0_u^+$ state, 1u states cannot be responsible for the observed δ' anomaly at $v' = 76$. The positive value of δ' is due to the dominant influence of *gerade* states (Ref. 4). Solid lines are *ab initio* calculations from the potential curves of Ref. 9 and matrix elements of Table I within the second-order theory approximation (Refs. 10 and 11) for J' = 0 levels.

tion as

$$\mathcal{H}_p = \mathcal{U} + \mathcal{H}_{hf} = \mathcal{U} + \mathcal{H}_{MD} + \mathcal{H}_{EQ}$$

$$= \frac{-h^2}{2\mu r_{ab}^2}\, \vec{j}(\vec{L} + \vec{S}) + \sum_{i=a}^{b} \sum_{k=1}^{2} Q^k(\vec{I}_i) V_{ei}^{\ k},$$

where a and b refer to the two nuclei, Q^k and V^k are tensorial operators of rank k acting on nuclear and electronic coordinates, respectively, and magnetic dipolar ($k = 1$) and electric quadrupolar ($k = 2$) terms are the only ones to be considered. All hf matrix elements can then be calculated from a general relationship which will be given in a forthcoming paper.[10] We have evaluated (Table I) the electronic matrix elements on a separated-atom Heitler-London basis which should be a good approximation for high v' levels.[11] As we are interested in the $^2P_{3/2}$-$^2P_{1/2}$ dissociation limit, ten basis states[9] are involved in the calculation. They are constructed from the atomic wave functions $|j = \frac{3}{2}, m_{3/2}\rangle$ and $|j = \frac{1}{2}, m_{1/2}\rangle$ centered on nuclei a or b. It is easy to see that the parametric part of the electronic matrix elements depends only on the quantities $_i\langle jm_j|$ $\times V_q^k |jm_j'\rangle_i$ ($k = 1, 2$; $i = a, b$) which can be deduced from experimentally known hf atomic parameters: the electric quadrupole constant $\frac{1}{2}e\,Q_{5/2}\,q_{3/2} = 1146$ MHz[12] and the two magnetic dipole constants $a_{3/2} = 827$ MHz[12] and $a_{1/2} = 6586$ MHz.[13] The matrix elements in Table I show that the strongest perturbations affecting the

TABLE I. Values (in megahertz) of the gyroscopic ($\mathcal{U}$), hf magnetic dipolar (V^1), and hf electric quadrupolar (V^2) off-diagonal electronic matrix elements between $B\,0_u^+$ and all other basis states sharing the same $^2P_{3/2}$-$^2P_{1/2}$ dissociation limit (in the order of Table II of Ref. 9). The actual wave functions are linear combinations of the basis functions; for instance, for the "1'g" state we have "1'g" $= 0.84|1'g\rangle + 0.54|1''g\rangle$ (Ref. 9). $\langle \mathcal{U} \rangle$ is calculated with $r_{ab} = r_+ = 10$ Å.

State	$\langle \mathcal{U} \rangle / [2J(J+1)]^{1/2}$	$\beta\, gI_a \langle V^1 \rangle$	$\frac{1}{2}e\,Q_{5/2}\langle V^2 \rangle$
0_g^+	0	0	−573
0_u^-	0	−2882	0
0_g^-	0	3709	0
0_u^+	0	0	−573
"1'g"	0	−3491	0
"1''g"	0	1013	810
"1'u"	170	5830	0
"1''u"	100	1013	810
2g	0	0	810
2u	0	0	810

$B\,0_u{}^+$ state could come from magnetic dipole interactions with the $1'u$, $0_g{}^-$, $1'g$, and $0_u{}^-$ basis states, the corresponding nuclear-spin selection rules being $\Delta I = \pm 1$ for g states and $\Delta I = 0$ for u states.[4]

The δ' anomaly for $v' = 76$ cannot be attributed to a perturbation by the $1'u$ state since C' is regular (Fig. 1). Now the vibrational overlap between $B\,0_u{}^+$ and the levels of interest can be calculated[14] from potential curves of Ref. 9. Only the "$1'g$" (Table I) gives nonnegligible overlap at about the same energy as $B\,0_u{}^+$ and can lead to strong perturbations in the observed region.

The definitive evidence of the $B\,0_u{}^+$–"$1'g$" hf perturbation is obtained from direct diagonalization of the related interaction matrix for each value of the total angular momentum F'. In these large submatrices (45×45 for $F'-J'=0$) almost all main parameters can be calculated and held fixed in the fits: (i) first- and second-order hf parameters of $B\,0_u{}^+$ (eQq', C', δ', d') calculated as stated previously without the "$1'g$" perturbation; (ii) first-order quadrupolar and magnetic hfs of "$1'g$"; (iii) the off-diagonal matrix elements $B\,0_u{}^+$–"$1'g$" (Table I); (iv) the Franck-Condon overlap. The only adjustable parameters are $\Delta E_{vv'} = E_{\text{"}1'g\text{"}}(v, J=0) - E_{B\,0_u{}^+}(v', J'=0)$ and the rotational constant B_v of "$1'g$" (the rotational constants in $B\,0_u{}^+$ are fixed at their known values[15]).

In this manner, it has been possible to interpret the perturbation of the 77-0 band for which five well isolated lines [$P(28)$, $R(27)$, $R(19)$, $R(11)$, and $R(0)$] were available in our observations. These five lines give homogeneous results, leading to a value $B_v = 120 \pm 5$ MHz for the rotational constant of the perturbing "$1'g$" vibrational level and $\Delta E_{vv'} = 4.5 \pm 0.5$ GHz.

Figure 2 reports the experimental and theoretical hfs of the almost unblended 75-0, 78-0, and 79-0 bandheads. In this region of large internuclear distances the rotational splitting at the origin of the bands in $B\,0_u{}^+$ is smaller ($\sim 200\times J$ MHz) than the hf splitting (~ 2000 MHz); because $\mathcal{H}_{\text{EQ}}$ couples different rotational levels, J' is no longer a good quantum number. Then a superhyperfine structure[16] in the origin of these $B\,0_u{}^+$ levels is observed. As a consequence we must diagonalize together the fine and hyperfine interaction matrices including the first six J' levels in order to fit the structures in Fig. 2. The fit of the 75-0 and 79-0 bandheads, located outside the strong perturbation region, could be obtained with the usual second-order effective parameters;
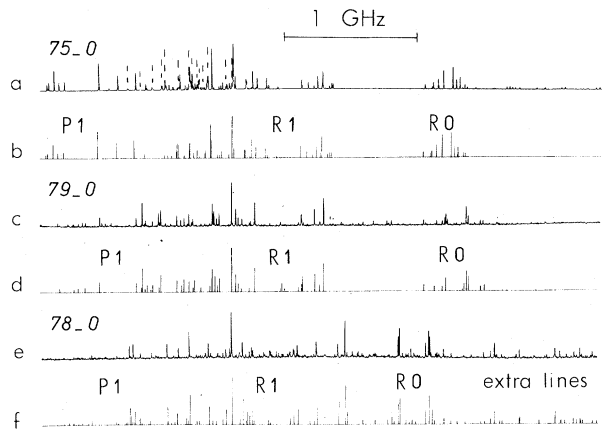

FIG. 2. (a), (c), and (e) Experimental recordings of the superhyperfine structure of the 75-0, 79-0, and 78-0 bandheads; dashed lines belong to other bands. (b) and (d) Second-order fits for the first two bands with the following parameters (in megahertz): $eQq' = -538(5)$, $C' = 3.60(0.20)$, $\delta' = 5.70(0.10)$, $d' = -2.90(0.10)$ for 75-0; $eQq' = -457(10)$, $C' = 7.60(0.20)$, $\delta' = 21(2)$, $d' = -10.5(1.0)$ for 79-0. (f) Result of a direct "$1'g$"– $B\,0_u{}^+$ diagonalization for the 78-0 bandhead with the following ab initio calculated parameters: $eQq' = -573$, $C' = 6.1$ ($B\,0_u{}^+$); $eQq = -224$, $C = 1943$ ("$1'g$"); $\langle 0_u{}^+|V^1|\text{"}1'g\text{"}\rangle = -2340$, $\langle 0_u{}^+|V^2|\text{"}1'g\text{"}\rangle = -446$ ["$1'g$" level is a mixing of states: "$1'g$" $=0.84\,|1'g\rangle + 0.54\,|1''g\rangle$ (Ref. 9)]; the fitted parameters are $\Delta E_{vv'} = 1800$ and $B_v = 100$.

for the 78-0 bandhead, on the other hand, its was necessary to diagonalize the "$1'g$"–$B\,0_u{}^+$ interaction matrix as explained above. A striking consequence of this procedure is the interpretation of the extra lines appearing on the high-frequency side of the 78-0 bandhead. They correspond to the forbidden "$1'g$"–$X\,0_g{}^+$ transitions which are made allowed by the ortho-para mixing of "$1'g$" with $B\,0_u{}^+$ through hf pertrubations. Depending on the hyperfine sublevels, the mixing coefficient can go up to 14%.

The existence of regions where the ortho-para symmetry is not valid allows violation of the usually very strict selection rule sym $\nleftrightarrow$ antisym[3] and permits a number of unusual observations. This u-g hf perturbation makes precise the assumption of Chevaleyre et al. about the unexplained transitions observed by Danyluk and King[17] from the $B\,0_u{}^+$ state [γ is $B\,0_u{}^+$("$1'g$") → $1u$ and δ is $B\,0_u{}^+$("$1'g$") → $0_u{}^+$ (or may be $2u$)]. Moreover the observed perturbed levels (and probably others at higher v') can serve as a first step for the excitation of nearly all the u or g high-lying ionic states. New and interesting possibilities are opened for the characterization

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of the numerous levels at the dissociation limits through double-resonance methods. Also, in collisional processes the very strict selection rule $\Delta J = \pm 2$ no longer holds and for instance $\Delta J = \pm 1$ rotational relaxed lines can be populated from the perturbed $B\,0_u{}^+$ levels.

Finally a survey of atomic hfs shows that a similar situation is likely to be met in many other molecules.

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