

ROTATIONAL SPECTRA OF THE $\text{FSO}_3\cdot$ RADICAL IN THE ν_6 DEGENERATE EXCITED VIBRATIONAL STATE



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INTRODUCTION

Fluorosulfate radical, $\text{FSO}_3\cdot$, is a symmetric top molecule belonging to C_{3v} point group in its ground state. Under this symmetry, the fluorosulfate radical has three A , and three E normal vibrations. The degenerate vibrational fundamentals ν_5 and ν_6 are pushed to the unusually low energies of 426 and 162 cm^{-1} ^[1,2], respectively, probably as a consequence of a strong vibronic interaction with the lowest excited electronic 2E state. Analysis of the lowest-lying fundamental vibrational level, degenerate ν_6 , is the aim of this study. It can be analyzed as an isolated vibrational level since the nearest perturber, the $2\nu_6$, lies about 200 cm^{-1} higher (Figure 1).

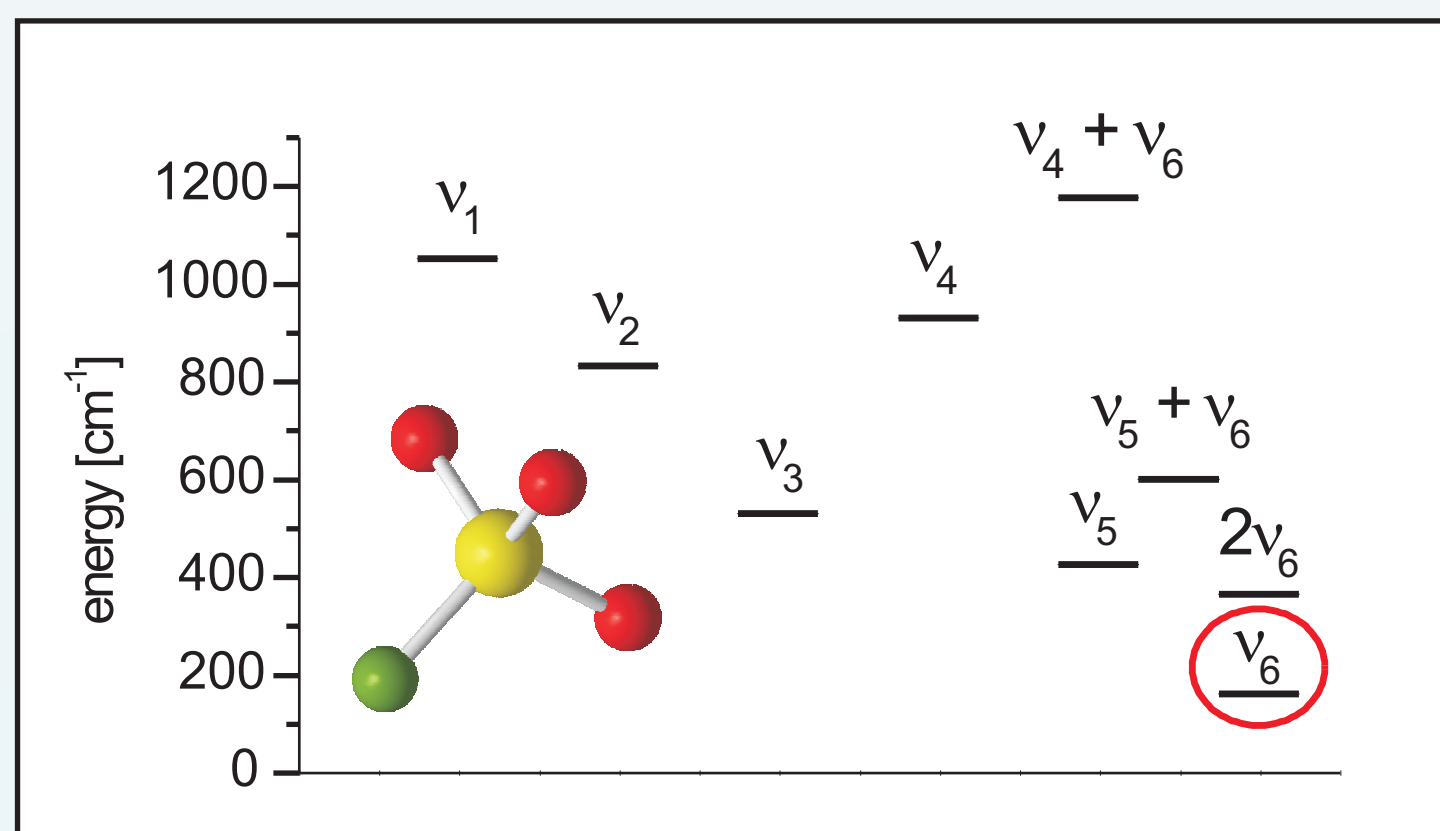


Figure 1: The lowest vibrational energy levels in the $\text{FSO}_3\cdot$ radical.^[1]

NONDEGENERATE VS. DEGENERATE EXCITED VIBRATIONAL STATE

The nondegenerate states fluorosulfate radical spectra exhibit the spin statistic weights that are a consequence of the Pauli principle which is applied to three identical bosons (Figure 1). In the vibrational ground state, which is an example of the nondegenerate state, the Pauli principle excludes all rotational states with the quantum numbers $K = 1, 2, 4, 5, 7, \dots$ and the measured spectrum contains the lines with $K = 0, 3, 6, 9, \dots$ only. The same spin statistic is held for all the totally symmetric (A) excited vibrational states. The entirely different situation is for the degenerate vibrational states. Using the same arguments for the E excited vibrational states, the Pauli principle excludes the rotational states with the quantum numbers $K = 0, 3, 6, 9$ etc., and only the lines with $K = 1, 2, 4, 5, 7$ etc. can be observed.

EXPERIMENT

Recently, ground state rotational transitions of the $\text{FSO}_3\cdot$ radical were measured and assigned in the region 93 - 280 GHz for the first time^[3]. From observed rotational transitions the set of molecular parameters was derived. The determined rotational constant B was then used for the identification procedure of transitions in the excited state. Measurements have been done by the Prague millimeterwave spectrometer (Figure 2) by the same way and with the same experimental conditions as in the case of the ground state (pressure about 6 μbar , pyrolysis of bis(fluorosulfonyl) peroxide at temperature about 440 K). In our new measurements, a special radical cell, which allows a 3 kHz Zeeman modulation, was used. By this manner, all the nonradical lines were suppressed (see Figure 3). The search of the excited vibrational transitions was carried out with help of overview scans. Then the groups of radical lines repeating along about $2B$ were searched in these overview scans. An example of measured overview spectra for $N' = 23$ is shown in the Figure 4. Finally, the rotational constant B_{ν} was estimated and the Loomis-Wood type diagram was plotted from the obtained frequencies (see Figure 5).

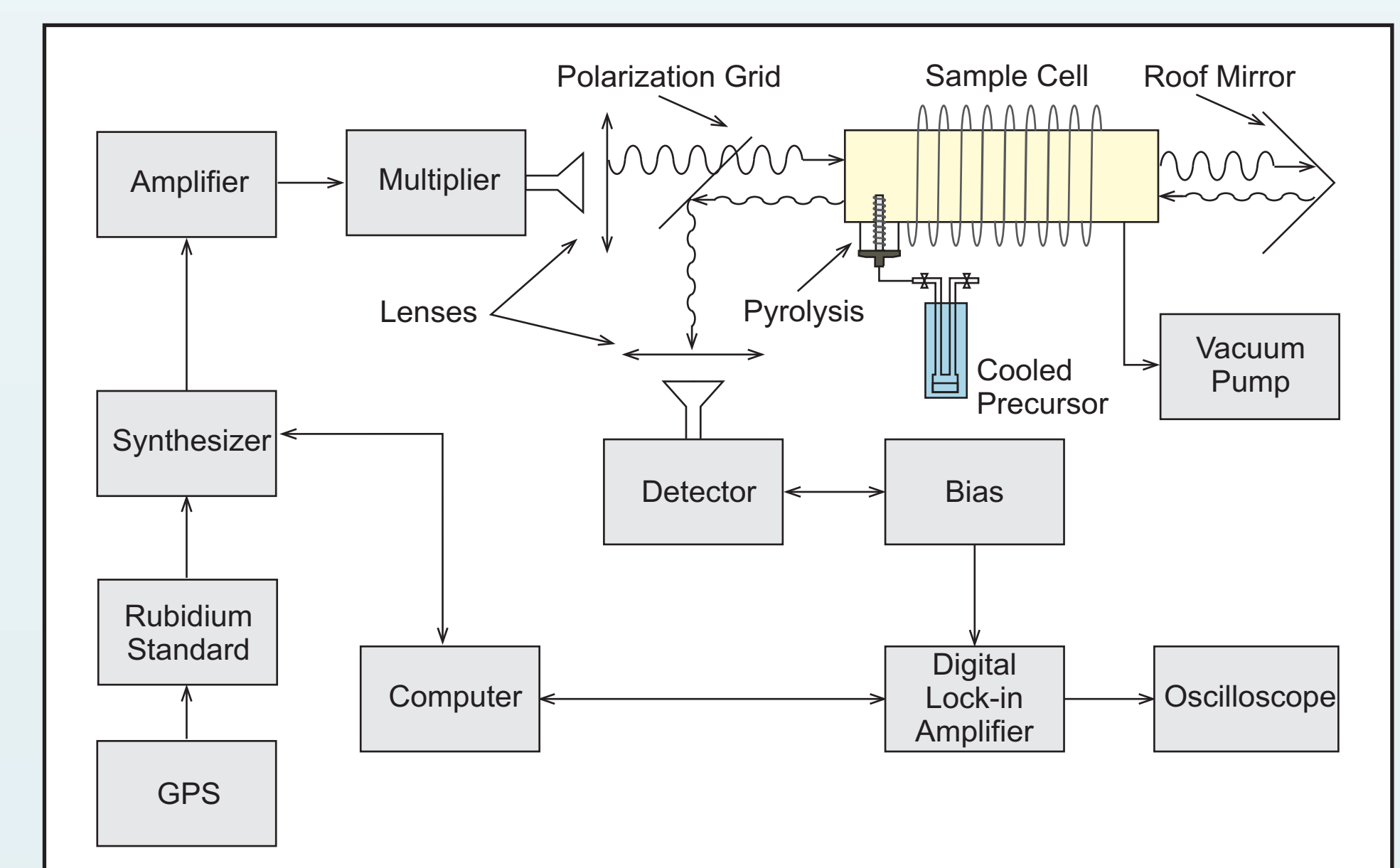


Figure 2: Prague millimeterwave spectrometer set-up.

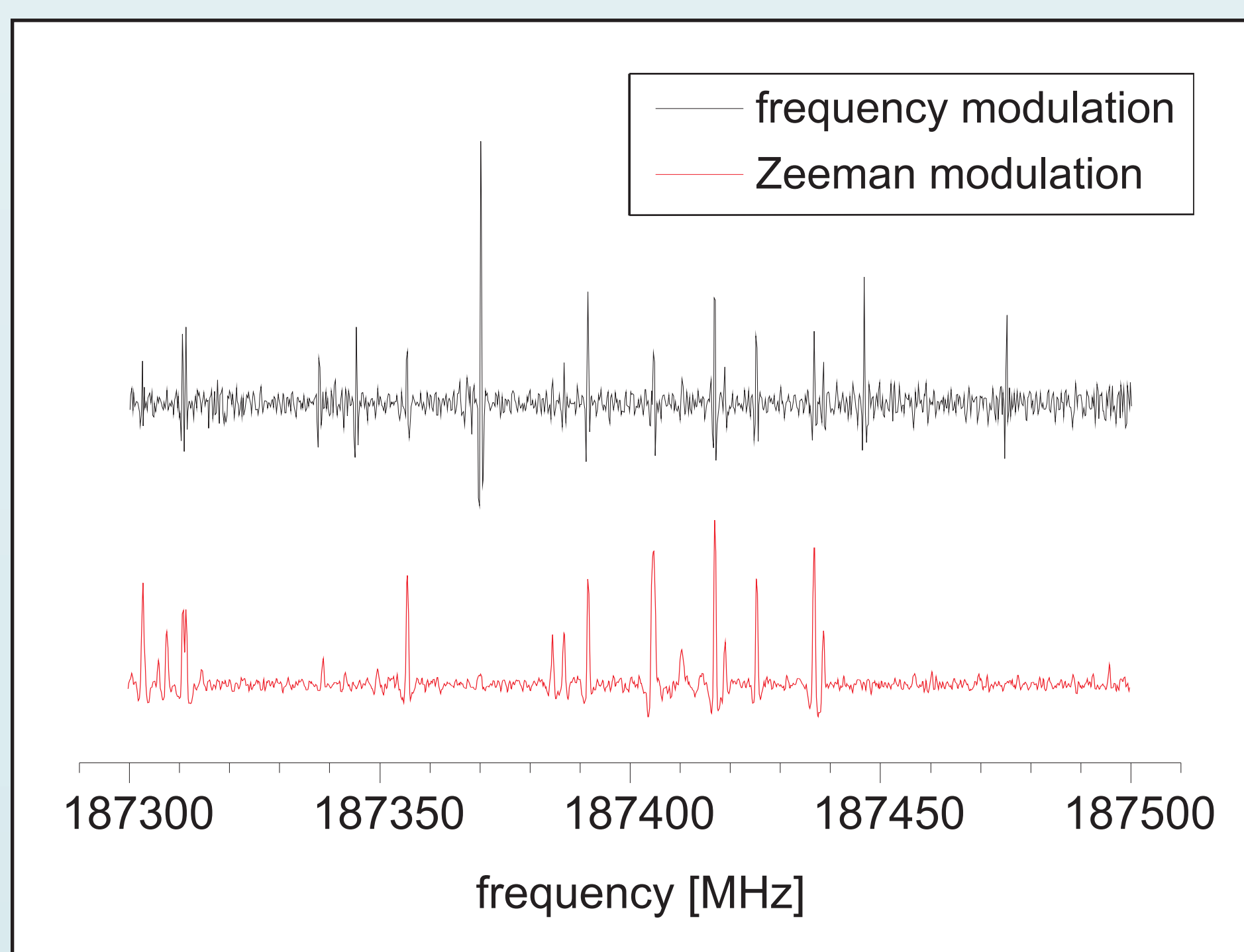


Figure 3: Illustration of the part of the spectrum measured in both the frequency (black line) and Zeeman (red line) modulation. The missing lines correspond to the nonradical species.

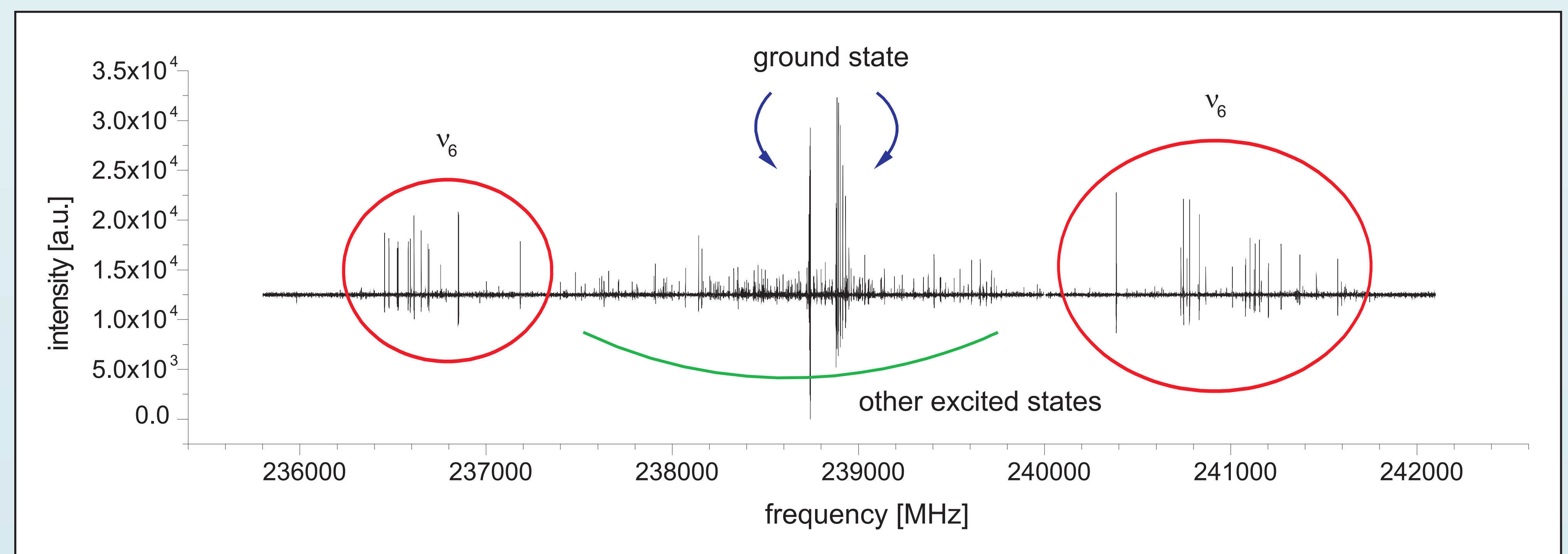


Figure 4: An overview rotational spectrum of the $\text{FSO}_3\cdot$ radical. In the middle of the picture the ground state rotational transitions can be seen. On the left and right side, two structures of the rotational transitions in the ν_6 excited state are probably located. The small lines around the ground state lines may belong to the other excited vibrational states.

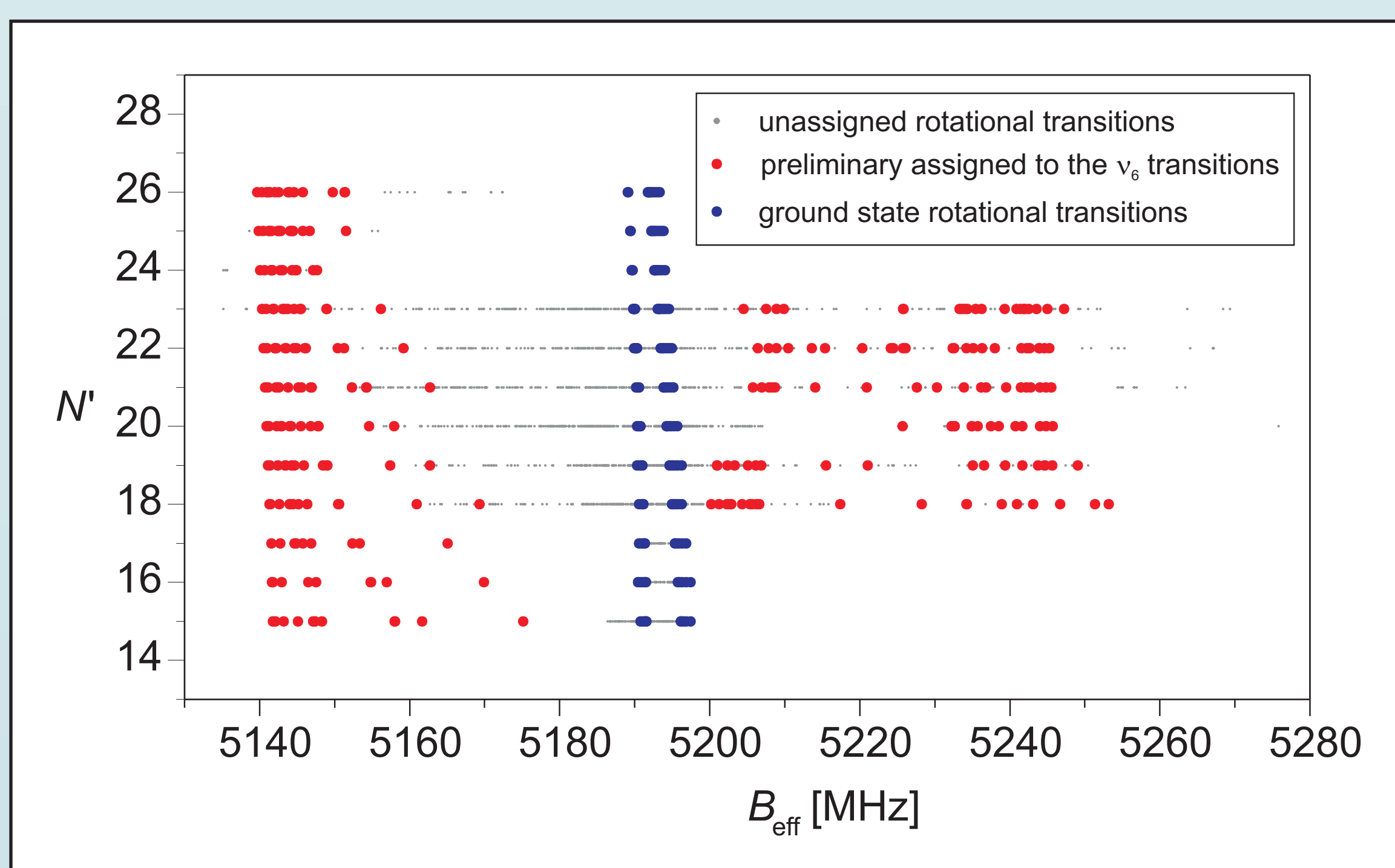


Figure 5: Loomis-Wood type diagram plotted from measured frequencies as the dependence of the upper rotational quantum number N' on $B_{\text{eff}} = \nu/2N'$

CONCLUSION

Rotational spectra of the $\text{FSO}_3\cdot$ radical in the degenerate excited vibrational state were measured in the frequency region 154 – 267 GHz ($N'' = 14 - 25$).

In the Figure 4 there is a big amount of rotational transitions. Since we used the Zeeman modulation (we see only radical species) we believe that these lines are rotational transitions in the excited vibrational states of the $\text{FSO}_3\cdot$ radical because of a significant number of low-lying vibrational levels. Besides the degenerate vibrational fundamentals ν_5 and ν_6 , the nondegenerate ν_3 fundamental band was observed at 531 cm^{-1} . Therefore, these lines may belong to the rotational transitions in the degenerate excited vibrational states $\nu_6^{l=\pm 1}, 2\nu_6^{\pm 2}, \nu_5^{\pm 1}, 3\nu_6^{\pm 1}, \nu_5^{\pm 1} + \nu_6^{\pm 1}, \nu_3^0 + \nu_6^{\pm 1}$ etc. at the energies of approximately 162, 366, 426, 590, 601, 690 cm^{-1} , respectively, as well as to those in the nondegenerate vibrational states $2\nu_6^0, \nu_3^0, 3\nu_6^{\pm 3}, \nu_5^{\pm 1} + \nu_6^{\mp 1}$ etc. located at about 366, 531, 590 and 601 cm^{-1} above the ground state, respectively.^[1]

The continuation of this study will be based on the measurement of lower frequencies to observe $kl = 1$ and $kl = -2$ l -type doublets or only crossing of lines with different K quantum numbers and the assignment of quantum numbers.

ACKNOWLEDGEMENTS

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