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Landé factor measurements in the $B^3\Sigma_u^-$ state of $^{80}\text{Se}_2$: a test of molecular perturbations (*)

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Résumé. — Nous avons mesuré les facteurs de Landé de 180 niveaux dans l'état $B^3\Sigma_u^-$ de $^{80}\text{Se}_2$ par la méthode des battements quantiques Zeeman. Nos mesures montrent la grande sensibilité du facteur de Landé aux perturbations moléculaires. Une interprétation préliminaire de ces résultats est proposée.

Abstract. — We have measured the Landé factor values of 180 rotational levels in the $B^3\Sigma_u^-$ state of $^{80}\text{Se}_2$ by the Zeeman quantum beats method. Our measurements show the great sensitivity of the g_J values to molecular perturbations. A preliminary interpretation of these results is proposed.

1. Introduction. — The study of atomic and molecular excited states by the quantum beats method has become increasingly popular since the advent of pulsed tunable lasers (a number of references are given in the review by S. Haroche [1]). For molecular problems there have been measurements of a few Landé factor values in the $B^3\Pi_{ou}^+$ state of I_2 [2] (Zeeman quantum beats).

However, we present here the first systematic study of Landé factors in molecular excited states. This work has been carried out on the $B^3\Sigma_u^-$ state of Se_2 and shows mainly the dramatic sensitivity of the Landé factor values upon local perturbations of the molecular state ; from these measurements a much more precise understanding of those perturbations becomes possible.

2. Experimental arrangement. — We have studied about 180 rotational levels in the $v' = 0$ to 6 vibrational levels of the $B^3\Sigma_u^-$ ($\Omega = 0^+$) state of Se_2 [3]. Optical excitation is produced by a nitrogen laser pumped dye laser operating in the 3 600 Å to 4 250 Å spectral range. The laser spectral width is about 2 GHz, which generally allows excitation of a single rotational vibrational level. Molecular fluorescence is viewed through a spectrometer of modest resolu-

tion ; the structure of the fluorescence spectrum, and the laser frequency measurement with a precision of 0.3 cm^{-1} allow an unambiguous assignment of the excited state.

The time dependence of the fluorescence intensity following a laser pulse is observed by means of a Tektronix R 7912 Transient Digitizer, and averaged over about a thousand laser shots. The dye laser polarization is perpendicular to a magnetic field **B** which is applied around the selenium cell. The fluorescence light is analysed through a linear polarizer perpendicular to **B**.

With these experimental conditions the time dependence of the fluorescent intensity is a cosine modulated exponential decay. The modulation frequency equals twice the molecular Larmor frequency [2].

This makes possible the direct measurement of the Landé factor parameter g_J with a precision up to 3 %.

3. Results. — The Landé factor variations as a function of the J value are displayed on figures 1-7 for the $v' = 0$ to 6 vibrational levels of $\text{B}0_u^+$. At the moment we have not performed systematic measurements in the $\text{B}1_u$ state because of assignment problems due to the poorer quality of the molecular parameters of the $\text{B}1_u \rightarrow \text{X}1_g$ transitions. The whole set of our experimental results clearly show two characteristic features of Landé factor variations in the $\text{B}0_u^+$ state :

1° For levels far from any local perturbation (the $v' = 2$ is the best example), g_J values are essen-

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Figs. 1-7. — $g_J = f(J)$ variations in the $v' = 0$ to 6 , vibrational levels of the state $B0_u^+$ in Se_2 .

tially J independent. As we have shown in a previous paper [4], these Landé factor values are mainly due to the $B0_u^+ \leftrightarrow B1_u$ mixing induced by the off-diagonal part of the rotational Hamiltonian $\mathcal{H}_{N,D} = -2BJ.S$.

2° On the other hand, a great number of local perturbations appear on the $g_J = f(J)$ curves, as very important deviations from the aforementioned constant value. As the J value goes through such a perturbation, the Landé factor first increase a little, then suddenly diminishes when J equals the most perturbed level value. Then, the g_J value slowly goes up again towards a value which seems slightly lower than the low J value.

Our results show again most of the local perturbations in the $B0_u^+$ state of Se_2 , which were first detected by absorption spectroscopy [3]. It seems worthwhile to point out that all the perturbations observed by Barrow *et al.* are weak perturbations, i.e. the energy shifts are all less than 5 cm^{-1} and noticeable only for a very small number of J values. Those same perturbations observed through the Landé factor values appear very important, for g_J may even change sign in some cases. Moreover, the perturbation shown here near $v' = 3$, $J' = 109$, is to our knowledge, reported for the first time.

The state(s) perturbing the $B0_u^+$ state are very badly known, for they do not appear in the absorption spectra; the only spectroscopic information about them, is through the appearance of extra-lines in the $X0_g^+ \rightarrow B0_u^+$ absorption spectra, near the points of maximum perturbation. On the contrary, the g_J measurements of the *perturbed* as well as *perturbing* states, when possible, give a much more precise knowledge either of the nature of the perturbing state or of that of the coupling Hamiltonian.

Without going into the details of such an analysis, we wish to show here how a second order perturbation theory may be used to understand the main features of our results.

4. Interpretation of results. — Let us consider two normalized molecular states noted $|1\rangle$ and $|2\rangle$, whose electronic and vibrational energies are E_1^0 and E_2^0 . The rotational constants of these states are, in general, different, say B_1 and B_2 . The energies of the two levels corresponding to the same J values are then :

$$\begin{cases} E_1 = E_1^0 + B_1 J(J+1) \\ E_2 = E_2^0 + B_2 J(J+1) \end{cases}$$

A local perturbation may happen between those two states, when $E_1(J) \simeq E_2(J)$. Let W_{12} be the matrix element of the molecular Hamiltonian between 1 and 2. This perturbation gives rise, for example, for level 1 to a shift

$$\Delta E_1 = \frac{|W_{12}|^2}{E_1(J) - E_2(J)}$$

and to a change in the molecular wave function such that

$$|\tilde{1}\rangle = |1\rangle + \frac{W_{12}}{E_1 - E_2} |2\rangle.$$

The study of the energy shifts $\Delta E_1(J)$ around the J value of *crossing* has been up to now the main source of information on the perturbations between molecular states. Nevertheless, one may also notice that around the crossing point, the exact wave functions are superpositions of pure state 1 or 2 wave functions. All molecular properties directly linked to those wave functions are therefore modified. This is the case, for example, of excited level lifetimes [5], and also for Landé factor values, which are the mean values of the operator

$$\frac{(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{J}}{J(J+1)}.$$

One then finds, for a perturbed molecular state :

$$g_J = g_1 + \frac{|W_{12}|^2 (g_2 - g_1)}{(E_1(J) - E_2(J))^2} + 2 \operatorname{Re} \frac{W_{12}}{E_1(J) - E_2(J)} g_{12}$$

with the notation :

$$g_{12} = \langle 1 | \frac{(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{J}}{J(J+1)} | 2 \rangle.$$

The variation of the g_J values around the crossing of the $|1\rangle$ and $|2\rangle$ rotational series, is then the sum of a variation which is even with regard to $(E_1 - E_2)(J)$ due to the $(g_2 - g_1)$ term, and another one which is odd due to the g_{12} contribution which is clearly what we experimentally observed. This shows, in particular, that $g_{12} \neq 0$, which confirms that the states perturbing $B0_u^+$ between $v' = 0$ to $v' = 6$ are all 1_u states (for the Zeeman Hamiltonian can not connect $\Omega = 0$ states at first order) [6].

Let us look now at the most intense perturbations (for the level $v' = 1, 4, 5$); the most perturbed rotational levels (v, J) are split into two components. The resulting two levels with the same J value have different Landé factors, whose measurement adds considerably to the available information. We will not comment longer upon this point in this short note, keeping a detailed study for a future paper.

Let us just point out a few particular features :

i) The $J' = 41$, $v' = 6$ level is, from R. F. Barrow [3] accidentally predissociated, i.e. it corresponds to a three-level crossing : the beat structure results from a superposition of several frequencies and we have not analysed it.

ii) For the $v' = 5$ level, the scattering of the g_J values is much beyond the experimental uncertainties.

In that case, it will be necessary to take into account second-order terms in the Zeeman interaction.

The whole set of these preliminary results shows how useful may be a systematic measurement of molecular Landé factors. We have shown the influence of coupling between the fine structure levels $\Omega = 0$ and $\Omega = 1$ of $B^3\Sigma_u^-$ (which gives here the *non perturb-*

ed g_J values) and that of local perturbations caused by other nearby electronic levels, which are otherwise very badly known. Furthermore the lifetimes of the levels we have studied could be measured simultaneously with the Landé factors, which would still add to our information upon the various perturbations we have observed.

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