Temperature dependence of N_2-, O_2-, and air-broadened half-widths of water vapor transitions: insight from theory and comparison with measurement

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Theory

Semi-classical formalism of Robert and Bonamy

- Complex formalism - halfwidths and line shifts
- Free from cut-off procedure and adjustable parameters
- Trajectories from solution of Hamilton's eqs. or R-B parabolic approximation
- General spherical tensor expansion for the intermolecular potential

Intermolecular Potential

H_2O-N_2 and H_2O-O_2 systems

- Leading electrostatic components: d-q, q-q
- Atom-atom potential: expanded to 8th order
- The vibrational dependence of the isotropic potential uses the induction and London dispersion potentials

Spherical Tensor Expansion of the Potential

$$V = \sum_{\substack{\ell_1 \ell_2 \\ \ell}} \sum_{\substack{n_1 \\ m_1 m_2 \\ m}} \sum_{w,q} \frac{U(\ell_1 \ell_2 \ell, n_1 w q)}{R^{q+\ell_1+\ell_2+2w}}$$

$$\otimes C(\ell_1 \ell_2 \ell, m_1 m_2 m) \mathrm{D}^{\ell_1}_{m_1 n_1}(\Omega_1) \mathrm{D}^{\ell_2}_{m_2 0}(\Omega_2) \mathrm{Y}_{\ell m}(\omega)$$

- where $C(\ell_1\ \ell_2\ \ell;\ m_1\ m_2\ m)$ is a Clebsch-Gordan coefficient, $\Omega_1=(\alpha_1, \beta_1, \gamma_1)$ and $\Omega_2=(\alpha_2, \beta_2, \gamma_2)$ are the Euler angles describing the molecular fixed axis relative to the space fixed axis. $\omega = (\theta,\phi)$ describes the relative orientation of the centers of mass.
- Electrostatic interactions: q=1 and w=0
- Atom-atom interactions: q=12 or 6 and w defined by the order of the expansion where *Order*$=\ell_1+\ell_2+2w$

S_1 term

Depends strongly on the vibrational dependence of polarizability. The coefficients for H_2O are taken from the work of Luo et al. J. Chem. Phys. **98**, 7159 (1983).

$$\alpha = 9.86 + 0.29\left(v_1 + \tfrac{1}{2}\right) + 0.03\left(v_2 + \tfrac{1}{2}\right) + 0.28\left(v_3 + \tfrac{1}{2}\right)$$

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Note, stretch modes have roughly the same contribution.

Halfwidth and Line Shift in RB theory

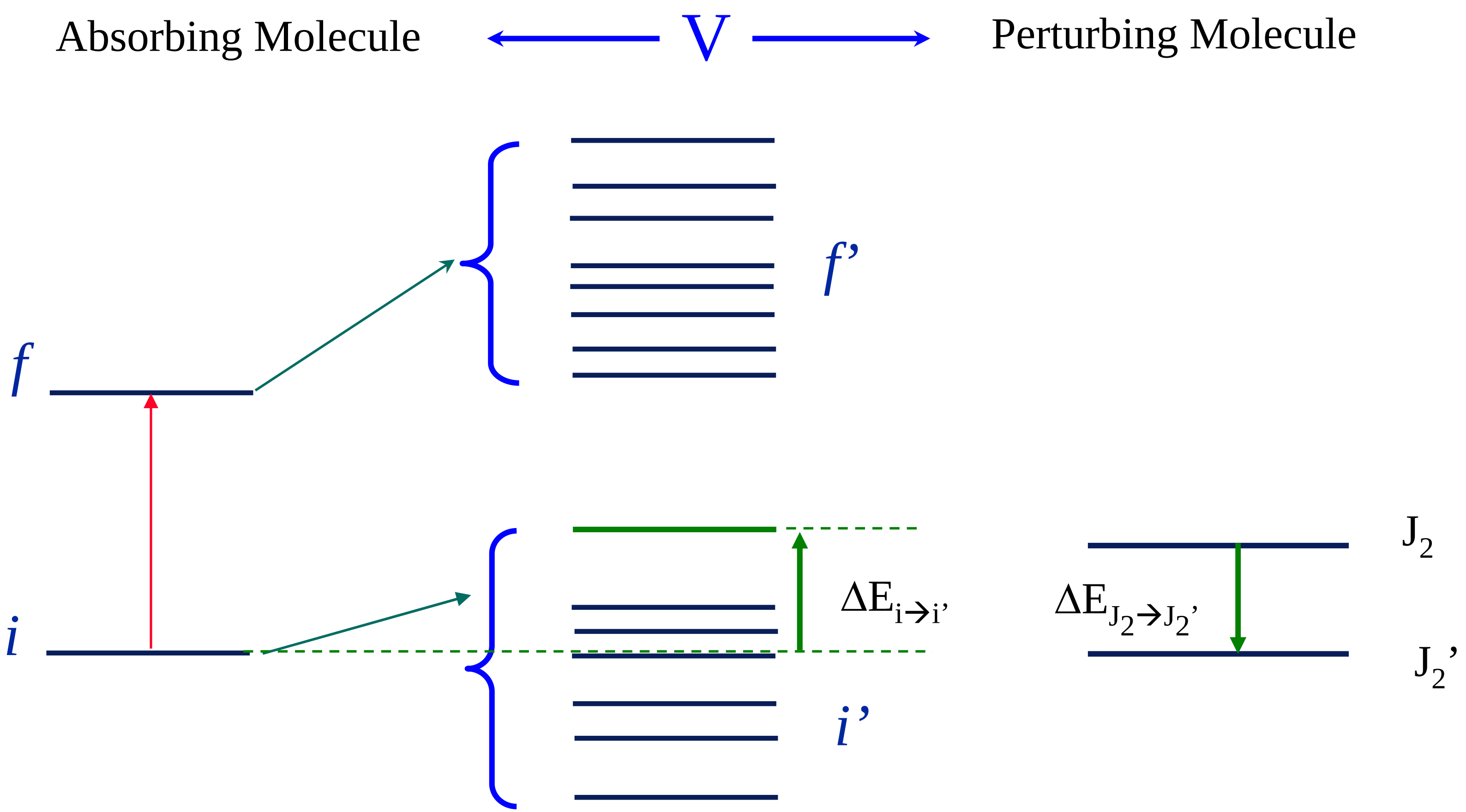
$$(\gamma - i\delta)_{f \leftarrow i} =$$

$$\frac{n_2}{2\pi c}\left\langle \mathrm{v} \times \left[1 - e^{-{}^{R}S_2(f,i,J_2,v,b)} e^{-i\left[S_1(f,i,J_2,v,b) + S_2(f,i,J_2,v,b)\right]} \right] \right\rangle_{v,b,J_2}$$

Real terms

Imaginary terms

Connecting states



optical transitions

collisionally induced transitions

N_2 and O_2 as perturbers

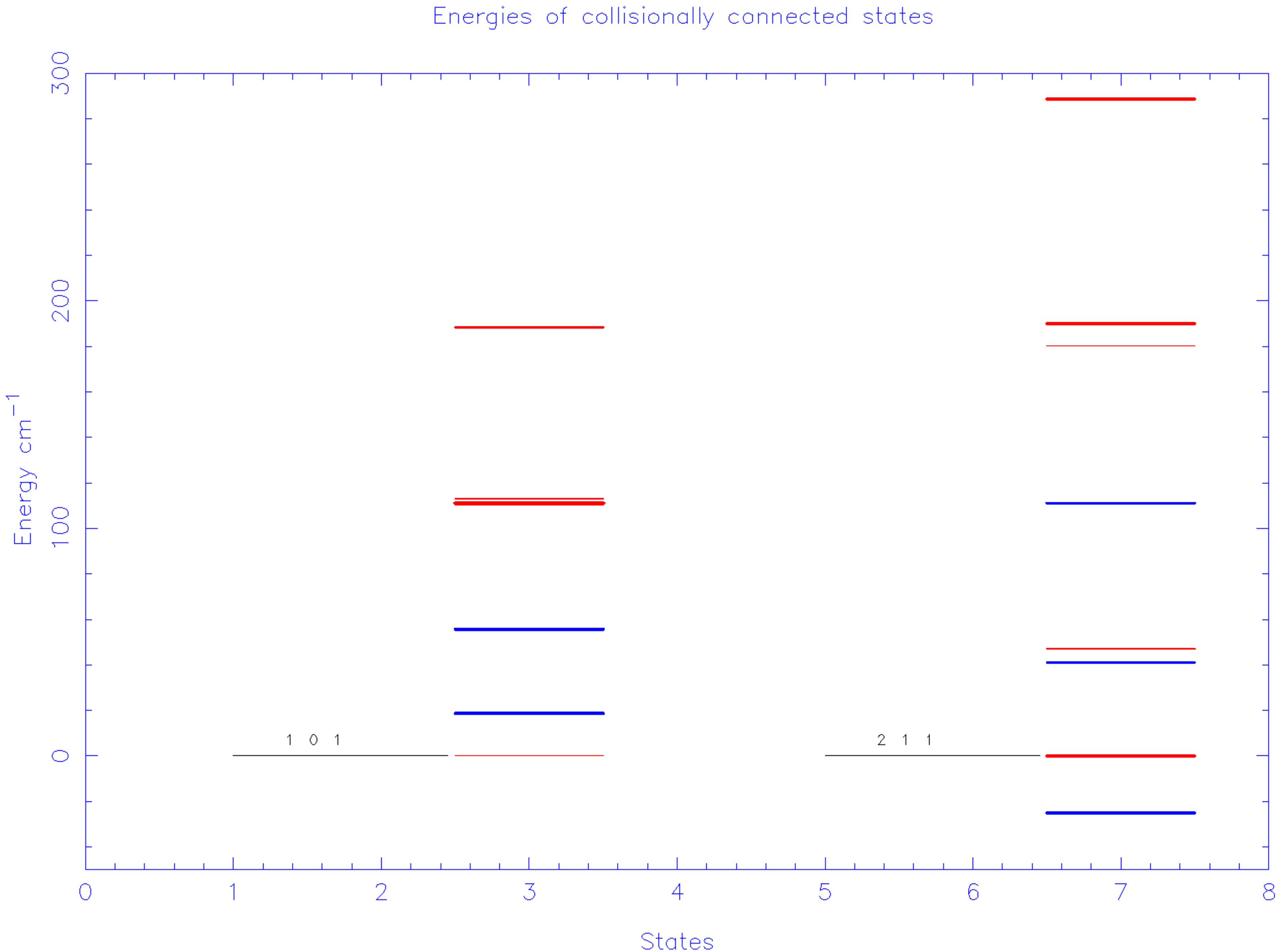
$B(N_2) = 2.0006\ cm^{-1}$ $B(O_2) = 1.4377\ cm^{-1}$

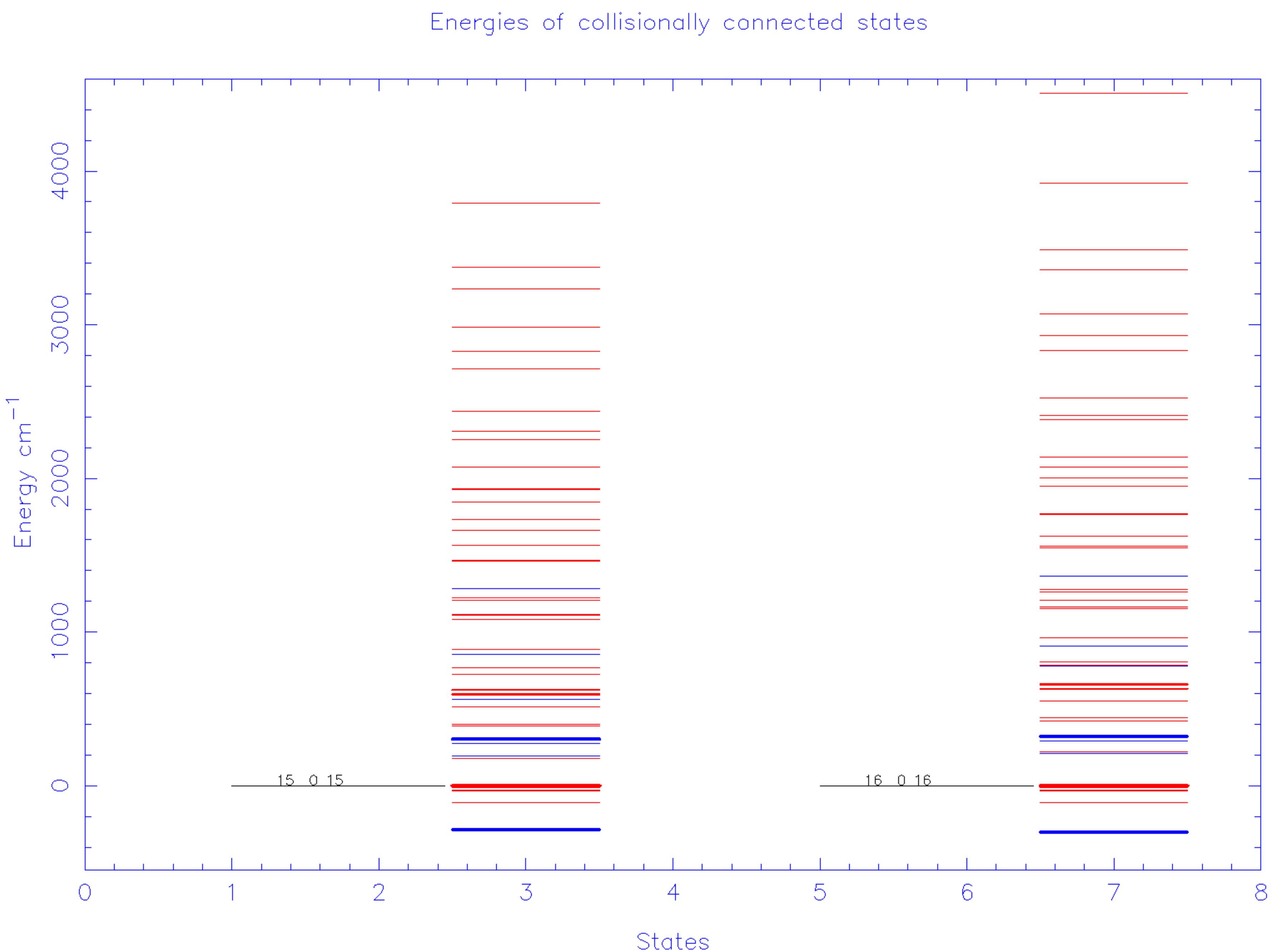
Energy gaps

~ 24 to $960\ cm^{-1}$ ~ 17 to $690\ cm^{-1}$

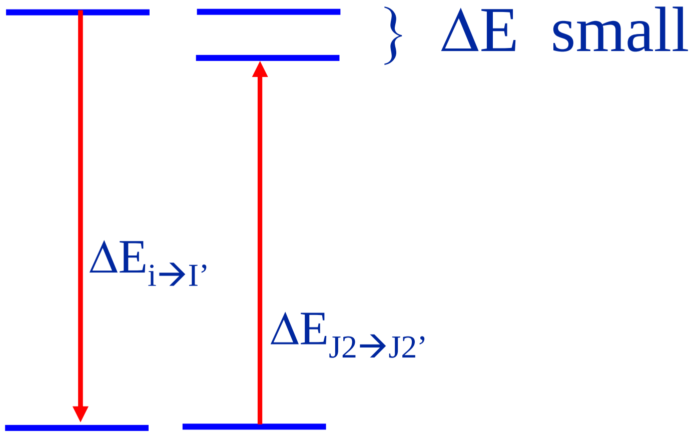
Most probable states

$\Delta E = \sim 150\ cm^{-1}$ $\Delta E = \sim 110\ cm^{-1}$


Energies of collisionally connected states
Energy cm^{-1}
300
200
100
0
1 0 1
2 1 1
0
1
2
3
4
5
6
7
8
States

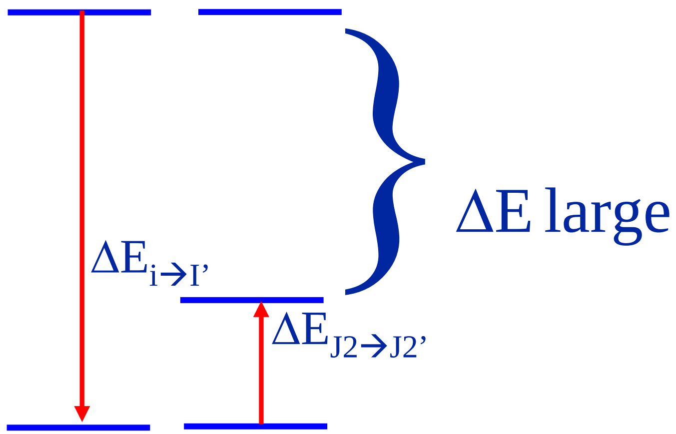

Energies of collisionally connected states
Energy cm^{-1}
0
1000
2000
3000
4000
15 0 15
16 0 16
0
1
2
3
4
5
6
7
8
States

Low J transitions



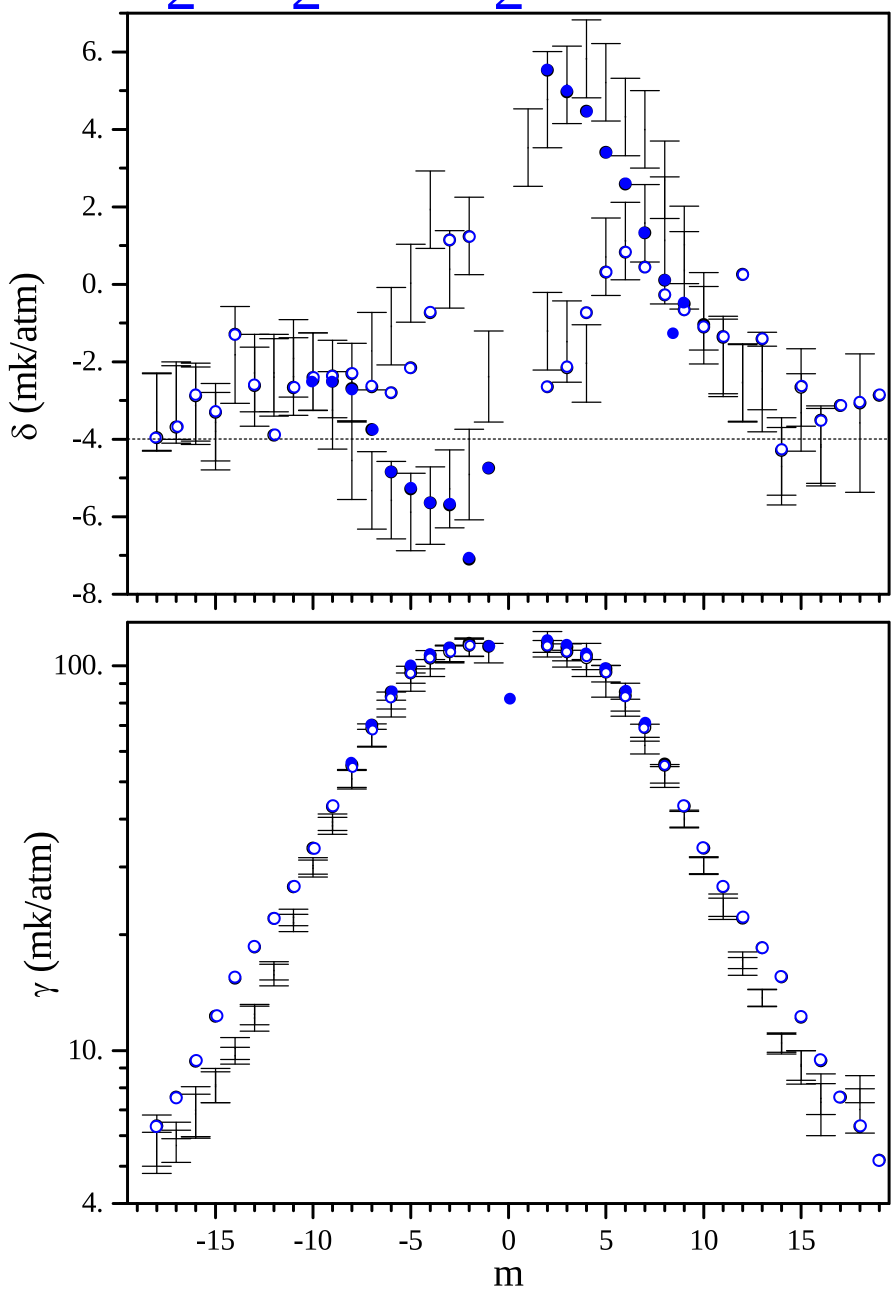
On resonance collisions, collisional contributions dominate the half-width

High J transitions



Off-resonance collisions, collisional contributions small, half-width dominated by vibrational terms.

ν_2 H_2O-N_2 P and R Doublet Transitions



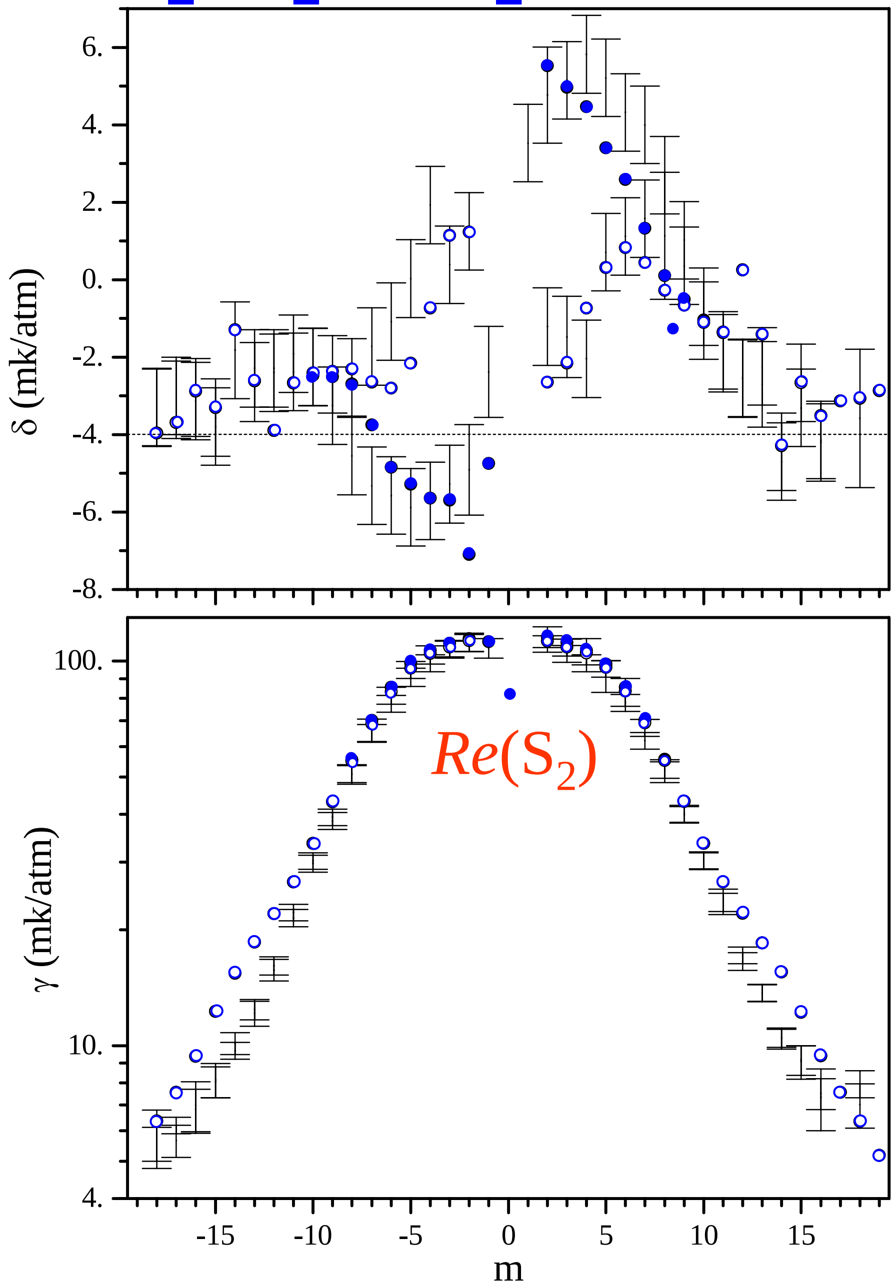
$(J\pm1_{1,J\pm1} \leftarrow J_{0,J}$ and $J\pm1_{0,J\pm1} \leftarrow J_{1,J})$

● and ○ are calculated values associated with P and R lines such that (Ka'-Ka")=(J'-J") and (Ka'-Ka")=-(J'-J"), respectively.

The horizontal dashed line indicates the pure dephasing contribution

Gamache and Hartmann, JQSRT **83**, 119–147 (2004).

ν_2 H_2O-N_2 P and R Doublet Transitions



($J\pm1_{1,J\pm1} \leftarrow J_{0,J}$ and $J\pm1_{0,J\pm1} \leftarrow J_{1,J}$)

● and ○ are calculated values associated with P and R lines such that (Ka'-Ka")=(J'-J") and (Ka'-Ka")=-(J'-J"), respectively.

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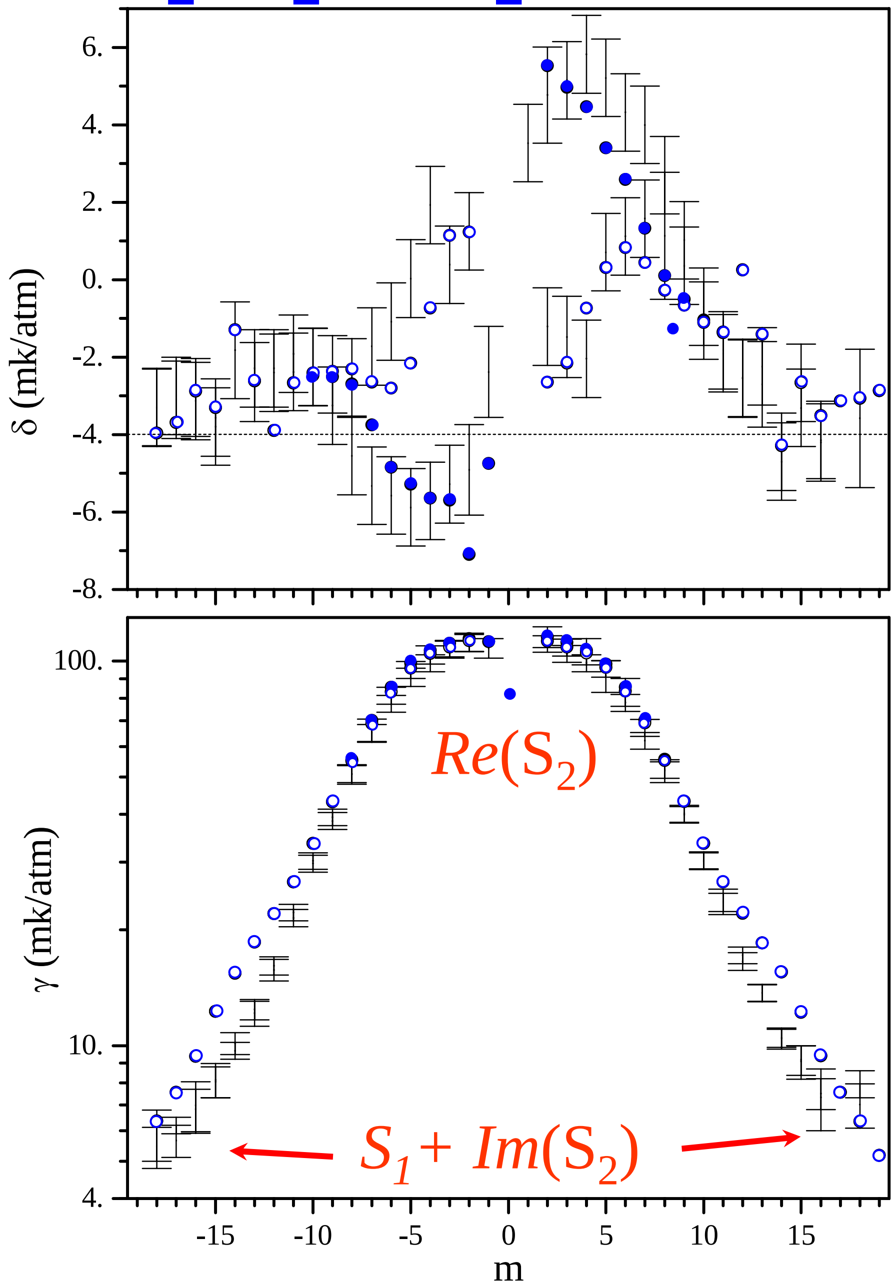
Gamache and Hartmann, JQSRT **83**, 119–147 (2004).

ν_2 H_2O-N_2 P and R Doublet Transitions



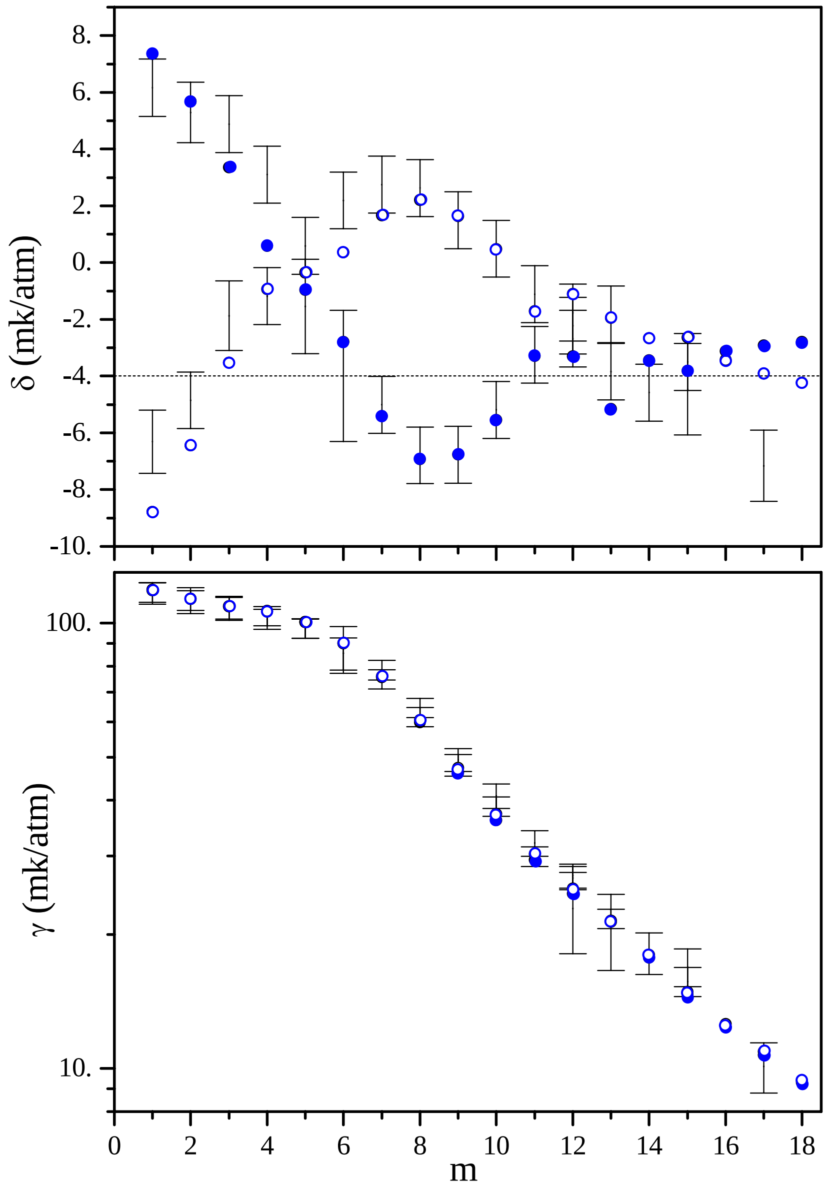
($J\pm1_{1,J\pm1}\leftarrow J_{0,J}$ and $J\pm1_{0,J\pm1}\leftarrow J_{1,J}$)

● and ○ are calculated values associated with P and R lines such that (Ka'-Ka")=(J'-J") and (Ka'-Ka")=-(J'-J"), respectively.

The horizontal dashed line indicates the pure dephasing contribution

Gamache and Hartmann, JQSRT **83**, 119–147 (2004).

ν_2 H_2O-N_2 Doublet Q-branch Transitions



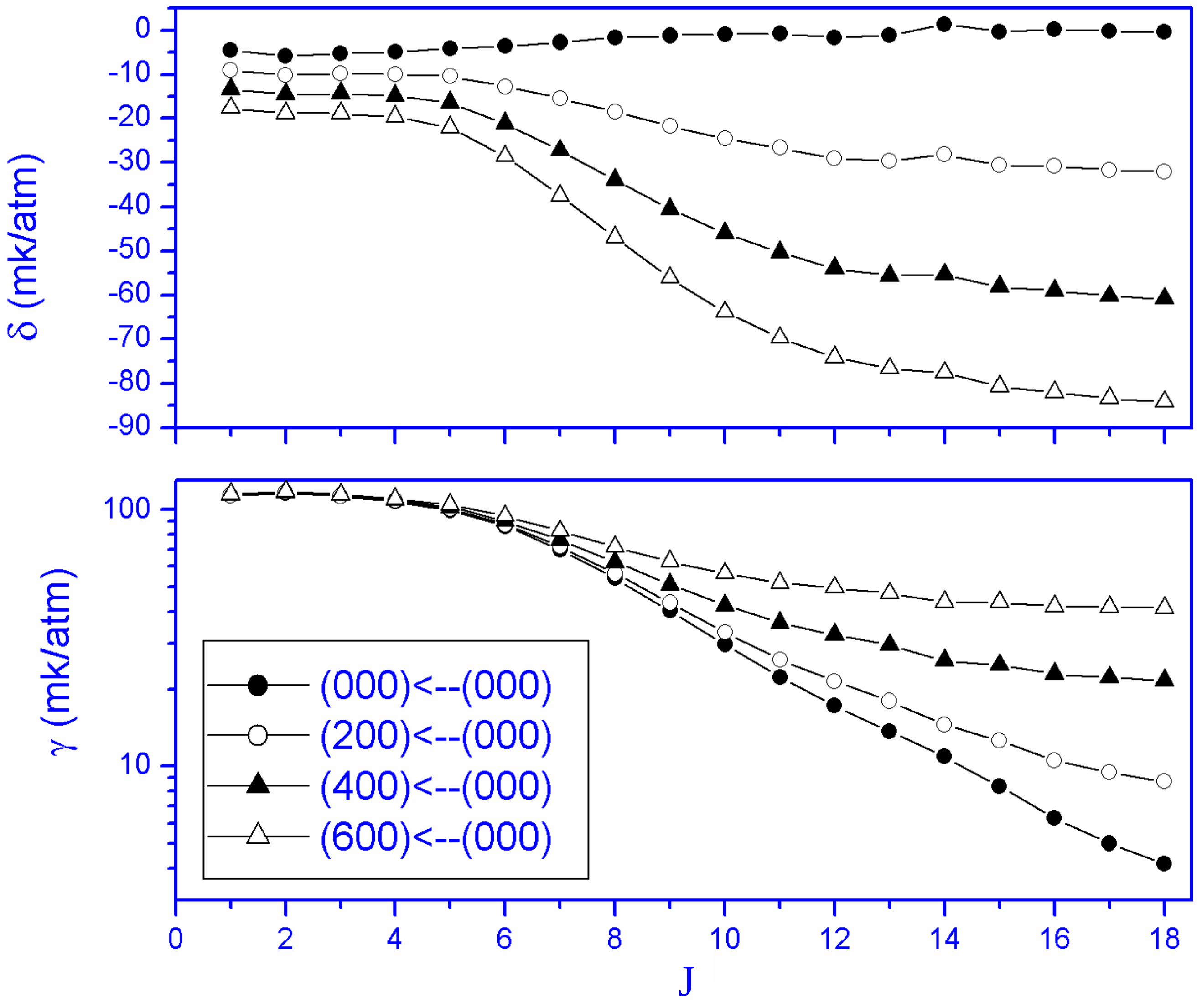
The J $_{1,J-1}$←J $_{0,J}$ and J $_{0,J}$←J $_{1,J-1}$) Q line doublets of the ν_2 band.

I are experimental values. ● and ○ are calculated values of the Ka'-Ka"=1 and Ka'-Ka"= -1 transitions, respectively.

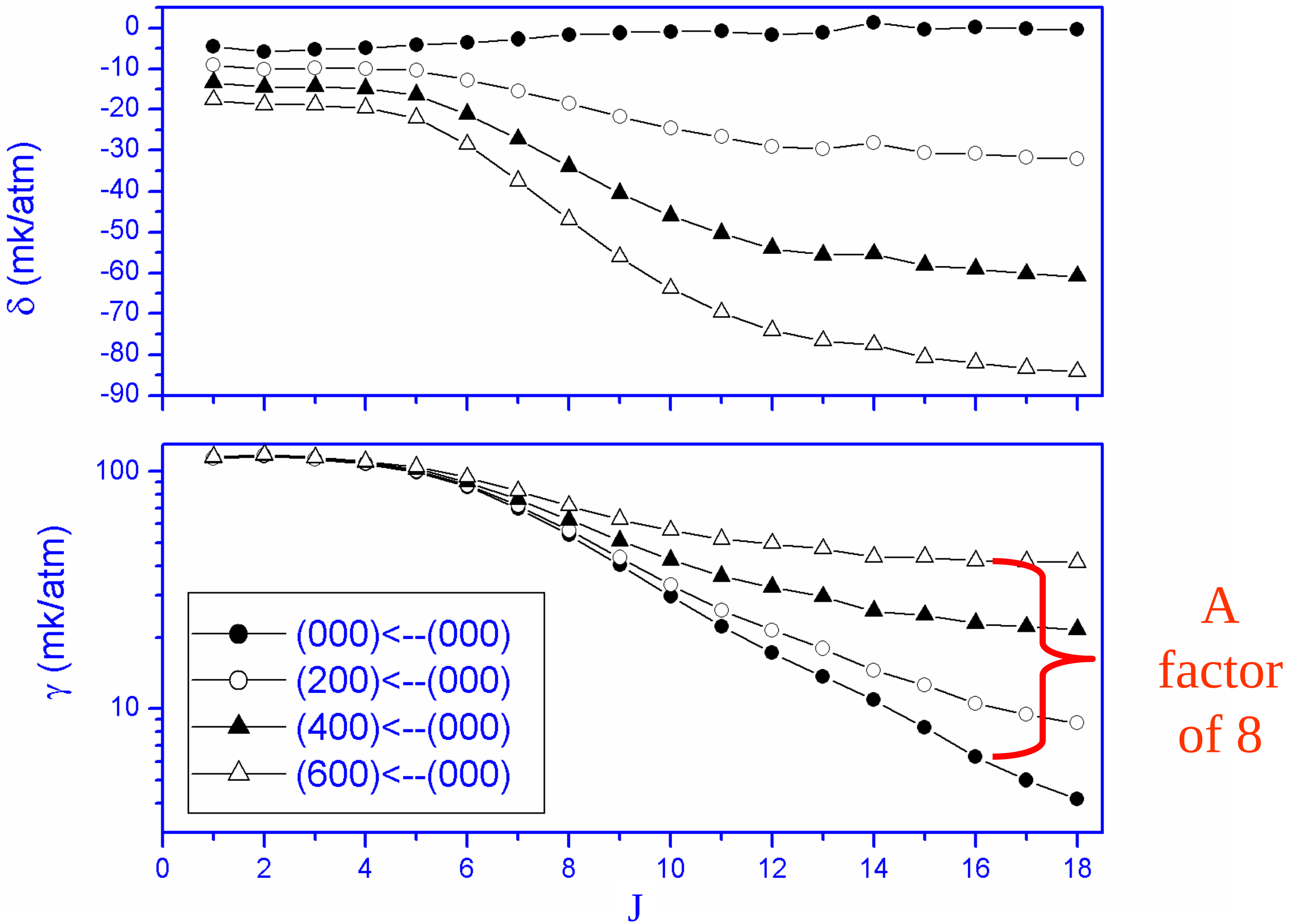
The horizontal dashed line indicates the pure dephasing contribution

Gamache and Hartmann, JQSRT **83**, 119–147 (2004).

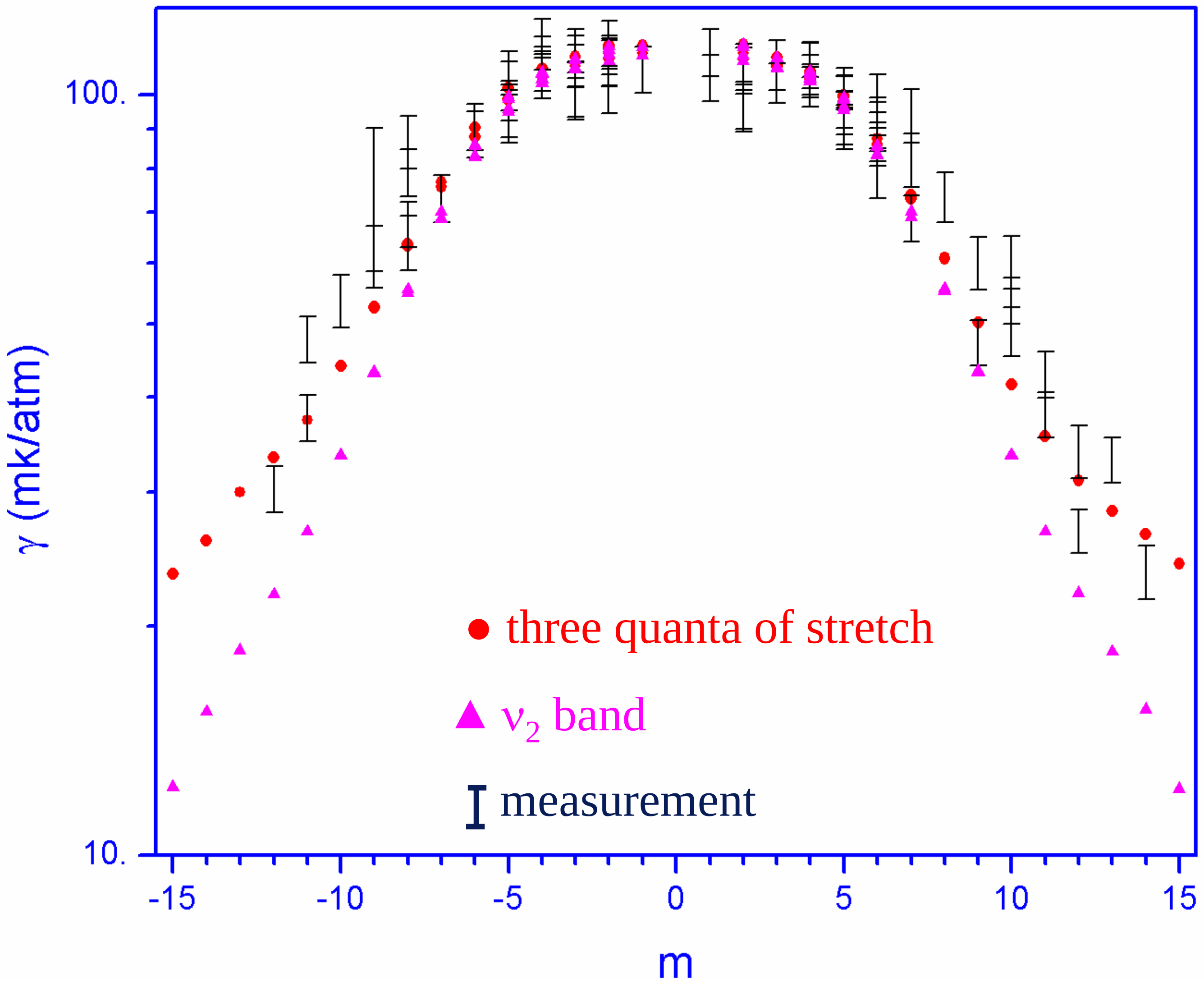
Calculated H_2O-N_2 γ and δ for the $J\text{-}1_{0,J-1} \leftarrow J_{1,J}$ transitions



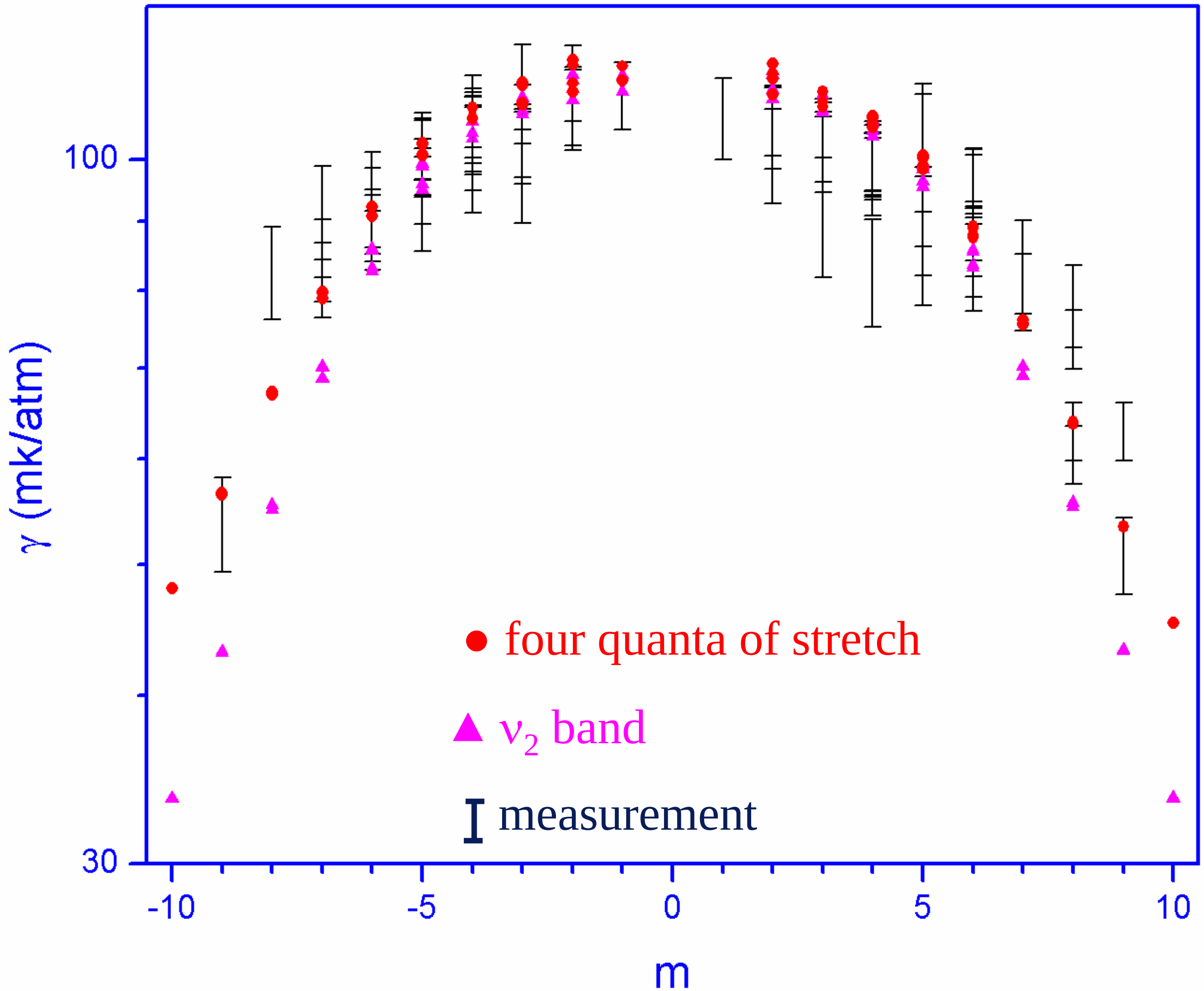
Calculated H_2O-N_2 γ and δ for the $J\text{-}1_{0,J-1} \leftarrow J_{1,J}$ transitions



Transitions with Kc=J in bands involving three quanta of stretching vibration



Transitions with Kc=J in bands involving four quanta of stretching vibration



Calculations agree well with measurement.

What can theory tell us about the temperature dependence of the half-width?

Temperature Dependence "Rule-of-thumb"

For "on resonance" collisions the temperature dependence of the half-width is given by

$$\gamma \;\alpha\; T^{-\frac{(n+4)}{2n}}$$

Interaction	n	Interaction	n
d-d	4	d-q, q-d	6
q-q	8	dispersion	10

Temperature Dependence of γ

- Power law form

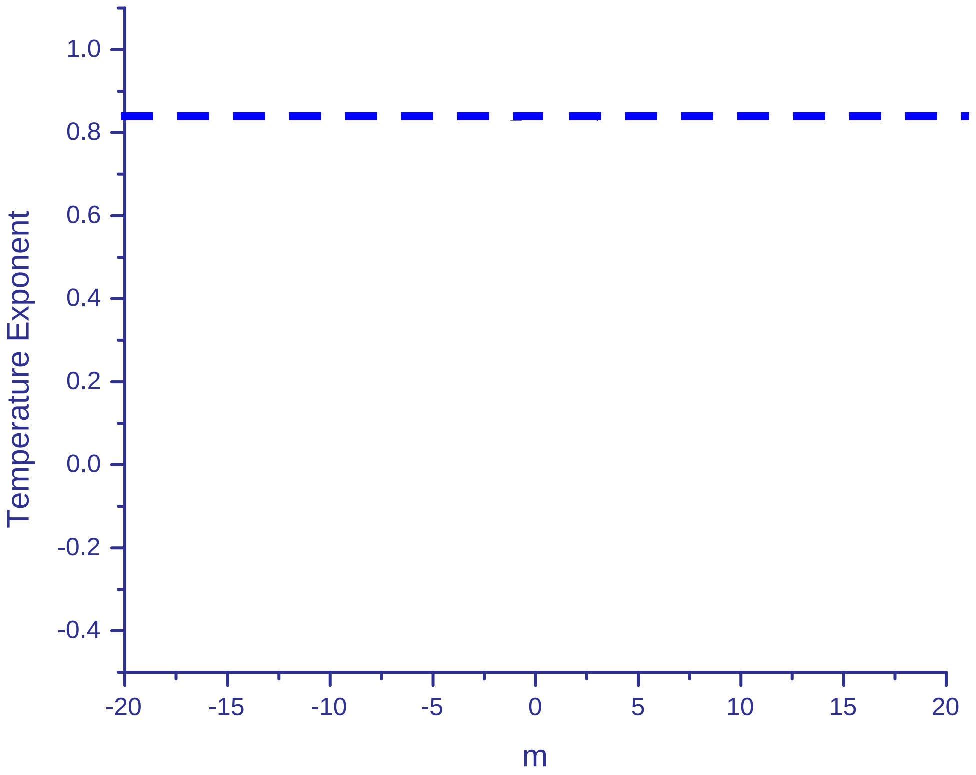
$$\gamma(T) = \gamma(T_0)\left[\frac{T_0}{T}\right]^N$$

- In practice plot (fit)

$$\ln\left\{\frac{\gamma(T)}{\gamma(T_0)}\right\} = N \ \ln\left\{\frac{T_0}{T}\right\}$$

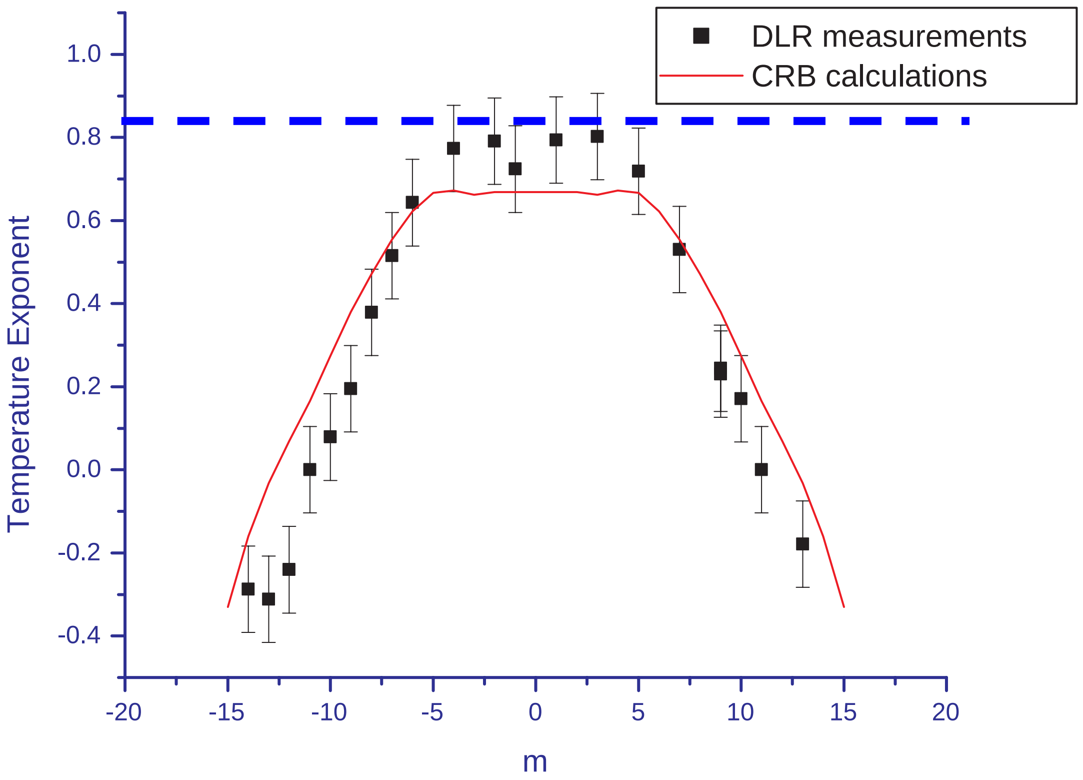
H_2O-N_2 system

"Dipole-Quadrupole" system – "rule-of-thumb" gives temperature dependence of 5/6



H_2O-N_2 system

"Dipole-Quadrupole" system – "rule-of-thumb" gives temperature dependence of 5/6

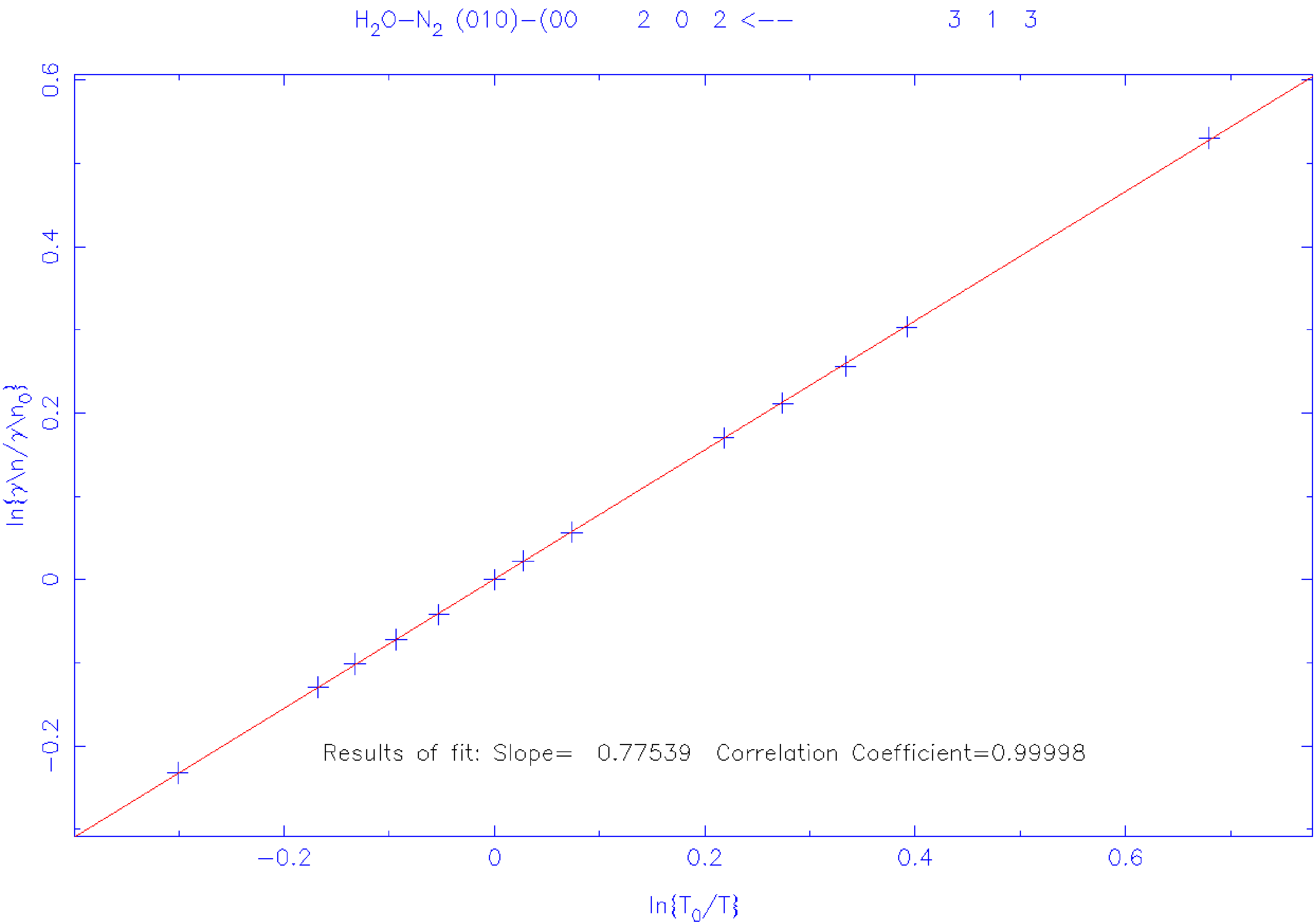


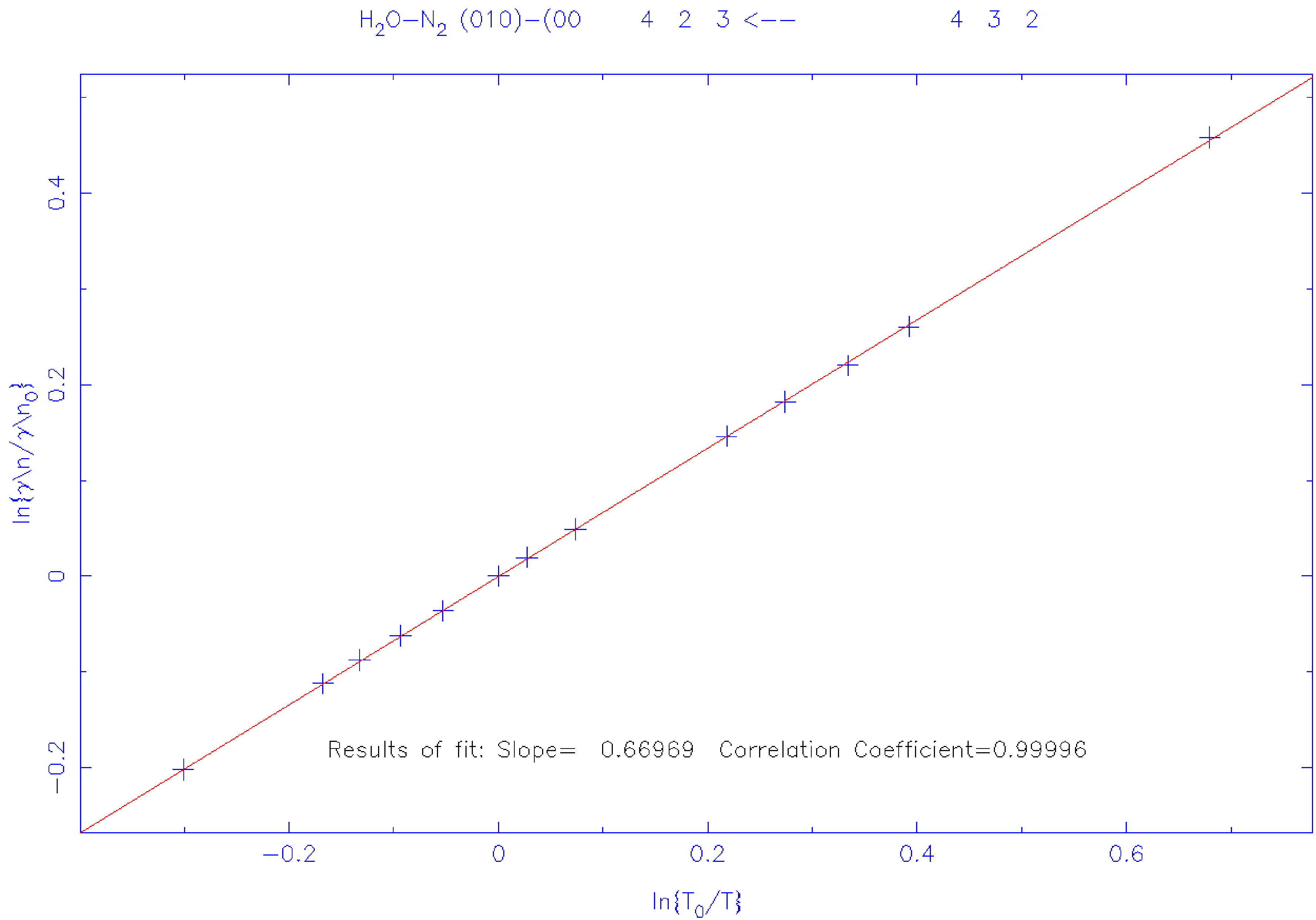
T-dependence for individual lines

13 temperatures studied from 150-400 K
150., 200., 212., 225., 238., 275.,
288., 296., 312., 325., 338., 350., 400.K

Low J”

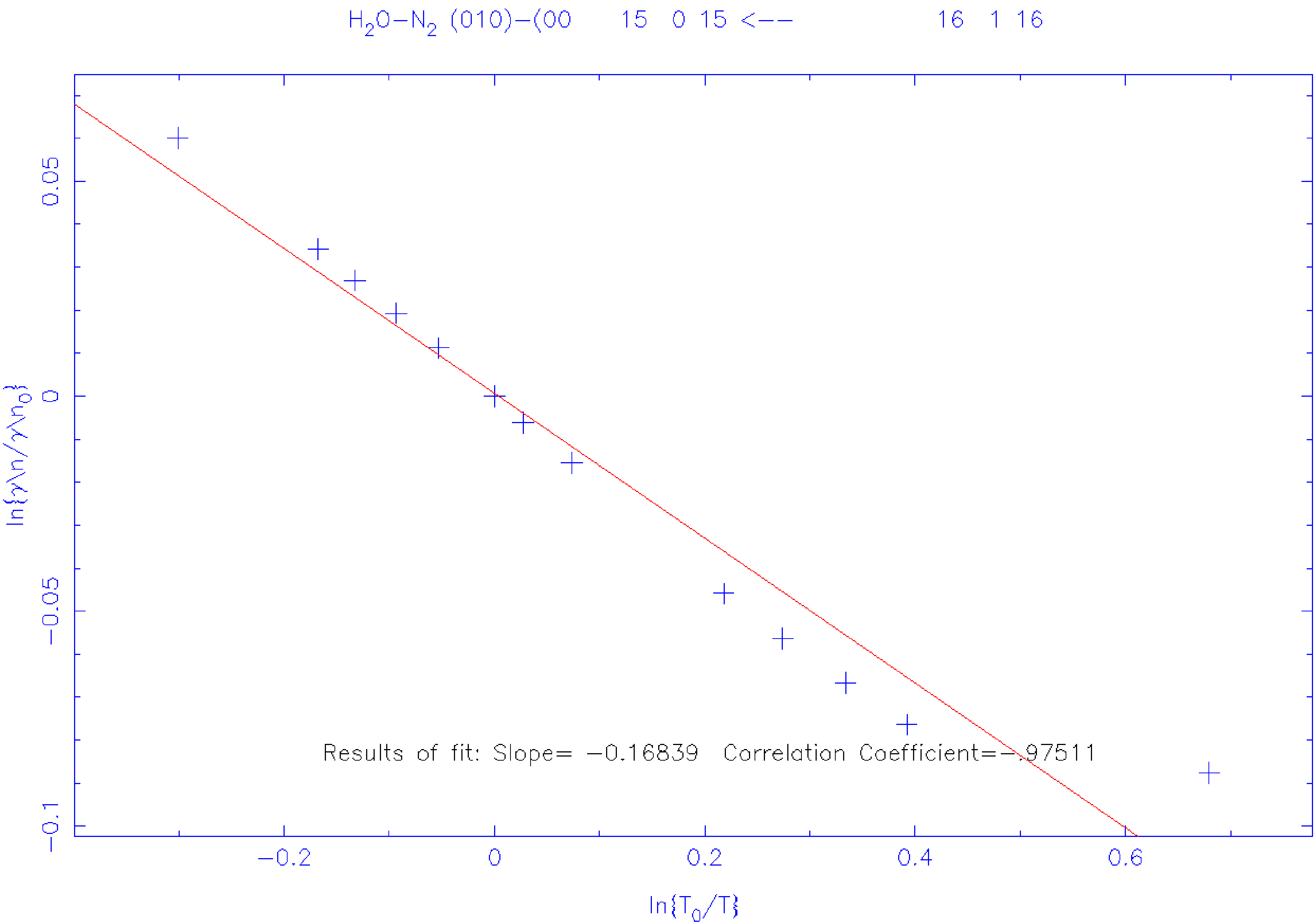
half-widths are dominated by rotational contributions (S_2, on resonance).

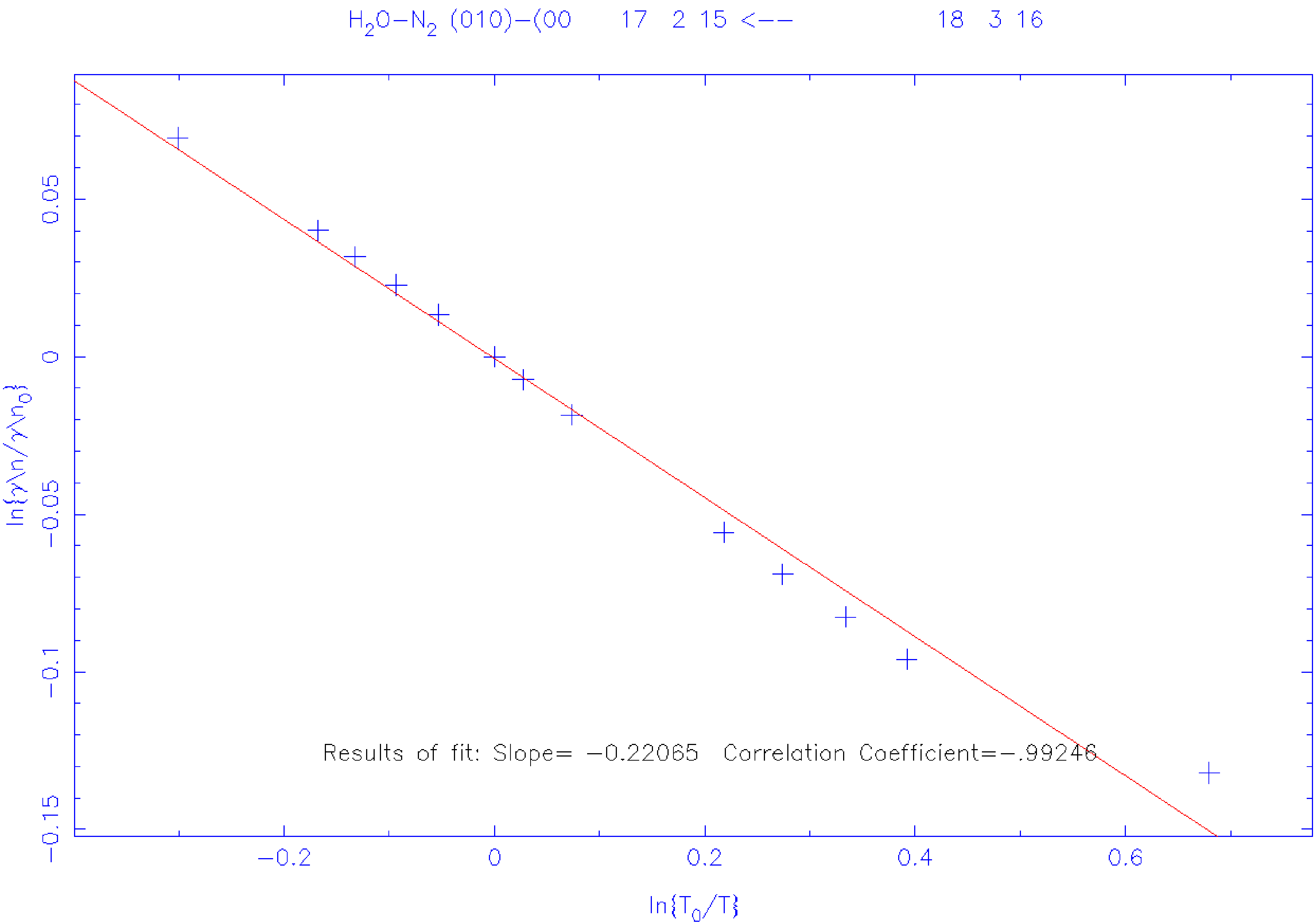

H2O–N2 (010)–(00 2 0 2 <-- 3 1 3
Results of fit: Slope= 0.77539 Correlation Coefficient=0.99998
ln{γ\n/γ\n0}
ln{T0/T}
0.6
0.4
0.2
0
−0.2
0.6
0.4
0.2
0
−0.2

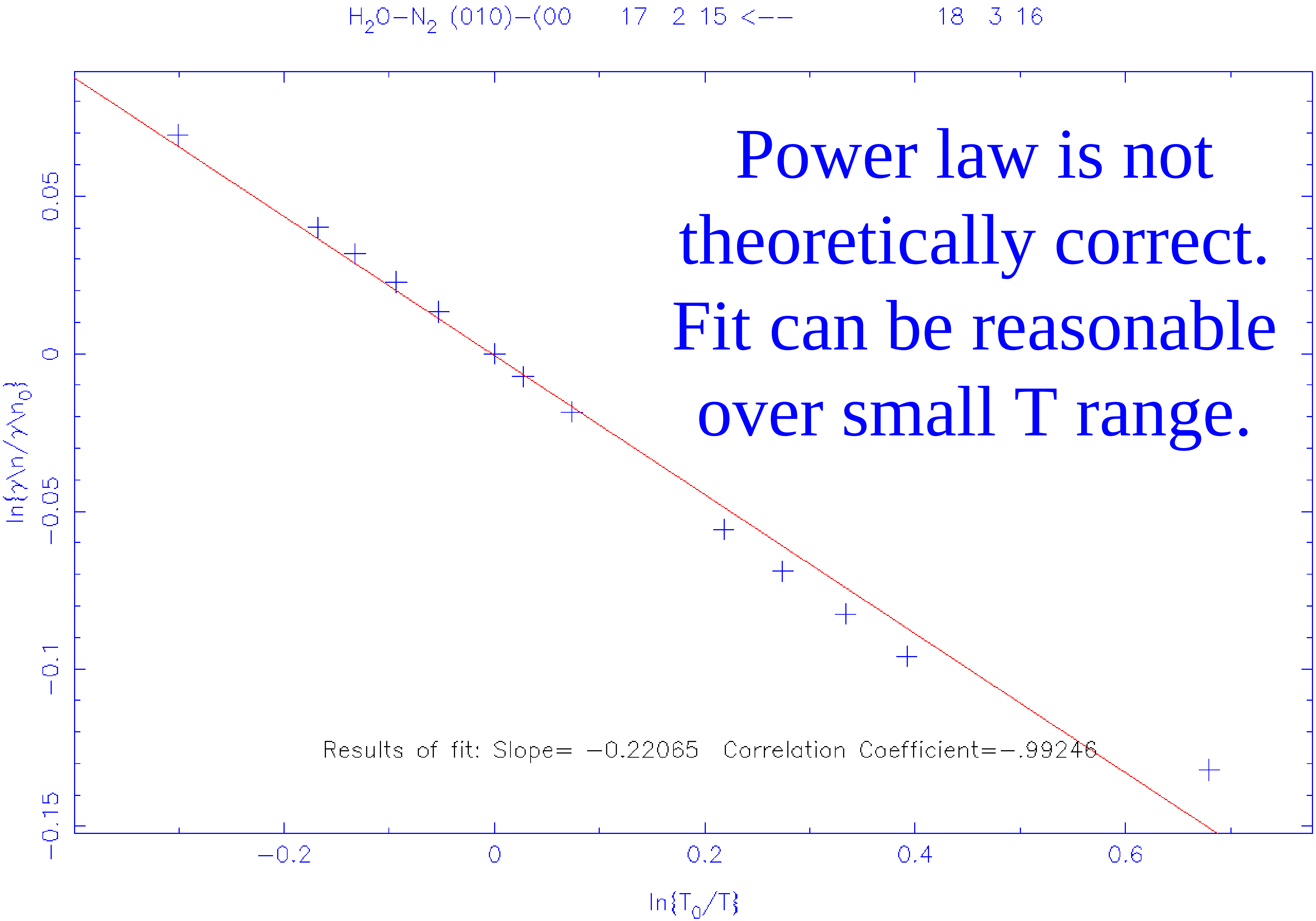

H2O-N2 (010)-(00 4 2 3 <-- 4 3 2
Results of fit: Slope= 0.66969 Correlation Coefficient=0.99996
ln{T0/T}
ln{γ\n/γ\n0}
-0.2
0
0.2
0.4
0.6

High J”

half-widths are dominated by vibrational contributions (S_1, off resonance).


H2O-N2 (010)-(00 15 0 15 <-- 16 1 16
0.05
0
-0.05
-0.1
ln{γ\n/γ\n0}
-0.2
0
0.2
0.4
0.6
ln{T0/T}
Results of fit: Slope= -0.16839 Correlation Coefficient=-.97511

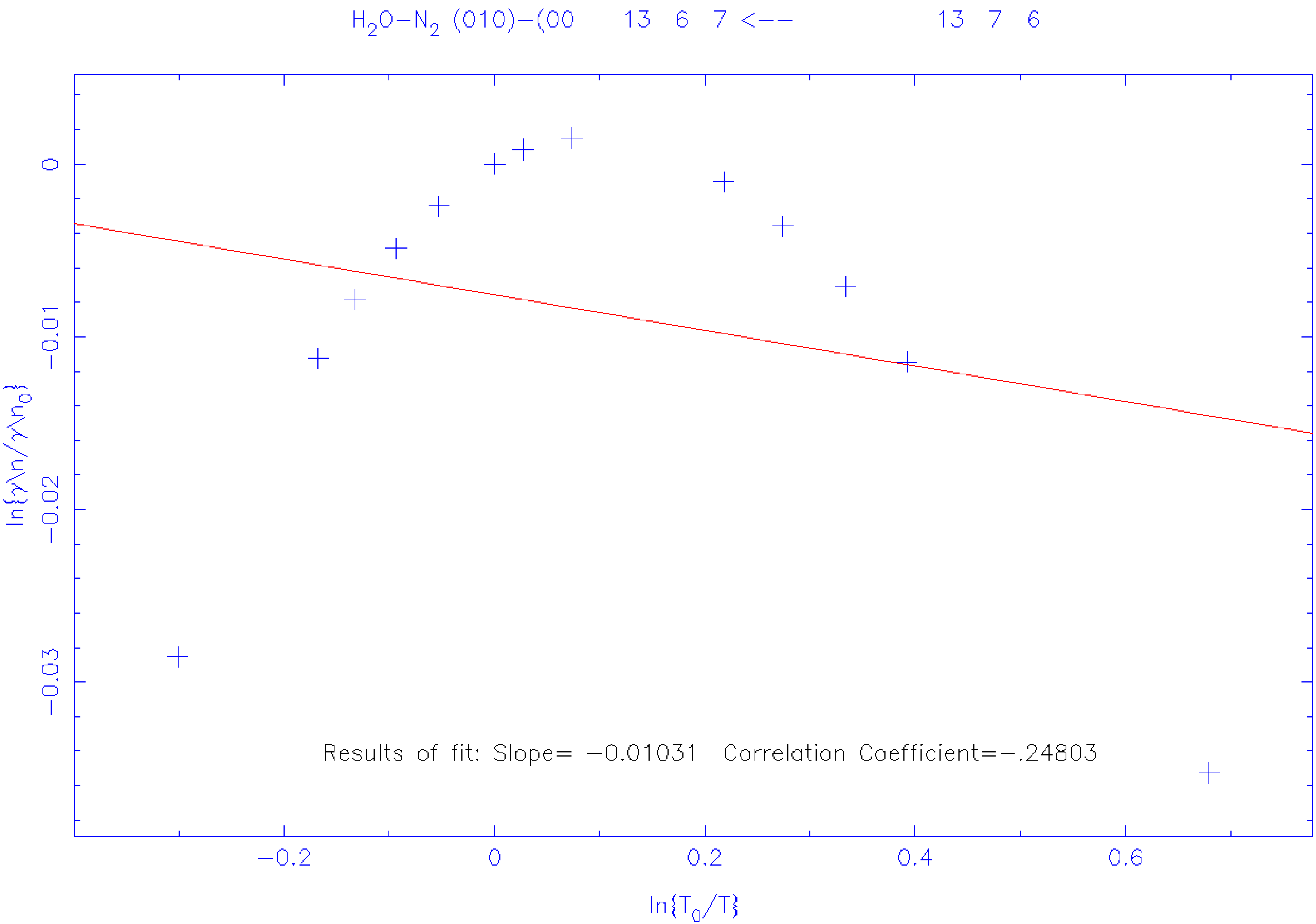

H_2O-N_2 (010)-(00 17 2 15 <-- 18 3 16
0.05
0
-0.05
-0.1
-0.15
ln{γ\n/γ\n$_0$}
-0.2
0
0.2
0.4
0.6
ln{T_0/T}
Results of fit: Slope= -0.22065 Correlation Coefficient=-.99246



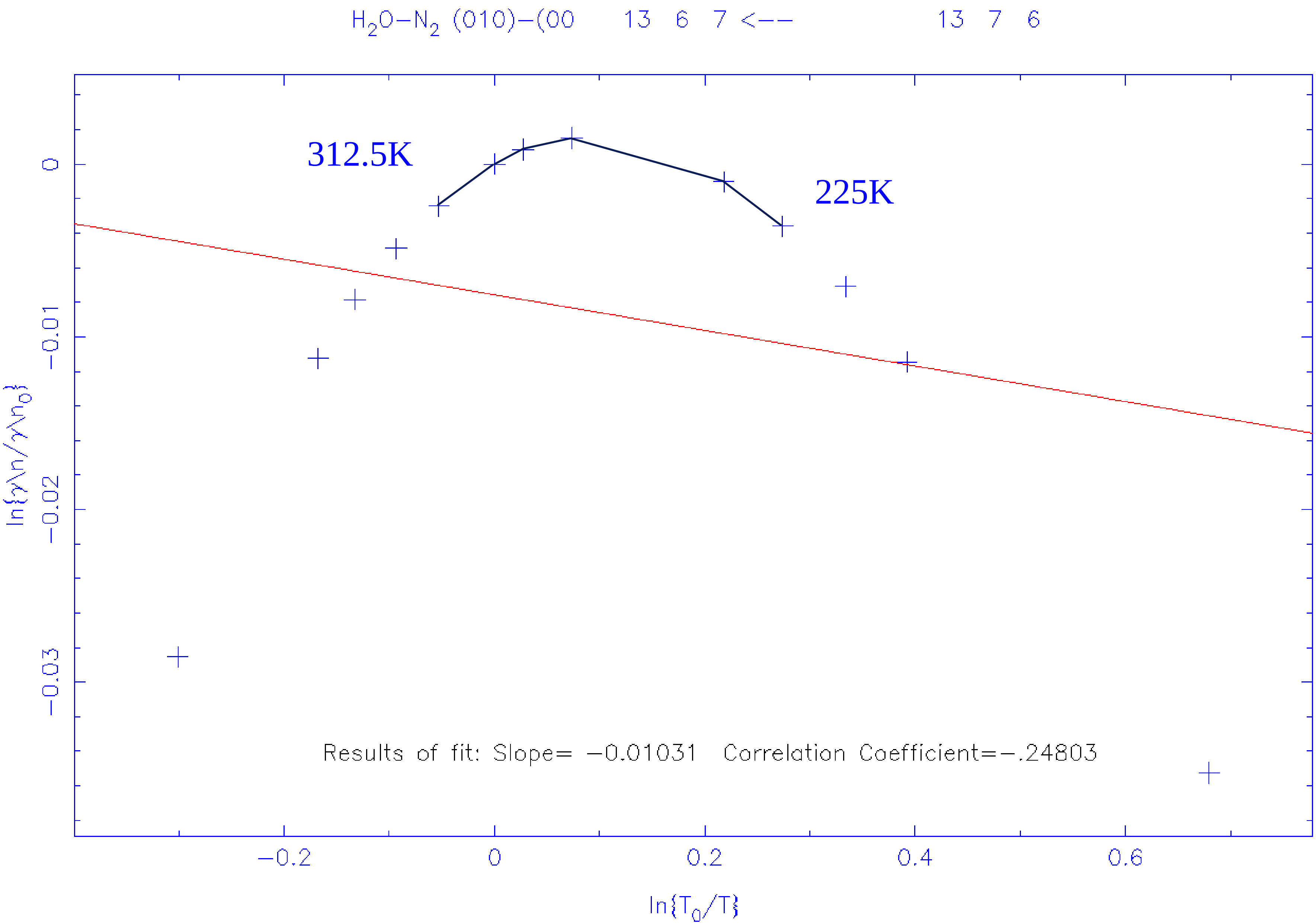
Power law is not theoretically correct.
Fit can be reasonable over small T range.

Intermediate J”

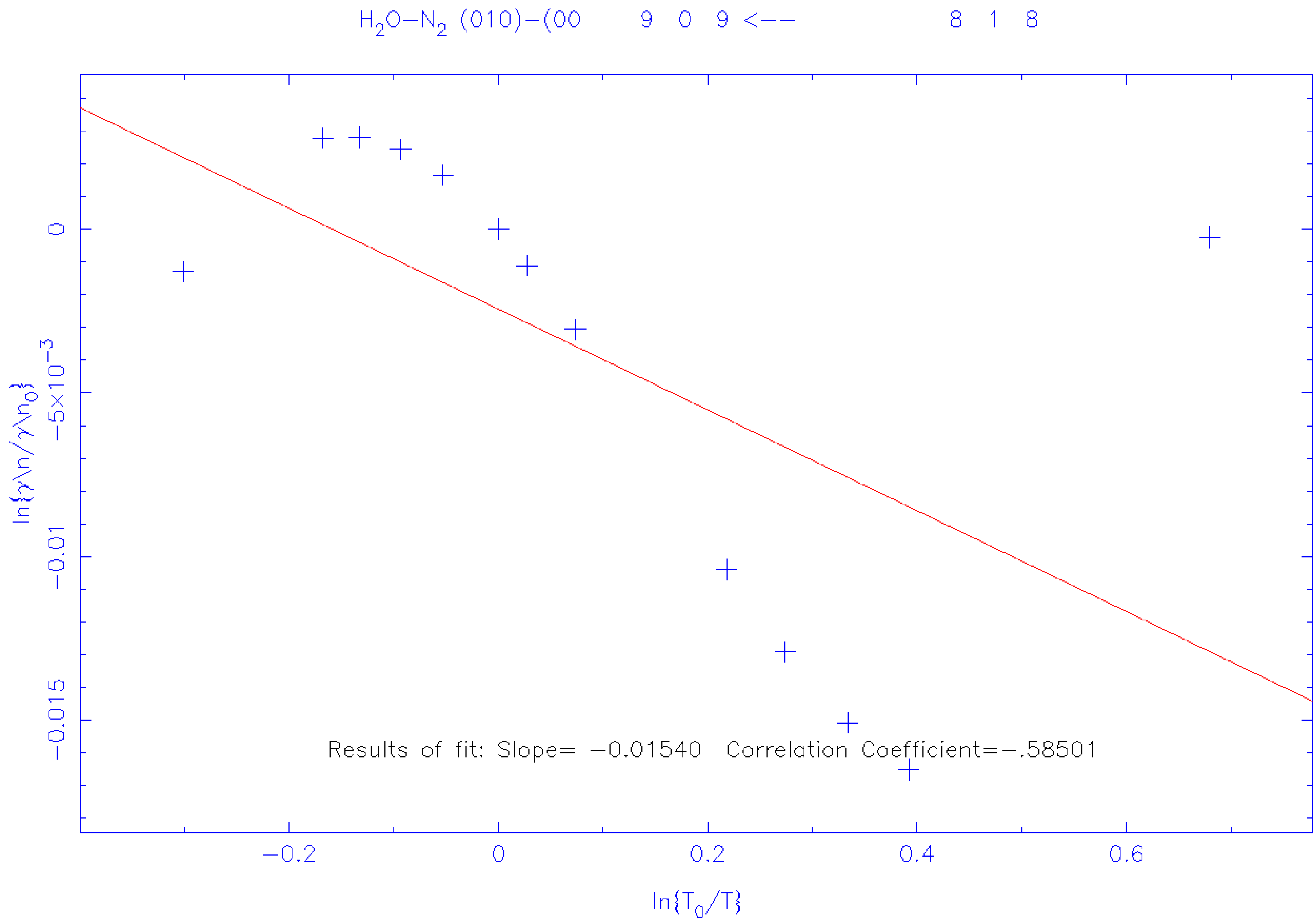
a mixture of rotational and vibrational contributions. (S_1 and S_2)



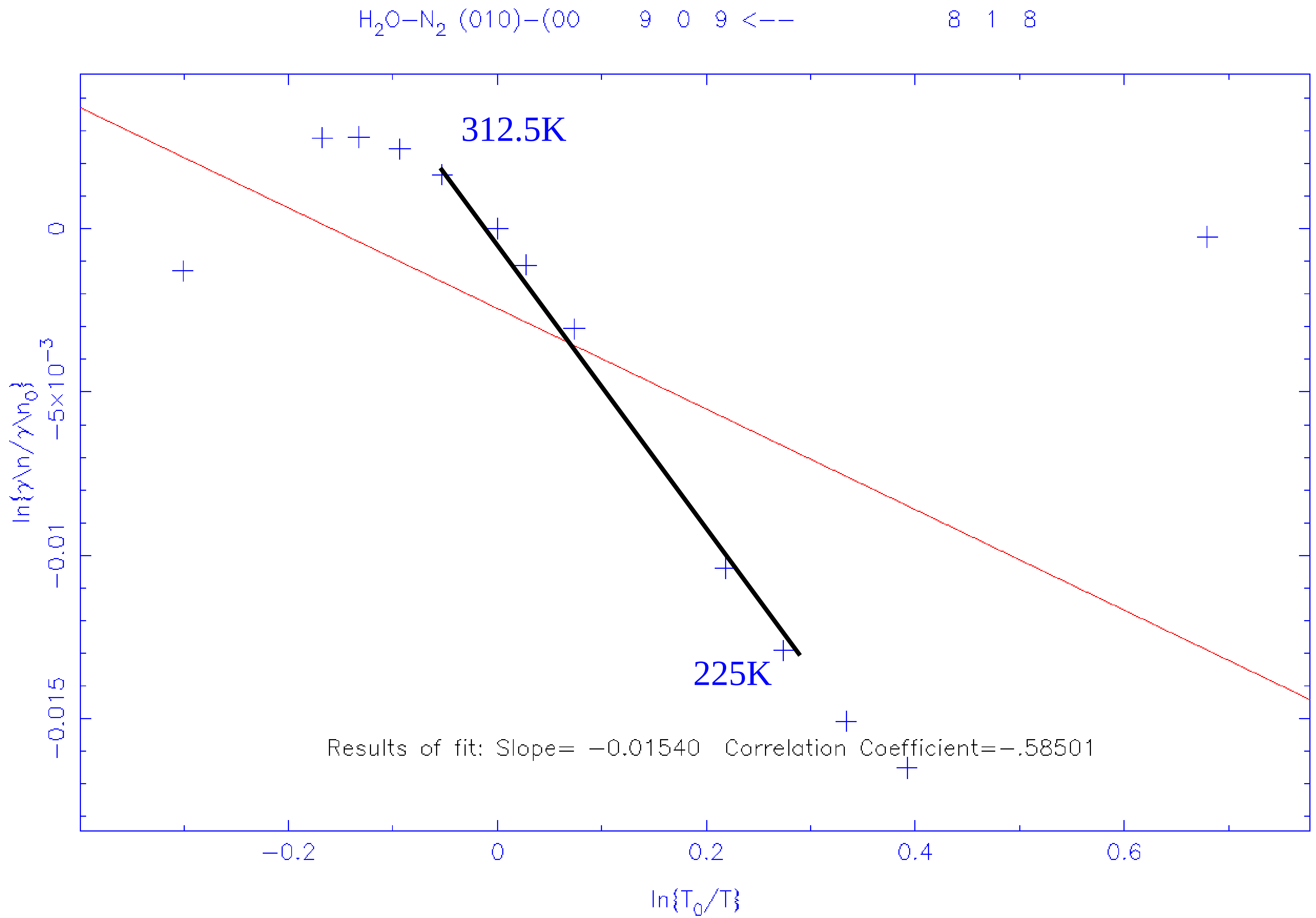
H_2O-N_2 (010)-(00 13 6 7 <-- 13 7 6
0
-0.01
-0.02
-0.03
$\ln\{\gamma\backslash n/\gamma\backslash n_0\}$
-0.2
0
0.2
0.4
0.6
$\ln\{T_0/T\}$
Results of fit: Slope= -0.01031 Correlation Coefficient=-.24803



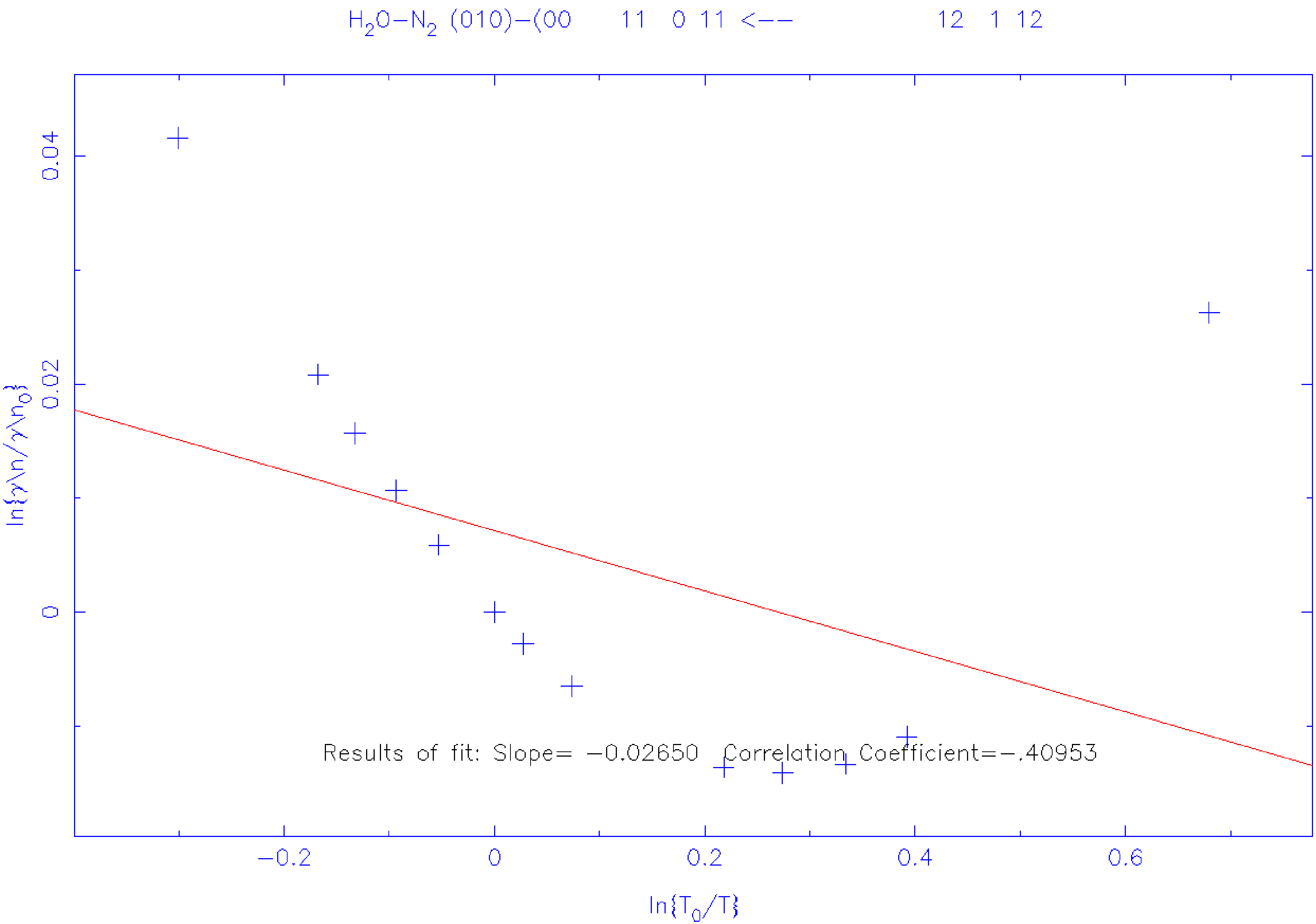
H2O-N2 (010)-(00 13 6 7 <-- 13 7 6
312.5K
225K
0
-0.01
-0.02
-0.03
ln{γ\n/γ\n0}
-0.2
0
0.2
0.4
0.6
ln{T0/T}
Results of fit: Slope= -0.01031 Correlation Coefficient=-.24803



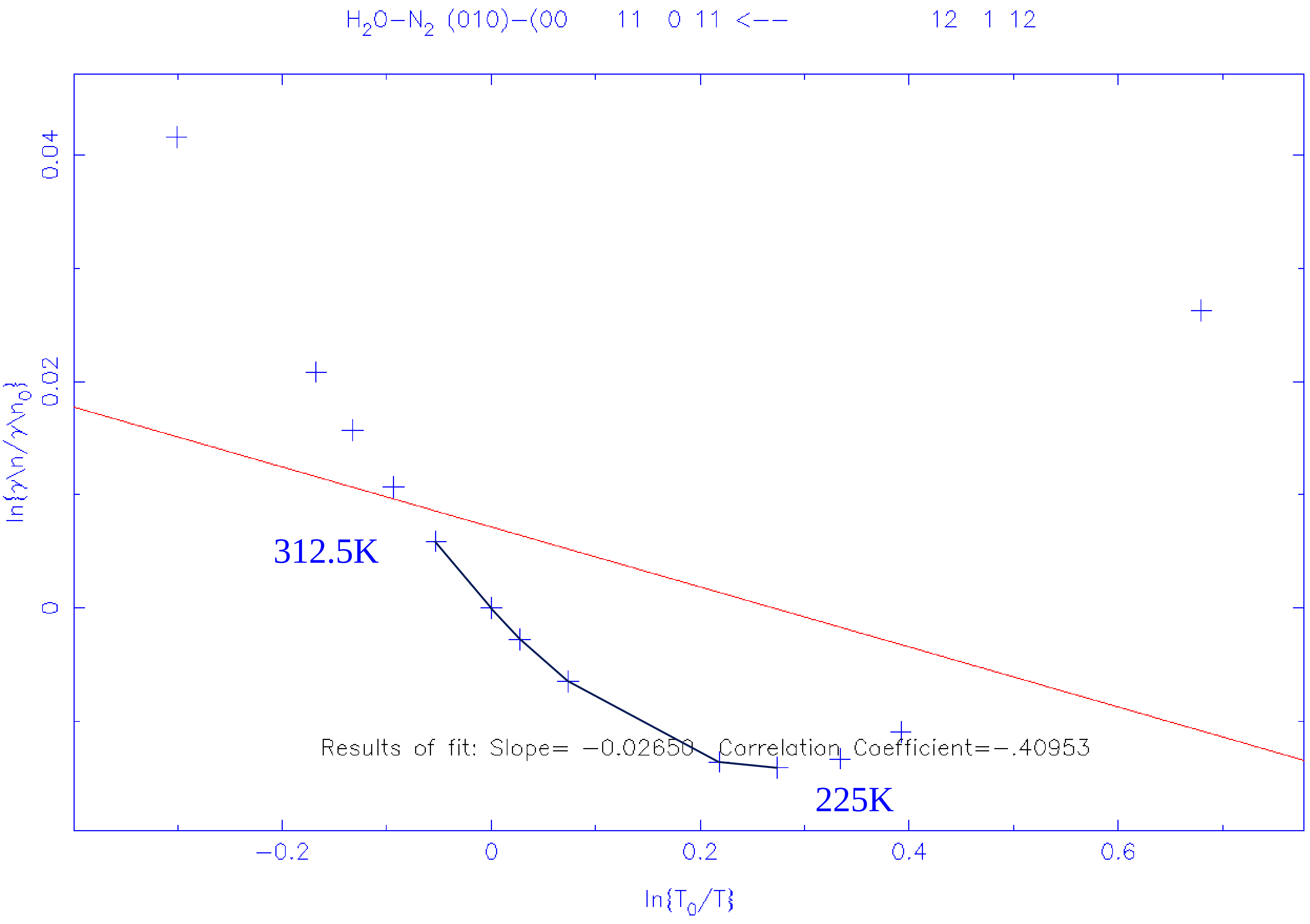
H2O-N2 (010)-(00 9 0 9 <-- 8 1 8
0
-5x10^-3
-0.01
-0.015
ln{γ\n/γ\n0}
-0.2
0
0.2
0.4
0.6
ln{T0/T}
Results of fit: Slope= -0.01540 Correlation Coefficient=-.58501



H2O–N2 (010)–(00 9 0 9 <-- 8 1 8
312.5K
225K
Results of fit: Slope= –0.01540 Correlation Coefficient=–.58501
ln{γ\n/γ\n0}
ln{T0/T}
0
–5×10–3
–0.01
–0.015
–0.2
0
0.2
0.4
0.6



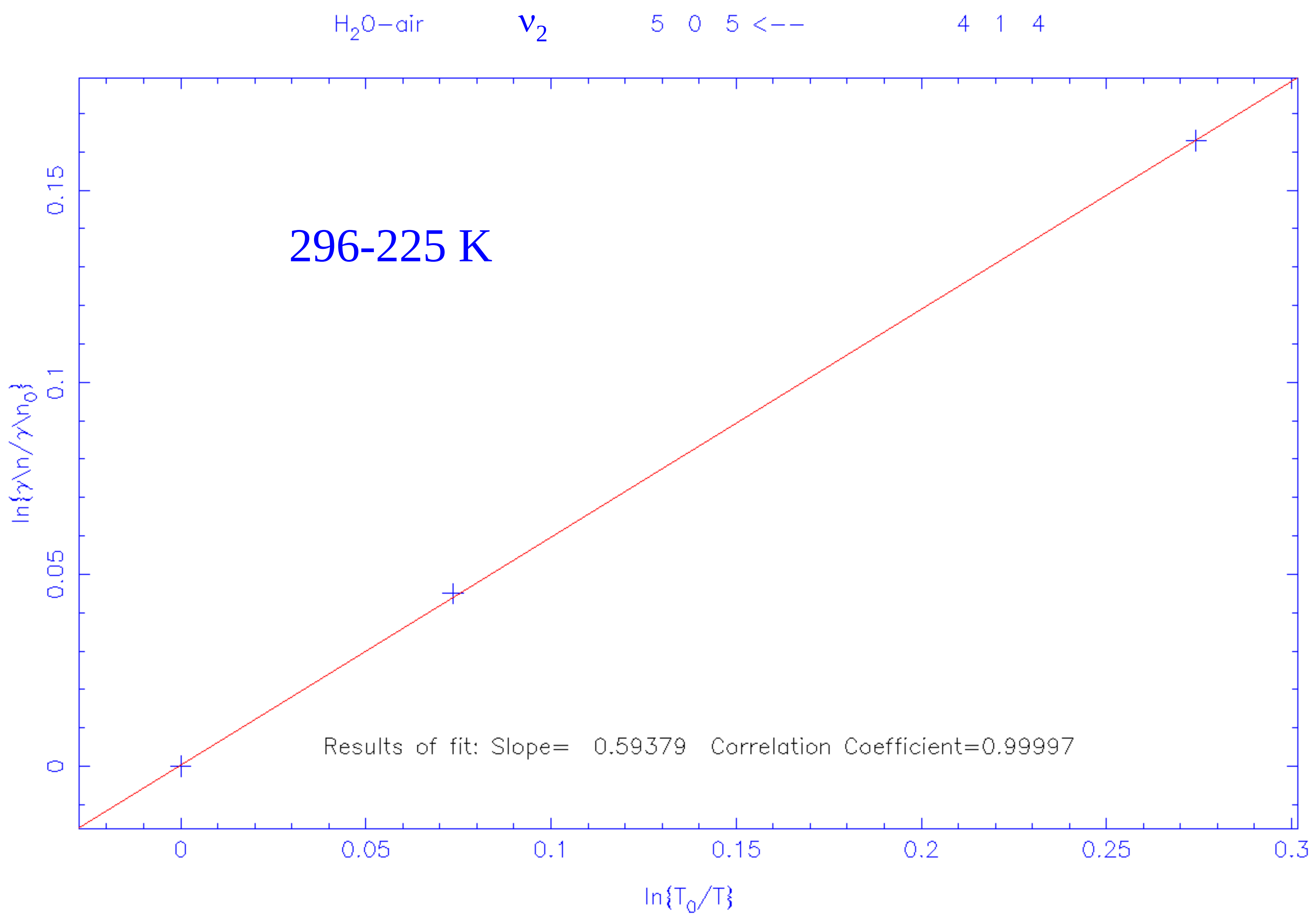
H_2O-N_2 (010)-(00 11 0 11 <-- 12 1 12
0.04
0.02
0
ln{γ\n/γ\n$_0$}
-0.2
0
0.2
0.4
0.6
ln{T_0/T}
Results of fit: Slope= -0.02650 Correlation Coefficient=-.40953



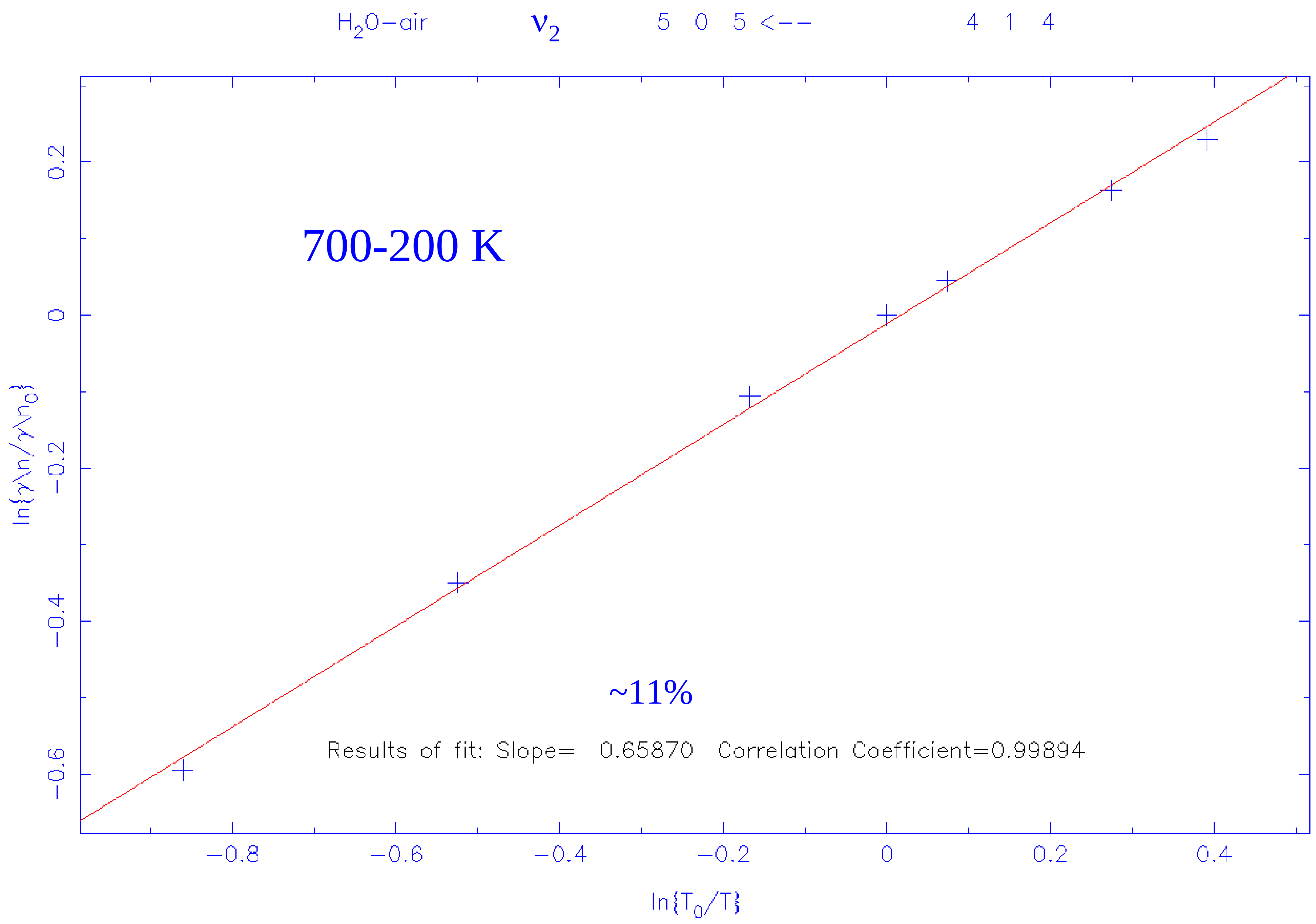
H2O-N2 (010)-(00 11 0 11 <-- 12 1 12
0.04
0.02
0
ln{γ\n/γ\n0}
312.5K
225K
Results of fit: Slope= -0.02650 Correlation Coefficient=-.40953
-0.2
0
0.2
0.4
0.6
ln{T0/T}

Temperature Range of the fit

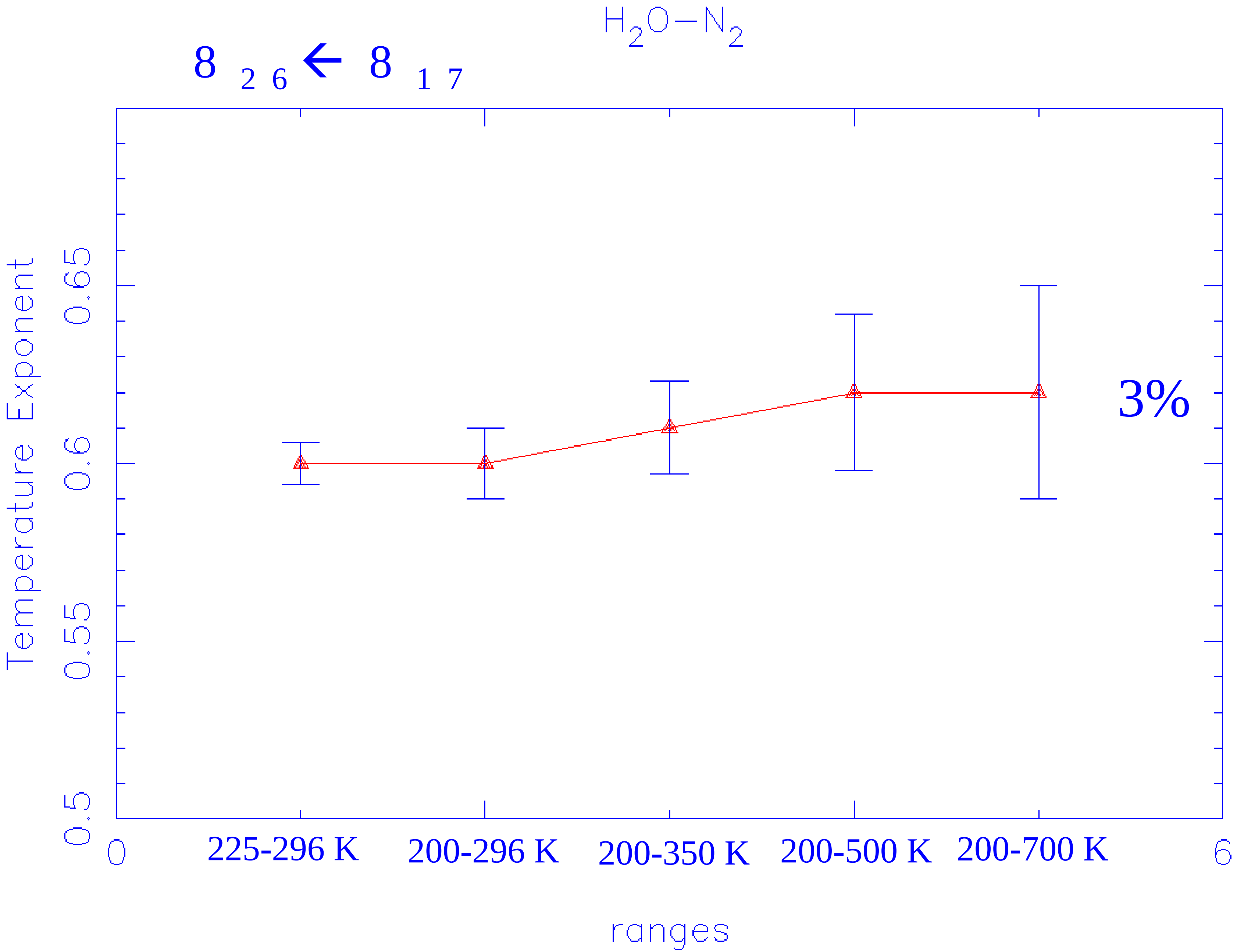
The derived temperature exponents are dependent on the range of the fit.



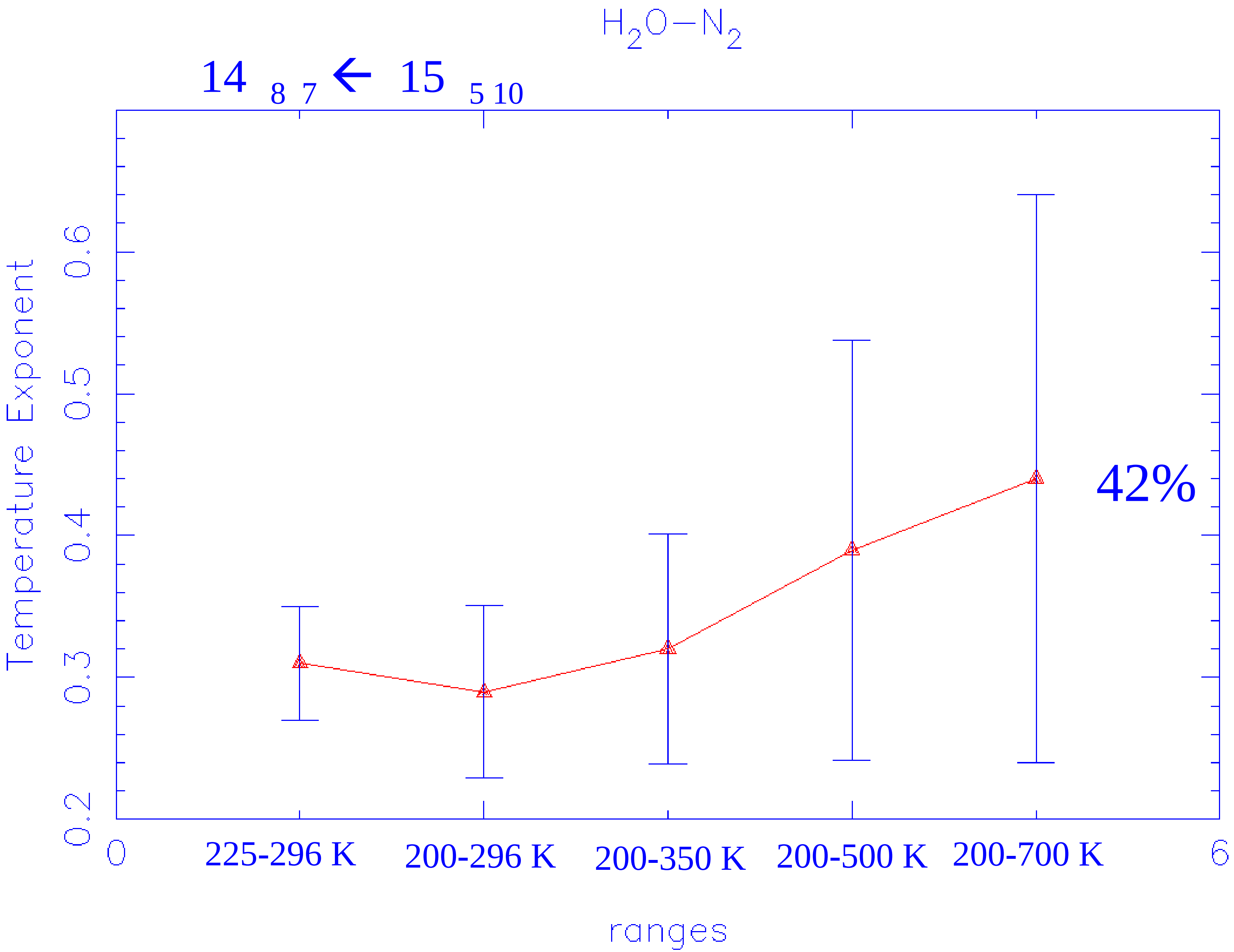
H_2O-air
ν_2
5 0 5 <--- 4 1 4
296-225 K
Results of fit: Slope= 0.59379 Correlation Coefficient=0.99997
0 0.05 0.1 0.15 0.2 0.25 0.3
0 0.05 0.1 0.15
ln{T0/T}
ln{γ\n/γ\n0}



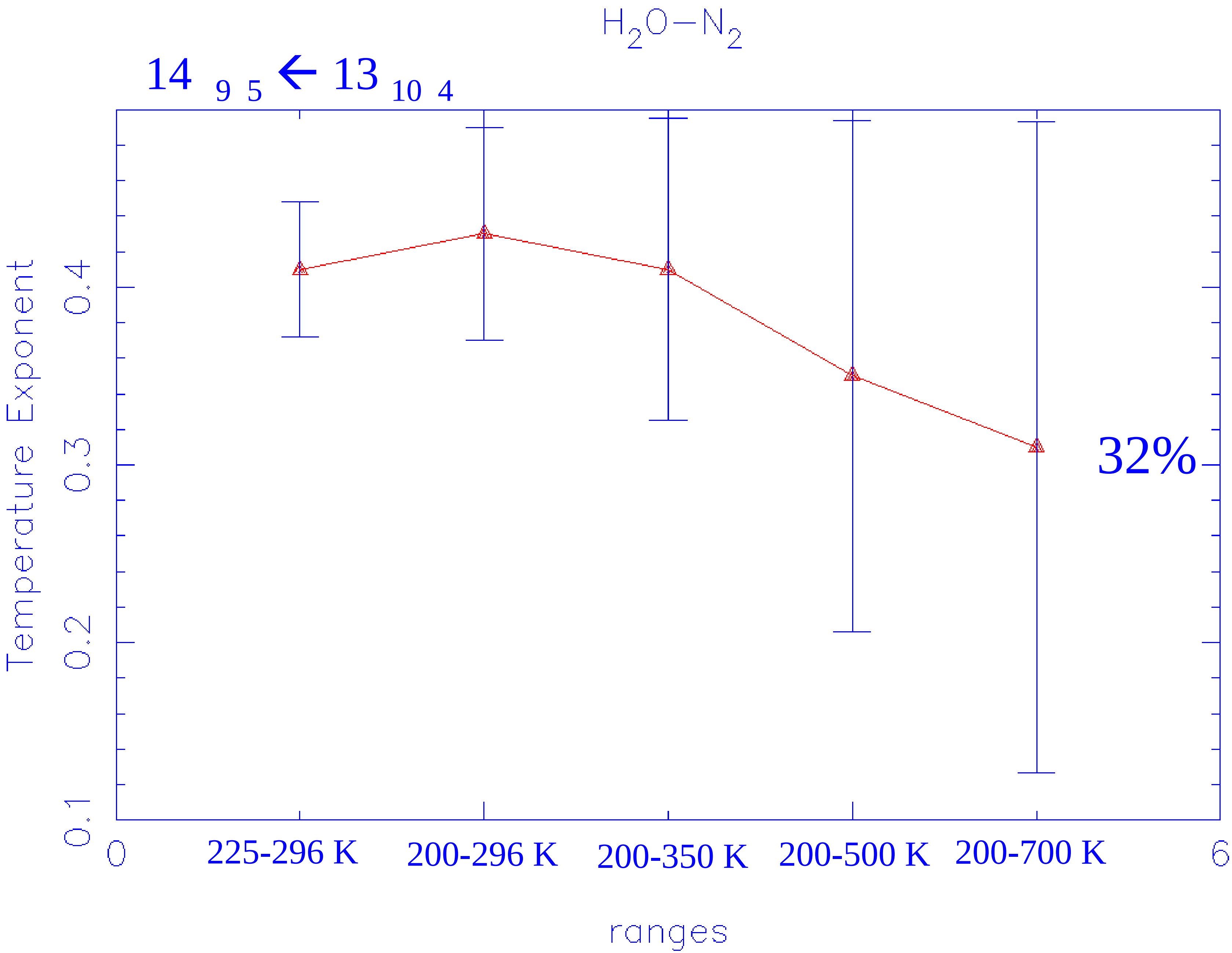
H2O-air
ν2
5 0 5 <-- 4 1 4
700-200 K
~11%
Results of fit: Slope= 0.65870 Correlation Coefficient=0.99894
ln{γ\n/γ\n0}
ln{T0/T}
0.2
0
−0.2
−0.4
−0.6
−0.8
−0.6
−0.4
−0.2
0
0.2
0.4

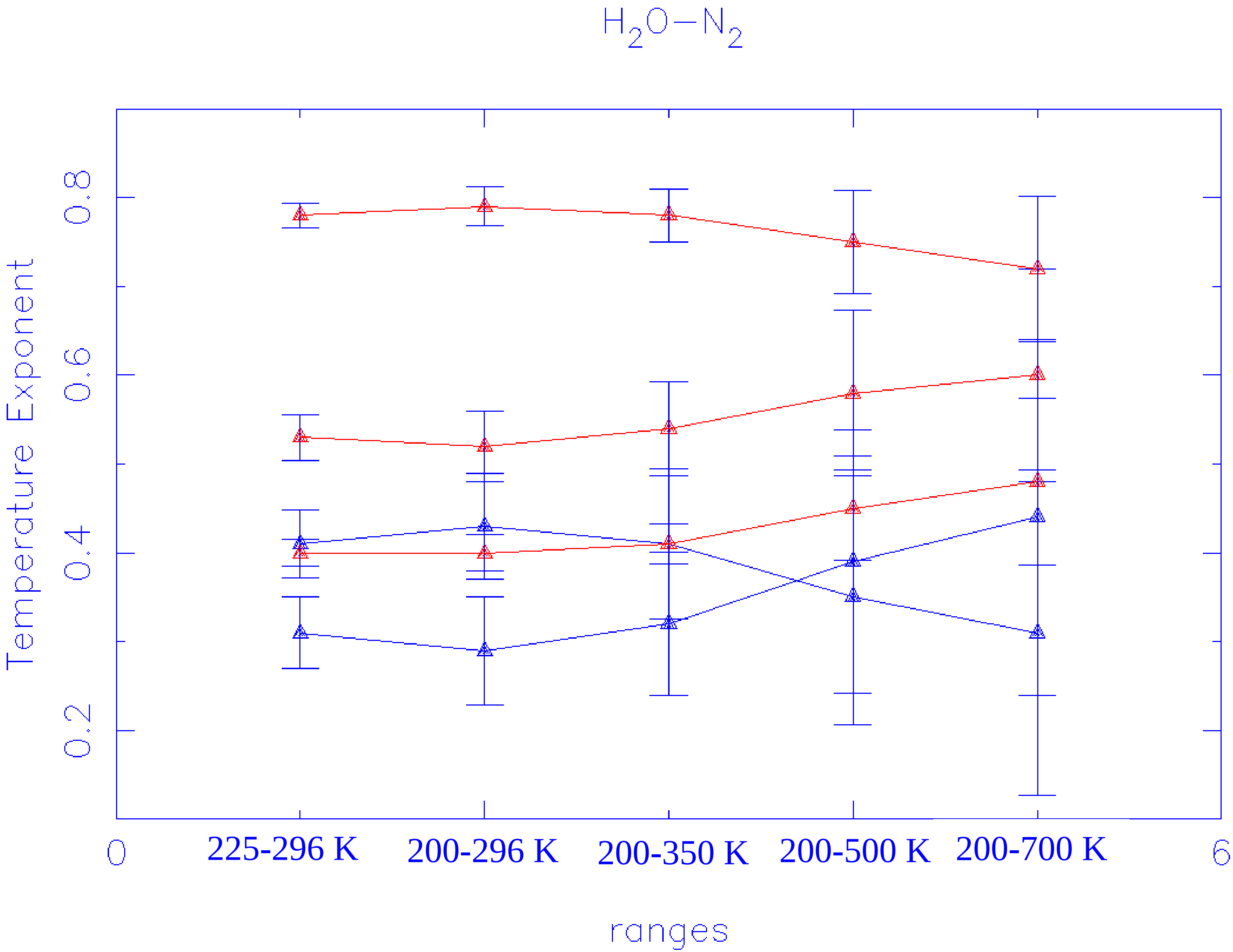


H_2O-N_2
$8_{26} \leftarrow 8_{17}$
Temperature Exponent
0.5
0.55
0.6
0.65
0
225-296 K
200-296 K
200-350 K
200-500 K
200-700 K
6
ranges
3%



H_2O-N_2
14 8 7 ← 15 5 10
Temperature Exponent
0.2
0.3
0.4
0.5
0.6
0
225-296 K
200-296 K
200-350 K
200-500 K
200-700 K
6
ranges
42%


H2O—N2
14 9 5 ← 13 10 4
Temperature Exponent
0.1
0.2
0.3
0.4
0
225-296 K
200-296 K
200-350 K
200-500 K
200-700 K
6
ranges
32%



H2O—N2
Temperature Exponent
0.2
0.4
0.6
0.8
0
225-296 K
200-296 K
200-350 K
200-500 K
200-700 K
6
ranges

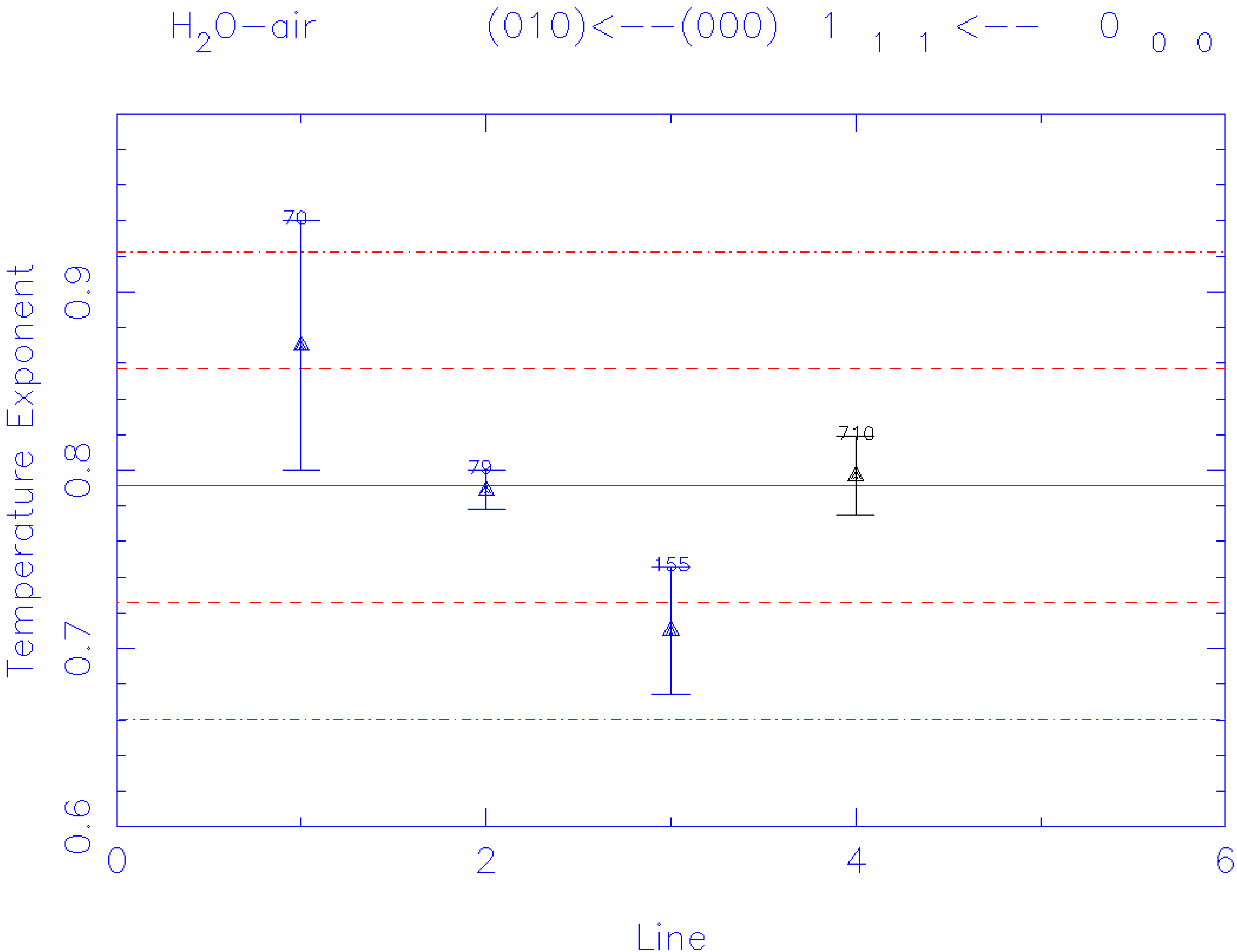
Comparison with measurement

Calculations are Ref 710, fit to 4 temperatures: 200, 225, 275, 296 K

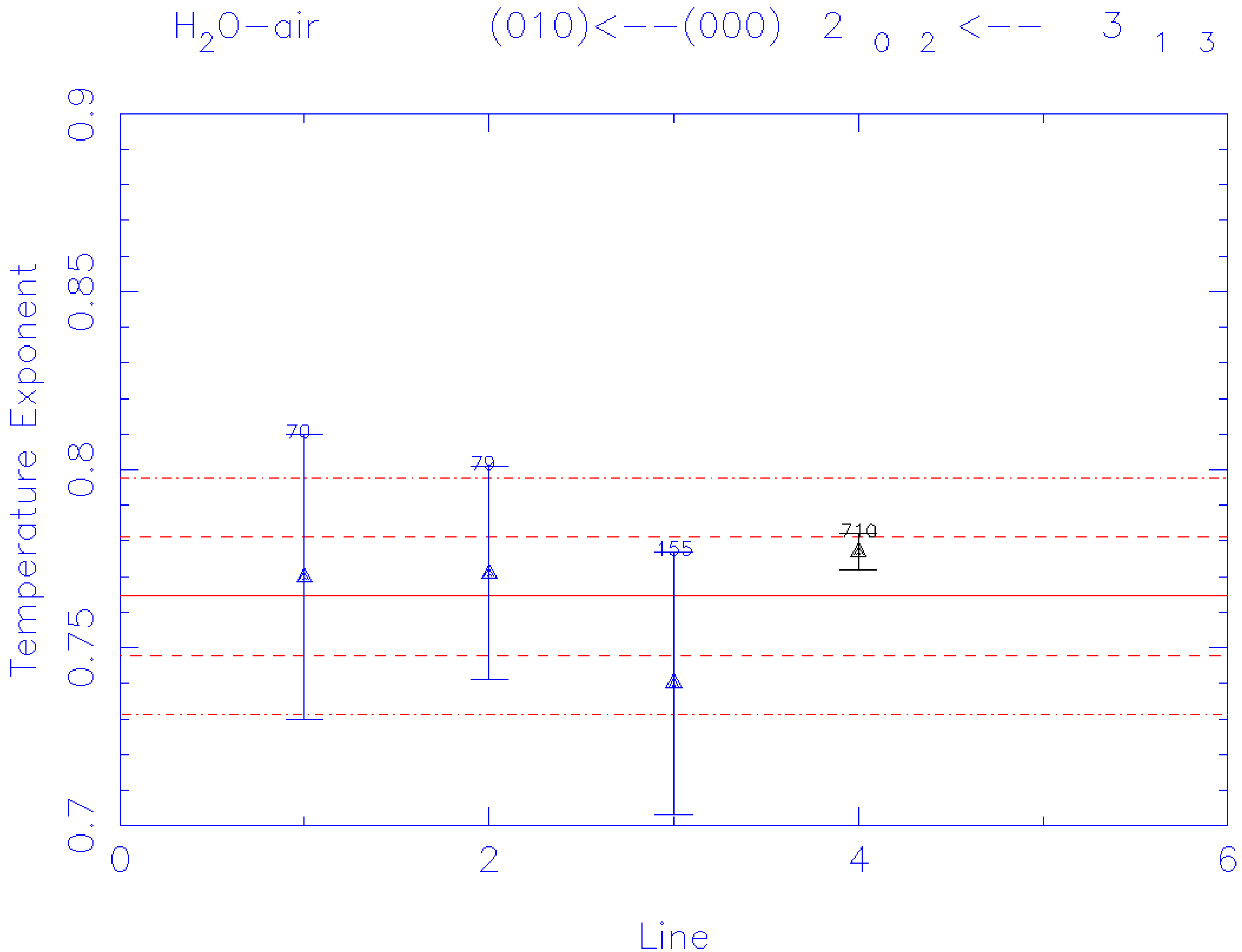
Ref 70 Remedios, J. J., PhD University of Oxford, (1990)

Ref 79 Q. Zou and P. Varanasi, P., J. Quant. Spectrosc. Radiat. Transfer, **82,** 45-98 (2003).

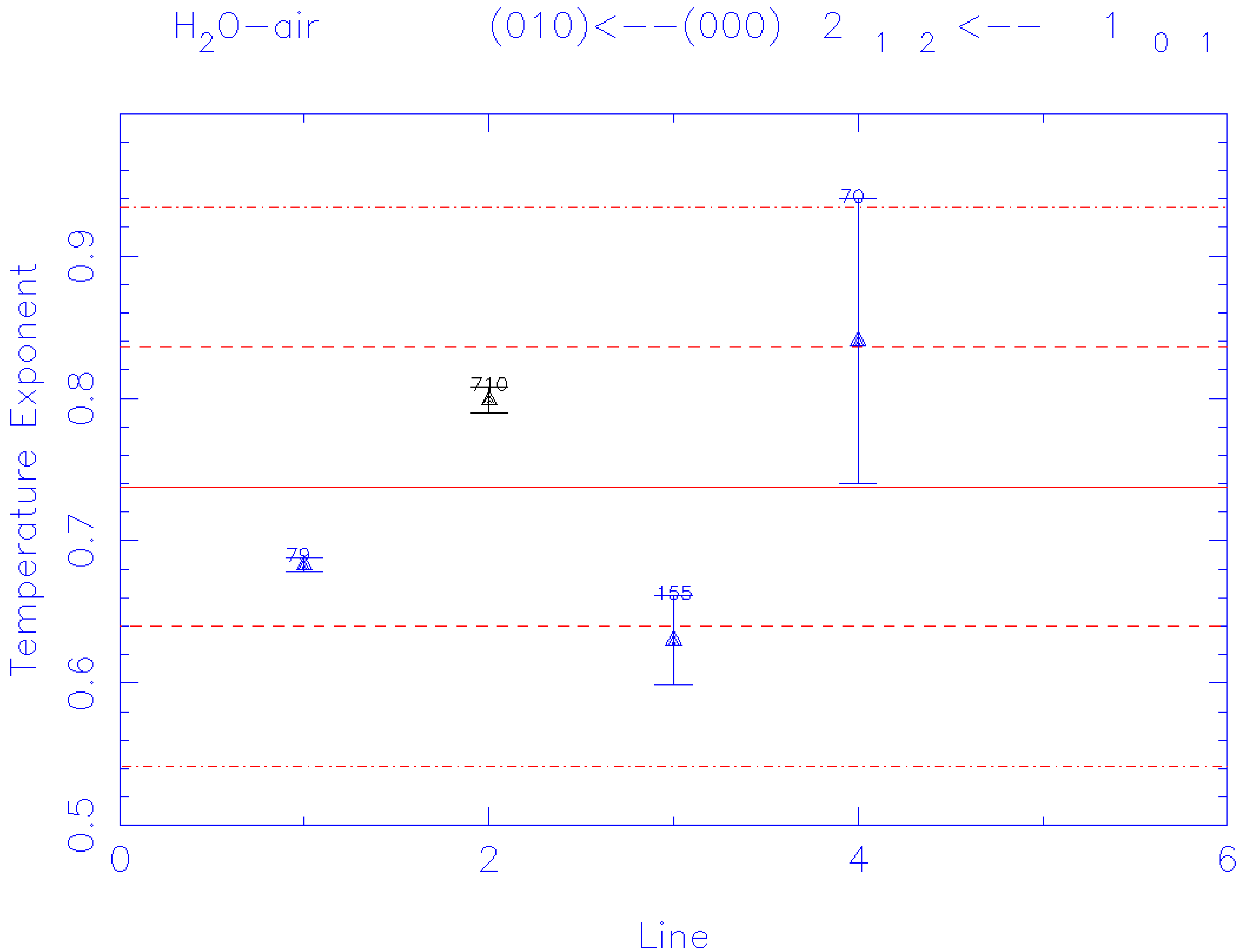
Ref 155 M. Birk and G. Wagner, DLR, Private Communication, 2006. (5% error bar added)



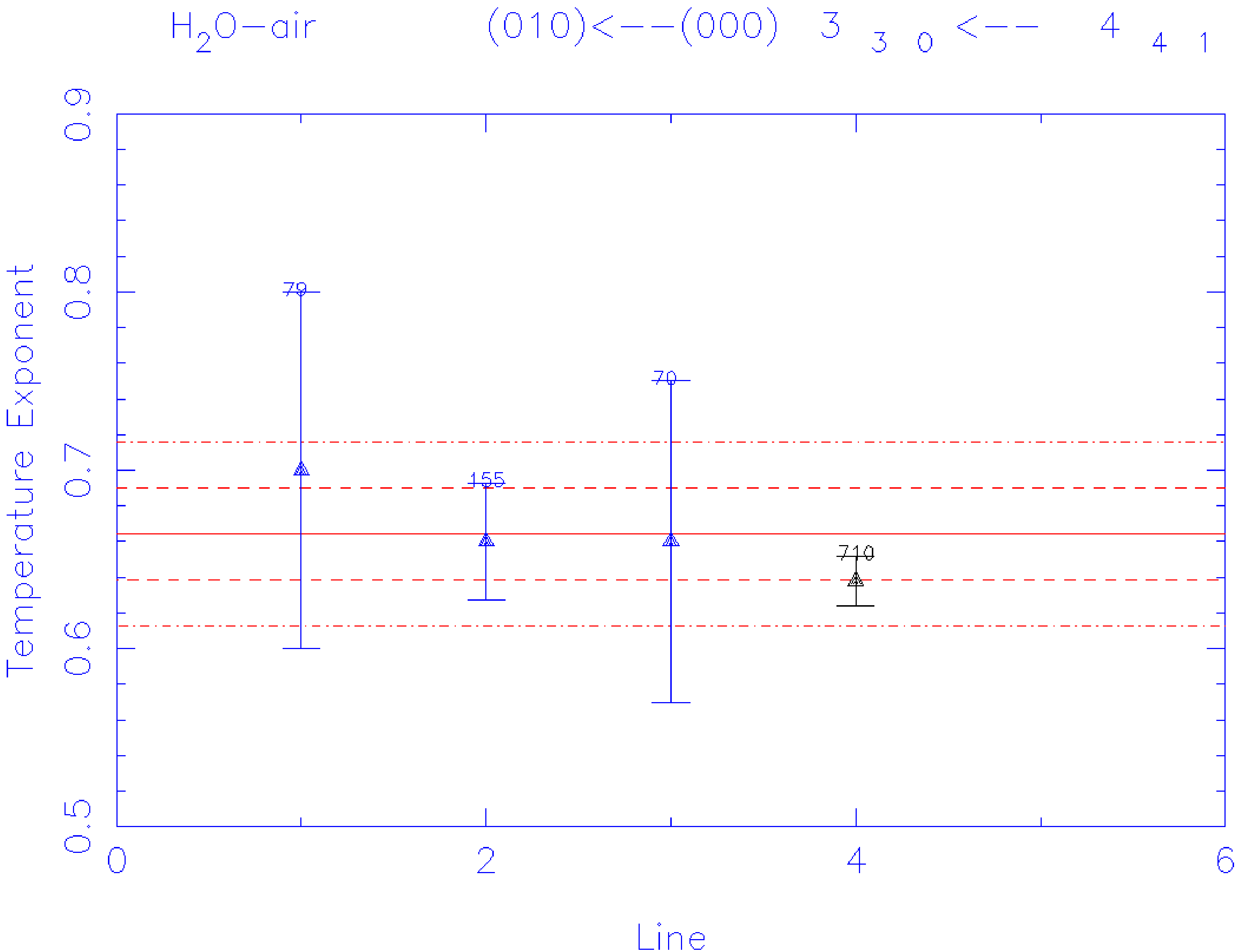
H2O−air
(010)<−−(000) 1 1 1 <−− 0 0 0
Temperature Exponent
0.6
0.7
0.8
0.9
0
2
4
6
Line
70
70
155
710



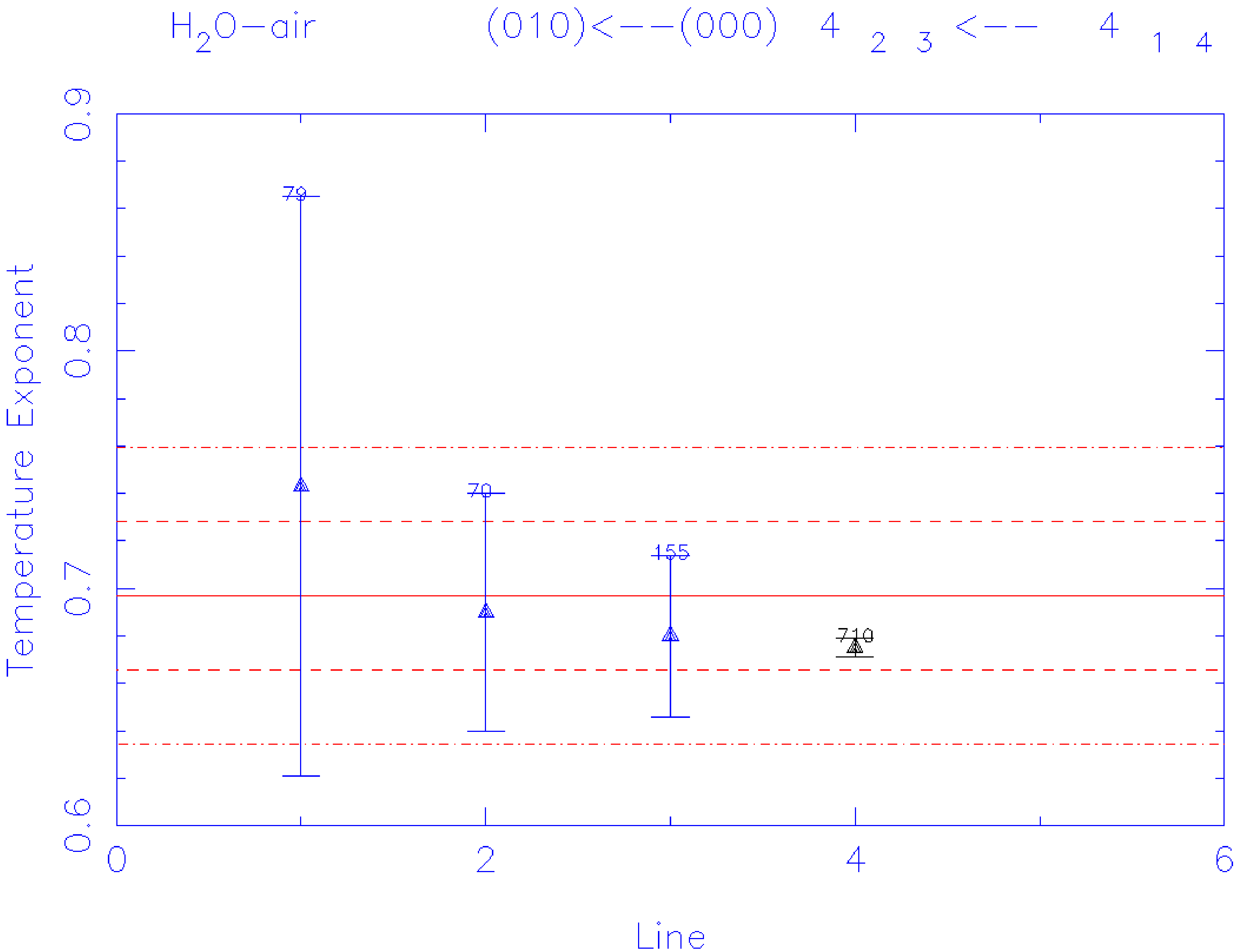
H_2O–air
(010)<−−(000) 2 0 2 <−− 3 1 3
Temperature Exponent
0.7
0.75
0.8
0.85
0.9
0
2
4
6
Line
70
70
155
710



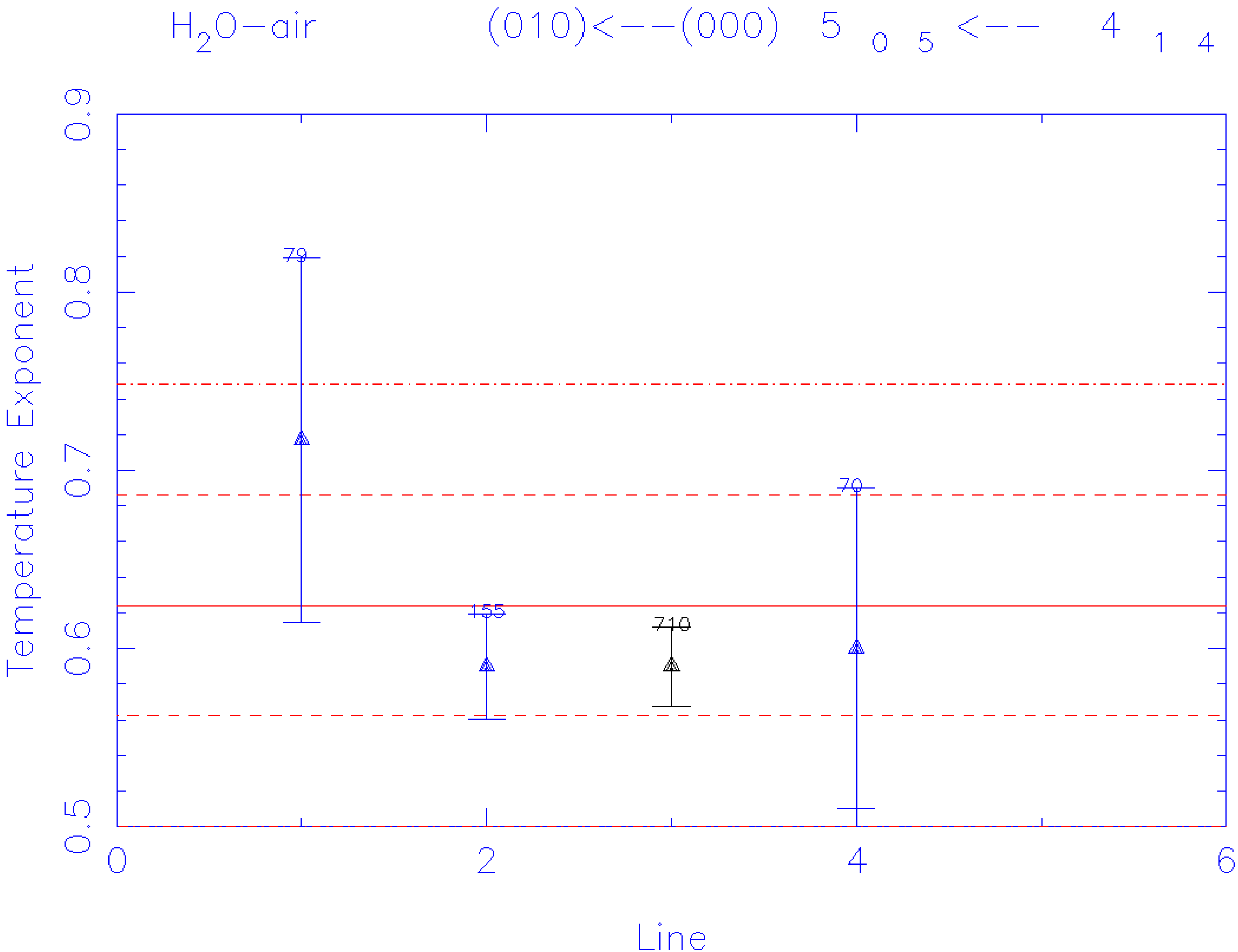
H2O-air (010)<--(000) 2 1 2 <-- 1 0 1
Temperature Exponent
0.5
0.6
0.7
0.8
0.9
0
2
4
6
Line
79
710
155
70



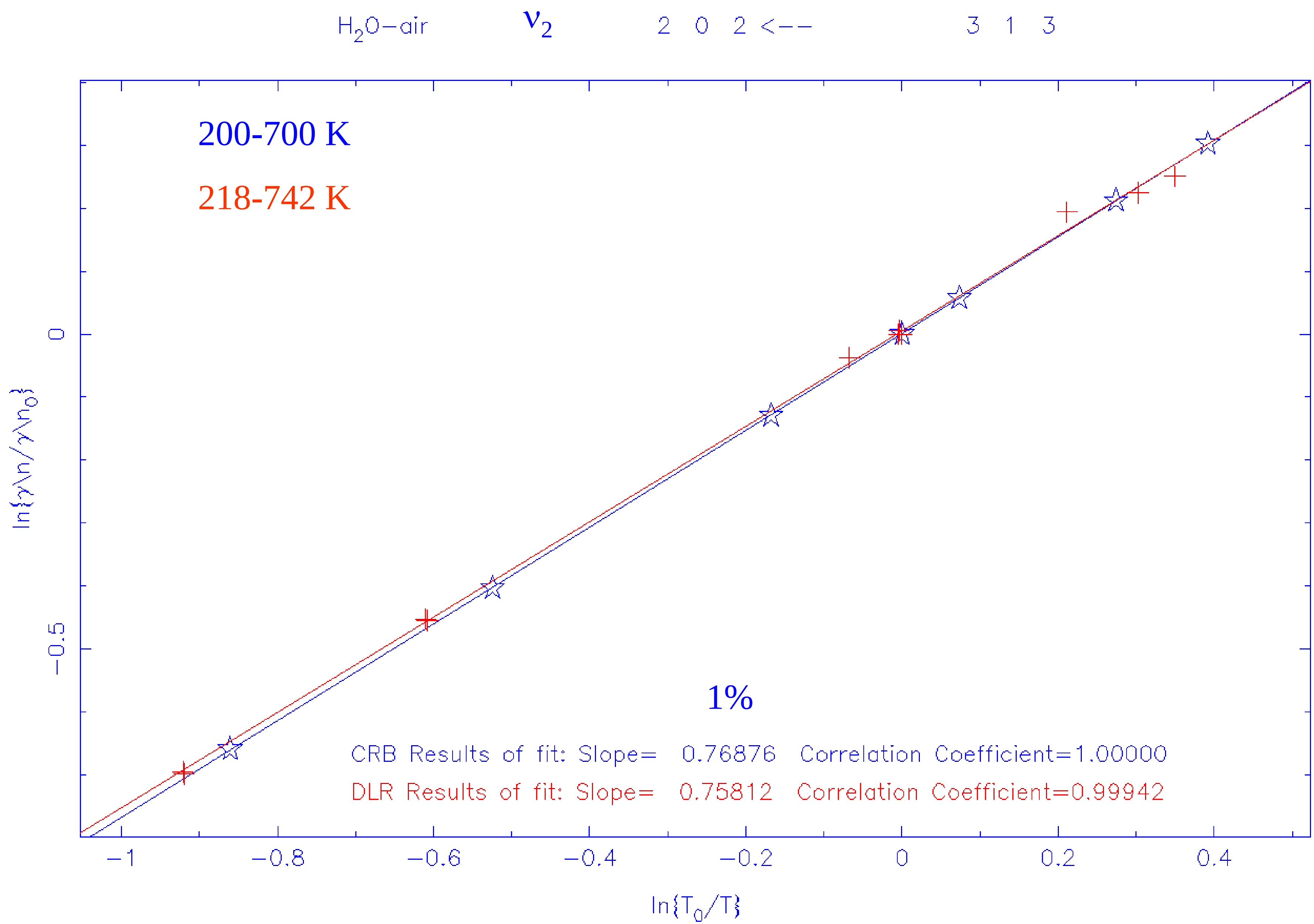
H_2O-air (010)<--(000) 3_{30}<-- 4_{41}
Temperature Exponent
0.5
0.6
0.7
0.8
0.9
0
2
4
6
Line
79
155
70
710



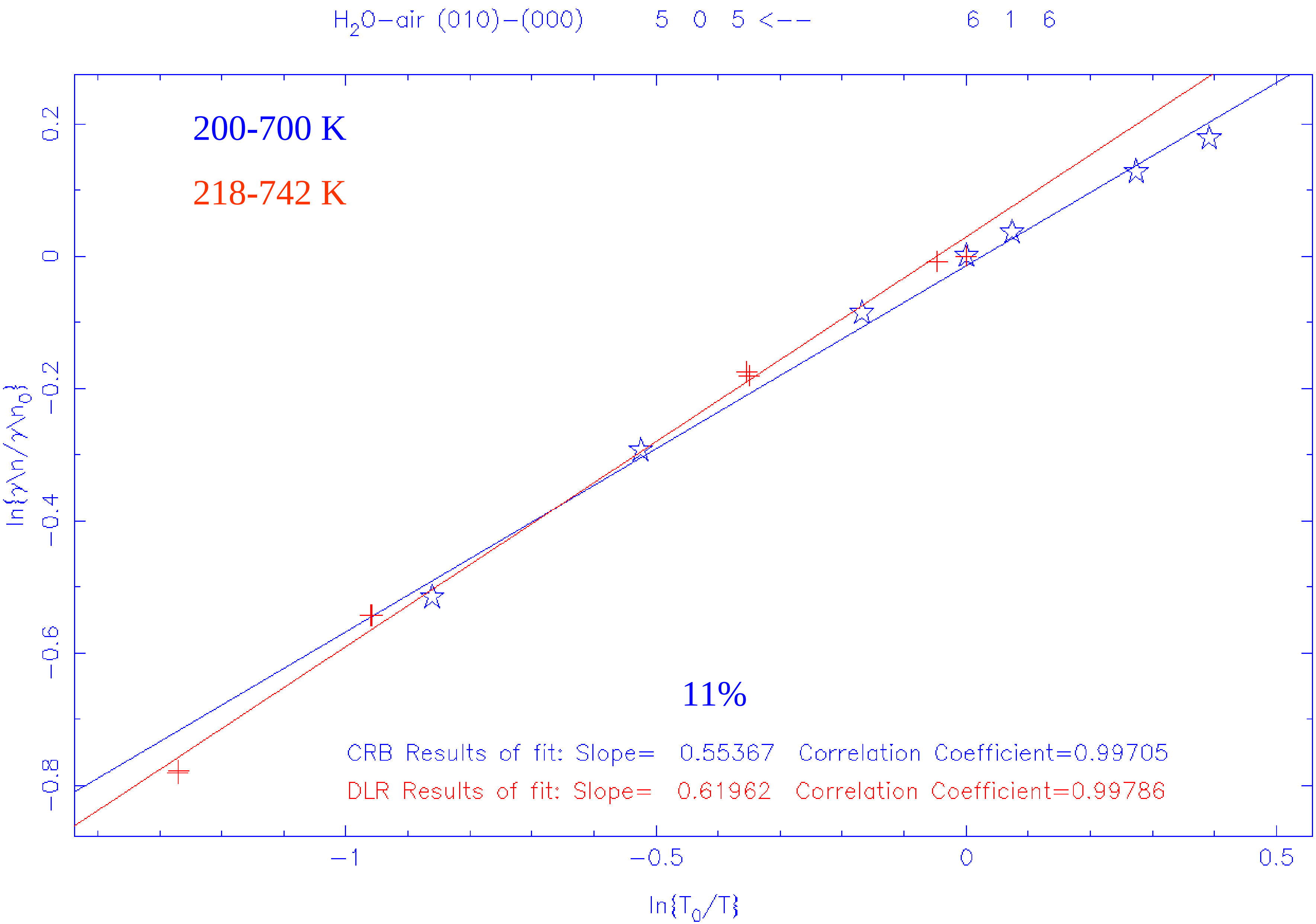
H2O−air
(010)<−−(000) 4 2 3 <−− 4 1 4
Temperature Exponent
0.9
0.8
0.7
0.6
79
70
155
710
0
2
4
6
Line



H_2O-air
(010)<--(000) 5 0 5 <-- 4 1 4
Temperature Exponent
0.5
0.6
0.7
0.8
0.9
0
2
4
6
Line
79
155
710
70

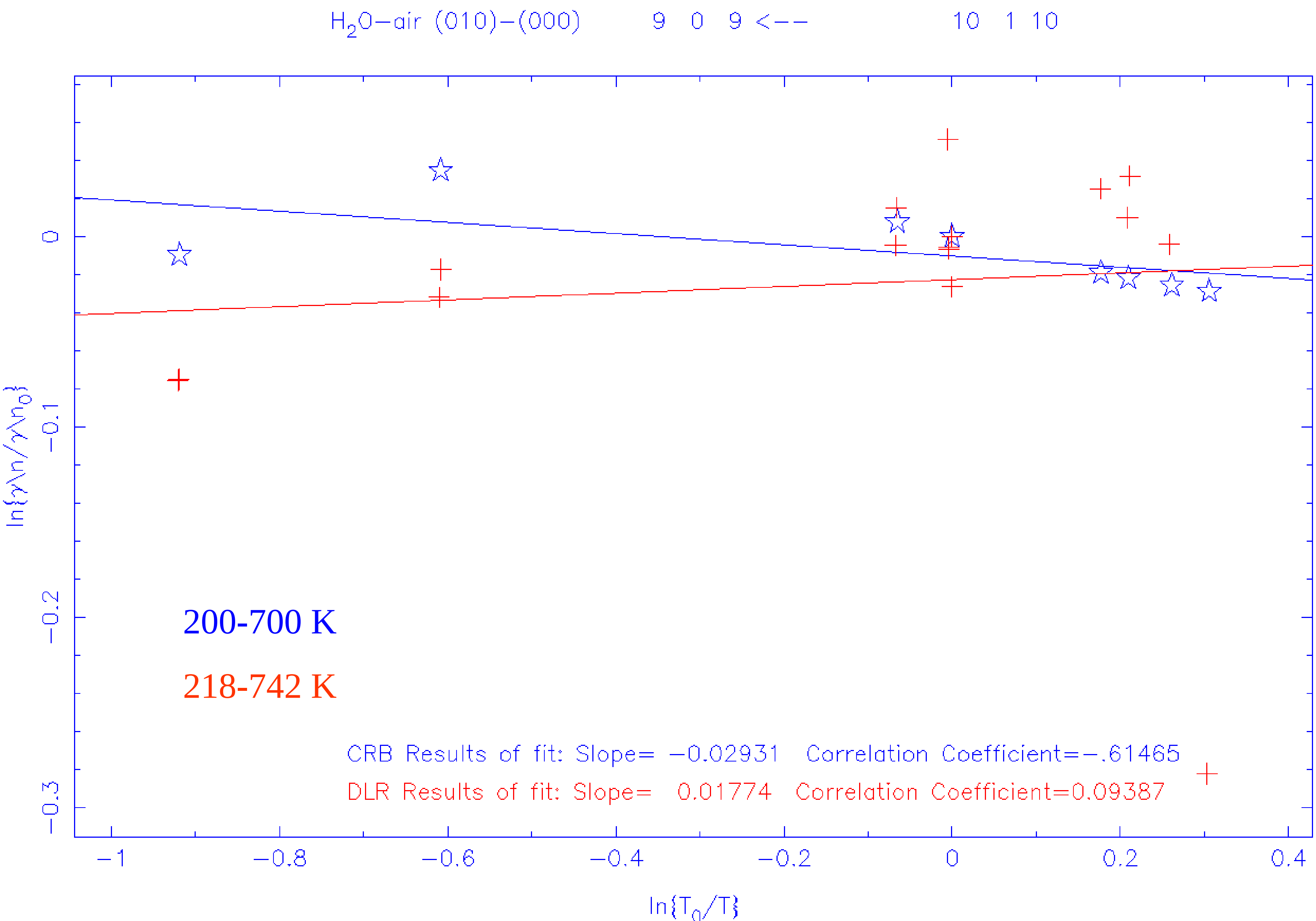


H2O−air ν2 2 0 2 <−− 3 1 3
200-700 K
218-742 K
1%
CRB Results of fit: Slope= 0.76876 Correlation Coefficient=1.00000
DLR Results of fit: Slope= 0.75812 Correlation Coefficient=0.99942
0
−0.5
ln{γ\n/γ\n0}
−1
−0.8
−0.6
−0.4
−0.2
0
0.2
0.4
ln{T0/T}

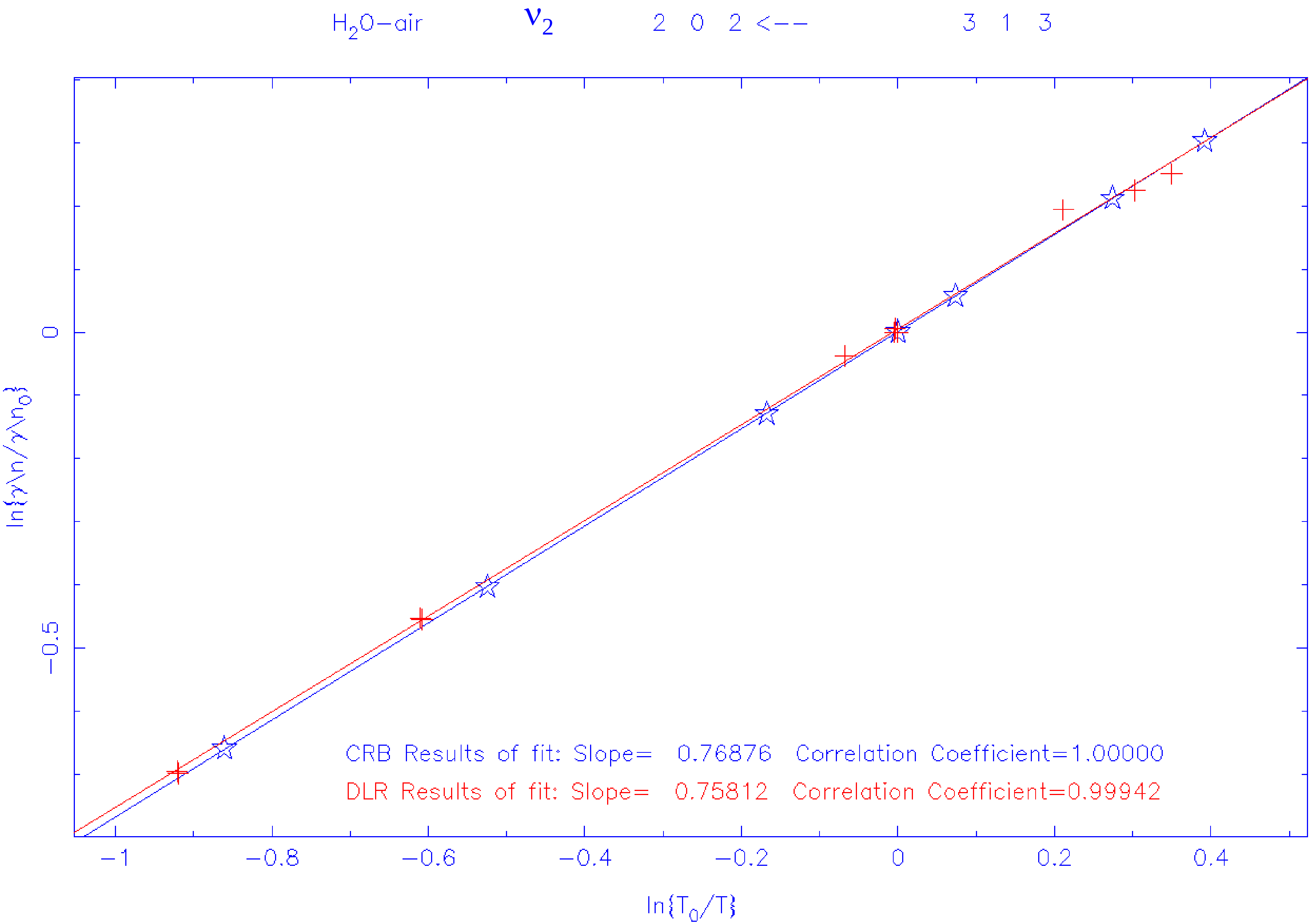


H2O–air (010)–(000) 5 0 5 <-- 6 1 6
200-700 K
218-742 K
11%
CRB Results of fit: Slope= 0.55367 Correlation Coefficient=0.99705
DLR Results of fit: Slope= 0.61962 Correlation Coefficient=0.99786
ln{γ\n/γ\n0}
ln{T0/T}
0.2
0
−0.2
−0.4
−0.6
−0.8
−1
−0.5
0
0.5

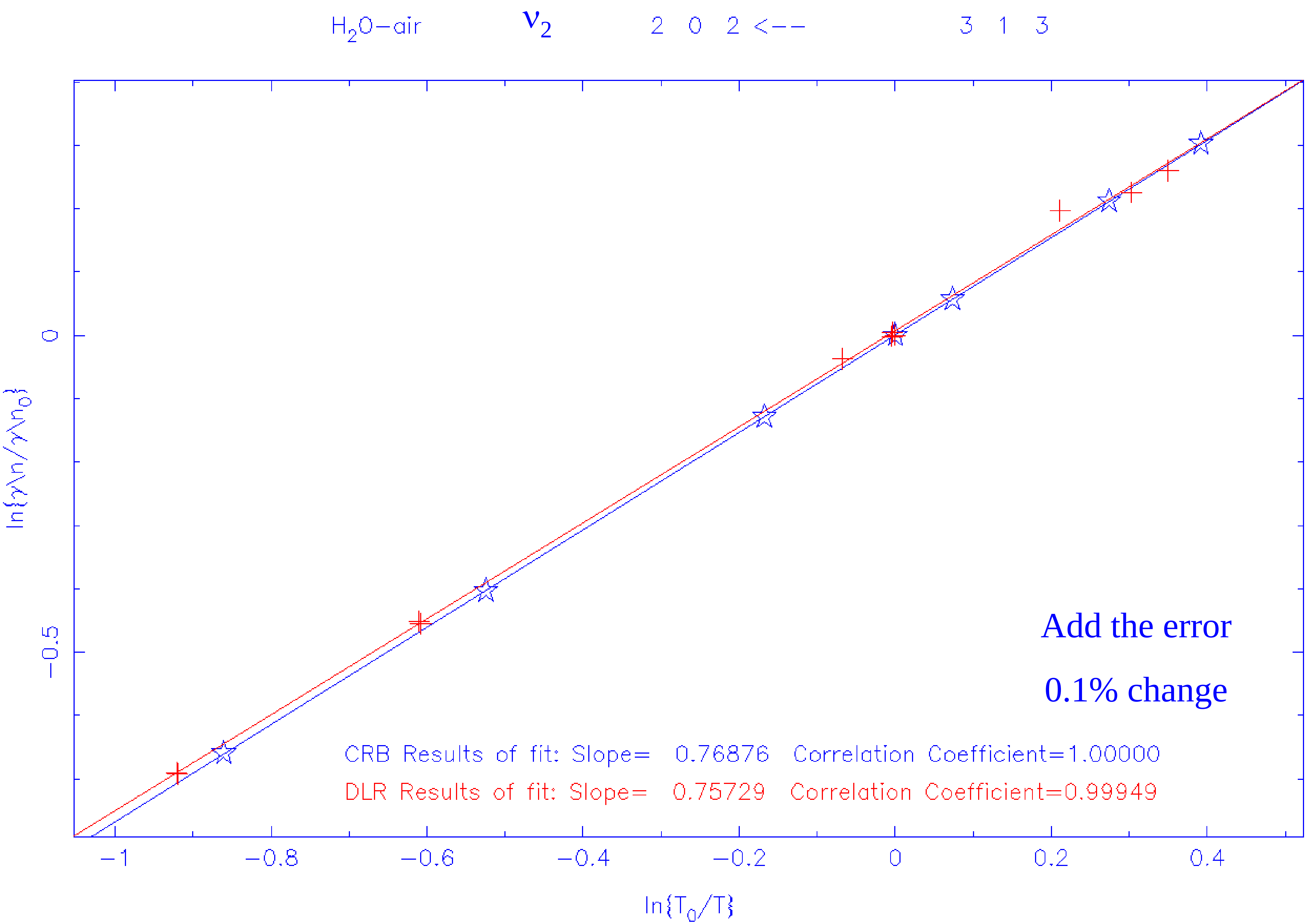
Intermediate J line



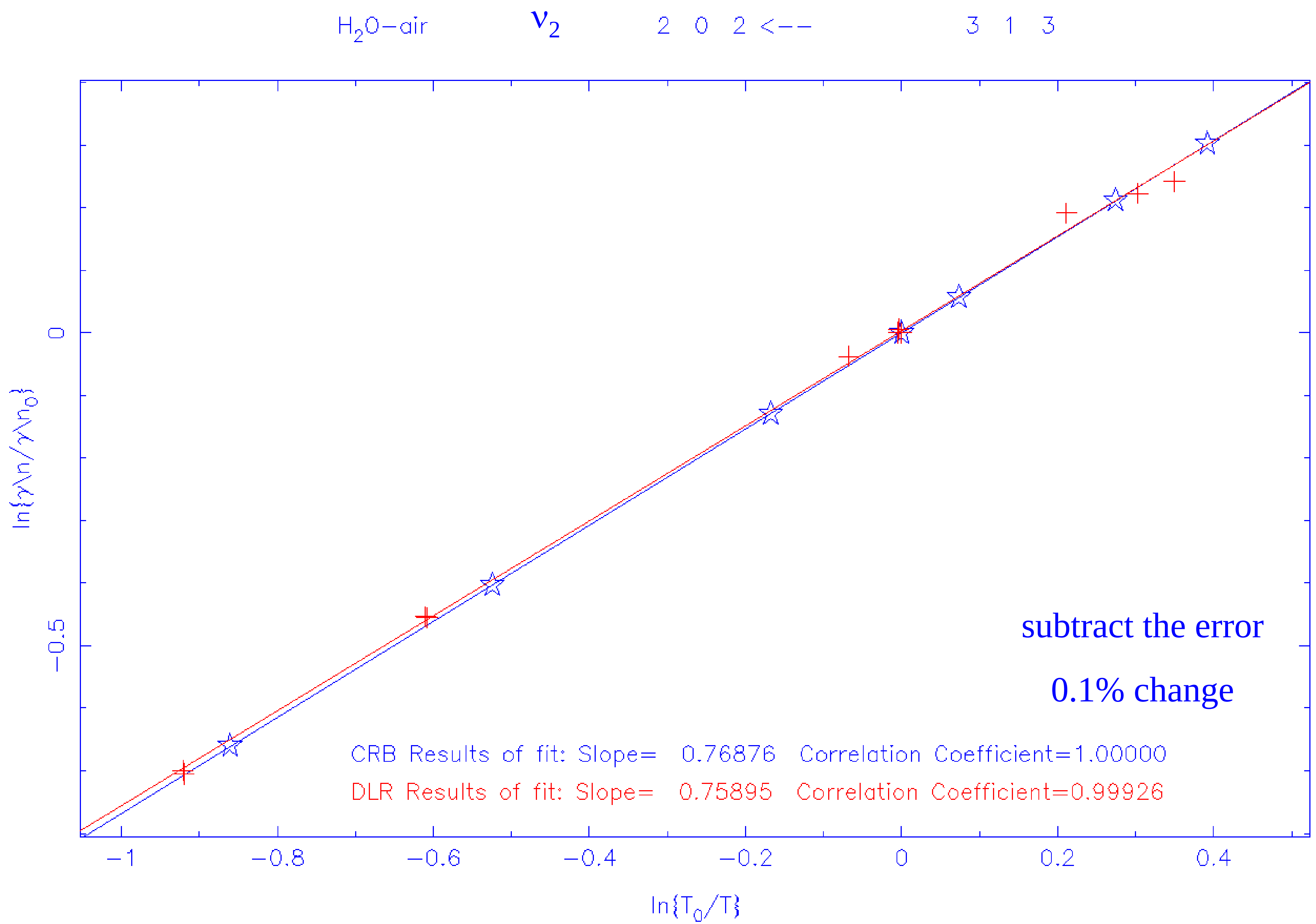
Temperature exponent
and
error in the measurement



H2O-air ν2 2 0 2 <-- 3 1 3
ln{γ\n/γ\n0}
0
-0.5
-1
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
ln{T0/T}
CRB Results of fit: Slope= 0.76876 Correlation Coefficient=1.00000
DLR Results of fit: Slope= 0.75812 Correlation Coefficient=0.99942



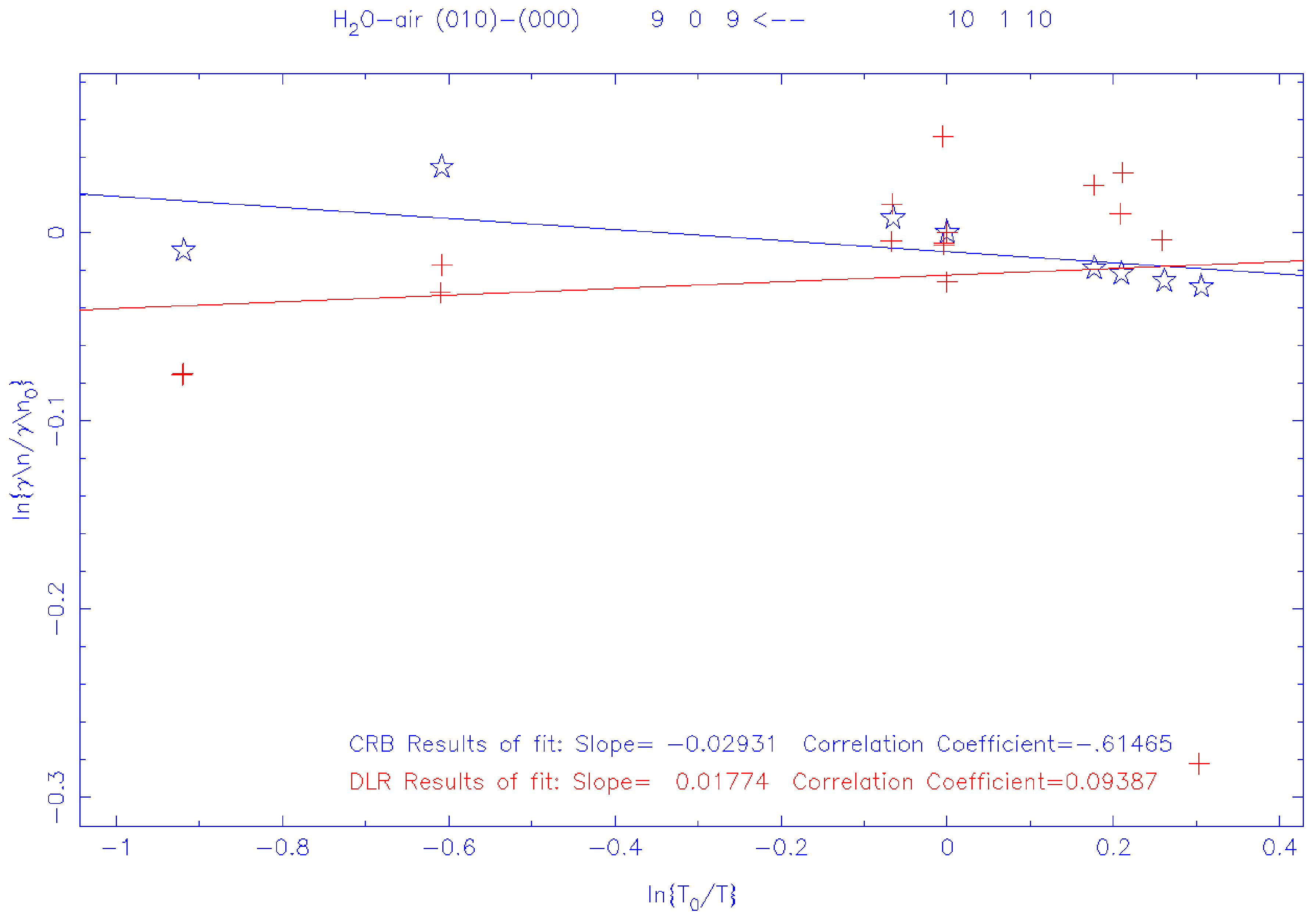
H2O−air ν2 2 0 2 <-- 3 1 3
ln{γ\n/γ\n0}
ln{T0/T}
0
−0.5
−1
−0.8
−0.6
−0.4
−0.2
0
0.2
0.4
Add the error
0.1% change
CRB Results of fit: Slope= 0.76876 Correlation Coefficient=1.00000
DLR Results of fit: Slope= 0.75729 Correlation Coefficient=0.99949



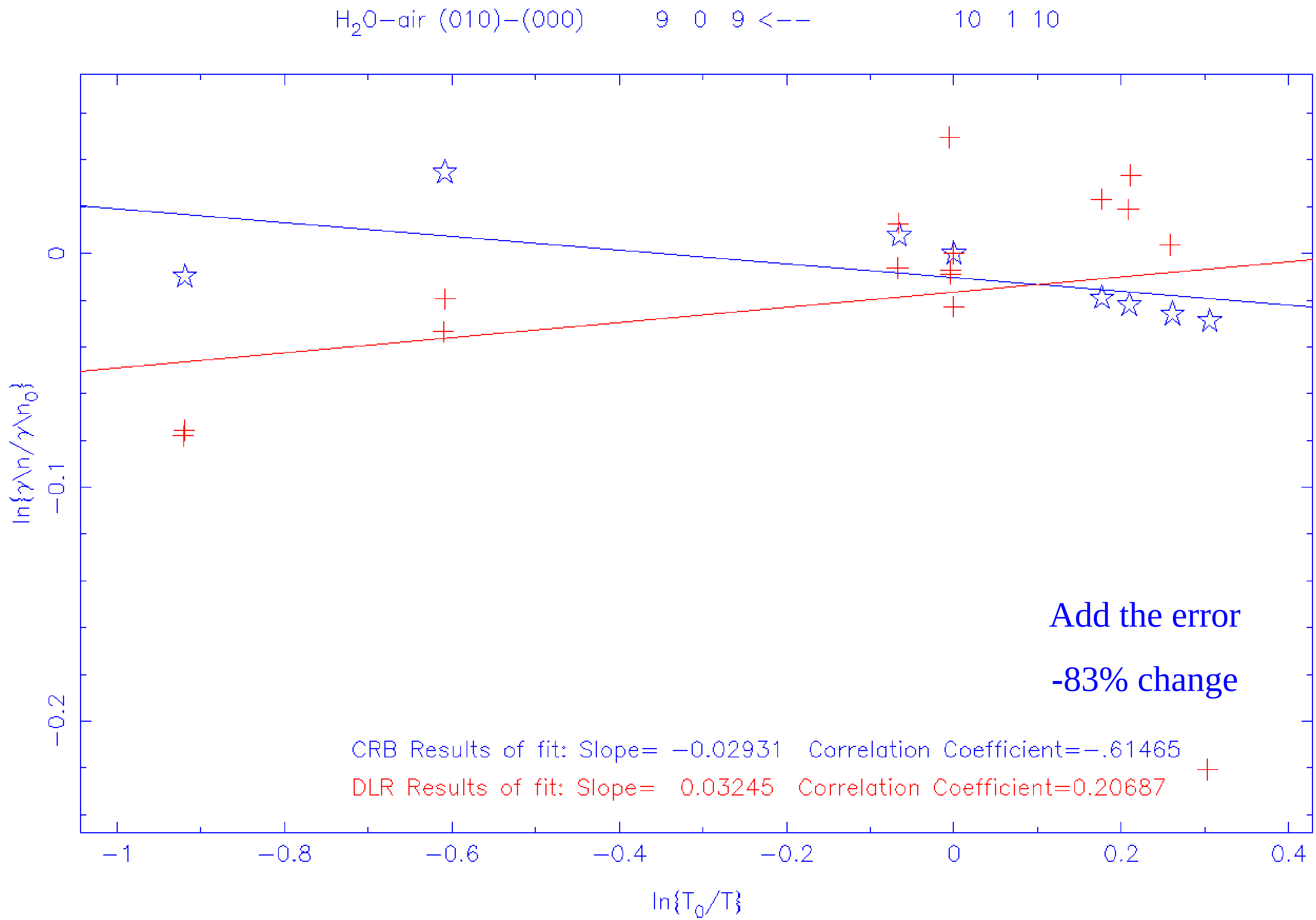
H2O-air ν2 2 0 2 <-- 3 1 3
ln{γ\n/γ\n0}
0
-0.5
-1
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
ln{T0/T}
subtract the error
0.1% change
CRB Results of fit: Slope= 0.76876 Correlation Coefficient=1.00000
DLR Results of fit: Slope= 0.75895 Correlation Coefficient=0.99926

$9_{0\ 9} \leftarrow 10_{1\ 10}$

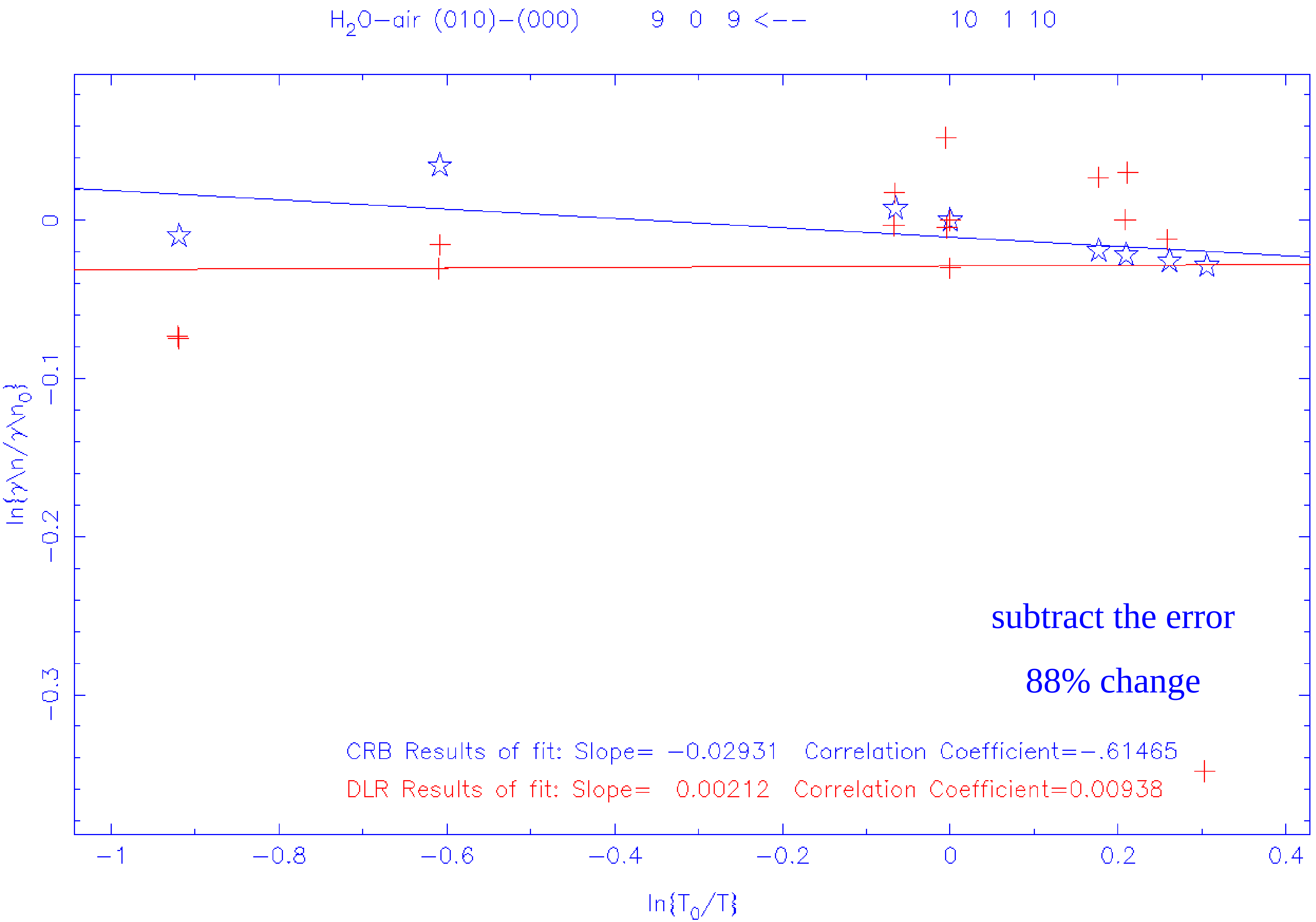
218.393	0.020190313	0.0013993286
228.380	0.026663998	0.00035951458
239.380	0.027640273	0.00019956876
240.140	0.027037898	0.00039908337
247.833	0.027456045	9.9119296e-005
295.700	0.026773004	0.00014984890
295.700	0.026076377	0.00023978278
296.830	0.026616405	0.00010993732
296.890	0.026599465	8.8987300e-005
297.290	0.028175650	0.00011905204
315.990	0.027183601	8.9289202e-005
316.345	0.026646532	0.00010977972
543.220	0.026312130	9.0967588e-005
544.310	0.025933295	0.00010529308
741.850	0.024836019	0.00012515789
742.940	0.024825009	7.8498053e-005



H2O−air (010)−(000) 9 0 9 <−− 10 1 10
ln{γ\n/γ\n0}
ln{T0/T}
CRB Results of fit: Slope= −0.02931 Correlation Coefficient=−.61465
DLR Results of fit: Slope= 0.01774 Correlation Coefficient=0.09387



H_2O—air (010)—(000) 9 0 9 <-- 10 1 10
$\ln\{\gamma\backslash n/\gamma\backslash n_0\}$
0
−0.1
−0.2
−1
−0.8
−0.6
−0.4
−0.2
0
0.2
0.4
$\ln\{T_0/T\}$
Add the error
-83% change
CRB Results of fit: Slope= −0.02931 Correlation Coefficient=−.61465
DLR Results of fit: Slope= 0.03245 Correlation Coefficient=0.20687

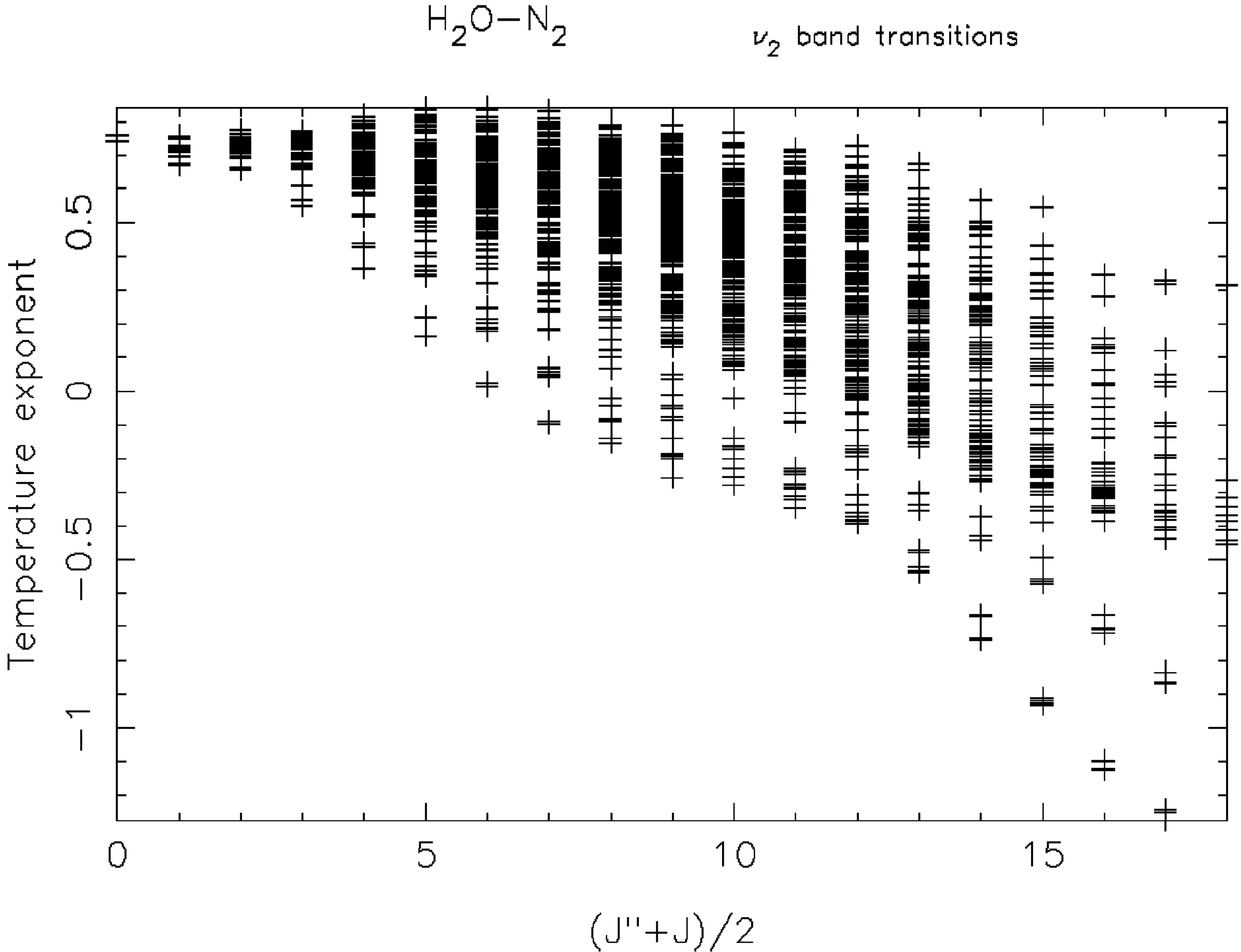


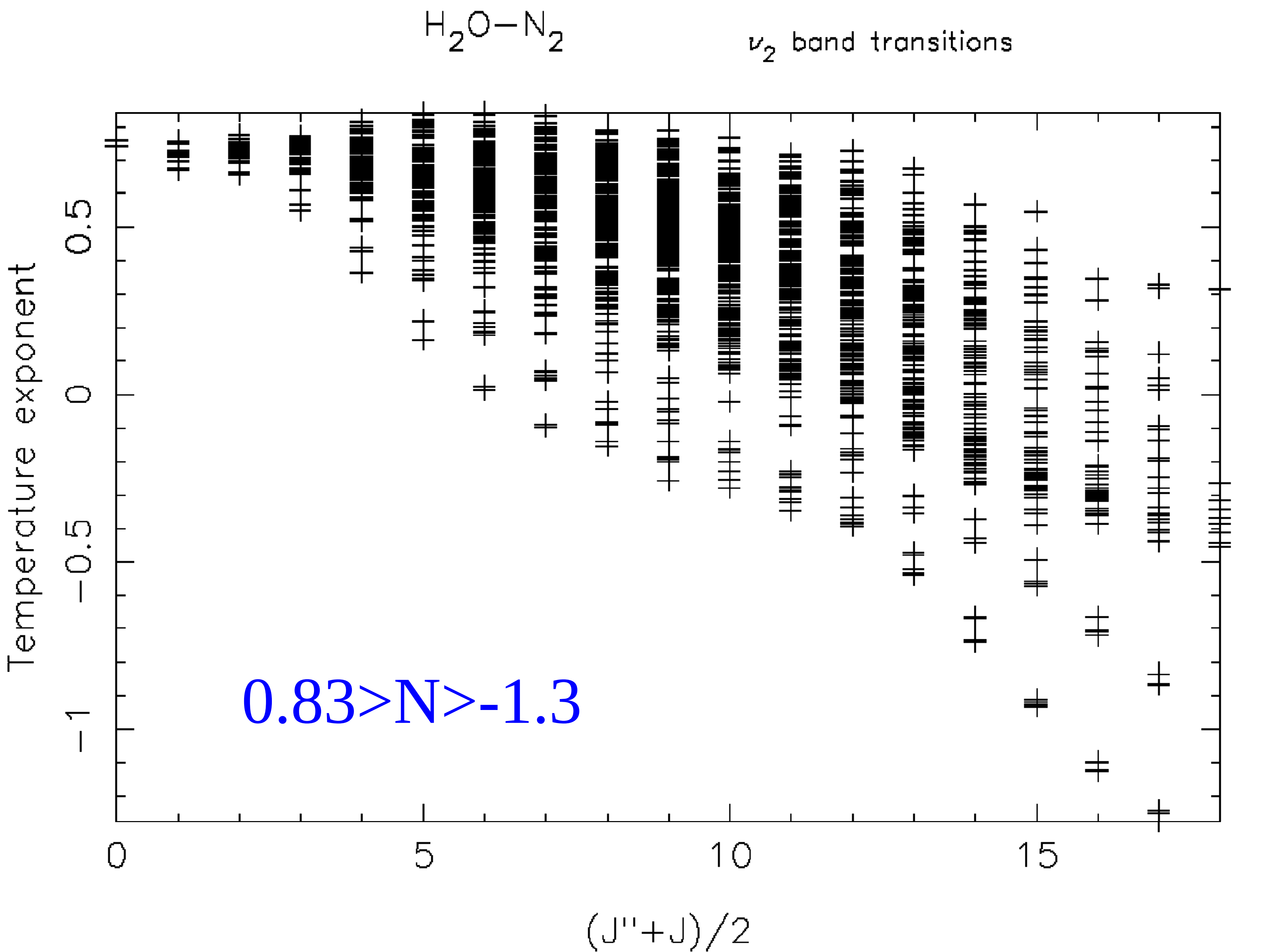
H2O–air (010)–(000) 9 0 9 <-- 10 1 10
subtract the error
88% change
CRB Results of fit: Slope= –0.02931 Correlation Coefficient=–.61465
DLR Results of fit: Slope= 0.00212 Correlation Coefficient=0.00938
ln{T0/T}
ln{γ\n/γ\n0}
0
–0.1
–0.2
–0.3
–1
–0.8
–0.6
–0.4
–0.2
0
0.2
0.4

HITRAN Algorithm
for temperature exponents of H_2O

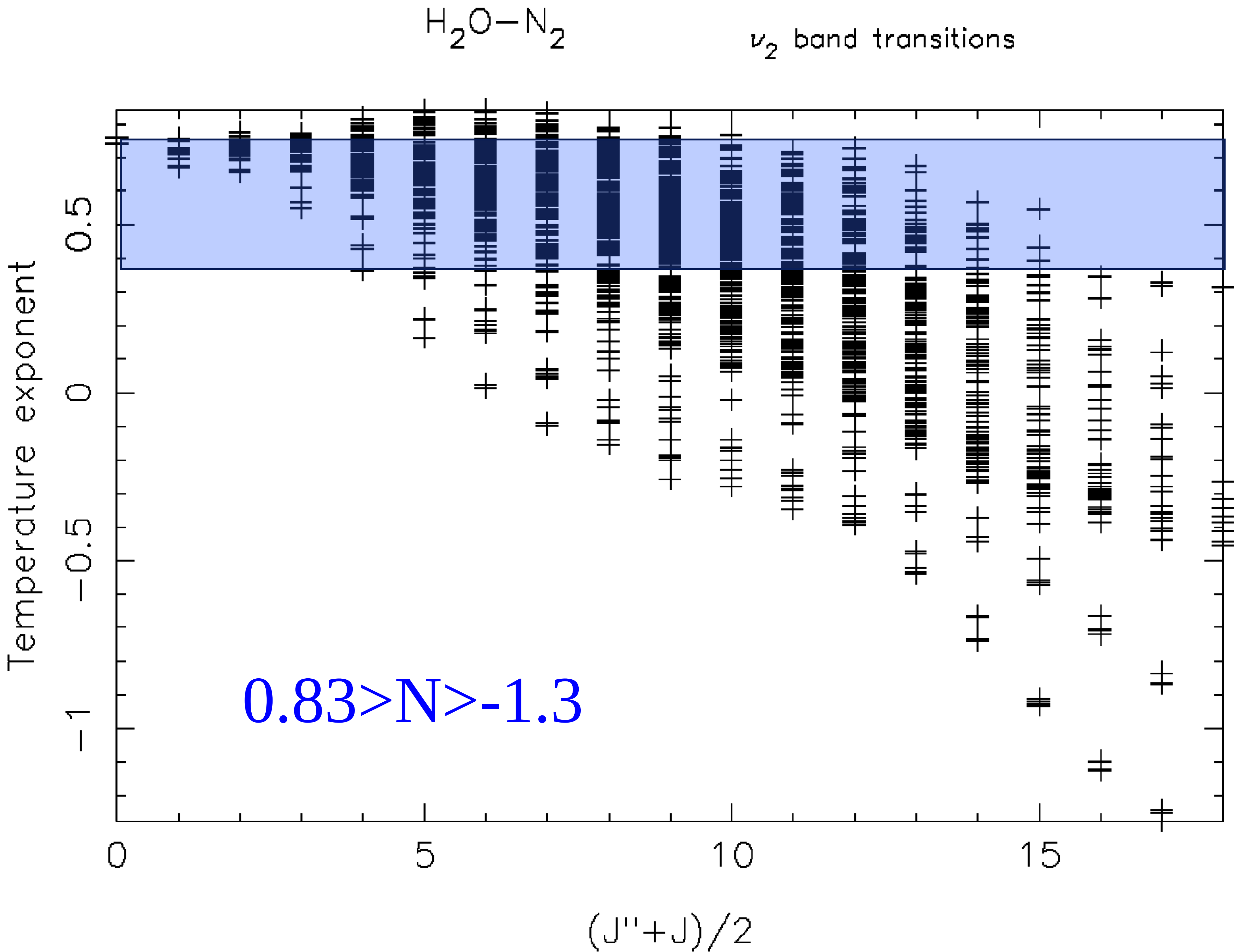
Temperature exponents on the HITRAN database

J	N	J	N
0	0.78	9	0.49
1	0.78	10	0.45
2	0.78	11	0.41
3	0.77	12	0.39
4	0.73	13	0.37
5	0.69	14	0.36
6	0.64	15	0.36
7	0.59	16	0.38
8	0.53	17	0.41


H_2O-N_2
ν_2 band transitions
Temperature exponent
0.5
0
−0.5
−1
0
5
10
15
(J''+J)/2



H2O–N2
ν2 band transitions
Temperature exponent
0.5
0
−0.5
−1
0
5
10
15
(J''+J)/2
0.83>N>-1.3



H_2O-N_2
ν_2 band transitions
Temperature exponent
(J''+J)/2
0.5
0
−0.5
−1
0
5
10
15
0.83>N>-1.3

Conclusions

- When γ an N are from rotational contributions. Vibrational dependence of γ is small, N is positive and follows the power law.

Conclusions

- When γ an N are from rotational contributions. Vibrational dependence of γ is small, N is positive and follows the power law.
- When γ an N are from vibrational contributions. Vibrational dependence of γ is large, N can be negative, the power law is approximate.

Conclusions

- When γ an N are from a mix of rotational and vibrational contributions. N is not described by the power law expression.

Conclusions

- When γ an N are from a mix of rotational and vibrational contributions. N is not described by the power law expression.
- N is dependent on the temperature range of the fit.

Conclusions

- When the temperature range is large, the power law becomes less valid.
- N is sensitive to the error in the half-width (R. R. Gamache, Eric Arié, Corinne Boursier, and Jean-Michel Hartmann, "A Review of Pressure-Broadening and Pressure-Shifting of Spectral Lines of Ozone," Spectrochimica Acta A **54**, 35-63 (1998).)

Acknowledgments

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