

HALF-WIDTHS AND LINE SHIFTS FOR  
TRANSITIONS IN THE  $\nu_3$  BAND OF METHANE  
IN THE 2726-3200  $\text{CM}^{-1}$  SPECTRAL REGION FOR  
ATMOSPHERIC APPLICATIONS



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# abstract

Complex Robert-Bonamy calculations of the pressure-broadened half-width and the pressure induced line shift are made for some four thousand transitions in the  $\nu_3$  band of methane with  $N_2$ ,  $O_2$ , and air as the perturbing gases. This work focuses on A and F symmetry transitions in the spectral range 2726 to 3200  $cm^{-1}$ . More work is needed on the intermolecular potential before calculations can be made for the E-symmetry transitions. The calculations are made at 225 and 296K in order to determine the temperature dependence of the half-width. The calculations are compared with measurements. These data are to support remote sensing of the Earth and Titan atmospheres.



# Complex Robert-Bonamy Theory

The model chosen is the semiclassical complex formalism of Robert and Bonamy (CRB) for several reasons.

- 1) The formalism is complex valued, yielding halfwidths and line shifts from a single calculation.
- 2) The cumulant expansion incorporated in the RB formalism allows for the inclusion of higher order terms in the S matrix, eliminating an awkward cutoff procedure that characterized earlier theories.
- 3) The intermolecular dynamics are treated more realistically than in earlier theories, i.e. using curved rather than straight line trajectories.
- 4) Connected to item (3) is the incorporation in the CRB theory of a short range (Lennard-Jones 6-12) atom-atom component to the intermolecular potential. This component has been shown to be essential for a proper description of pressure broadening.



# Halfwidth and Line Shift in RB theory

In computational form the half-width and line shift are usually expressed in terms of the Liouville scattering matrix

$$(\gamma - i\delta)_{f \leftarrow i} = \frac{n_2}{2 \pi c} \sum_{J_2} \langle J_2 | \rho_2 | J_2 \rangle \int_0^\infty v f(v) dv \int_0^\infty 2\pi b \left[ 1 - e^{-\{S_1 + \text{Im}(S_2)\}} e^{-\text{Re}(S_2)} \right] db$$

where  $n_2$  is the number density of perturbers and the average is over all trajectories given by impact parameter  $b$  and initial relative velocity,  $v$ , and initial rotational state,  $J_2$ , of the collision partner.

# Mean-relative thermal velocity approximation

$$\gamma = \frac{n_2 \bar{v}}{2\pi c} \sum_{J_2} \langle J_2 | \rho_2 | J_2 \rangle \int_0^{\infty} 2\pi b db \left[ 1 - \cos \{ S_1 + \text{Im}(S_2) \} e^{-\text{Re}(S_2)} \right]$$

Terms from  
imaginary part

Form from  
cumulant expansion

$$\delta = \frac{n_2 \bar{v}}{2\pi c} \sum_{J_2} \langle J_2 | \rho_2 | J_2 \rangle \int_0^{\infty} 2\pi b db \left[ \sin \{ S_1 + \text{Im}(S_2) \} e^{-\text{Re}(S_2)} \right]$$

From measurements of the half-width the following conclusions are reached:

The vibrational dependence of the half-width has been found to be of order a few percent for low J lines, but can be of order 20% for high J lines.

The half-widths decrease with J” but there is no simple propensity rule to describe the behavior and the branch dependence is small; of order a few percent.



Devi *et al.* (*J. Mol. Spectrosc.* **157** (1993) 95-111.)  
have found A, E and F symmetry level transitions  
have almost the same average pressure-broadening  
coefficient.

The dependence on the perturbing molecule/atom  
show the ratios as being somewhat constant,  
indicating that predictions for other perturbers can  
be obtained once the ratio of one transition is  
known.

The shifts demonstrate a marked dependence on  
vibrational band. From the studies made the  
results indicate that most of the shifts are negative  
and transition dependent.

# Calculations

The 2004 HITRAN database contains some 251 440 methane transitions. Considering only bands of  $^{12}\text{CH}_4$  between 9 and 1.6  $\mu\text{m}$  with the sum of line intensities greater than  $10^{-20} \text{ cm}^{-1}/(\text{molecule}\cdot\text{cm}^{-2})$  yields a list of over one hundred thousand transitions.

Here, we focus on the region 2726 to 3200  $\text{cm}^{-1}$ , which still contains over twenty five thousand transitions for  $^{12}\text{CH}_4$ . The dominant band in this region is the  $\nu_3$  band centered at 3018  $\text{cm}^{-1}$ .





# Calculations

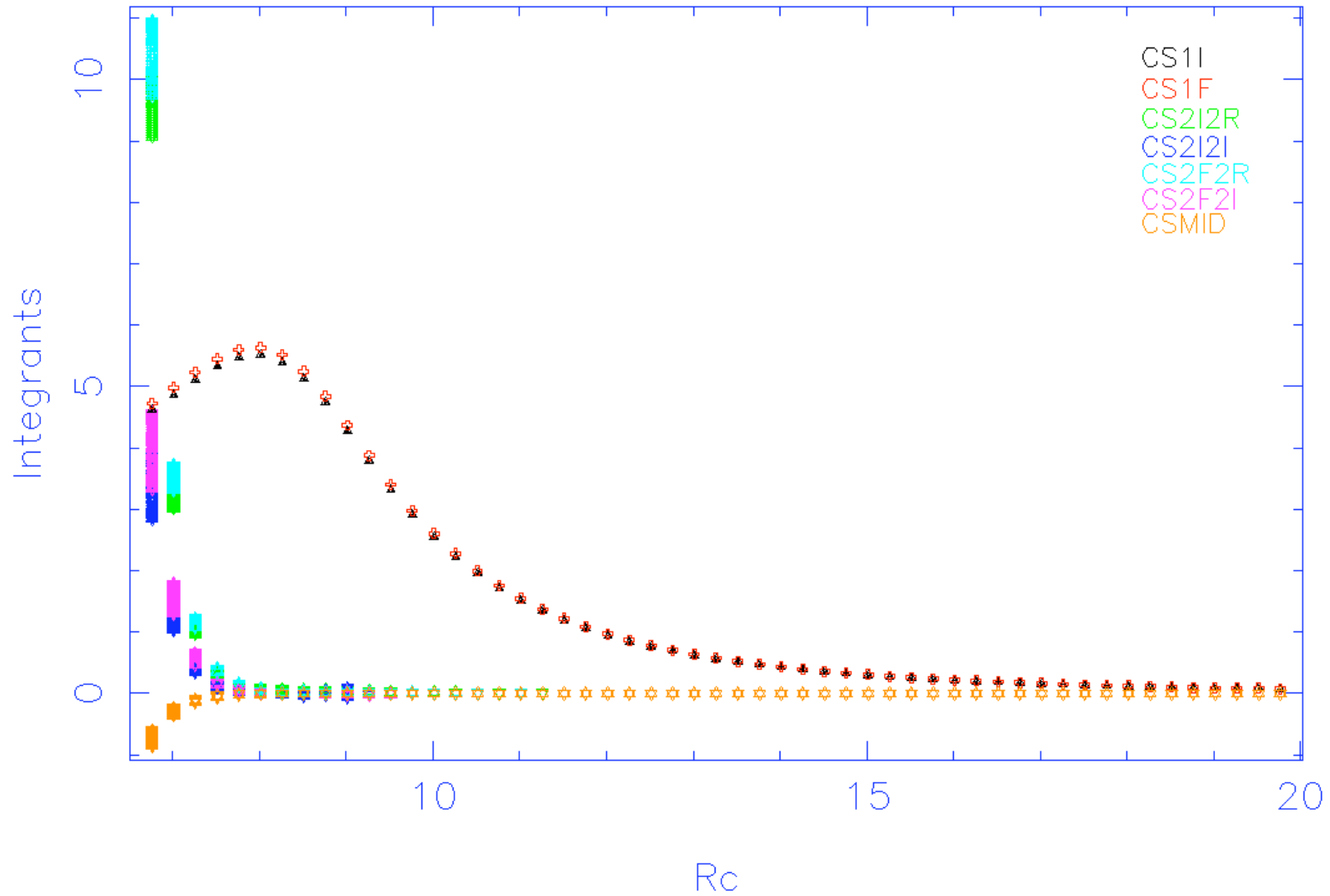
In the present work we find convergence of the atom-atom part of the intermolecular potential is obtained at 12<sup>th</sup> order for transitions involving A- and F-symmetries.

However, for E-symmetry transitions the results show that the calculations are not converged even at 14<sup>th</sup> order of expansion. Since it is the current limit of the codes, results for E symmetry transitions are not reported here.



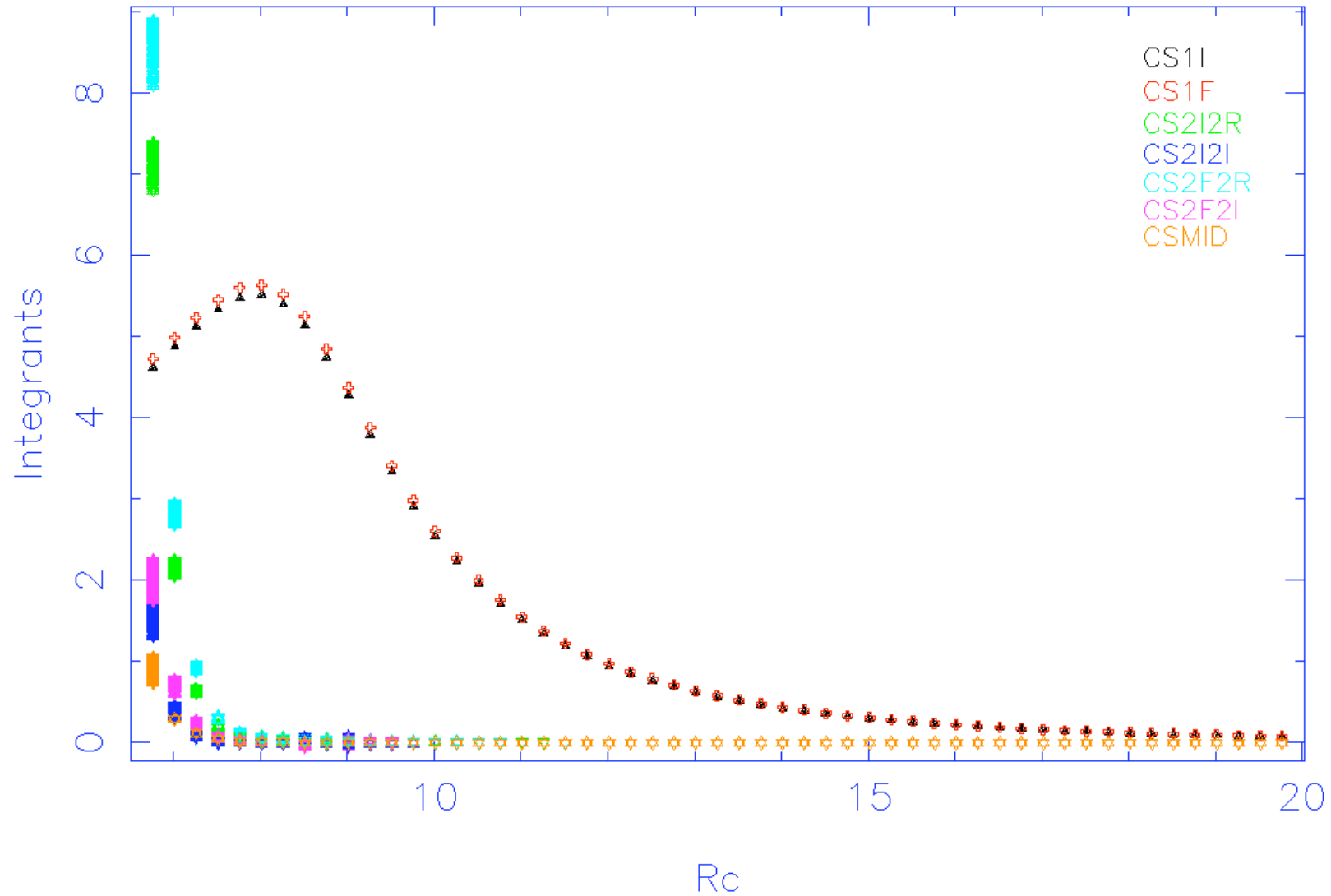
# Components of the integrand

CH<sub>4</sub>-N<sub>2</sub> (Symmetry-A)



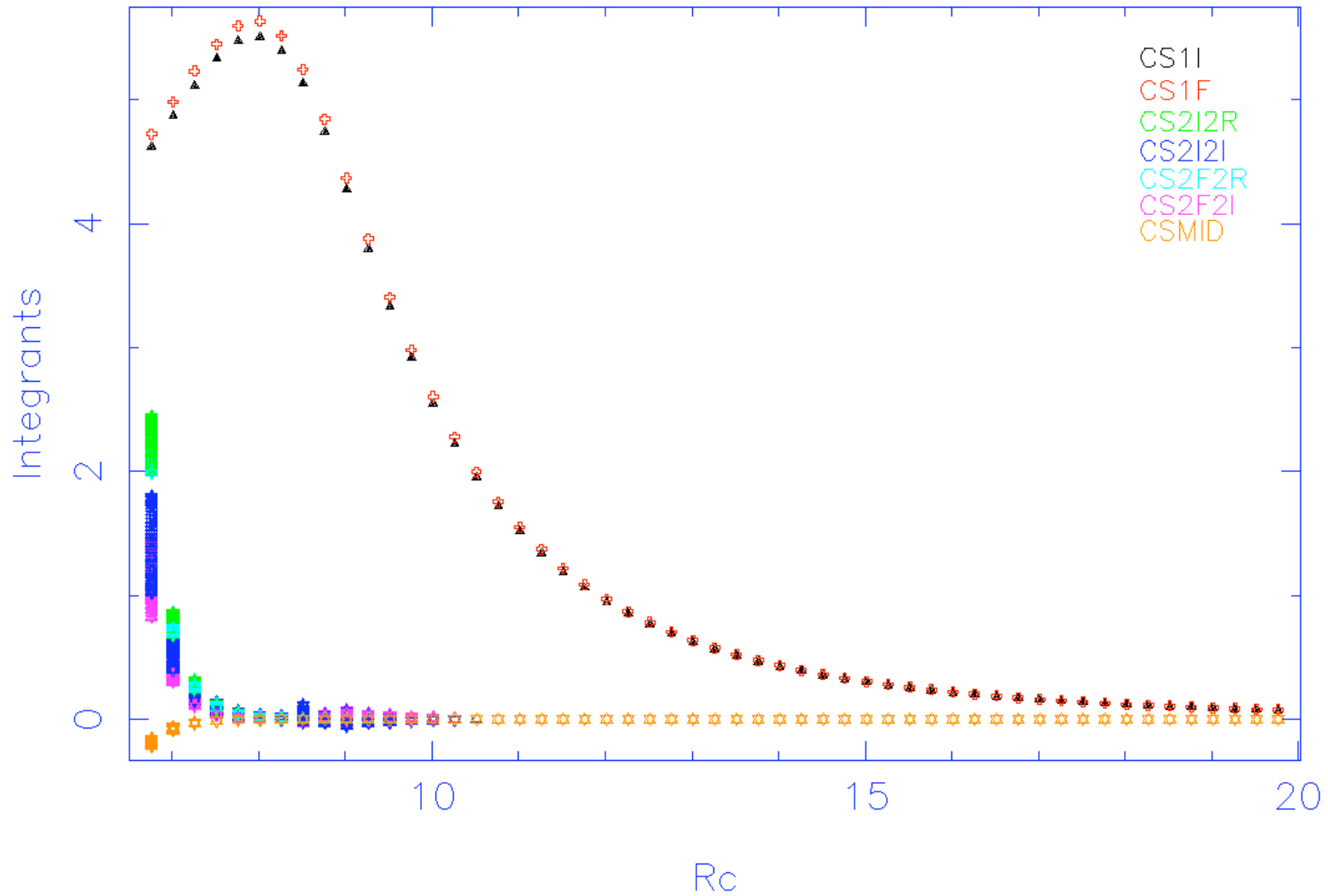
# Components of the integrand

CH<sub>4</sub>-N<sub>2</sub> (Symmetry-F)



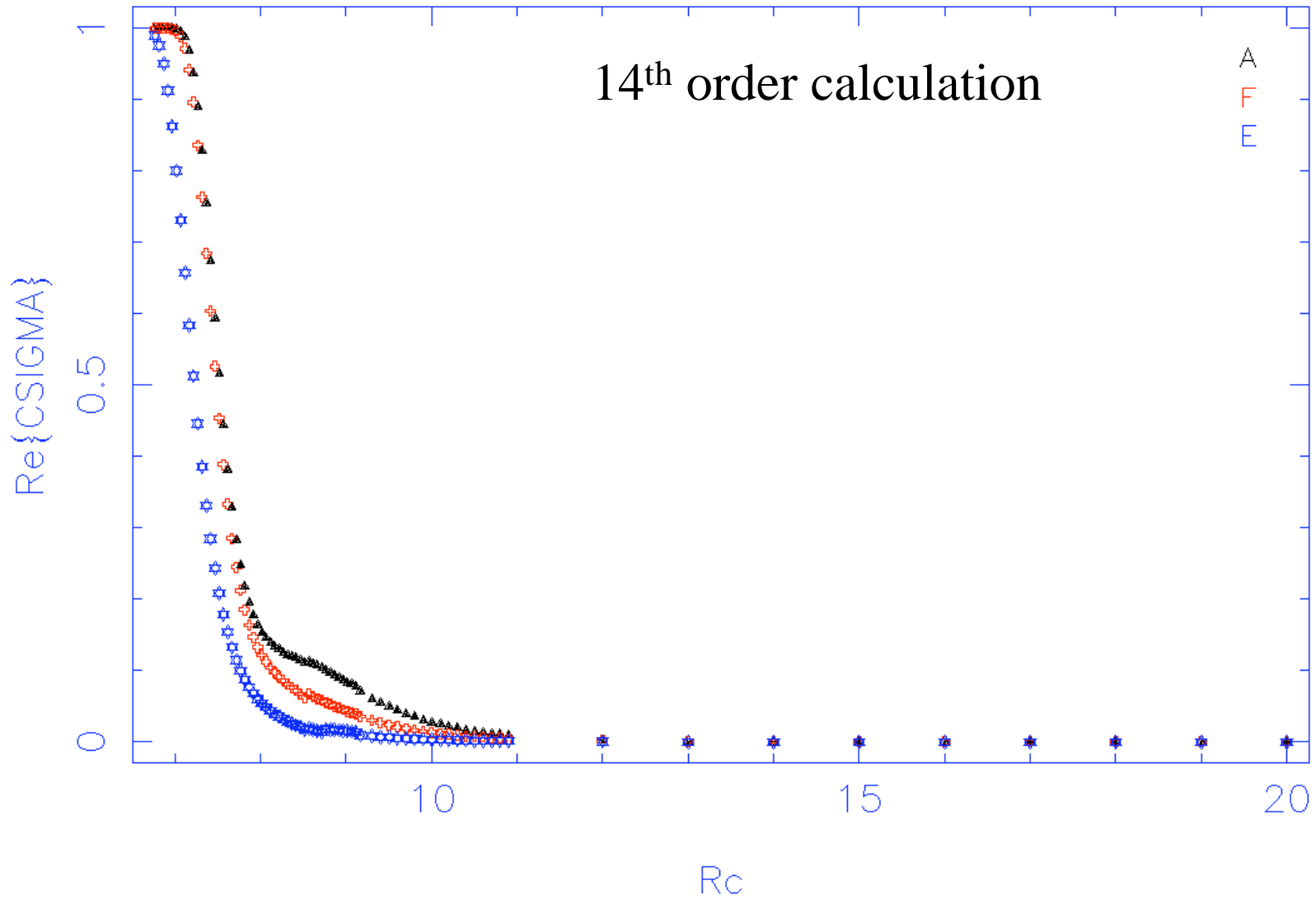
# Components of the integrand

CH<sub>4</sub>-N<sub>2</sub> (Symmetry-E)



# Real part of the integrand

CH<sub>4</sub>-N<sub>2</sub> for J=8



# Calculations

From the remaining A- and F-symmetry transitions we were able to make calculations for

524 A-symmetry transitions and

3596 F-symmetry transitions;

4120  $\nu_3$  transitions total.



# Preliminary Calculations

Combination rules → atom-atom parameters with large uncertainty

An initial calculation of the 52 A- and F-symmetry transitions for which Pine (*J. Chem. Phys.* **97** (1992) 773-785.) made N<sub>2</sub>- and O<sub>2</sub>-broadening measurements was done yielding -8.8 and 15.0 percent difference, respectively.



# Preliminary Calculations

To adjust the atom-atom parameters six transitions (1 A- and 5 F-species) and five F-symmetry transitions were chosen for N<sub>2</sub>- and O<sub>2</sub>-broadening, respectively.

Results of fit gives:

perturber	average percent difference
N <sub>2</sub>	0.15
O <sub>2</sub>	-2.1



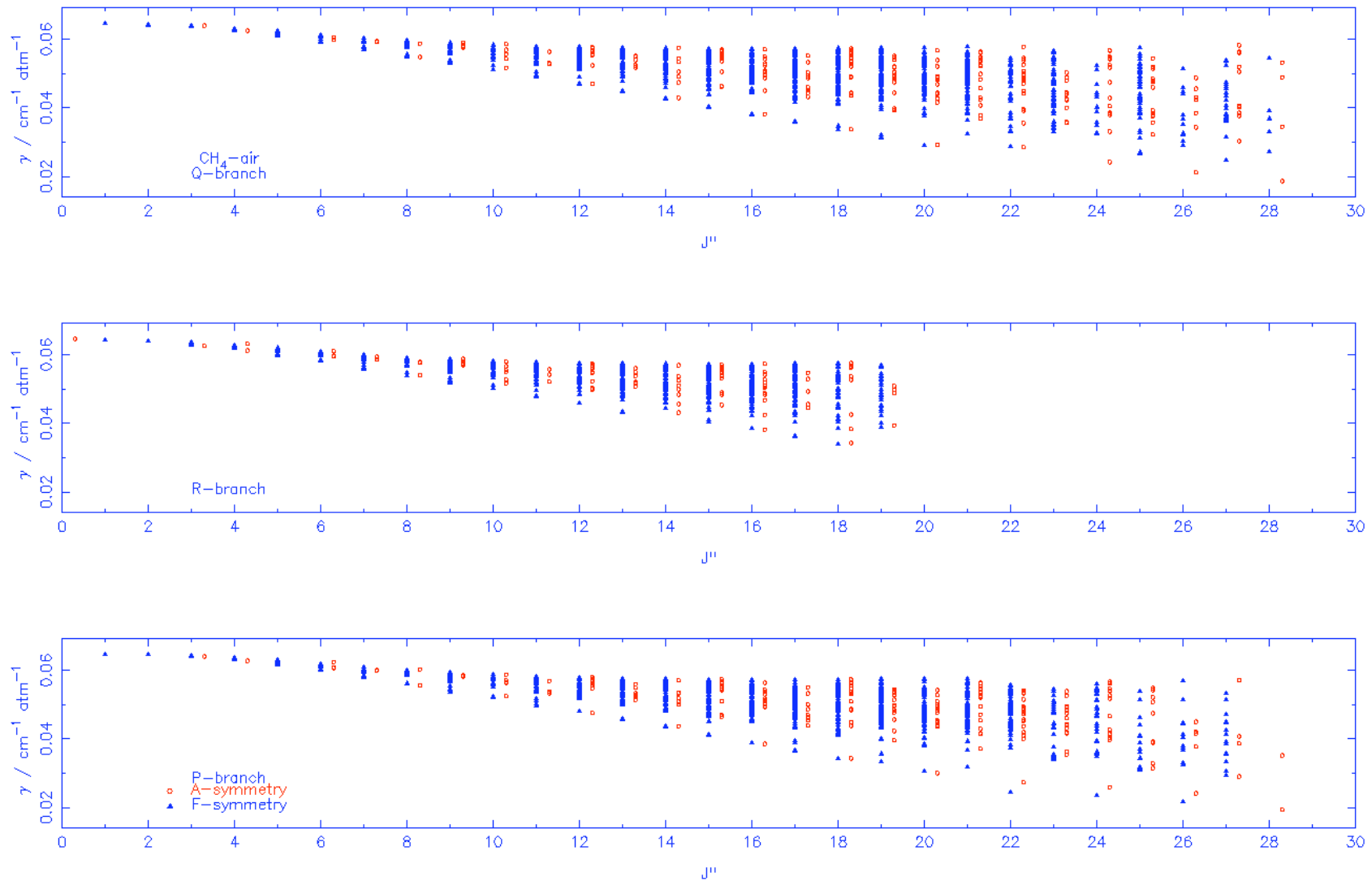
# Atom-atom coefficients

Pair	$\varepsilon/k_B$ (K)		$\sigma$ /(Å)	
	initial	final	initial	final
H-N	20.50	20.50	3.00	2.85
C-N	34.30	32.59	3.45	3.45
H-O	24.15	24.15	2.84	2.70
C-O	40.43	38.01	3.28	3.02

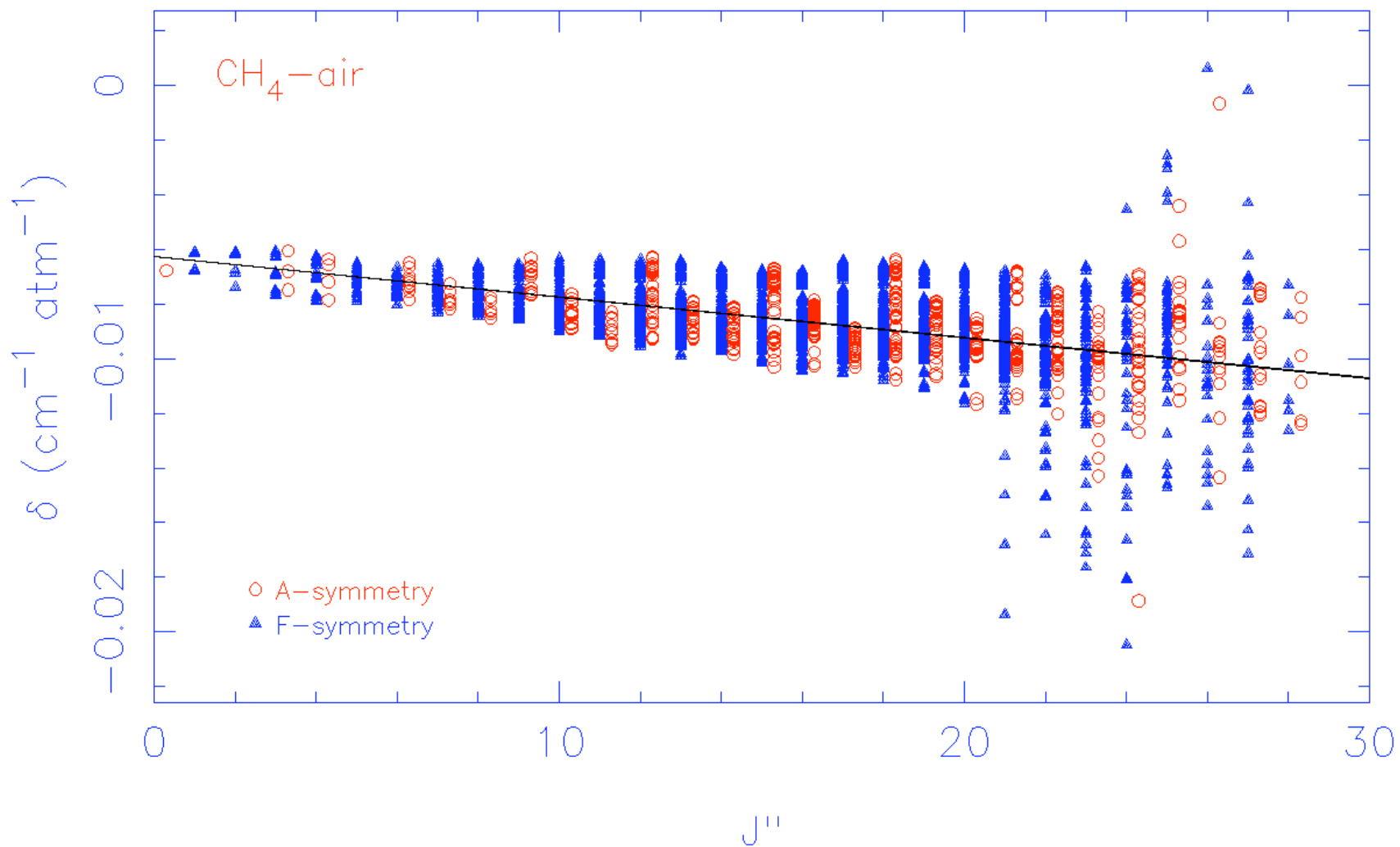
All other molecular constants are the best literature values.

Perturber	$\gamma_{\min}^*$	$\gamma_{\max}^*$	$\delta_{\min}^*$	$\delta_{\max}^*$	$N_{\min}$	$n_{\max}$
N <sub>2</sub>	0.0169	0.0657	-0.0208	0.0009	-0.546	0.759
O <sub>2</sub>	0.0251	0.0606	-0.0194	-0.0004	-0.047	0.752
air	0.0186	0.0646	-0.0205	0.0006	-0.398	0.757

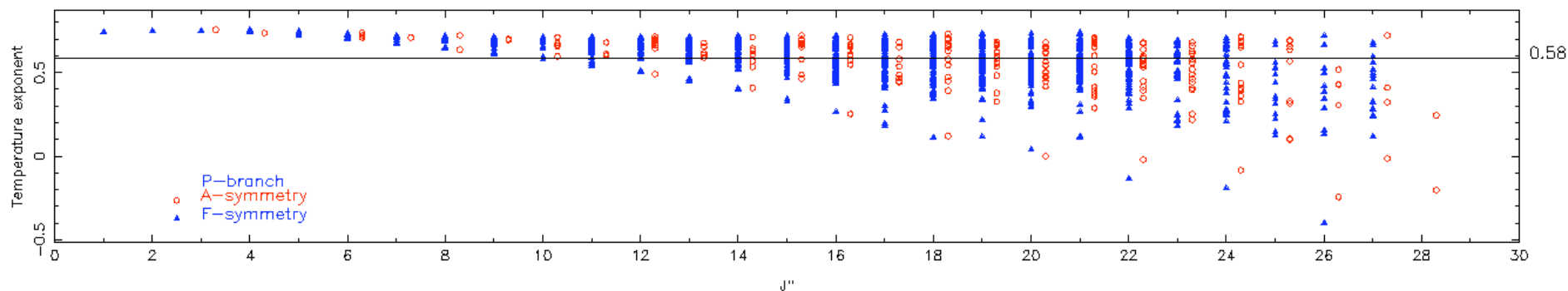
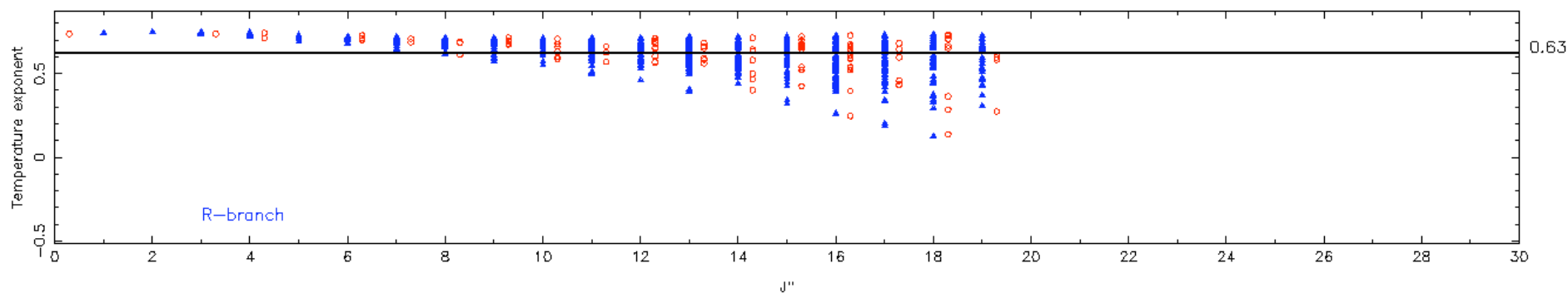
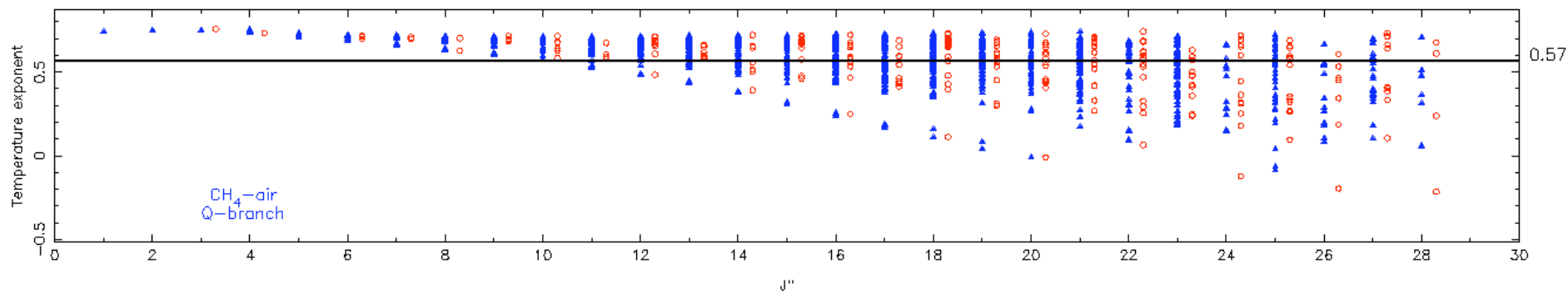
Minimum and maximum values of the half-width, line shift, and temperature dependence of the half-width (temperature exponent) for N<sub>2</sub>-, O<sub>2</sub>-, and air-broadening of methane



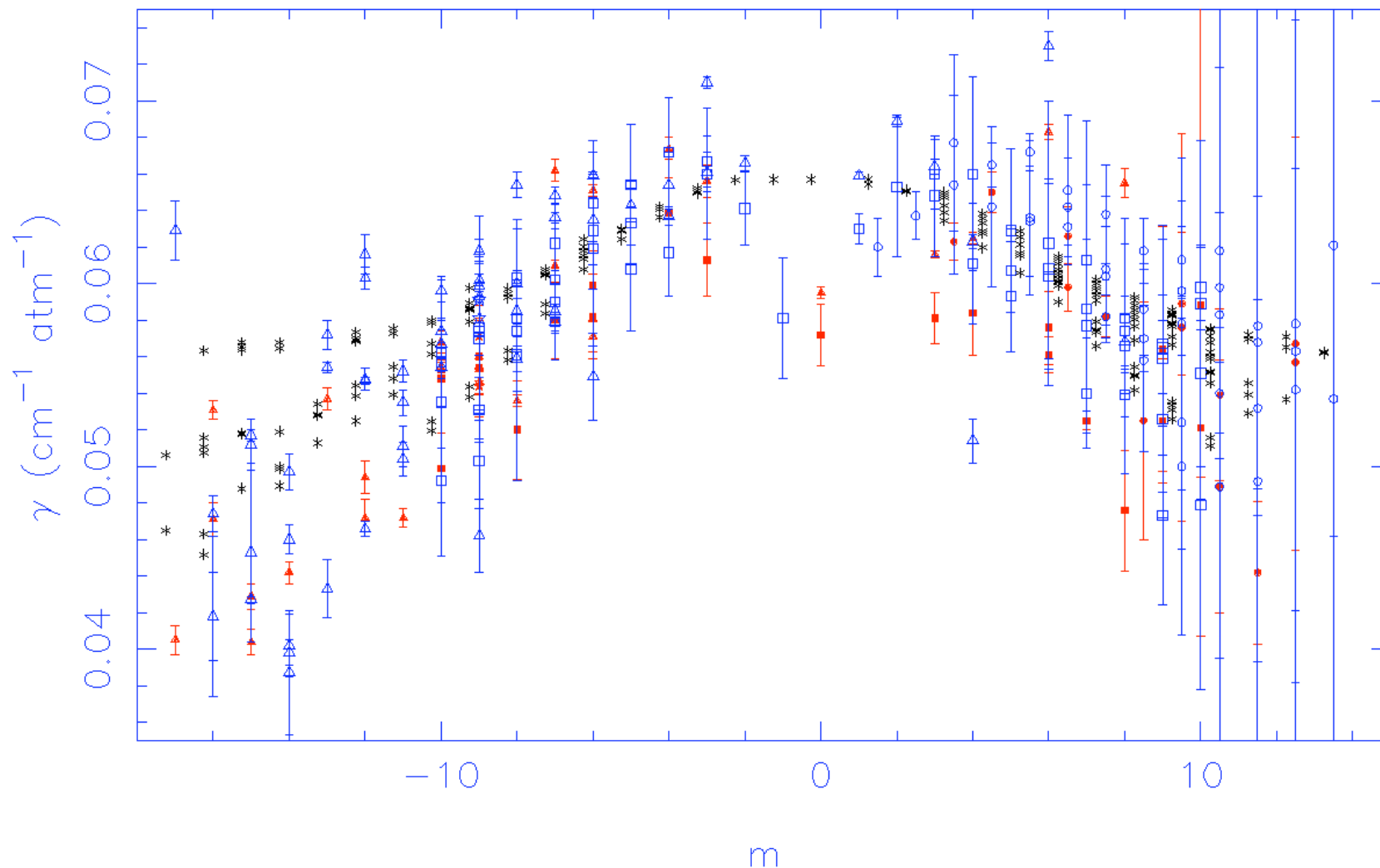
Calculated air-broadened half-widths of CH<sub>4</sub> versus J''.



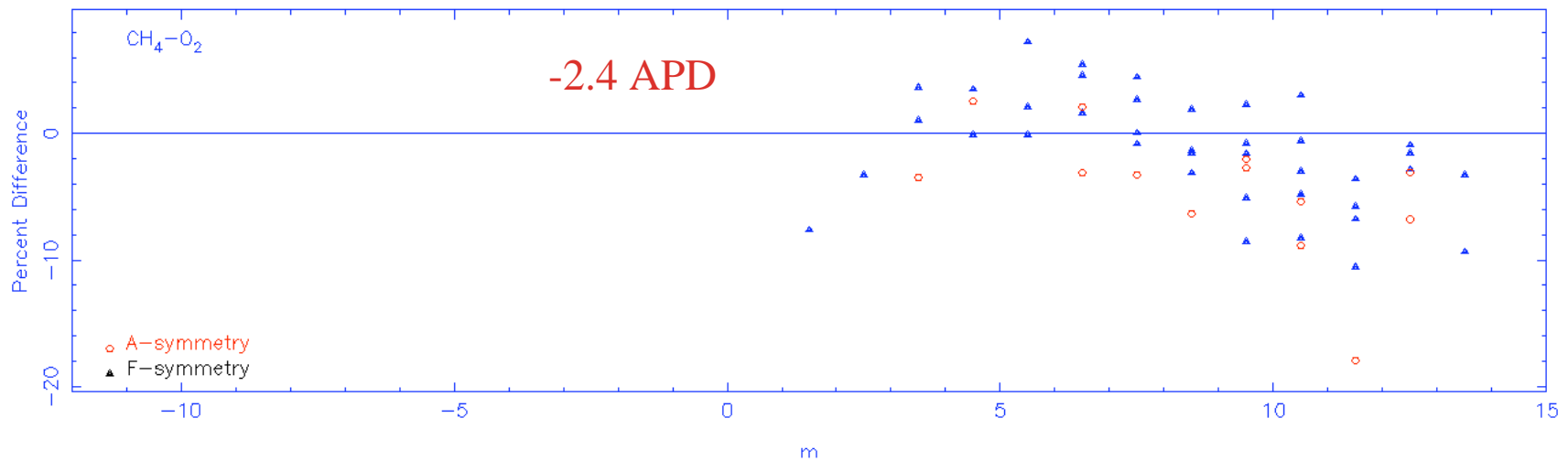
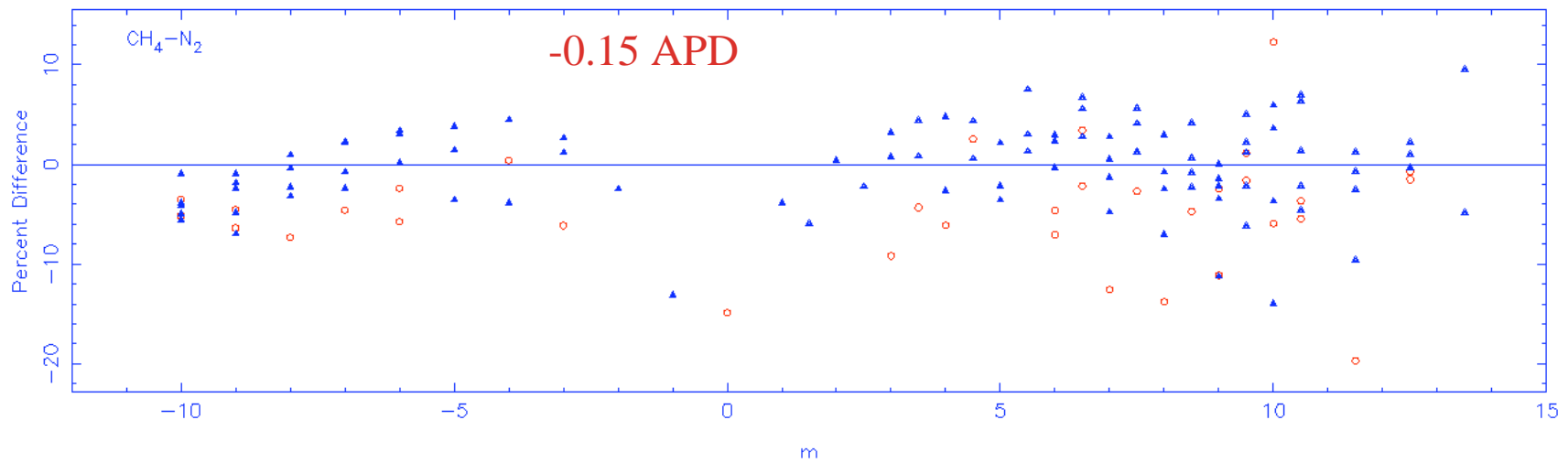
Air-induced line shifts for  $\nu_3$  transitions of methane versus  $J''$ .



Temperature exponents for air-broadened half-widths of  $\nu_3$  transitions of CH<sub>4</sub> versus  $J''$ .



Measured  $N_2$ -broadened half-widths with error bars and the CRB calculated half-widths (\* symbol) are plotted versus  $m$ . The measurements are Pine 1992 A-species solid circle, F-species open circle, Pine 1997 A-species solid square, F-species open square, Benner *et al.* 1993 A-species solid delta symbol, F-species open delta symbol, and Mondelain *et al.* 2007 A-species solid star symbol, F-species open star symbol



Percent difference between the CRB calculations and the N<sub>2</sub>- and the O<sub>2</sub>- broadening data of Pine (1992 and 1997) versus  $m$ .

## *Predicting half-widths*

9 and 1.6  $\mu\text{m}$  with  $S_v > 10^{-20} \text{ cm}^{-1}/(\text{molecule}\cdot\text{cm}^{-2})$   
➤ one hundred thousand transitions



# Predicting half-widths

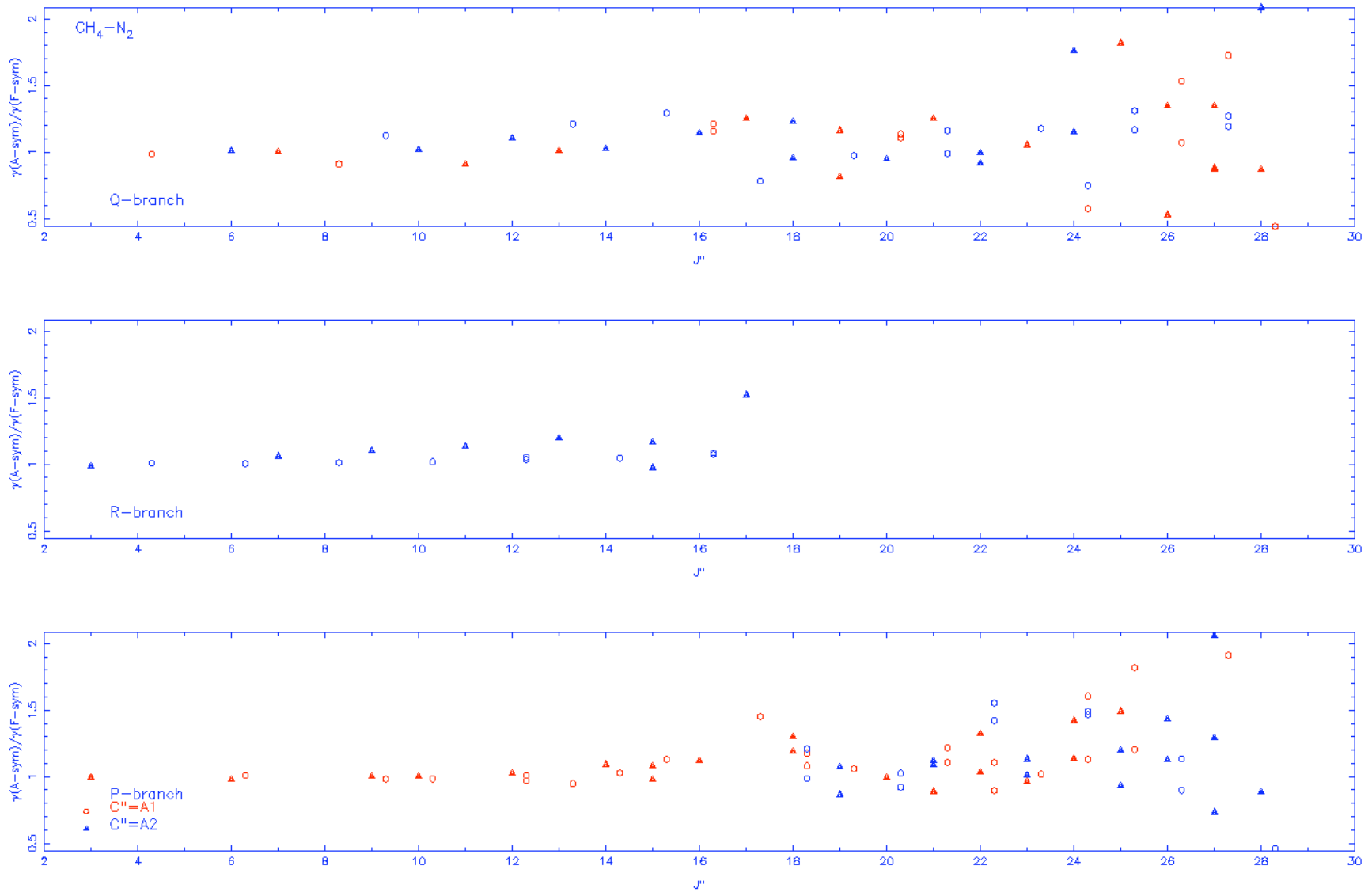
Is it possible to predict half-widths for A-/F-species transitions from F-/A-species transitions with the same quantum numbers?

The pairs of lines are chosen such that the upper and lower rotational quantum numbers are the same, the  $A_1$  symmetry is paired with the  $F_1$  symmetry and the  $A_2$  symmetry is paired with the  $F_2$  symmetry, the lower order index values are the same.

Because the allowed order index for A- and F-symmetry states are quite different, the pairs were created from the minimum  $N'$  and for the maximum  $N'$  of each symmetry species.

For example the line

$J' A_1 N'_{\min} \leftarrow J'' A_2 N''$  is paired with  $J' F_1 N'_{\min} \leftarrow J'' F_2 N''$ .



Ratios of A-symmetry transitions to corresponding F-symmetry transition versus  $J''$ .

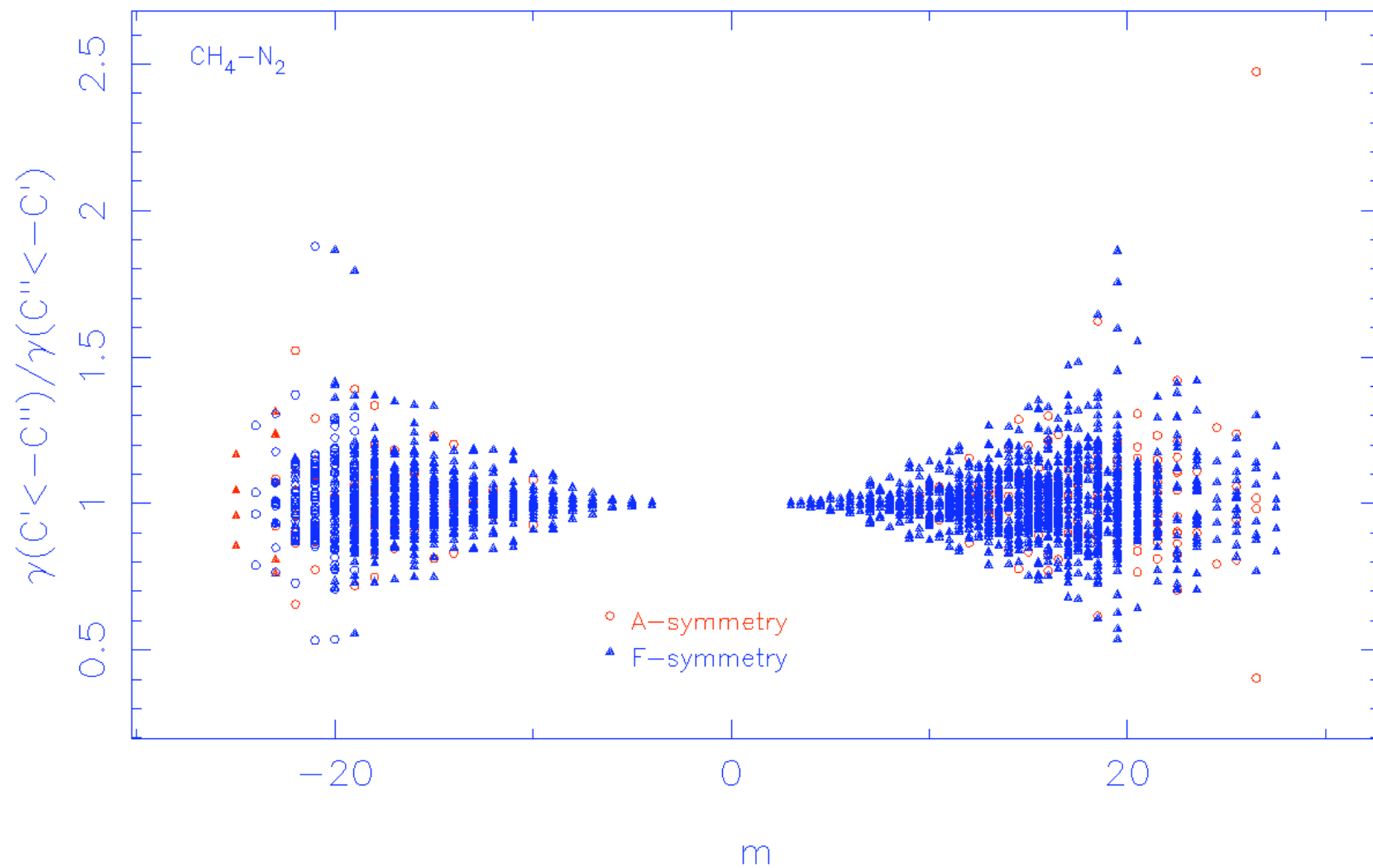
# Predicting half-widths

Is it possible to predict half-widths for transitions of the same overall symmetry species, i.e.  $C''=A_1$  to predict  $C''=A_2$ , etc?

Transitions are chosen such that

$$J' A_1 N' \leftarrow J'' A_2 N'' \text{ is paired with } J' A_2 N' \leftarrow J'' A_1 N''$$

with a similar pairing for F-symmetry



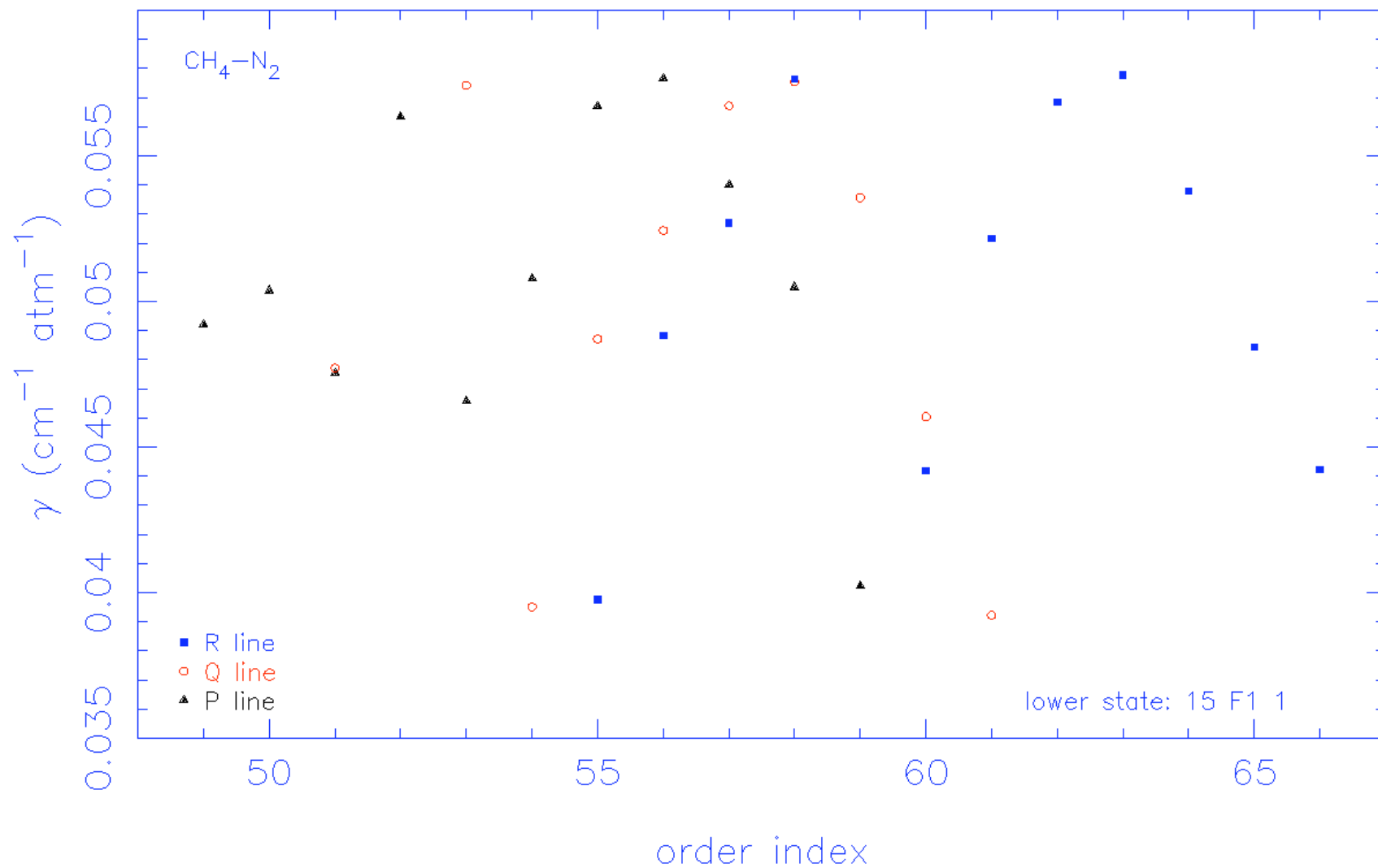
Ratios of transitions with upper and lower symmetries interchanged versus  $m$ .

# Predicting half-widths

Is it possible to predict half-widths for transitions of the same  $J$  and symmetry species from lines with different upper state counting (order) indices, i.e.  $N'=5$  to predict  $N'=1$ , etc?

To test the effect of the upper states on the calculation, we randomly looked through the  $N_2$ -broadening data file and selected the 15 F1 1 lower state. This lower state is involved in transitions to 32 upper states; eleven to 14 F2 states, ten 15 F2 states, and eleven 16 F2 states.





N<sub>2</sub>-broadened half-widths for  $\nu_3$  transitions of methane with lower state 15 F1 1.

# Predicting half-widths

Is it possible to predict half-widths for methane transitions by scaling as a function of perturbing molecule?

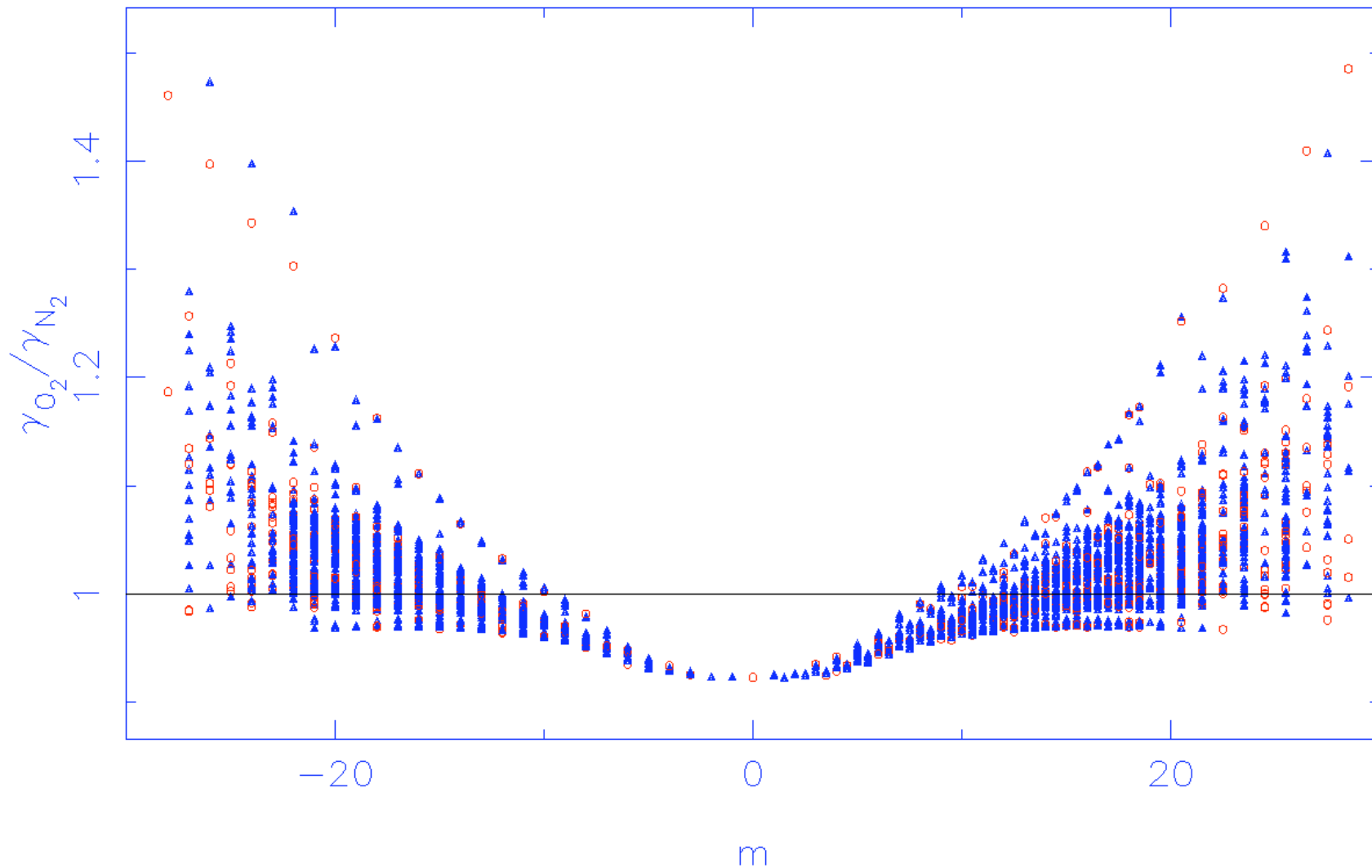
Using the CRB calculated N<sub>2</sub>-, O<sub>2</sub>-, and air-broadened files, the ratios

$$\gamma(\text{O}_2)/\gamma(\text{N}_2)$$

$$\gamma(\text{air})/\gamma(\text{N}_2)$$

were determined and plotted.





Ratios of O<sub>2</sub>-broadened half-width to corresponding N<sub>2</sub>-broadened half-width for v<sub>3</sub> transitions of CH<sub>4</sub> versus m.



# Conclusion

- Calculations of the pressure-broadened half-width, the pressure induced line shift, and the temperature dependence of the half-width have been made for nitrogen-, oxygen-, and air-broadening of  $\nu_3$  transitions of  $\text{CH}_4$  in the 2726 to 3200  $\text{cm}^{-1}$  region of the spectrum. The calculations were made at two temperatures, 225 and 296 K, and for rotational states with  $J \leq 28$ .
- Because of limitations in the current codes only A- and F symmetry transitions were considered.
- Calculations were made for 4120 A- and F- symmetry transitions in this region. The final list of transitions is comprised of 524 A-symmetry transitions and 3596 F-symmetry transitions. The calculations did not take into account any line coupling effects.

- From the calculations the temperature dependence of the nitrogen-, oxygen-, and air-broadened half-widths were determined.
- Calculations of  $\gamma$  compared with Pine's measurements give reasonable percent differences and standard deviations.
- However, Mondelain *et al.* have demonstrated that retrievals of methane volume mixing ratios from balloon spectra made using slightly different line shape parameters show noticeable effects. Thus our calculations are not yet at the level desired by all researchers for terrestrial atmospheric applications but certainly are an improvement of the estimated values.

- The accuracies needed for Titan remote sensing are less stringent (5-10%) and the CH<sub>4</sub>-N<sub>2</sub> calculations presented here meet that criterion.
- The comparisons for the line shifts were not as good.
- This may be due in part to the magnitude of the parameter as well as the uncertainty in the parameters used in the calculation (vibrational-dependence of the polarizability of methane and the atom-atom coefficients).

# Future work

- While the agreement with the measured data of Pine gives good statistics (see above) the differences vary between roughly  $\pm 10\%$  with a few stray points.
- The fact that the calculations cannot yet be done for E-symmetry transitions is a concern.
- Investigate the form of intermolecular potential used in the calculations and the parameters used with emphasis on reducing the spread in the agreement with Pine and being able to compute E-symmetry transitions as well.
- Wavefunctions for  $\nu_4$  states available, which will allow the consideration of vibration dependence of the half-widths and line shifts ( $\nu_3$  vs.  $\nu_4$ ).
- Extend calculations to other broadening species, i.e.  $H_2$  and He.

# Acknowledgement

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