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Hyperfine predissociation in the B state of iodine investigated through lifetime measurements of individual hyperfine sublevels

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Résumé. — L'iode présente le phénomène de prédissociation hyperfine à la suite duquel les différents sous-niveaux hyperfins d'un même niveau rovibronial doivent avoir des durées de vie différentes. Ceci a été vérifié directement pour la première fois par des mesures de durée de vie par niveau hyperfin. On a ainsi déterminé :

\[ \Gamma_{\text{rad}} = (0.314 \pm 0.018) \times 10^6 \text{ s}^{-1}, \]

ainsi que les paramètres de prédissociation rotationnelle et hyperfine \( C_v = (5.85 \pm 0.65) \text{ s}^{-1/2} \) et \( a_v = (-142 \pm 5) \text{ s}^{-1/2} \), pour le niveau \( v = 43 \) de l'état \( B^0_u+ \).

Abstract. — Iodine exhibits the phenomenon of hyperfine predissociation, by which the different hyperfine sublevels of the same rovibronic level are given different lifetimes. This has been verified for the first time by the direct lifetime measurement technique. We determined \( \Gamma_{\text{rad}} = (0.314 \pm 0.018) \times 10^6 \text{ s}^{-1} \) and the rotational and hyperfine predissociation parameters \( C_v = (5.85 \pm 0.65) \text{ s}^{-1/2} \) and \( a_v = (-142 \pm 5) \text{ s}^{-1/2} \) for the \( v = 43 \) level of the \( B^0_u^+ \) state.

1. Introduction. — The dynamics of molecular excited states is an important chapter of present-day molecular physics. In this respect, studies of predissociation phenomena are of special interest. The case of the iodine B state is a particularly good example of such investigations. In addition to the already known magnetic [1] and gyroscopic [2] predissociation, a third mechanism, hyperfine predissociation [3] was recently discovered. The theory of these processes, all due to the coupling of the \( B^3 \Pi_{0u} \) state with the same \( 1\Pi_u \) dissociative state, has been completely worked out [4].

The hyperfine structure of rovibronic levels of the B state is now well known. For not too low values of the rotational quantum number \( J \), each rotational level \( J'' (J') \) is split into 21 or 15 hyperfine sublevels according to whether \( J'' (J') \) is odd (even) or even (odd). The combination rules prevailing in this case give rise to 21 (15) main hyperfine components for each rotational transition. Due to the hyperfine relaxation mechanism, the different hyperfine sublevels will have different lifetimes, with the following consequences :

— The overall decay of the population of a given rovibronic level \( J' \) of the B state will be non-exponential and its apparent lifetime will depend on whether \( J' \) is even or odd [3] ;

— the different hyperfine components of a given rovibronic transition will have anomalous intensities [5], and different linewidths [6].

These three consequences have been borne out by three series of experiments [3, 5, 6] which already verified the essential correctness of the theory of hyperfine predissociation [4]. The most direct consequence of this theory, namely the difference in lifetimes between different hyperfine sublevels had, however, never been verified in some detail. In this paper, we describe the experiments we have performed on this point and their comparison with theory.
2. Experimental. — Lifetime measurements were obtained by the standard technique of monitoring the decay of the fluorescence light originating from the level under investigation following a pulsed excitation of this level. Our laser-excited collimated supersonic beam apparatus [7] had many desirable features for such experiments and had only to be modified in order to give it time-resolved capabilities. As the P(13) and R(15) 43-0 iodine lines were well suited to this study, we chose as an excitation source the 514.5 nm radiation of a single-mode Ar$^+$ laser (Fig. 1). Its output frequency was stabilized by two successive servo-loops. The first one (prestabilization) locked the Ar$^+$ laser frequency to a high quality stable reference cavity. The residual frequency jitter, already reduced by precautions such as mechanical decoupling of the laser structure from the vibrations due to cooling water around the discharge tube, was narrowed down to a few megahertz. The remaining thermal drifts of the reference cavity were then suppressed by locking it, through the standard third derivative technique, to the saturated absorption peaks produced in an iodine reference cell.

The fluorescence decay technique calls for an exciting light pulse with fall time much shorter than the ~ 1 μs expected decay times and a reasonably good extinction ratio. An acousto-optic modulator is well suited for this purpose. Such a device, quite adequate as concerns the response time (200 ns), unfortunately presents a correct extinction ratio (1/5 000) only on the first order diffracted light beam, whose frequency is shifted from the incident light frequency by an amount equal to the acoustic driving frequency $N$. Such a light beam, crossing the iodine beam, was accordingly completely out of resonance with respect to a given hyperfine component, when the Ar$^+$ laser was locked on the same component of the iodine reference cell. However, as the selected tuning range of driving frequency $N$ (50 $< N <$ 90 MHz) is greater than the frequency differences between the hyperfine components of interest, it was possible to lock the laser frequency to one hyperfine component in the cell and to excite the neighbouring one in the jet by adjusting the acoustical frequency $N$.

The exciting laser beam ($\sim$ 500 mW) was sent perpendicularly to the iodine supersonic beam. The resulting fluorescence light was collected by a photomultiplier followed by a fast amplifier-discriminator (50 MHz) and a multichannel analyser. The model used was developed in our laboratory and had 1 024 channels with a dynamic range of 24 bits each. The time interval between two successive channels was 500 ns. A clock provided the necessary synchronizing pulses between the channel scan and the operation of the RF gate acting on the light modulator. In order to get a good signal to noise ratio, as many as 10$^6$ scans were accumulated in the multichannel analyser. The data were then transferred into a minicomputer (Exorset 30) which enabled the visualization of the obtained curves and the calculation of the corresponding time constants.

3. Results. — The hyperfine sublevels belonging to the $v' = 43$, $J' = 12$ and 16 rotational levels of the...
BOu state have been analysed. The relevant transitions in the excitation spectrum are displayed on figure 2a. Figure 2b shows the decays observed for three hyperfine sublevels. From these curves, one deduces the corresponding lifetimes: results obtained for all the levels studied are gathered in table I. The existence of hyperfine predissociation is made immediately apparent by the large variation of observed lifetimes between different hyperfine sublevels.

The iodine molecules in our supersonic molecular beam experience essentially no collisions. On the other hand, no magnetic predissociation takes place in the absence of any magnetic field. As a result, the decay rate $\Gamma$ of a given hyperfine sublevel is given by the relation (4):

$$\Gamma = \Gamma_{\text{rad}} + \Gamma_{\text{rot}} + \Gamma_{\text{hf}} + \Gamma_{\text{int}}$$

(1)

where $\Gamma_{\text{rad}}$ is the radiative decay rate, $\Gamma_{\text{rot}}$ is the gyroscopic predissociation rate, $\Gamma_{\text{hf}}$ is the hyperfine predissociation rate, and $\Gamma_{\text{int}}$ takes into account the interference effect between the two later mechanisms.

The different rate constants are given by the following formulas:

$$\Gamma_{\text{rot}} = c_{\alpha}^2 [1 + p_v J(J + 1) + \cdots] J(J + 1)$$

$$\Gamma_{\text{hf}} = \frac{1}{3} a_v^2 [1 + p_v J(J + 1) + \cdots] \left[ \sum_{\ell} \alpha^2 (I, \ell, J, F) \left( I^2 + \frac{3(I, J)^2 + \frac{3}{2} (I, J) - I^2 J^2}{(2J - 1)(2J + 3)} \right) \right]$$

$$\Gamma_{\text{int}} = -\sqrt{2} a_v c_v [1 + p_v J(J + 1) + \cdots] \left[ \sum_{\ell} \alpha^2 (I, \ell, J, F) I, J \right]$$

The coefficients $a_v$ and $c_v$ are essentially under the dependence of the Franck-Condon overlap between the BOu $v$ level of interest and the $^1 \Pi_{1u}$ state responsible for the predissociation; the $[1 + p_v J(J + 1) + \cdots]$ factor takes into account a possible J dependence of this overlap. On the other hand, the coefficients $\alpha$ come from the fact that, due to quadrupolar hyperfine interaction, $I'$ is not a good quantum number. These coefficients are obtained by diagonalizing the hyperfine Hamiltonian.

In the present case (low J value) the $p_v$ influence is negligible. We are thus left with the three constants $\Gamma_{\text{rad}}, a_v$ and $c_v$ to account for the observed lifetimes. Every hyperfine sublevel measurement was repeated several times. The parameters are directly determined from the whole set of measurements with a non-linear least-squares fit by a gradient method. We obtain:

$$\Gamma_{\text{rad}} = (0.314 \pm 0.018) \times 10^6 \text{ s}^{-1}$$

$$c_v = (5.85 \pm 0.65) \text{ s}^{-1/2}$$

$$a_v = (-142 \pm 5) \text{ s}^{-1/2}$$
Table II. — Calculated contributions to $\Gamma_F$ of $\Gamma_{\text{int}}$ and $\Gamma_{\text{hf}}$ (Eq. (1)) for the hyperfine components of the P(13) 43-0 line, with $\Gamma_{\text{rot}} = 0.535 \times 10^4 \text{ s}^{-1}$, and $\Gamma_{\text{rad}} = 31.4 \times 10^4 \text{ s}^{-1}$.

<table>
<thead>
<tr>
<th>Component</th>
<th>$\Gamma_{\text{hf}}$ ($10^4 \text{ s}^{-1}$)</th>
<th>$\Gamma_{\text{int}}$ ($10^4 \text{ s}^{-1}$)</th>
<th>$\Gamma_F$ ($10^4 \text{ s}^{-1}$)</th>
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<tbody>
<tr>
<td>$a_1$</td>
<td>28.8</td>
<td>-7.65</td>
<td>53.0</td>
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<tr>
<td>$a_2$</td>
<td>2.55</td>
<td>-0.29</td>
<td>34.2</td>
</tr>
<tr>
<td>$a_3$</td>
<td>26.9</td>
<td>7.06</td>
<td>65.9</td>
</tr>
<tr>
<td>$a_4$</td>
<td>25.6</td>
<td>-6.71</td>
<td>50.8</td>
</tr>
<tr>
<td>$a_5$</td>
<td>5.11</td>
<td>0.97</td>
<td>38.0</td>
</tr>
<tr>
<td>$a_6$</td>
<td>6.47</td>
<td>-2.05</td>
<td>36.3</td>
</tr>
<tr>
<td>$a_7$</td>
<td>21.6</td>
<td>-5.57</td>
<td>48.0</td>
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<td>$a_8$</td>
<td>13.5</td>
<td>-3.87</td>
<td>41.5</td>
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<tr>
<td>$a_9$</td>
<td>8.45</td>
<td>2.35</td>
<td>42.7</td>
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<tr>
<td>$a_{10}$</td>
<td>11.5</td>
<td>4.06</td>
<td>47.5</td>
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<td>$a_{11}$</td>
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<td>$a_{14}$</td>
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<td>$a_{15}$</td>
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<td>$a_{16}$</td>
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<td>$a_{17}$</td>
<td>14.7</td>
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<td>$a_{18}$</td>
<td>5.95</td>
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<td>$a_{19}$</td>
<td>13.2</td>
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<td>43.6</td>
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<td>$a_{20}$</td>
<td>10.4</td>
<td>0.33</td>
<td>42.6</td>
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<tr>
<td>$a_{21}$</td>
<td>21.2</td>
<td>5.06</td>
<td>58.2</td>
</tr>
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</table>

where the quoted error corresponds to two standard deviations. Two standard deviations between observed and calculated decay rates are $0.013 \times 10^6 \text{ s}^{-1}$.

The calculated lifetimes (Table I) are in agreement with the measured ones within the estimated experimental error ($\pm 5\%$).

The determination of the three parameters allow to calculate the contributions to individual $\Gamma_F$ decay rate according to equation (1). The results are shown in table II for the P(13) 43-0 line. We can see that the $\Gamma_{\text{hf}}$ and $\Gamma_{\text{int}}$ terms are an order of magnitude higher than the pure rotational $\Gamma_{\text{rot}}$ decay rate, due to the low $J$ value. This leads to a variation of about a factor 2 between the individual lifetimes. We can remark that the lowest hyperfine predissociation influence corresponds to the line $a_5$ ($F - J = 0$), so for this line $\Gamma_F$ is close to $\Gamma_{\text{rad}} + \Gamma_{\text{rot}} \approx \Gamma_{\text{rad}}$. On the other hand, the largest hyperfine effects are observed for $a_1$ ($F - J = -5$) and $a_3$ ($F - J = +5$). This was pointed out [5] from intensity measurements.

Precise global lifetime measurements of the same levels were made by Paisner and Wallenstein [9]: $\tau_{\text{eff}} = 2.28 \pm 0.08 \mu \text{s}$, and Sakurai et al. [10]: $\tau_{\text{eff}} = 2.13 \pm 0.15 \mu \text{s}$. Our determinations permit the calculation of the same quantity using the approximation:

$$e^{-\Gamma_{\text{eff}} t} = \frac{\sum F}{\sum F} \frac{\sum I_F e^{-r_{\text{eff}} F}}{\sum I_F}$$

where $\Gamma_{\text{eff}} = \frac{1}{\tau_{\text{eff}}}$ is the global effective radiative decay rate. $I_F$ is the calculated hyperfine intensities following the relation:

$$I_F = I_{0F} \frac{\Gamma_{\text{rad}}}{\Gamma_F}$$

$I_{0F}$ being the hyperfine intensity expected without predissociation.

The approximation (3) appears to be valid for time intervals of more than $10 \tau_{\text{eff}}$ within less than 0.3% (relative deviation from a single exponential law). Finally, we obtain: $\tau_{\text{eff}} = (2.32 \pm 0.03) \times 10^{-6} \text{ s}$ in agreement with the results of references [9] and [10].

It is also remarkable that the indirect determination of $a_2^2 (a_2^2 = (12 \pm 5) \times 10^3 \text{ s}^{-1})$ from intensity measurements [8] by Vigue et al. [4] is in agreement with $a_2^2 = (10.2 \pm 1.5) \times 10^3 \text{ s}^{-1}$ deduced from our direct measurements.

Let us finally notice that our technique is the only precise way of determining the pure radiative decay rate $\Gamma_{\text{rad}}$ in the presence of hyperfine predissociation.

4. Conclusion. — The most direct method for lifetime measurement, the fluorescence decay technique, has been applied for the first time to the case of hyperfine sublevels. The results show the importance of hyperfine predissociation and provide the most straightforward verification of the corresponding theory [4]. It should be interesting to perform such experiments on other iodine levels, in particular near the dissociation limit of the B state [7], or on other molecules such as Bromine.

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