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## INTRODUCTION

The fluorosulfate radical  $\text{FSO}_3\cdot$  can be, in principle, considered as a trace atmospheric pollutant. It can act as a strong oxidizer and fluorinating agent.

The radical  $\text{FSO}_3\cdot$  is an open-shell system with one unpaired electron. The non-zero electronic angular momentum causes a fine splitting of rotational levels (electron spin-rotational interaction). Further hyperfine splitting of the  $J$  into the  $F$  levels results, likewise, from two possible orientations of the fluorine nuclear spin angular momentum ( $m_F = 1/2$  or  $-1/2$ ), and the mutual magnetic interaction of the electron and nuclear spins (dipolar and Fermi contact terms). An additional contribution to the fluorine hyperfine splittings is due to the nuclear spin-rotational interaction. This fluorine splitting is, however, very small and in rotational spectra of this radical nearly unresolved.

Recently, the  $\text{F}^{32}\text{S}^{16}\text{O}_3\cdot$  ground state rotational transitions were measured, assigned, and analysed in our laboratory [1] for the first time and we decided to continue with analysis of this interesting radical molecule. This study is focused on the ground state rotational spectra of the fluorosulfate radical isotopologues with  $^{32}\text{S}$ ,  $^{34}\text{S}$ ,  $^{16}\text{O}$ , and  $^{18}\text{O}$ . We present the actual status of our study - the first measurements of the  $\text{F}^{34}\text{SO}_3\cdot$  radical spectra.

## ZEEMAN MODULATION

To simplify our spectrum measurements and the spectrum analysis we developed a new spectrometer module - a special sample cell which makes the Zeeman effect possible and consequently the Zeeman modulation too (Figure 2). The oscillating magnetic field was generated by a set of the Helmholtz coils, whereas the corresponding modulation electronics was built in our

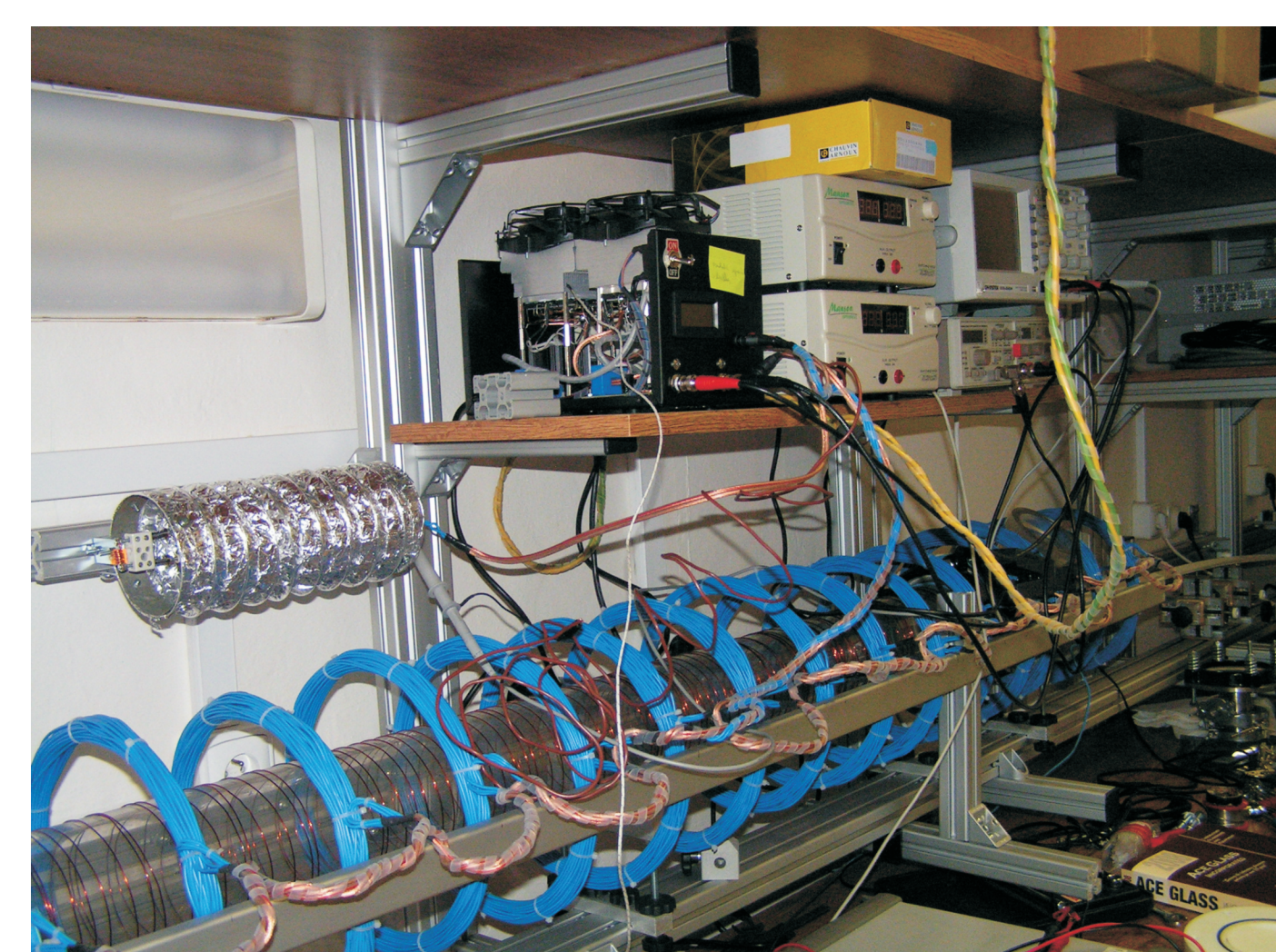


Figure 2: Zeeman modulation. Sample cell is encircled by Helmholtz coils (blue wire), which are fed by voltage from the power supply and connected to the modulator and they produce the magnetic field inside the sample cell.

laboratory. The magnetic field splits rotational energy levels belonging to the free radicals due to the molecular Zeeman effect while the energy levels of the close shell molecules are unaffected. The radicals carrying a nonzero magnetic dipole moment lose space degeneracy and the rotational levels are slightly split into  $2N+1$  sublevels ( $N$  is the rotational quantum number). This splitting reduces the line intensity and this fact can be used for the spectrum modulation. With the own built modulator we are able to modulate this magnetic field with the frequency up to 3kHz.

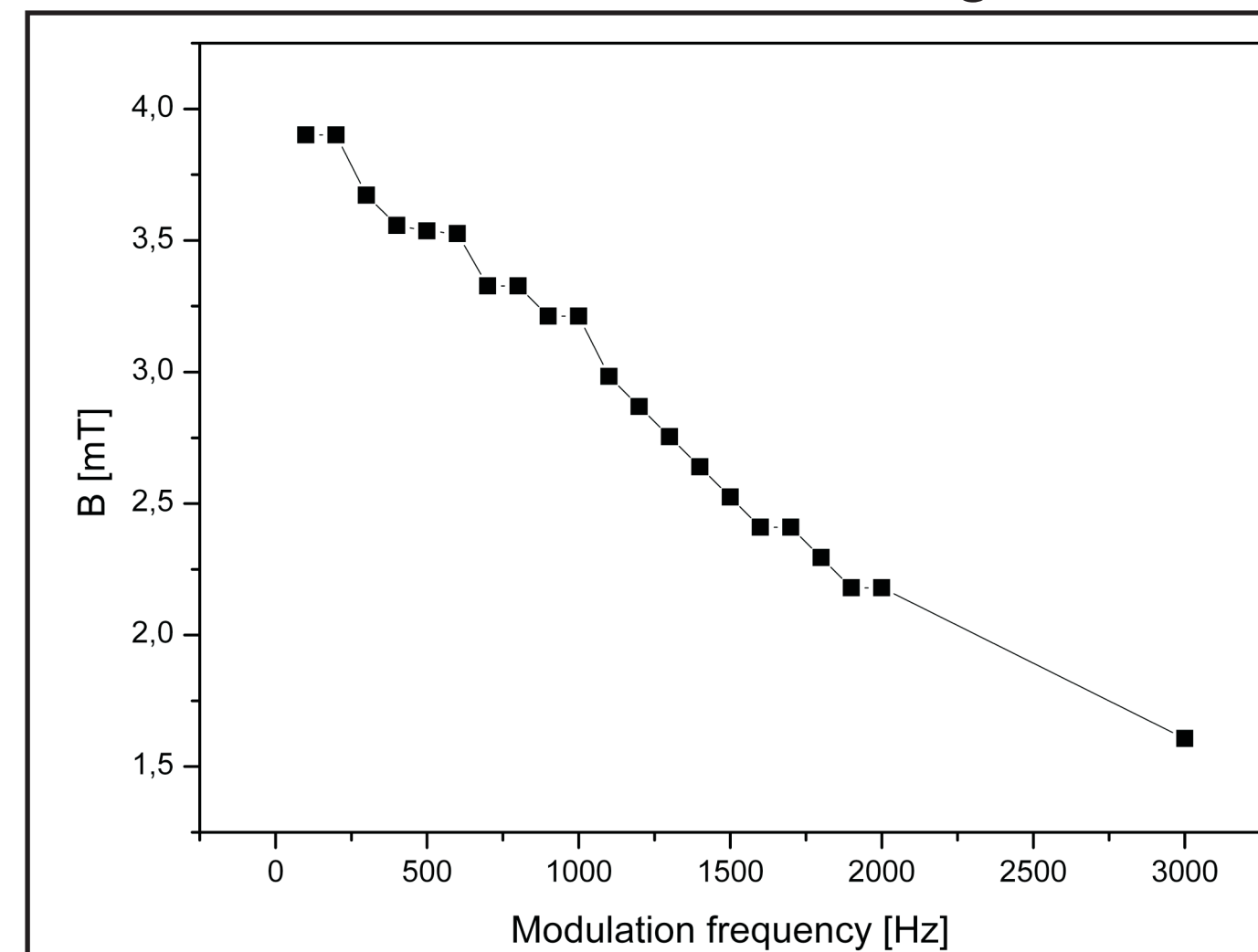


Figure 3: The parameters of the Zeeman modulation.

The generated magnetic field depends on the modulation frequency and we are able to generate magnetic field up to 4mT (modulation frequency 250Hz) at present (Figure 3). The suitable parameters for our experiments was modulation frequency 2 kHz and the magnetic field 2.7mT. We are continuously developing this modulation technique.

## EXPERIMENT

Rotational spectra of the  $\text{FSO}_3\cdot$  radical were measured by the Prague millimeterwave spectrometer (Figure 1) at a pressure about 10  $\mu\text{bar}$ . The fluorosulfate radical was produced by a low pressure pyrolysis of corresponding bis(fluorosulfonyl) peroxide at temperature about 440 K. All the spectra were measured using the frequency modulation technique in the second harmonic and the Zeeman modulation technique (Figure 4, see section Zeeman modulation below) to improve a sensitivity and to simplify measurements and analysis. The experimental lines were numerically treated to minimize effects of a spectral background and overlapping lines to enhance the frequency accuracy and spectral resolution. The accuracy was about 10kHz in the cases of well developed lines. Because of none previous study and predictions of this isotopologue  $\text{F}^{34}\text{SO}_3\cdot$  we took advantage of our previous work [1]. The first order estimations of molecular parameters were obtained by a quantum chemistry calculations [2]. On the basis of this simple predictions, the frequency range over  $2B$  (15 - 20 GHz) was continuously recorded. We also analyzed the spectra measured during our previous work [1]. In this interval, the groups of transitions (unambiguously identified as the radical lines, see

Zeeman modulation below) with spectral features predicted for the corresponding  $N$  quantum number were searched. Since the natural abundance of the  $^{34}\text{S}$  isotope is 4.19 % we looked for radical lines structure of  $\text{F}^{34}\text{S}^{16}\text{O}_3\cdot$  which are about 20 times weaker than the  $\text{F}^{32}\text{S}^{16}\text{O}_3\cdot$  lines. Rotational spectra of all these isotopologues were measured for the first time.

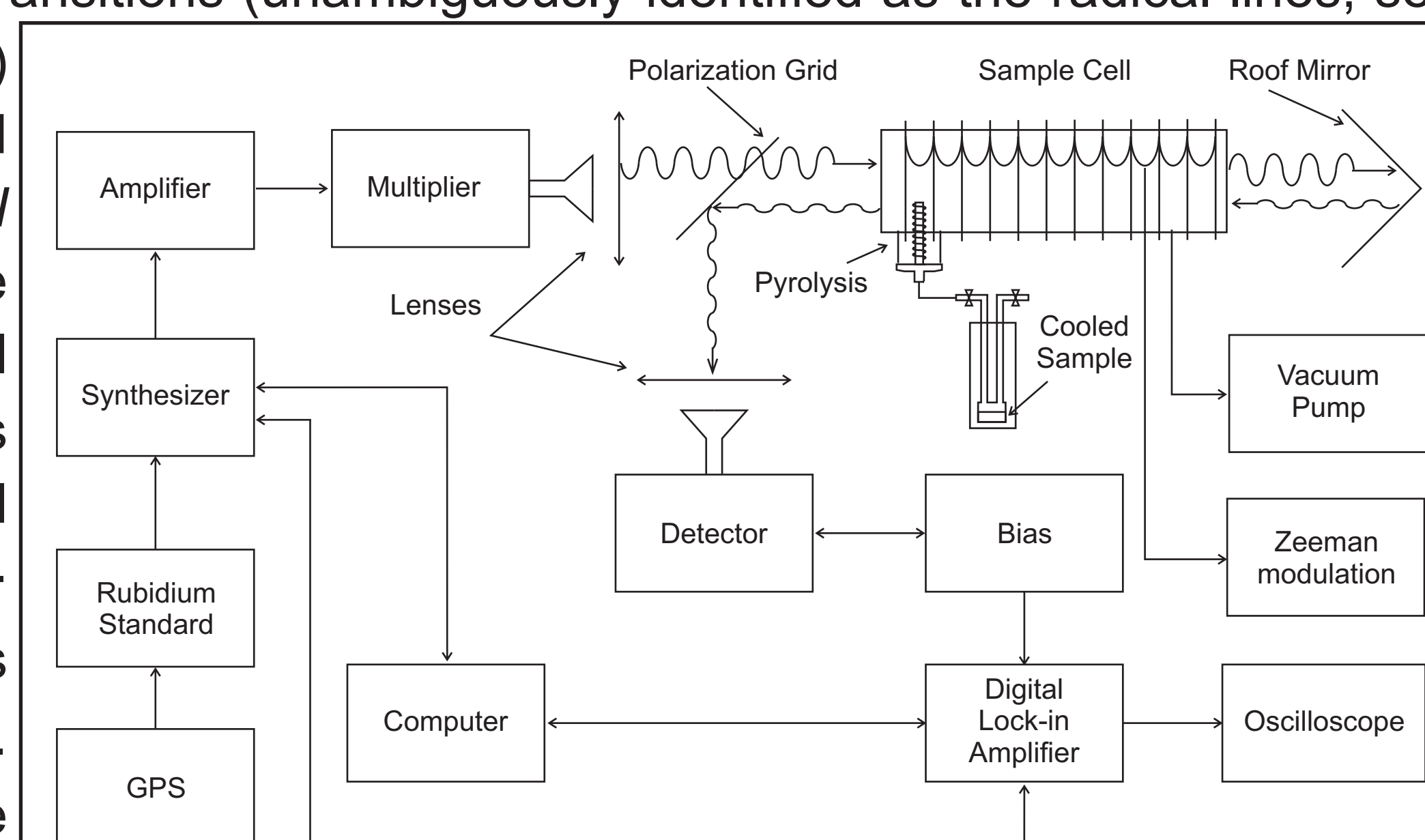


Figure 1: Prague millimeterwave spectrometer set-up with the Zeeman modulation module.

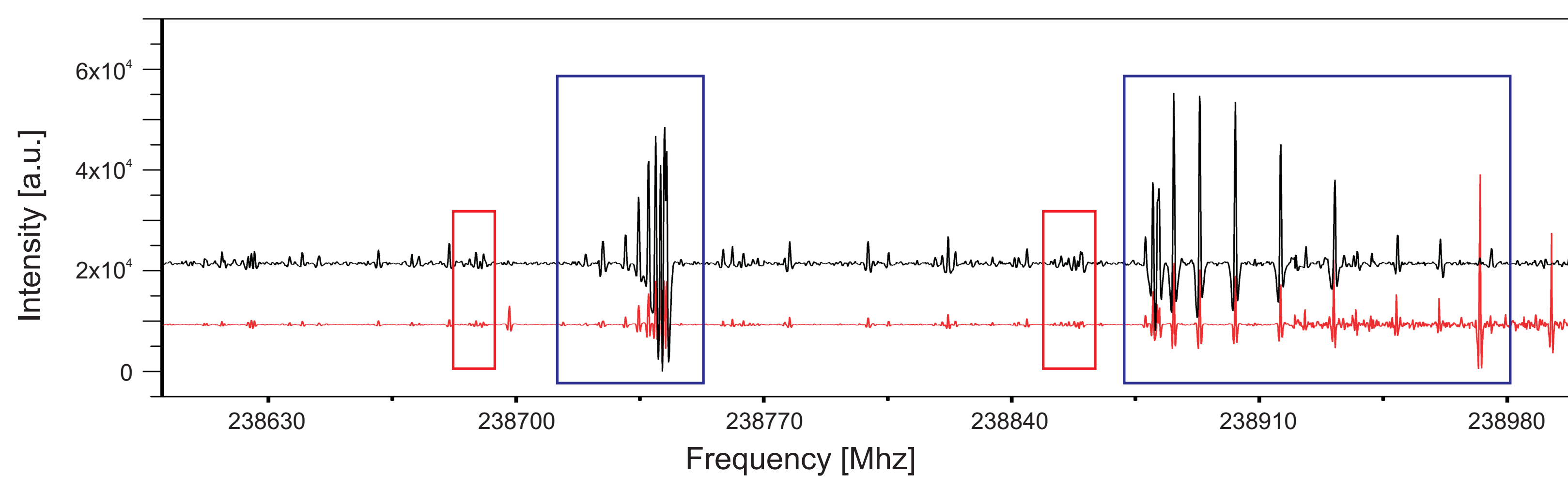


Figure 4: Measured spectra of the  $\text{F}^{34}\text{S}^{16}\text{O}_3\cdot$  radical using both, the frequency (red line) and Zeeman (black line) modulation. It is evident which lines do not belong to radical molecules (not visible in the Zeeman modulation spectra). In red box there are structures of fine splitting, which belongs to  $\text{F}^{34}\text{S}^{16}\text{O}_3\cdot$  isotopologue (Figure 5), and in blue box are fine splitting components of  $\text{F}^{32}\text{S}^{16}\text{O}_3\cdot$  radical.

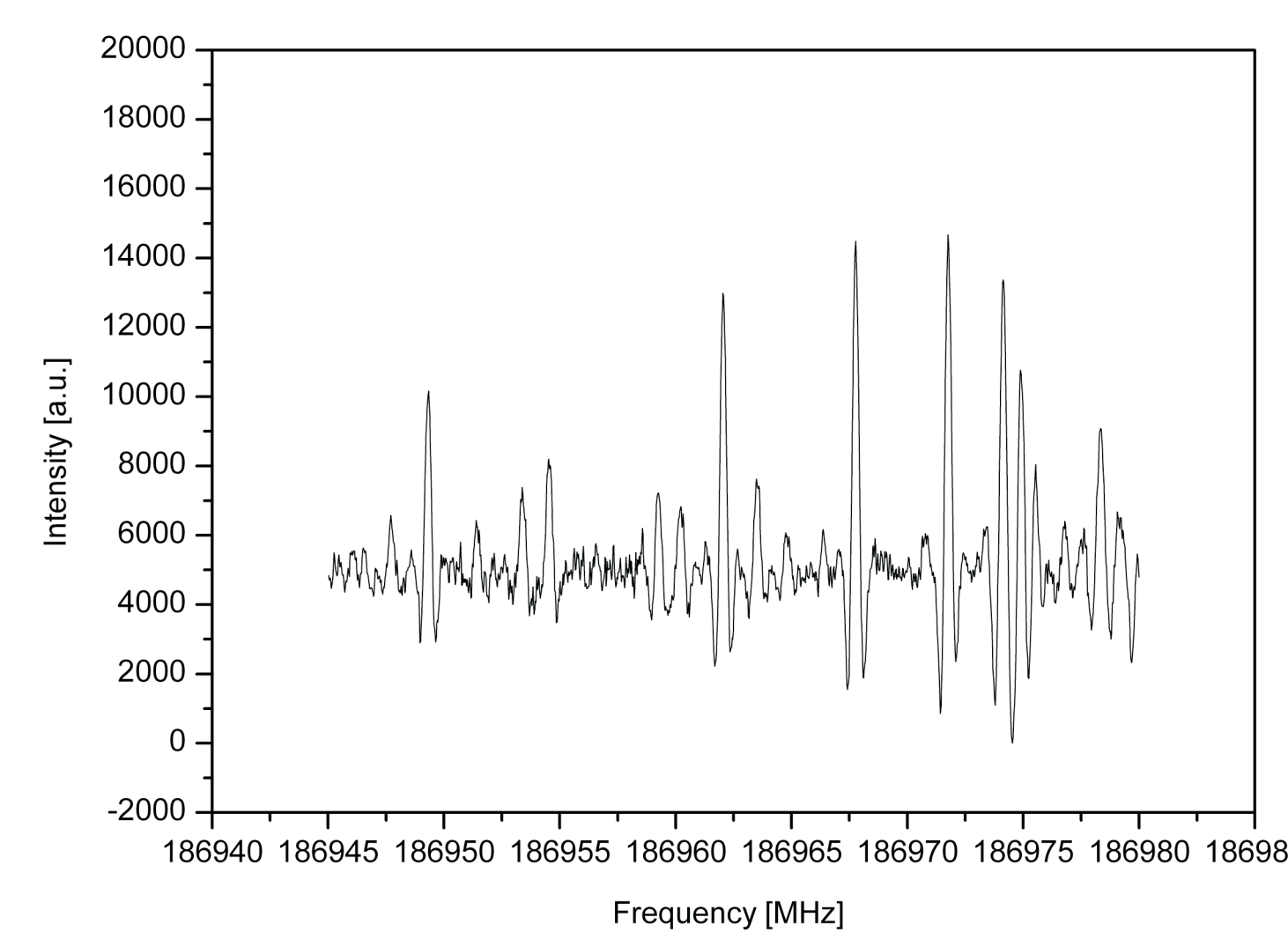


Figure 5: Part of the  $\text{F}^{32}\text{S}^{16}\text{O}_3\cdot$  radical spectrum.

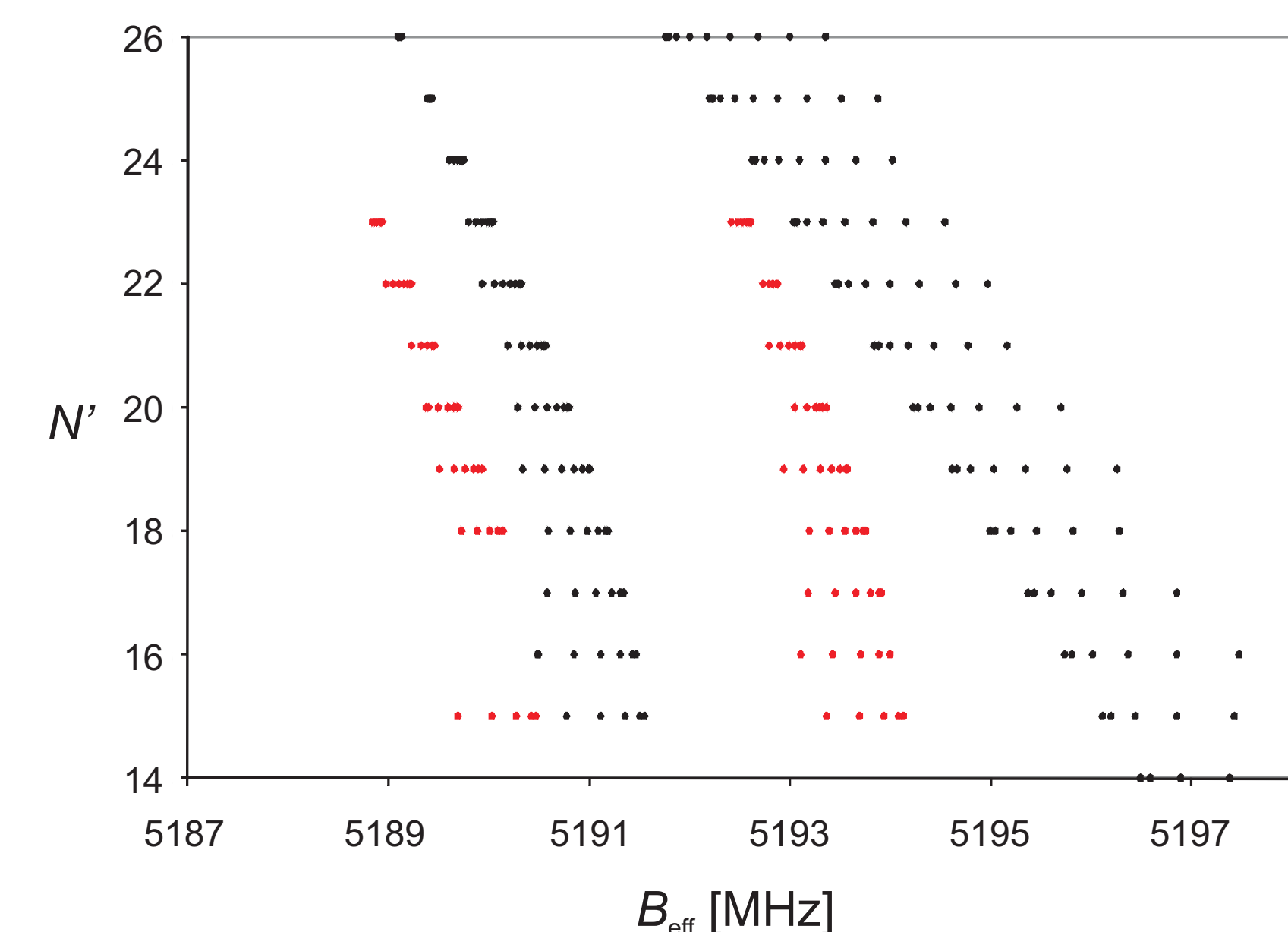


Figure 6: Loomis - Wood diagram of the  $\text{F}^{32}\text{S}^{16}\text{O}_3\cdot$  (black dots) [1] and  $\text{F}^{34}\text{S}^{16}\text{O}_3\cdot$  (red dots).

## REFERENCES

- [1] Lucie Kolesniková, Juraj Varga, Lucie Nová Stříteská, Helmut Beckers, Helge Willner, Friedhelm Aubke, and Štěpán Urban, The Journal of Chemical Physics 130, 184309 (2009).  
[2] Tereza Uhlíková, Lucie Kolesniková, Štěpán Urban, Ab initio calculations of isotopic shifts in rotational spectra of the  $\text{FSO}_3$  radical, Poster, This conference.

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