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LETTER TO THE EDITOR

Observation of Magnetic Hyperfine Structure in the Infrared Saturation Spectrum of $^{32}SF_6$

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The magnetic hyperfine structure of a vibration-rotation line was first observed for a $^{12}CH_4$ line at 3.39 μm (*1*). We report a similar observation for the P(33) A_2^1 Coriolis component of the ν_3 band of $^{32}SF_6$ close to the P(18) CO_2 line center at 945.98 cm^{-1} (*2*). This structure has been previously resolved with a free-running CO_2 laser (*3*). The spectrum presented here has been recorded by locking a CO_2 laser with a tunable frequency offset to a reference CO_2 laser slaved to a close-by PF_5 saturation peak. The lasers and the spectrometer have been described in previous papers (*4*, *5*). The spectrum exhibits seven resolved hyperfine components. This is consistent with the values allowed for the total nuclear spin of the fluorine atoms, I, in the involved vibration–rotation levels, since the theory predicts $I = 1$ and $I = 3$ for A_2 rovibronic states (*6*).

A first tentative fit is shown on the Fig. 1. The theoretical curve has been drawn by considering only the scalar spin-rotation interaction, $W_{SR}{}^S = -hc_a\mathbf{I}\cdot\mathbf{J}$. The coupling constant c_a has been fixed in the lower level to the microwave value, -5.27 kHz, given by Ozier, Yi, and Ramsey (*7*). The only adjustable parameters are the value of c_a in the upper level and the width of the Lorentzian used as line shape. The heights of the Lorentzians are deduced from the general formulae of intensities for saturation spectroscopy (*8*):

$$(2F_\lambda+1)^2(2F_\mu+1)^2\begin{Bmatrix} I & J_\lambda & F_\lambda \\ 1 & F_\mu & J_\mu \end{Bmatrix}^4 \sum_{k=0,1,2}(-1)^{q^-+q^+}(2k+1) \times\begin{pmatrix} k & 1 & 1 \\ 0 & -q^- & q^- \end{pmatrix}\begin{pmatrix} k & 1 & 1 \\ 0 & -q^+ & q^+ \end{pmatrix}\begin{Bmatrix} k & 1 & 1 \\ F_\lambda & F_\mu & F_\mu \end{Bmatrix}^2$$

where λ and μ label respectively the lower and upper hyperfine states for the low frequency recoil peaks and *vice-versa* for the high frequency recoil peaks. For this experi-

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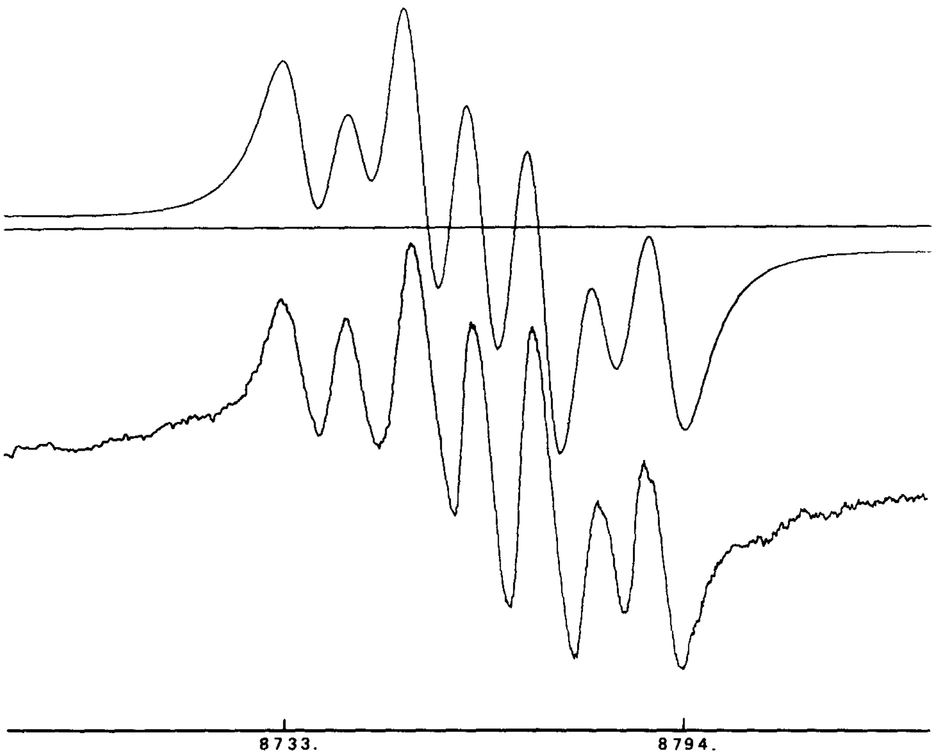

FIG. 1. (Lower curve). Derivative saturation spectrum of the P(33) A_2^1 Coriolis component of $^{32}SF_6$ at 28.35978049 THz (absolute frequency of the unresolved structure obtained through the beat note with a reference laser locked to a CO_2 saturated fluorescence peak). The reference laser is locked to a PF_5 line whose frequency is 8.763 MHz higher than the SF_6 line. The absolute frequency therefore increases from right to left. The SF_6 pressure is 60 μTorr and the peak-to-peak modulation depth is 2 kHz at 800 Hz. (Upper curve). Synthetic spectrum of the same A_2 line with a pure scalar spin-rotation interaction term. The line shape is Lorentzian with a half-width at half-maximum equal to 5.9 kHz; $\delta c_a = c_a$ (upper) $- c_a$ (lower) $= 0.125$ kHz.

ment $q^+ \equiv q^- = 1$ (retroreflected circularly polarized light) and for a $F \leftrightarrow F - 1$ hyperfine component the sum over k reduces to $(6F^2 - 1)/15F(2F - 1)(2F + 1)$. The Doppler generated level crossings are very small ($<1\%$) and have been neglected in the present case. We can see that the agreement between experimental and calculated curves is surprisingly good for such a simple theoretical approach. We find $\delta c_a = c_a$ (upper) $- c_a$ (lower) $= 0.125$ kHz; we must emphasize that this value is only effective and gathers all phenomena leading to the same $\mathbf{I} \cdot \mathbf{J}$ dependence for the energy levels. The final interpretation and the determination of physically meaningful constants will require the calculation of all the terms in the hyperfine Hamiltonian. The hyperfine structures of many other lines of the P, Q, and R branches of the ν_3 band and of "hot" bands of SF_6 can be reached with conventional or waveguide CO_2 lasers (*3*, *5*) and we have therefore the possibility to achieve a systematic study of hyperfine interactions for this molecule in the future.

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Note added in proof. Very similar structures have been observed for the R(28) A_2^0 and P(59) A_2^3 lines of SF_6, respectively, at 28.46469125 THz and 28.3062526 THz. The three values found for δc_a for the three lines are consistent with a spin–vibration interaction in the excited state.

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