

JSM2025



Journées de Spectroscopie Moléculaire

Grenoble, 10-12 mars 2025

Line parameters measurements and modeling for the $\nu_3+\nu_6$ band of CH_3F

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Why are we interested in HFCs (CH₃F)?

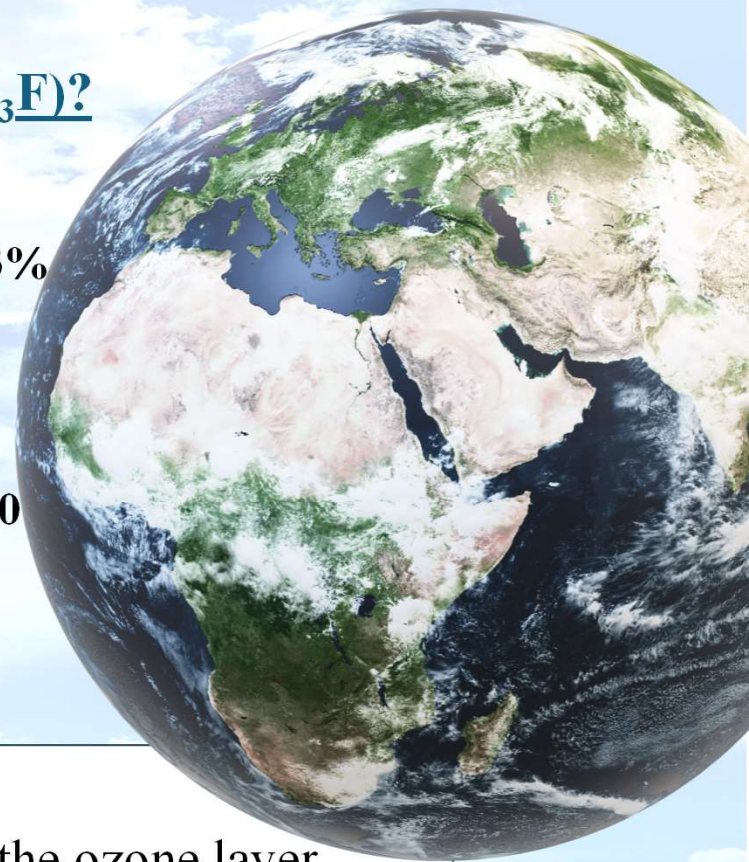
In 2021, **Hydrofluorocarbons (HFCs)** accounted for less than **3% of greenhouse gases (GHG)** emissions

[The 6th "AR6" report, IPCC 2021]

HFCs have a **Global Warming Potential (GWP)** of up to **14.600 CO₂ equivalent (CO₂ eq)** over 100 years

[The 6th "AR6" report, IPCC 2021]

HFCs are recognized as "**ozone friendly**", safe for the ozone layer



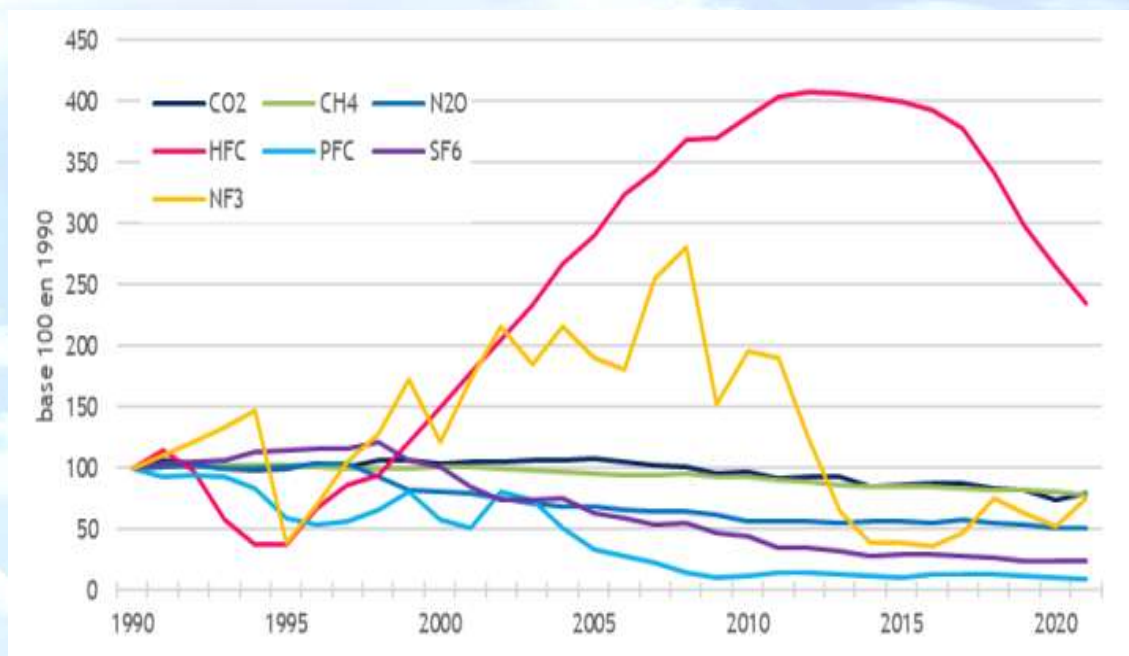
Why are we interested in HFCs (CH₃F)?



The 1987 Montreal Protocol :

HFCs have gradually replaced CFCs and HCFCs

[The 6th "AR6" report, IPCC 2021]



Relative evolution of different GHGs in France

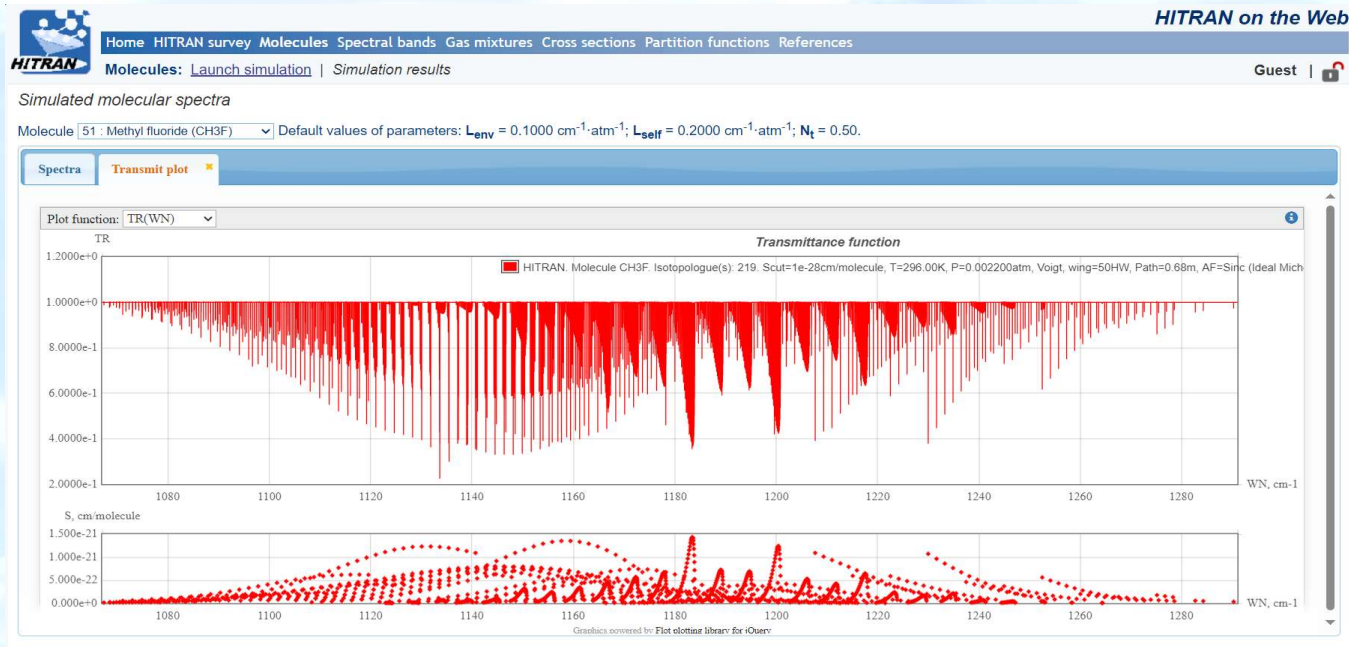
Why are we interested in HFCs (CH₃F)?



HITRAN data base contains **limited data** for the CH₃F molecule

Only between 1067 and 1291 cm⁻¹: the region of the ν_6 band

[D. Jacquemart *et al.*, JQSRT 2016]



Experimental conditions:

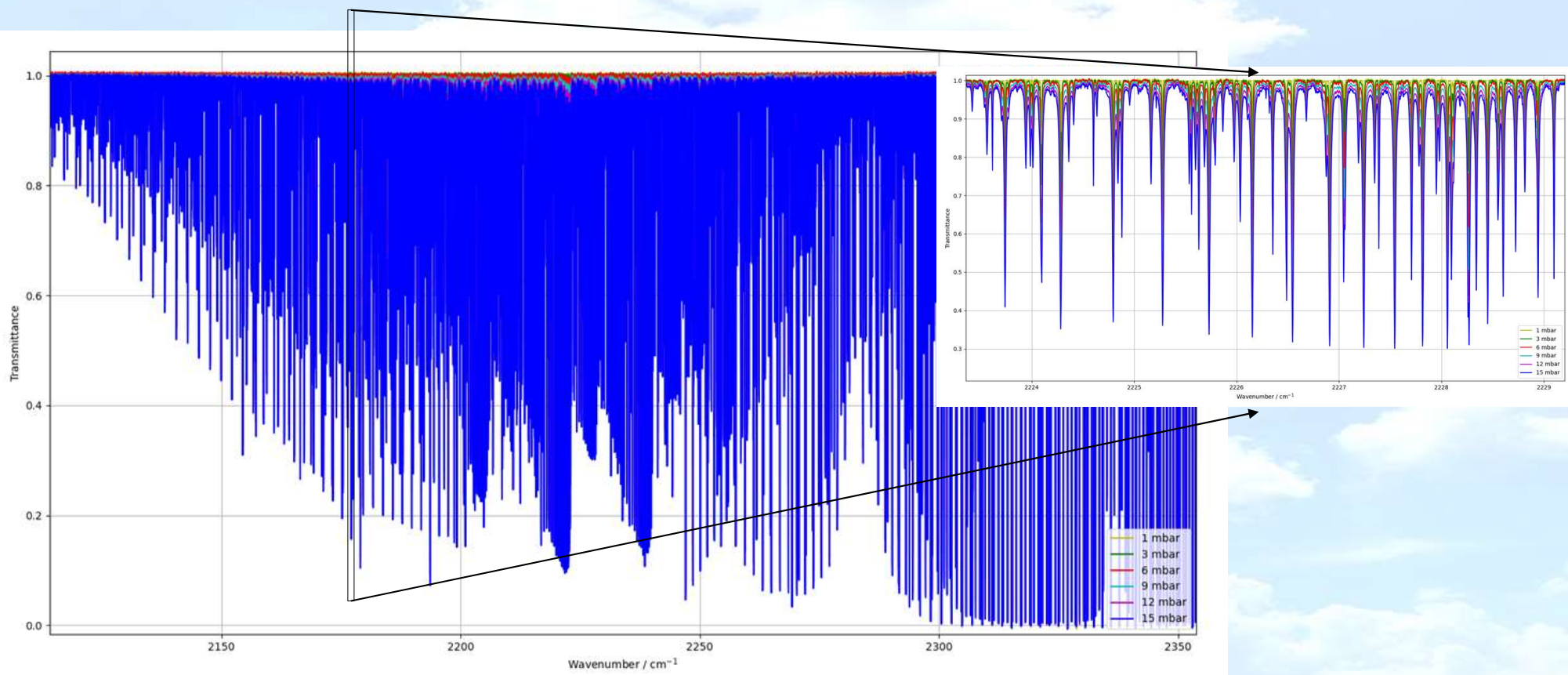
| Experimental parameters | |
|--|------------------|
| Resolution (cm^{-1}) | 0.003 |
| Optical cell length (m) | 8.29 |
| Signal-to-Noise Ratio | 557-935 |
| Useful spectra domain (cm^{-1}) | 1900-4300 |
| Temperature (K) | 294 |
| Source | Globar (SiC) |
| Detector | InSb |
| Cell | Multi-pass (2 m) |
| Separator | KBr |
| Spectra number | 6 |
| CH_3F pressure (mbar) | 1.01 - 14.97 |

Experimental conditions for recording the various CH_3F spectra



The 125HR TF spectrometer coupled with a 2 m multi-pass cell

Recorded spectra of CH₃F between 2100 and 2350 cm⁻¹ at all six pressures:

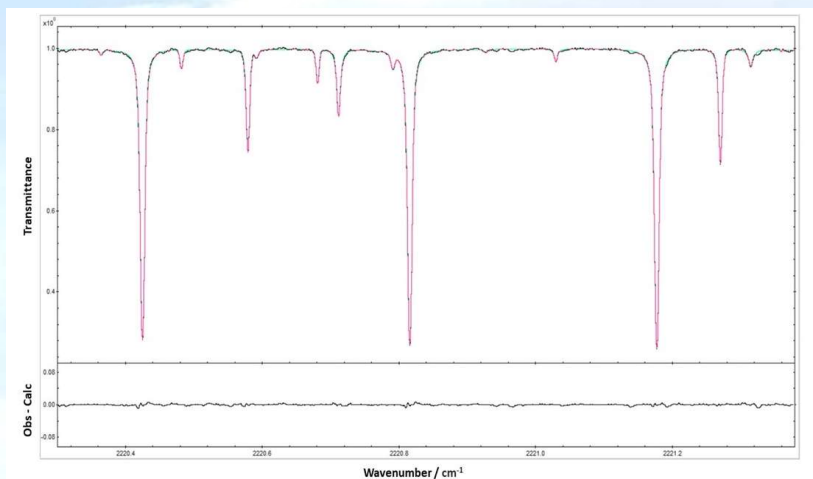


Spectroscopic parameters measurements:

By using the method of fitting the six spectra with the **Voigt profile**, we calculated the experimental spectroscopic parameters with

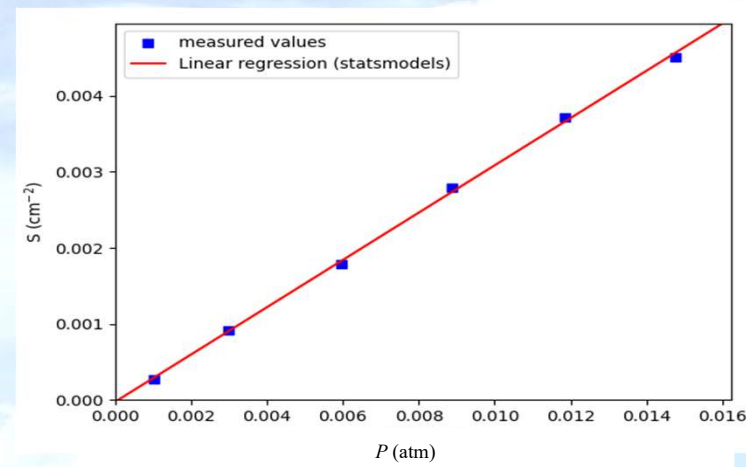
Wspectra [position (cm^{-1}), intensity (cm^{-2}) and width (cm^{-1})]

[Carleer MR., SPIE-ISOE, 2001]



Example of fit of some lines in the region between $2220.3 - 2221.3 \text{ cm}^{-1}$ recorded at 1.017 mbar.

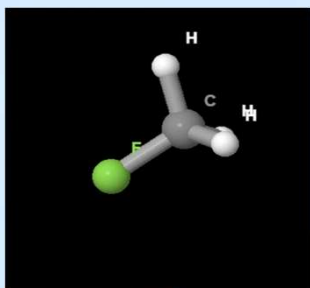
We determined the **absolute line intensities** ($\text{cm}^{-2} \cdot \text{atm}^{-1}$), by plotting the line's intensity against the six pressures and using the slopes of the resulting linear fits



Pressure dependence for the line $^P P (J=23, K=9)$.

➤ An **experimental linelist** (measured positions, intensities and widths) is prepared with **Wspectra**.

[Carleer MR., SPIE-ISOE, 2001]



CH₃F is a symmetric top molecule: C_{3v}

Polyad structure: $\tilde{\mathcal{H}} = \tilde{\mathcal{H}}_{\{P_0=GS\}} + \tilde{\mathcal{H}}_{\{P_1\}} + \dots + \tilde{\mathcal{H}}_{\{P_n\}}$

Systematic tensorial development: $H = \sum_{\text{all indexes}} t_{\{n_S\}\{m_S\}}^{\Omega(K,n\Gamma,\tilde{\Gamma})\Gamma_1\Gamma_2\Gamma} T_{\{n_S\}\{m_S\}}^{\Omega(K,n\Gamma,\tilde{\Gamma})\Gamma_1\Gamma_2\Gamma}$

[Champion, Can. J. 1977]
[Nikitin *et al.*, JMS 1997]

This work:
The parameters to be adjusted

The projection in the Hilbert subspace: $\tilde{H}^{\langle P_n \rangle} = P^{\langle P_n \rangle} \tilde{\mathcal{H}} P^{\langle P_n \rangle}$

The effective Hamiltonian (position analysis): $\tilde{H}^{\langle P_n \rangle} = \tilde{H}_{\{GS\}}^{\langle P_n \rangle} + \tilde{H}_{\{P_1\}}^{\langle P_n \rangle} + \dots + \tilde{H}_{\{P_n\}}^{\langle P_n \rangle}$

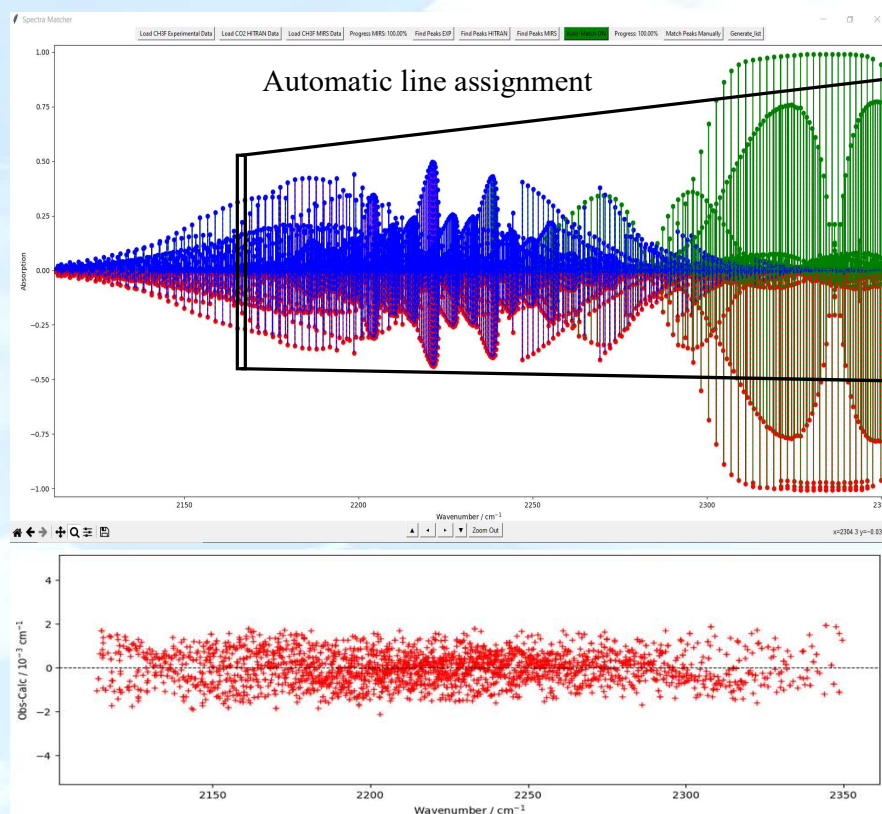
The same tensorial formula is applied to construct: **The effective dipole moment** (intensity analysis).

[Champion, Acad J. 1992]

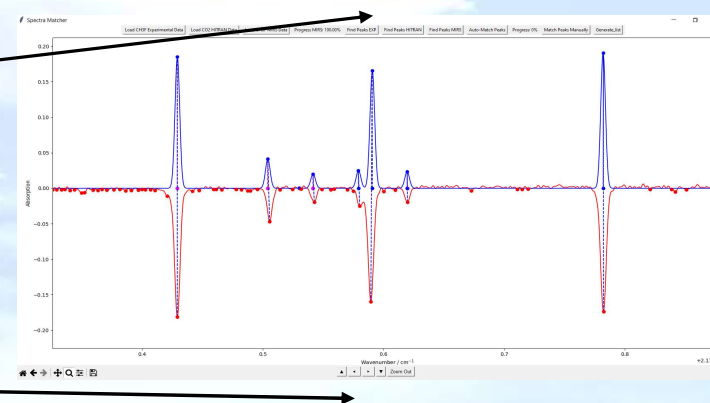
➤ **MIRS** was used to determine the **theoretical linelist** (predicted positions and intensities).

[Nikitin, Rey *et al.*, JQSRT 2012]

Line assignments (SpectraMatcher) and adjustment of the effective Hamiltonian parameters (MIRS)



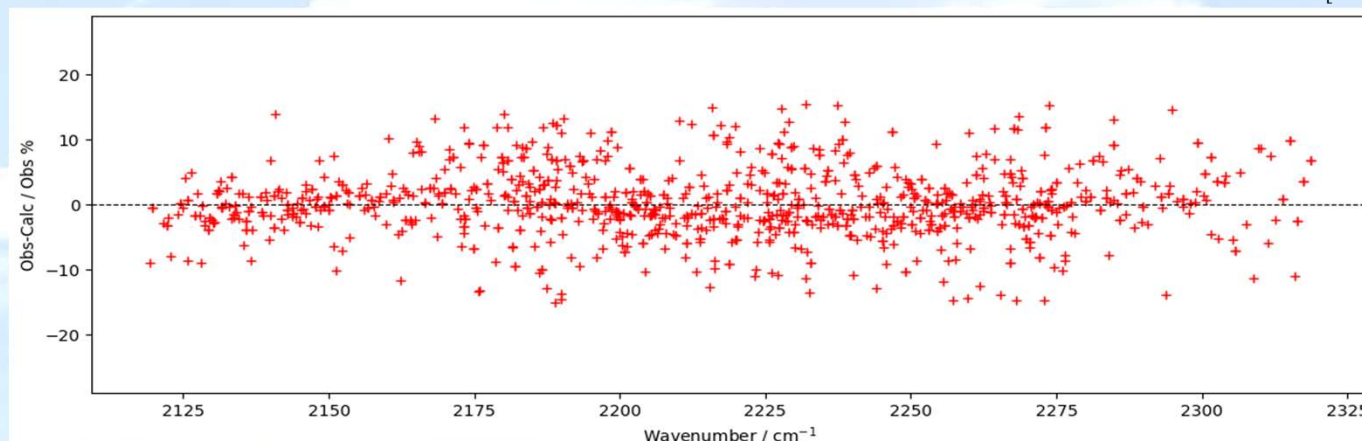
[Nikitin, Rey *et al.*, JQSRT 2012]



| | |
|-----------------------------------|-------|
| Assignment lines | 2521 |
| Adjusted parameters | 18/18 |
| RMS (10^{-3} cm^{-1}) | 0.73 |
| St Dev | 0.63 |
| J_{Max} | 45 |
| K_{Max} | 17 |

Positions fit statistics.

Adjustment of the dipole moment parameters (MIRS)

[Nikitin, Rey *et al.*, JQSRT 2012]

Residuals between adjusted and observed intensities

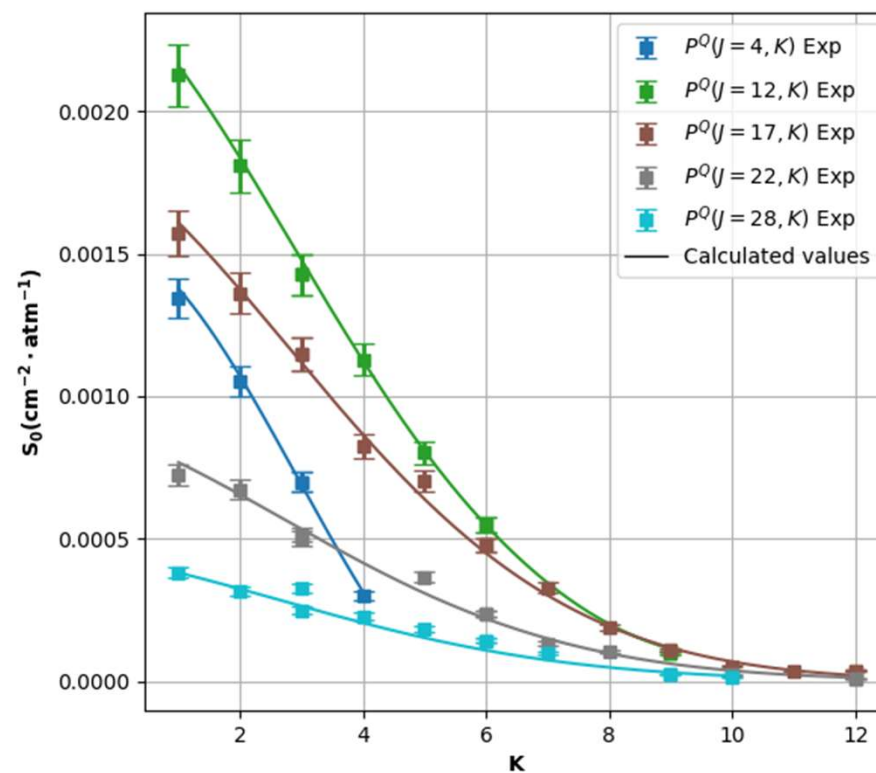
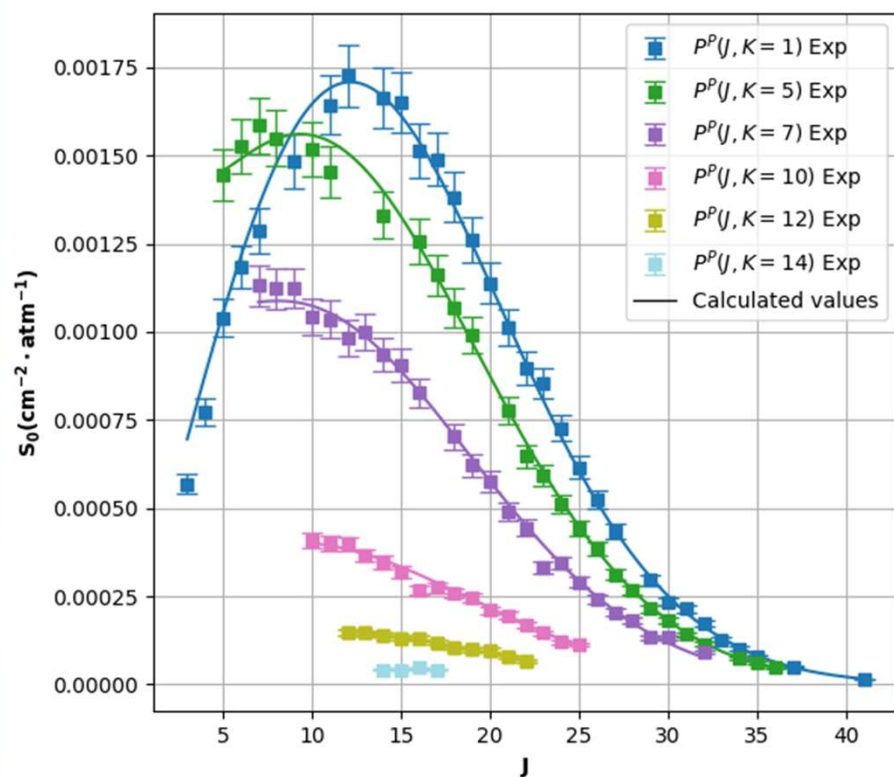
| Order | $\Omega(K, m)$ | Γv | $\Gamma v'$ | Values (D) |
|-------|----------------|------------|-------------|------------------|
| 0 | 0(0, 0A1) | 000000 E | 001001 E | -3.2339231176E-3 |
| 1 | 1(1, 1E) | 000000 A1 | 001001 A1 | 7.7650975311E-6 |
| | 1(1, 0A2) | 000000 E | 001001 E | -1.6373989157E-5 |
| | 1(1, 1E) | 000000 E | 001001 E | -7.4729237574E-5 |
| 2 | 2(2, 1E) | 000000 A1 | 001001 A1 | 5.7948003040E-8 |
| | 2(2, 2E) | 000000 A1 | 001001 A1 | 1.7863156497E-7 |
| | 2(0, 0A1) | 000000 A1 | 001001 A1 | -8.3328965882E-8 |
| | 2(2, 0A1) | 000000 A1 | 001001 A1 | 5.2419160544E-8 |
| | 2(2, 1E) | 000000 A1 | 001001 A1 | 2.0428254660E-6 |
| | 2(2, 2E) | 000000 A1 | 001001 A1 | -3.4810566631E-9 |

Effective Dipole Moment parameters of the v_3+v_6 band

| | |
|---------------------|-------|
| Assignment lines | 1081 |
| Adjusted parameters | 10/10 |
| RMS (%) | 5.02 |
| St Dev | 0.052 |
| J_{Max} | 45 |
| K_{Max} | 17 |

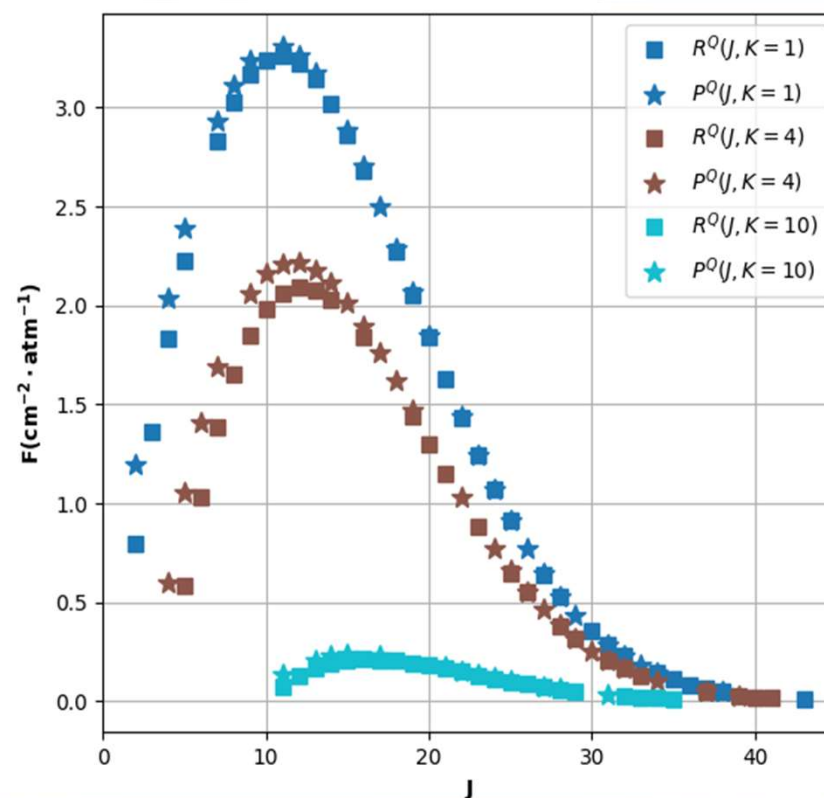
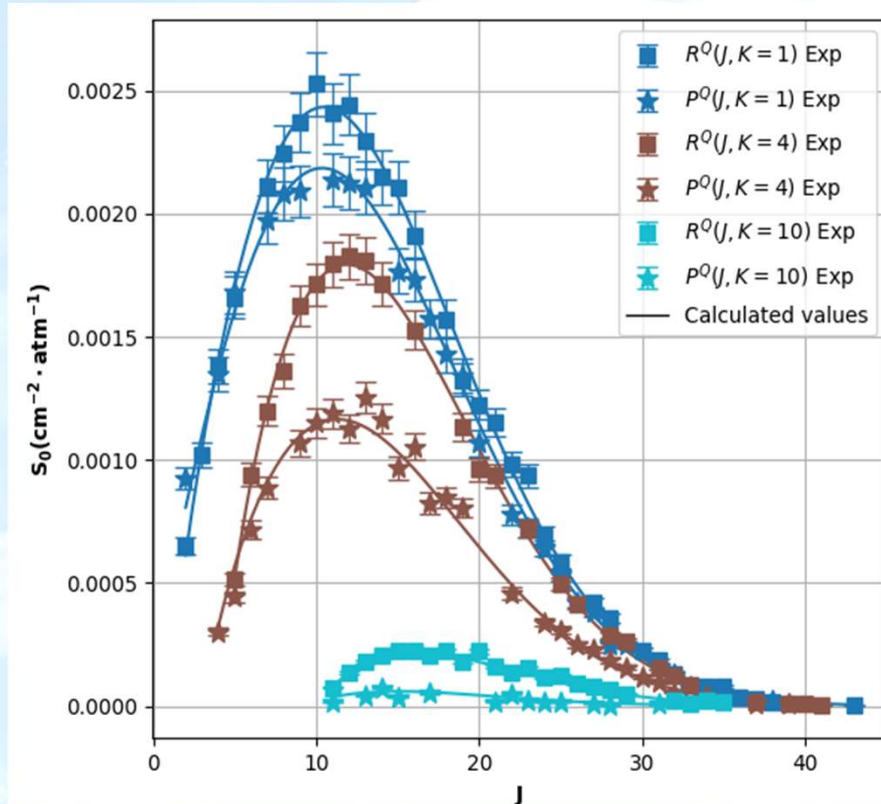
Intensity fit statistics.

Line intensity dependence on J and K



The x,y -Coriolis interaction between the $2\nu_3$ and $\nu_3+\nu_6$ bands

[Nakagawa *et al.*, Ch,S,J 1976]



Squared transition dipole moment, HW coefficient and vibrational dipole moment

$$\mu^2 = \frac{3hcTQ}{8\pi^3 N_0 T_0 l_a g_i} \frac{\exp\left[\frac{hc}{kT} E(J, K)\right]}{\left[1 - \exp\left(-\frac{hc}{kT} \sigma_{if}\right)\right] \sigma_{if} H_{\Delta J \Delta K}} S_0$$

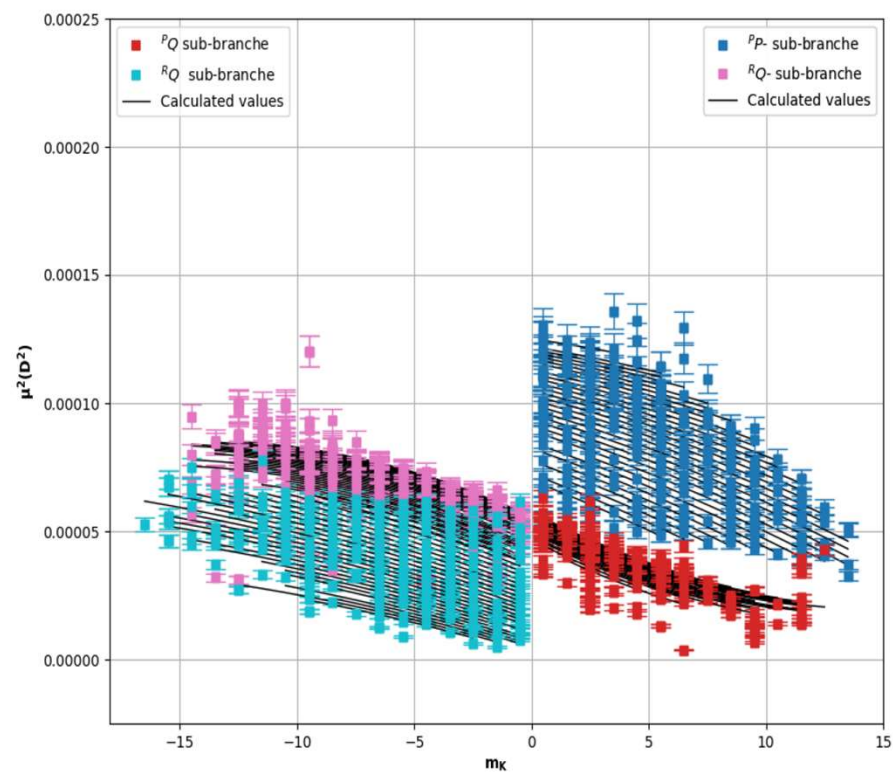
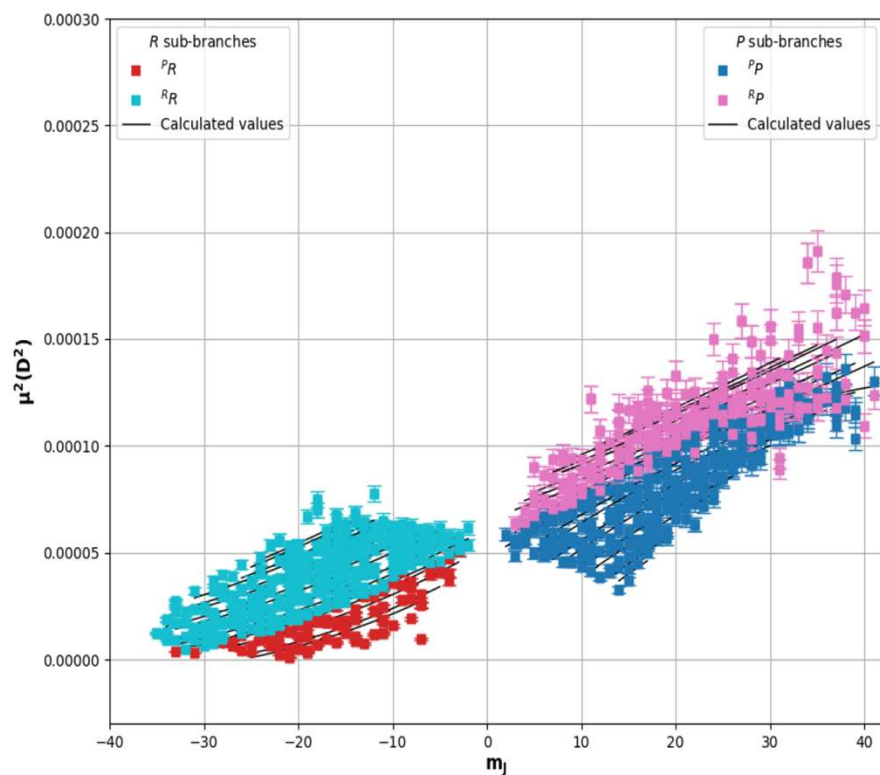
Watson Model $\mu^2 = \mu_v^2 \times F_{\Delta J, \Delta K}$

[Watson JKG, JMS 1992]

$$F_{\Delta J, \Delta K} = \left[\left(1 + A_J m_J + A_K m_K + A_{JJ(Q)} \overline{J(J+1)} - m_J^2 \right) + A_{JJ(PR)} m_J^2 + A_{KK} \overline{K^2} + A_{JK} m_J m_K \right]^2$$

| Branch | $\mu_v^2 \times 10^{-5}$ | $A_J \times 10^{-2}$ | $A_K \times 10^{-2}$ | $A_{JJ} \times 10^{-4}$ | $A_{KK} \times 10^{-3}$ | $A_{JK} \times 10^{-3}$ |
|--------|--------------------------|----------------------|----------------------|-------------------------|-------------------------|-------------------------|
| P_P | 5.4762 (125) | 4.9028 (98) | -7.0805 (110) | -3.6099 (67) | -1.4319 (89) | 1.3803 (103) |
| P_Q | 5.5765 (78) | --- | -5.7728 (92) | -1.6442 (135) | -0.5764 (142) | --- |
| P_R | 5.9191 (147) | 4.0793 (109) | -10.1143 (75) | 3.4393 (130) | 1.0292 (54) | -2.4560 (140) |
| R_P | 5.3879 (90) | 5.2547 (121) | -5.6687 (83) | -4.3868 (66) | 0.0720 (150) | 1.3187 (102) |
| R_Q | 5.6548 (134) | --- | -6.4299 (77) | -2.4145 (145) | -1.7927 (95) | --- |
| R_R | 5.4951 (112) | 4.1388 (85) | -7.4137 (123) | 3.8217 (68) | -1.2691 (148) | -0.6049 (97) |

Squared transition dipole moment

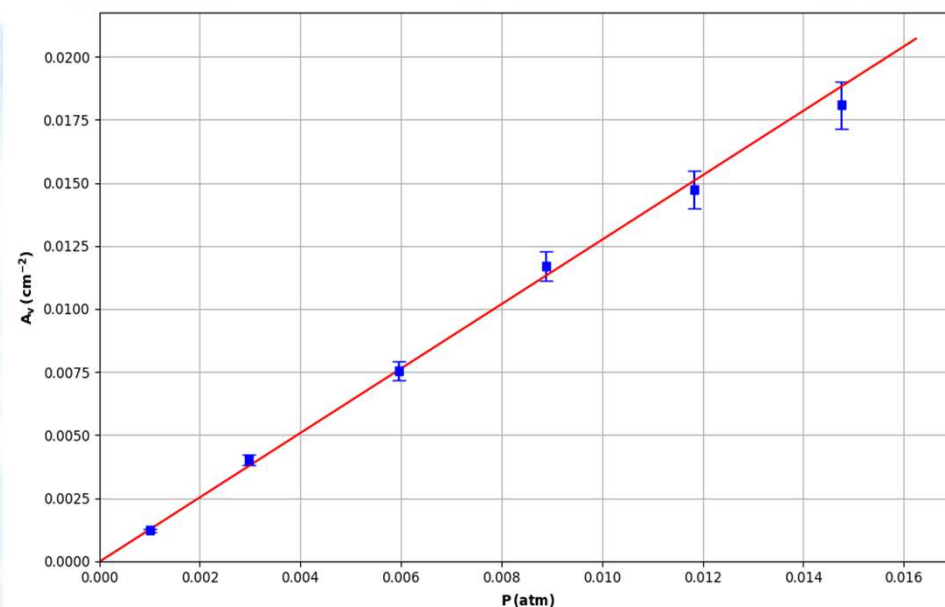
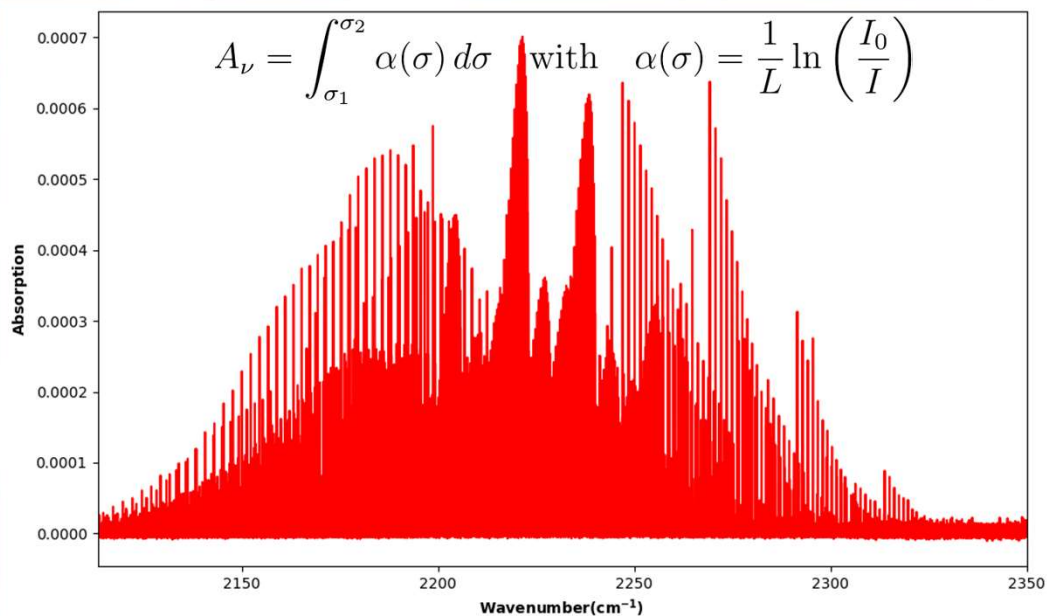


m_J - and m_K - rotational dependence of squared dipole moment coefficients.

Band intensity

$$S_\nu = \frac{8\pi^3 \sigma_\nu I_a N_L T_0}{3hcQ_\nu T} \mu_\nu^2$$

Band intensity based on vibrational dipole moment: **1.28 cm².atm⁻¹**



Band intensity using the surface method: **1.30 cm².atm⁻¹**

Self-broadening Coefficients and Empirical Modelling

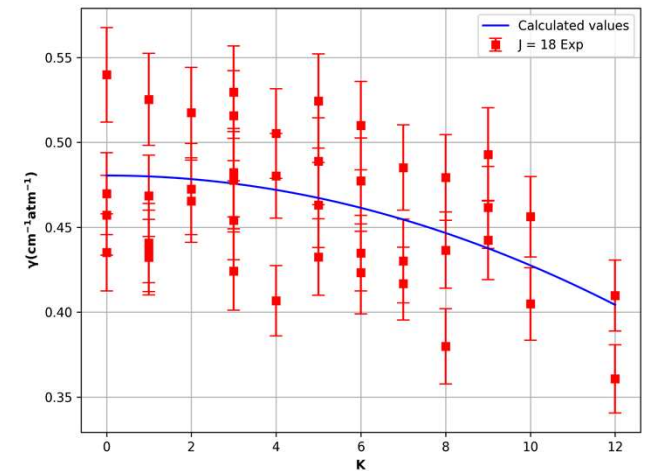
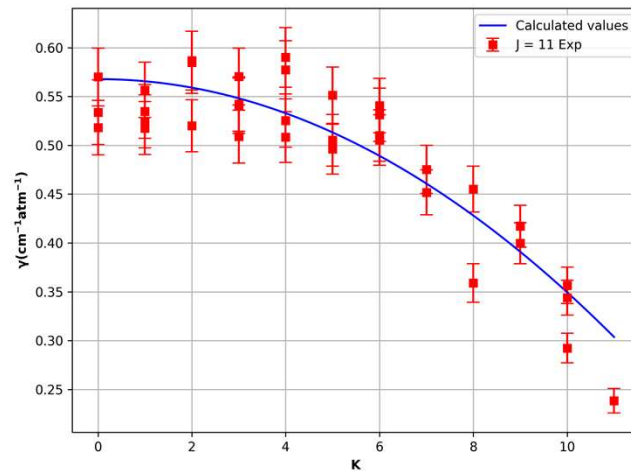
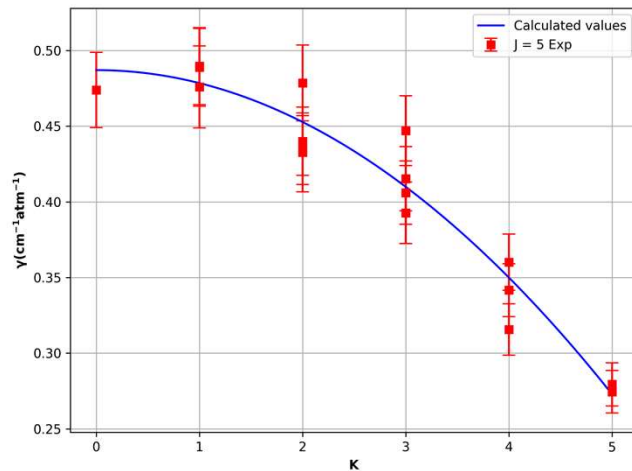
The model of Starikov [Starikov et al, Opt Spec 2005]

$$\gamma_0^{\text{Emp}} = x_1 + \frac{x_2}{\cosh [x_3(K'' - x_4)] \cosh [x_3(K' - x_4)]} + \frac{x_5}{\cosh [3x_3(K'' - x_4)] \cosh [3x_3(K' - x_4)]}$$

$$x_k = x_{k0} + x_{k1}(J'' + J'), \quad \text{with } k = 1 \rightarrow 5$$

 x_{10} x_{11} x_{20} x_{21} x_{30} x_{31} x_{40} x_{41} x_{50} x_{51}

0.6711 ± 0.0075 -0.0071 ± 0.0002 -0.5314 ± 0.0414 0.0235 ± 0.0022 -1.3469 ± 0.0903 0.097 ± 0.006 2.9367 ± 0.1066 0.0021 ± 0.0006 0.085 ± 0.0072 0.001 ± 0.0004



K - rotational dependence of self-broadening coefficients

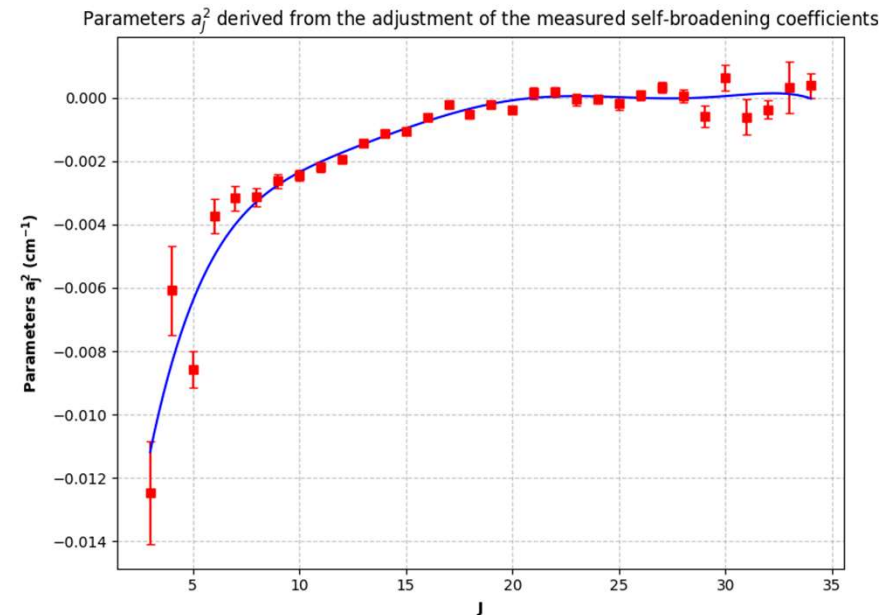
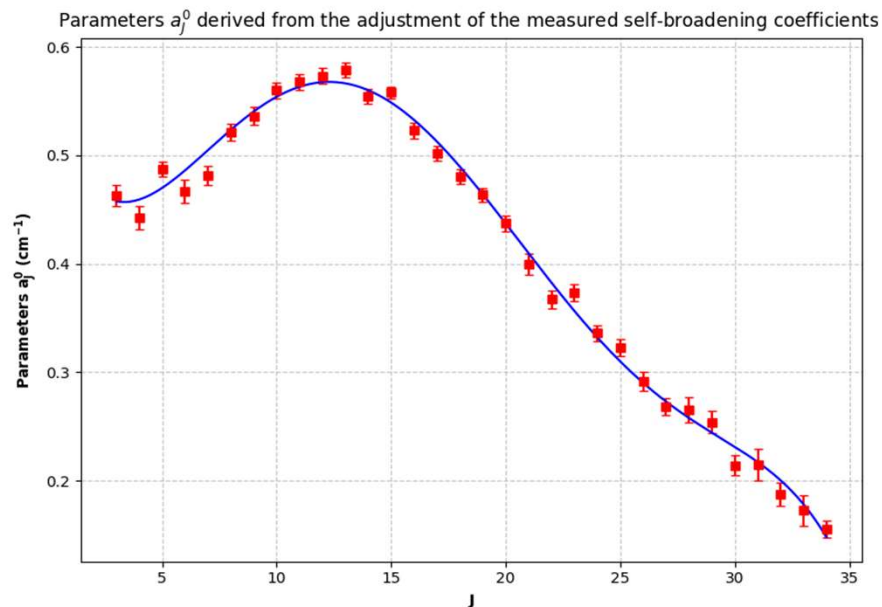
Self-broadening Coefficients and Empirical Modelling

The polynomial expansions

$$\gamma_J(K) = a_J^0 + a_J^2 K^2 \quad [\text{Predoi-Cross A et al, JMS 2006}]$$

$$a_{J,\text{self}}^0 = a_{\text{self}}^{0,0} + a_{\text{self}}^{0,1}J + a_{\text{self}}^{0,2}J^2 + a_{\text{self}}^{0,3}J^3 + a_{\text{self}}^{0,4}J^4 + a_{\text{self}}^{0,5}J^5$$

$$a_{J,\text{self}}^2 = a_{\text{self}}^{2,0} + a_{\text{self}}^{2,1}J + a_{\text{self}}^{2,2}J^2 + a_{\text{self}}^{2,3}J^3 + a_{\text{self}}^{2,4}J^4 + a_{\text{self}}^{2,5}J^5 + a_{\text{self}}^{2,6}J^6$$



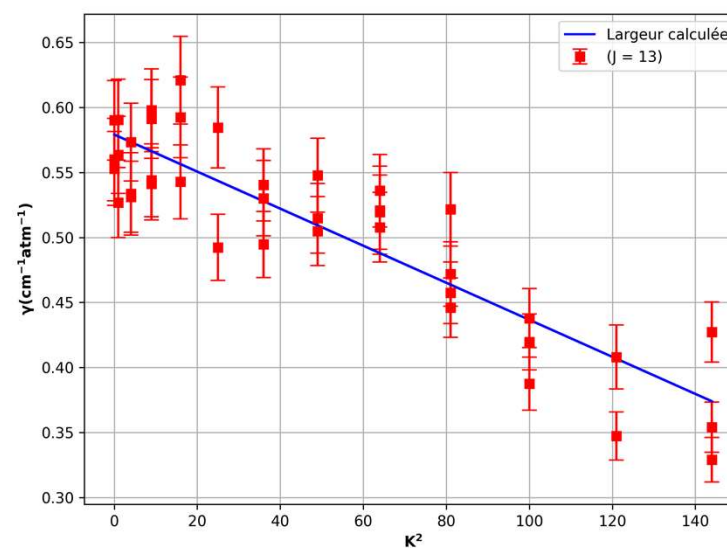
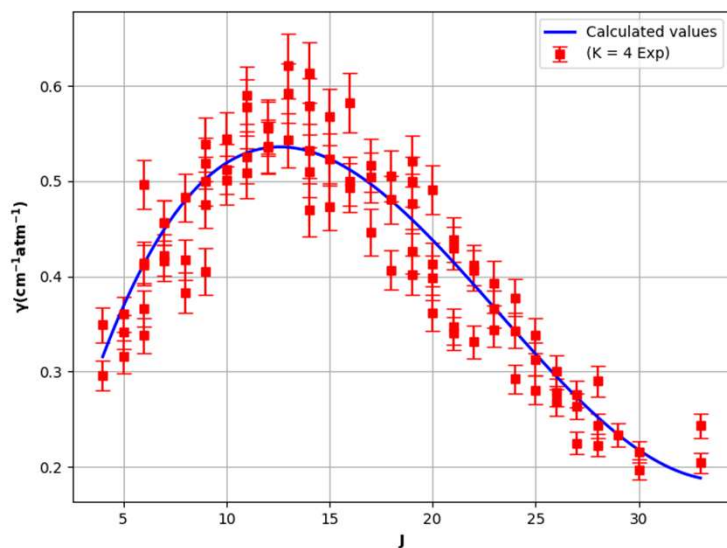
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Rotational dependence in J and K^2 of the squared dipole moment

- A complete study of the infrared spectra of the CH₃F molecule at different pressures, recorded using the Reims TF 125HR spectrometer, was undertaken.
- The theoretical model, built on irreducible tensor operators for symmetric top molecules, provided a robust framework for interpreting the observed transitions.
- The new **SpectraMatcher** facilitated an efficient and accurate comparison of experimental data with theoretical model.
- The effective Hamiltonian parameters for the $\nu_3+\nu_6$ band were fitted with an RMS of 0.7 mK (2521 lines were assigned). Additionally, the effective dipole moment parameters were optimized with an RMS of 5%.
- The intensity parameters were used to reproduce the measured line intensities (1867 lines) with an RMS of about 7 % $\nu_3+\nu_6$ band.
- The measured self-broadening coefficients (1205 lines) are reproduced with accuracy better than 11% using the Starikov model and around 9% using the polynomial expansions.

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Grenoble, 10-12 mars 2025

Thank you for your attention

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