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# Strong-Field Saturation Spectroscopy of Weak Hyperfine Crossover Resonances.

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**Abstract.** – We show that, thanks to a controlled use of strong laser fields in hyperfine spectroscopy of molecules, it is possible to record the crossover resonances between allowed $\Delta F = \Delta J$ lines and $\Delta F \neq \Delta J$ lines which are very weak for high $J$ lines. A demonstration experiment on the $Q(45)A_2^2$ line of the $\nu_3$ band of $SF_6$ yields very accurate values of the spin-rotation and spin-vibration constants, $c_a$ and $A$, whose ratio denotes the importance of purely vibrational effects.

The first goal of this letter is to demonstrate the possibility offered by modern saturation spectroscopy, to record very weak crossover resonances [1-4] between molecular hyperfine transitions of high rotational quantum number $J$, thanks to recent instrumental progress and especially through a controlled use of strong laser fields. This technique opens the way to direct high-accuracy measurements of energy splittings corresponding to a specific hyperfine interaction within a given vibration-rotational level. We illustrate this point in the case of the scalar nuclear spin-rotation interaction for $SF_6$. The second original contribution of the letter consists of conclusions that can be drawn from this measurement concerning the physics of this molecule.

To put right away our ideas in concrete form for what follows, we shall develop our reasoning preferentially on the system of hyperfine levels represented in fig. 1, corresponding to the line $Q(45)A_2^2$ of the $\nu_3$ band of $SF_6$ at 28 412 526 414.5 kHz. This line has been selected for our measurement because it is well isolated in the spectrum and can be easily reached with the $P(16)$ $CO_2$ laser line [5-7]. As we shall see, a $Q$ line presents narrow structures which are best suited for a measurement of the crossovers positions and the $A_2$ symmetry species restricts hyperfine interactions which need to be considered in first approximation, to the scalar spin-rotation and spin-vibration terms of the Hamiltonian [8, 9]

$$H_S/h = -c_a \boldsymbol{I} \cdot \boldsymbol{J} + A \boldsymbol{I} \cdot \boldsymbol{l}_3 ,$$

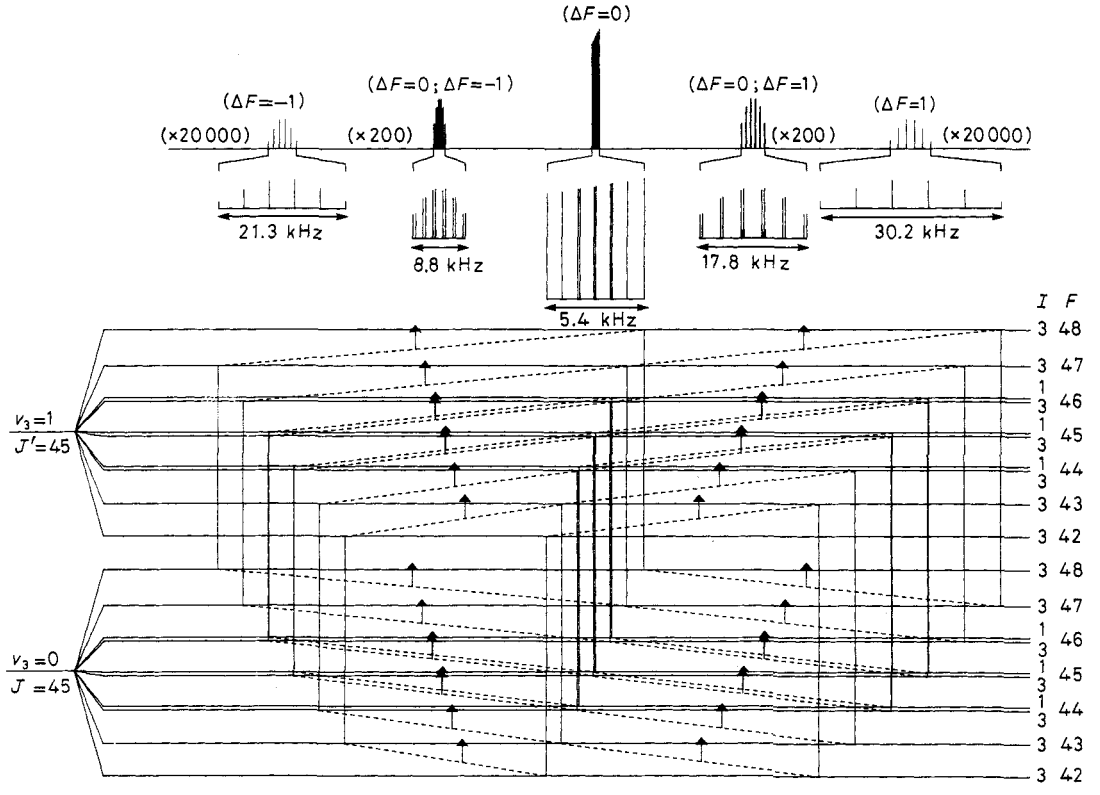


Fig. 1. – Calculated energy levels and saturation spectrum for the $Q(45)A_2^2$ line. Crossovers are denoted by a vertical arrow in the middle of the dotted lines joining their associated levels.

where $\boldsymbol{J}$, $\boldsymbol{I}$ and $\boldsymbol{l}_3$ are, respectively, the vibration-rotation, spin and vibrational angular momenta. Hyperfine terms of higher order with respect to vibration-rotation will be introduced here simply as a correction $\delta c_a$ to $c_a$ in the excited state, which has been calculated from the matrix elements of the corresponding operators and is given to a good approximation by the formula [10]

$$\delta c_a = \delta_0 c_a + \delta_1 c_a (-1)^{J'+J} (2J'+1) \begin{Bmatrix} J' & J' & 2 \\ 1 & 1 & J \end{Bmatrix} \begin{Bmatrix} J' & J' & 2 \\ 1 & 1 & J' \end{Bmatrix},$$

which yields $\delta c_a \approx -17.4$ Hz for $Q(45)$.

The lower and upper vibrational level energies are then, respectively, expressed by $E = -hc_a f(I, J, F)$ and $E' = -h(c_a + \Delta c_a) f(I, J', F')$ with $f(I, J, F) = (1/2)[F(F+1) - J(J+1) - I(I+1)]$ and an effective change in $c_a$ given by [8]

$$\Delta c_a = \delta c_a + A \frac{f(1, J', J)}{J'(J'+1)}.$$

The possible values for the spin quantum number are 1 and 3 for $A_2$ species lines. This leads to a spectrum which exhibits ten main lines $\Delta F = \Delta J$ with frequencies

$$-(c_a + \Delta c_a)\Delta J(F-J) - \Delta c_a f(I, J, F).$$

In the case of $Q$ lines, only the second term subsists, with a very small value for $\Delta c_a = \delta c_a - A/(J'(J+1))$ (of the order of $-19.6$ Hz for $Q(45)$), hence a very narrow structure. In addition to these main lines, there are eight $\Delta F = -1$ lines. To each of these, we can associate the two main lines sharing a common level with it: the frequency intervals are equal either to $c_a(F'+1)$ or to $(c_a + \Delta c_a)F$. These components are therefore also clustered in a packet located at about $c_a J$ and hence well isolated from the main lines. Similarly a second packet, on the high-frequency side of the main lines, comprises the eight $\Delta F = +1$ lines. Although their intensity is several hundred thousand times weaker than that of the main lines, we have been able to record the envelope of these packets using strong ($\sim 5$ mW) laser fields. However, under these conditions, the baseline distortions, to be described later, do not permit a good measurement of their position. Fortunately, two crossover resonances appear exactly half-way([1]) between weak $\Delta F = \pm 1$ line and their associated main hyperfine components and their intensity is intermediate between these parent lines. They cluster again as two unresolved sets of sixteen lines (with the narrowest spreading on the low-frequency side) at

$$\Delta^{\pm} = \mp (2J+1)\left(c_a + \frac{\Delta c_a}{2}\right)/4 + \frac{\Delta c_a}{2} \tag{1}$$

from the main lines (with the hypothesis of equal intensities within each multiplet). Therefore, thanks to a precise measurement of the splitting between the centre of either one of these packets and that corresponding to the main lines, one could hope to infer an accurate value for the constant $c_a$. In a second step, it is possible to make iterations between the recorded profile and the calculated spectrum taking into account relative intensities and all off-diagonal hyperfine interactions between $A_2$ states and neighbouring levels. We have included in our final computations all the couplings within a basis comprising the 9($E^4$, $F_1^7$, $A_1^2$, $F_1^8$, $F_2^7$, $A_2^2$, $F_2^8$, $E^5$ and $F_1^9$) rovibrational levels, that is all ($v = 0$) levels within $\pm 12$ MHz of $A_2^2$, resulting in a spectrum of 1702 lines. All these mixings do not yield any shift larger than 165 Hz for the energy levels and represent a few Hz correction to the measurement.

The spectrometer has been described before [7]. The data acquisition program is such that two lines can be recorded quasi-simultaneously with a number of sweeps and scanning orders which minimize the effect of the local oscillator frequency drifts (a few Hz/mn) even if the experimental conditions are very different for both lines. To record the crossover resonances, the laser power was varied between 50 $\mu$W and 1 mW with typically 10 to 20 sweeps of 500 points and a 100 ms time constant. Unfortunately, the crossovers ($\Delta F = 0$, $\Delta F = 1$) could not be measured because of their quasi-coincidence with an unidentified triplet (see fig. 2). For the main lines, the power was considerably smaller ($\sim 1$ $\mu$W) and 2 to 4 sweeps with a 30 ms time constant were sufficient to obtain a higher signal-to-noise ratio than in the case of crossovers. Line centre positions are then automatically obtained thanks to a nonlinear regression program fitting the lineshapes with Lorentzian derivatives and correcting for baseline tilts. The pressure in the cell was $\approx 1.5 \cdot 10^{-4}$ Torr and the linewidth was of the order of 3.5 kHz HWHM for the $\Delta F = 0$ lines and of the order of 6 kHz for the crossovers resulting in unresolved structures with respective half-widths of $\sim 4.5$ and 8 kHz. Figure 2 illustrates both kinds of structures in the strong field conditions required to observe the crossovers. These field conditions introduce a number of problems:

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([1]) Crossover resonances could be shifted owing to any anisotropy in the speed of light [11]. Such an anisotropy of either instrumental or preferred frame origin [12] is negligible here.

1) The increase of the laser power in the cell is obtained by reducing the attenuation of the laser beam before entering the cell, and therefore also the optical isolation. This results in an increase of the noise due to optical feedback and hence of the difficulty to record very weak lines. This problem is presently taken care of by the use of acousto-optic frequency shifters.

2) Strong laser fields induce large light shifts of crossover resonances [4] owing to off-resonant conditions with the strong coupled $\Delta F = 0$ transitions. An analysis made along the lines of ref. [4] shows that all crossover resonances ($\Delta F = 0$, $\Delta F = -1$) suffer from comparable blue shifts in good agreement with the observed shift. An extrapolation to zero power yields

$$\Delta^- = -(117.2 \pm 0.2)\,\text{kHz}$$

for the splitting between $\Delta F = 0$ lines and these crossovers, where the uncertainty comes for the major part from the light shift evaluation.

3) As can be seen in fig. 2, we observe a spectacular distortion of the main lines which develops as the field strength is increased: a narrow central dispersive feature, together with weak oscillations, appears on top of an asymmetric pedestal. The side oscillations affect the baseline to such an extent that the weak $\Delta F = \pm 1$ lines could not be measured accurately. These new phenomena originate from constructive or destructive interferences between the detuning and the phase shifts induced by wavefront curvature. A detailed experimental and theoretical investigation of this strong field behaviour has been undertaken [13] and will be presented elsewhere [14]. This strong lineshape distortion is of course absent in the weak-field conditions used to measure the position of the main lines.

From the measurement of the crossovers position extrapolated to vanishing laser field, one can deduce a preliminary value $c_a = -(5.15 \pm 0.01)$ kHz neglecting $\Delta c_a$ in (1). For each value of $c_a$ close to this starting value, it was possible to determine the other scalar hyperfine interaction constants $A$, $\delta_0 c_a$ and $\delta_1 c_a$ thanks to the set of measurements of the splittings between the main components $F = J \pm 3$ of all the rovibrational $A_{2u}$ lines recorded in the past [6, 8]—$P(33)A_2^1$, $P(59)A_2^3$, $P(84)A_2^1$, $R(28)A_2^0$, $R(66)A_2^0$, $R(72)A_2^3$ and $Q(54)A_2^2$—. In each case, the synthetic spectrum for the $Q(45)A_2^2$ line was fitted with the program which was used for the true experimental recording and this converged to the following values:

$$\begin{cases} c_a = -(5.140 \pm 0.010)\,\text{kHz}, & A = (4.707 \pm 0.015)\,\text{kHz}, \\ \delta_0 c_a = -(12.05 \pm 0.25)\,\text{Hz}, & \delta_1 c_a = -(40 \pm 3)\,\text{Hz}, \end{cases} \quad \text{(90\% confidence level)}$$

giving $\delta c_a = -(17.4 \pm 0.7)$ Hz for $Q(45)$. The sign of $c_a$ was also confirmed directly by the observation of the envelope of the crossovers between the $\Delta F = 1$ and $\Delta F = 0$ transitions for the $R(28)A_2^0$ line, which spreads unresolved on the lower frequency wing of the main structure.

The value obtained for $c_a$ is compatible with the measurement of Ozier *et al.* [15] which yielded $c_a = -(5.27 \pm 0.40)$ kHz. The higher accuracy of the present work is a consequence of two advantages of the optical method using crossovers over magnetic resonance in molecular beams:

1) The magnetic resonance method does not select any particular rotational state so that the spectrum is broadened by tensorial contribution of the various rotational states and it is necessary to assume that these contributions do not result in any shift on the average.

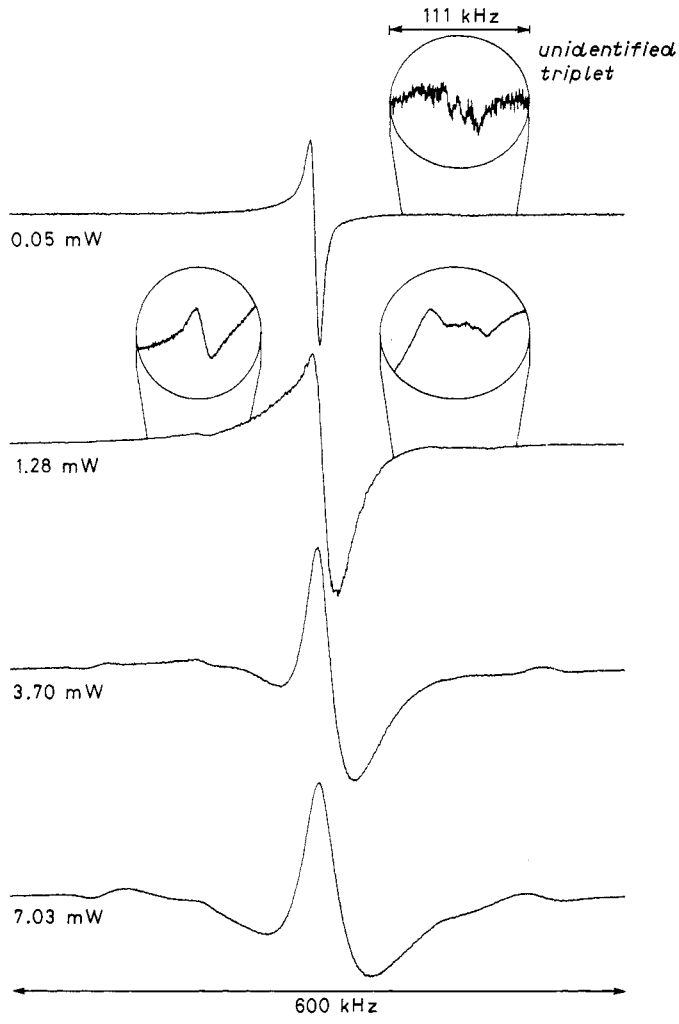


Fig. 2. – Experimental derivative spectrum of the $Q(45)A_2^2$ for increasing laser powers.

2) The magnetic resonance spectrum is still a difference ($\Delta F = \Delta m_I = 0$) spectrum ($\mp c_a m_I$, where $m_I$ is the projection of $\boldsymbol{I}$ on the magnetic field axis) between Zeeman sublevels, much less sensitive to $c_a$ than crossover positions which reveal the full hyperfine splitting itself.

The direct confirmation of the sign of $c_a$ and the knowledge of an accurate value for this constant, which was the worst known of all the main hyperfine interaction constants for $SF_6$, should lead to a better global understanding of these interactions. For example, it removes any ambiguity in the comparison between spin-rotation and spin-vibration interactions. It was speculated that these two constants could be equal [16]. The present accuracy rules out completely this hypothesis (which also runs into a sign problem) as well as the possibility of having a ratio of these constants equal to the Coriolis coupling constant $\zeta_3 = 0.693\,443$ [6] which was found to be the case for $^{189}OsO_4$ [17] and $^{187}OsO_4$. This difference which comes from vibrational corrections [18] will be justified in another paper by a calculation based on known molecular properties of both molecules.

With respect to saturated absorption experiments of the past we have demonstrated several points which bring an important methodological progress in the use of crossover resonances:

1) The access to much higher values of $J$, thanks to a strong laser field, has enabled us to choose the most judicious line in order to isolate the scalar interaction constants: symmetry $A_2$ and well isolated $Q$ line presenting narrow structures for the crossovers and for the main line.

2) These experiments have clearly shown the influence of light shifts for crossovers and of curvature-induced distortion for the main line. We have thus acquired a better understanding of lineshapes in strong laser field and we have found and indicated measurement procedures to correct for these effects or avoid them.

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