The Collision-Broadened Line Shape of CO_2 via the Complex Robert-Bonamy Method: *The Complexity of Simplicity*

Robert R. Gamache, Julien Lamouroux, Anne L. Laraia

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Why CO_2?

- Venus and Mars
  - Venus Express with Venus IR Thermal Imaging Spectrometer
  - Mars Reconnaissance Orbiter Mission with the Mars Climate Sounder

Why CO_2?

Earth

A well mixed greenhouse gas with a very long lifetime.

Measurements

Atmospheric Infrared Sounder (AIRS)

Infrared Atmospheric Sounder Interferometer (IASI)

Greenhouse Gas Observing Satellite (GOSAT)

Orbiting Carbon Observatory (OCO-2) *1% precision*

Previous calculations

Yamamoto *et al.* JQSRT 9, 371 (1969).

Bouanich and Brodbeck, JQSRT 14, 141 (1974)

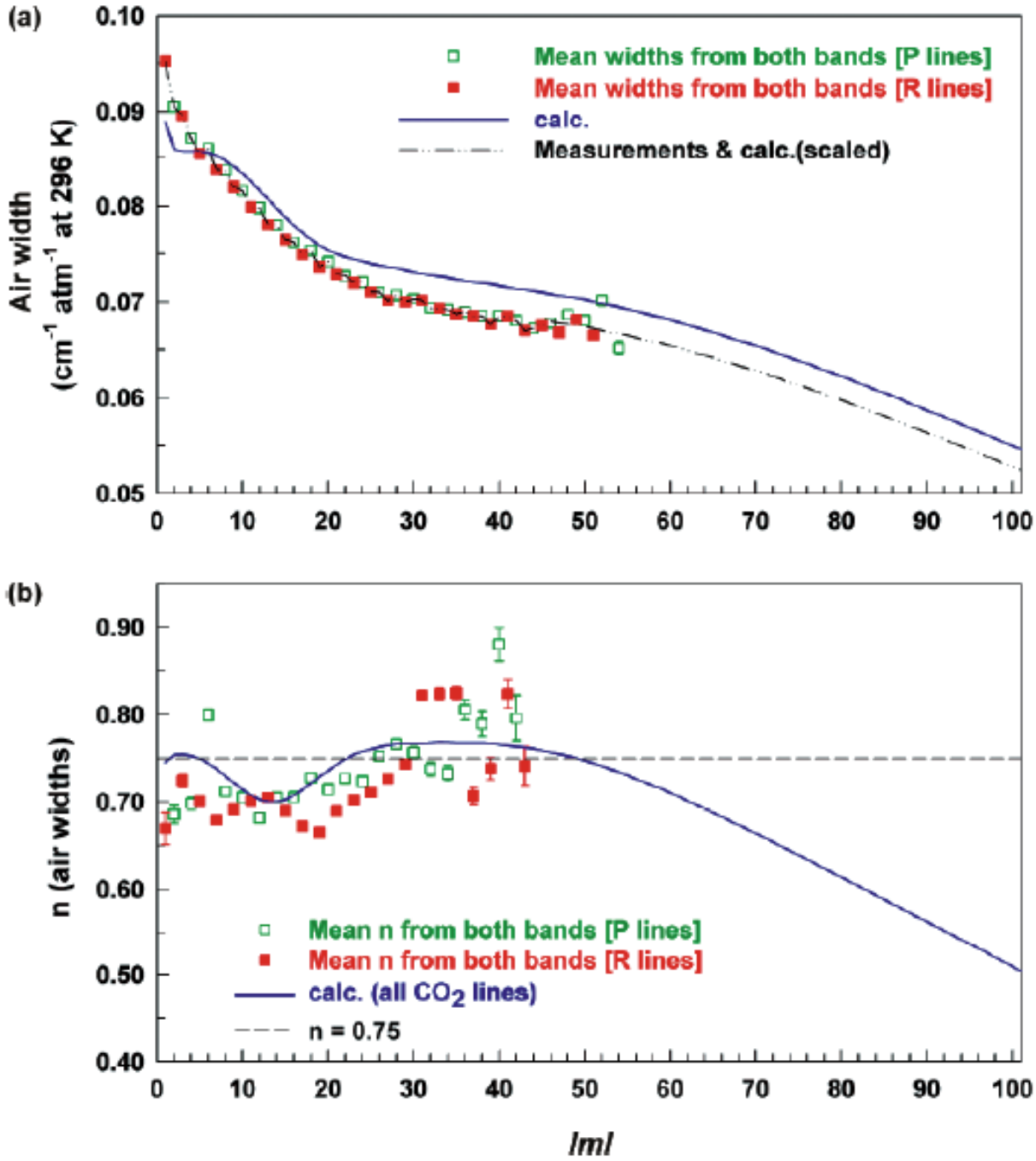
Boulet *et al.* Can. J. Phys. 50, 2178 (1972).

Arie *et al.*, Appl Opt. 25, 2584 (1986).

Rosenmann *et al.,* J. Chem Phys 88, 2999 (1988); JQSRT 40, 569 (1988), Appl. Opt 27, 3902 (1988).

Gamache and Rosenmann, "N_2-, O_2-, air-, and self broadening of CO_2 transitions and temperature dependence for HITRAN," unpublished data, 1992.

Predoi-Cross *et al.*, Can J. Phys. 87, 517 (2009); JQSRT 111, 1065 (2010).



Predoi-Cross , *et al*,.Can. J. Phys. **87**, 517-535 (2009)

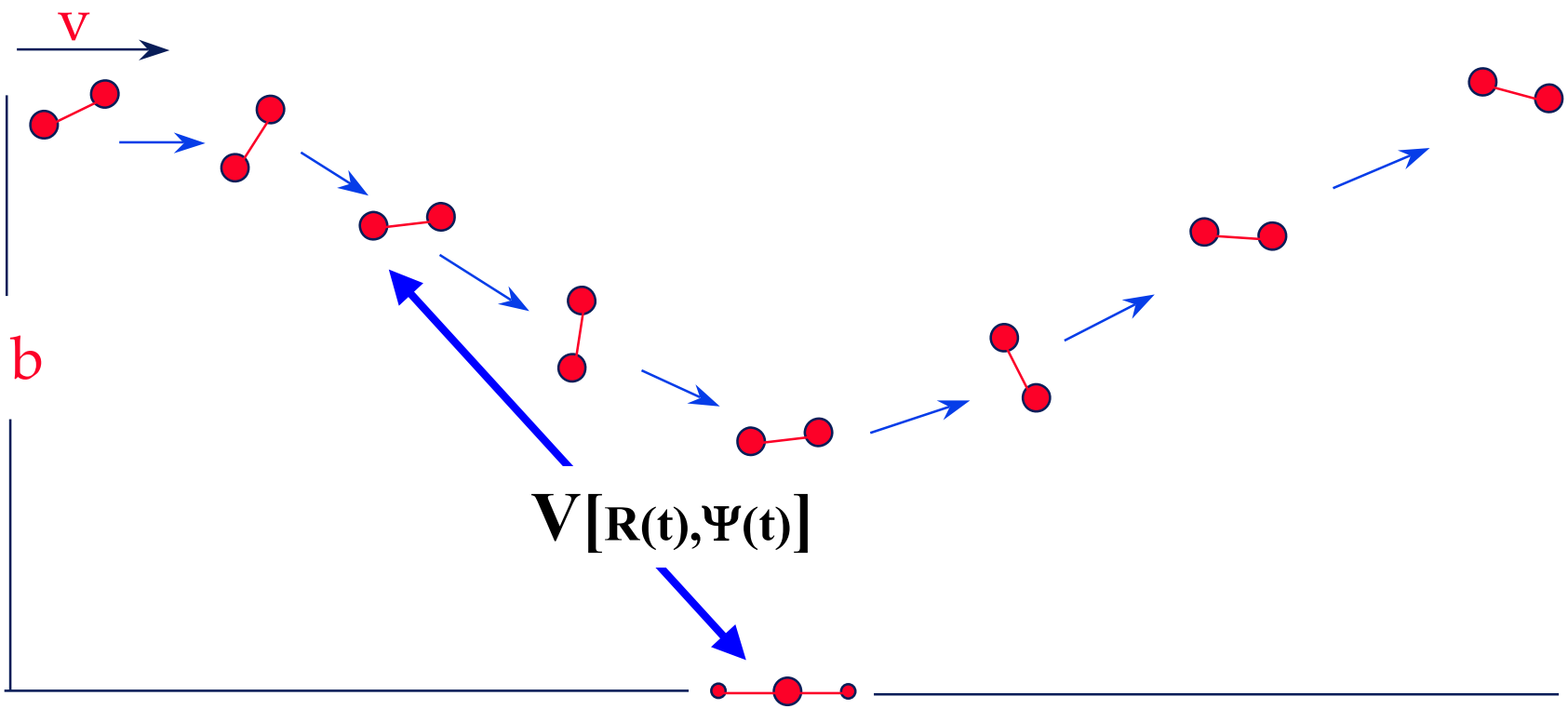
Semiclassical complex Robert-Bonamy theory

The half-width and line shift are

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

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.

Radiator - Perturber trajectory determined via the potential



The isotropic component of the atom-atom potential is used to define the trajectory of the collisions.

Trajectories: parabolic model or Hamilton's Equations

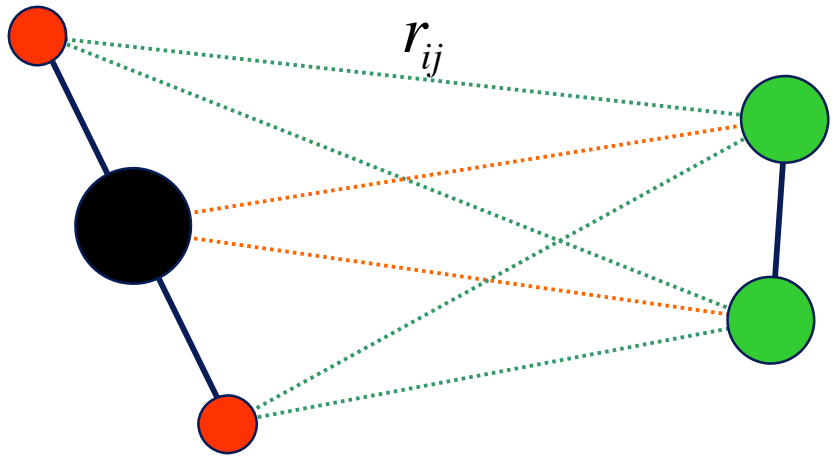
Potential Terms

The electrostatic potential is given by an expansion of the charge distribution in terms of the electric moments of the molecules

$$V_{1,2}^{elec} = \qquad V_{\theta_1 \theta_2}$$

Atom-Atom Potential

$$V^{at-at} = \sum_{ij} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$$



Lennard-Jones (6-12) parameters
CO_2-N_2

	N-O	N-C
σ/Å	2.55	2.77
ε/ k_B(K)	39.12	41.54

Spherical Tensor Expansion of the Potential

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

$$\otimes C\left(\ell_1 \ell_2 \ell, m_1 m_2 m\right) \mathrm{D}^{\ell_1}_{\mathrm{m}_1 n_1}\left(\Omega_1\right) \mathrm{D}^{\ell_2}_{\mathrm{m}_2 0}\left(\Omega_2\right) \mathrm{Y}_{\ell \mathrm{m}}\left(\omega\right)$$

- 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*$=\ell_1+\ell_2+2w$

CO_2

Linear molecule - Quadrupole moment

$$D^2_{-2\ 0},\ D^2_{0\ 0}, D^2_{2\ 0}$$

Wave functions - D^J_{00}

Reduced matrix elements - CO_2

$$\int \Psi_{i'} \; V \; \Psi_{i} \; d\tau \; \alpha \int D_{00}^{J_{i'}} \quad D_{k0}^{l_{1'}} \; D_{00}^{J_i} \; d\tau$$

$C(J_{i'}, \ell_{l'}, J_i; 0, k, 0)$

Only potential term remaining is

$$D_{00}^{2}$$

Trajectories

Parabolic Approximation

$$\int_0^{\infty} 2\pi b\,db \rightarrow \int_{r\,\min}^{\infty} 2\pi r_c\,dr_c \left(\frac{v_c'}{v}\right)^2$$

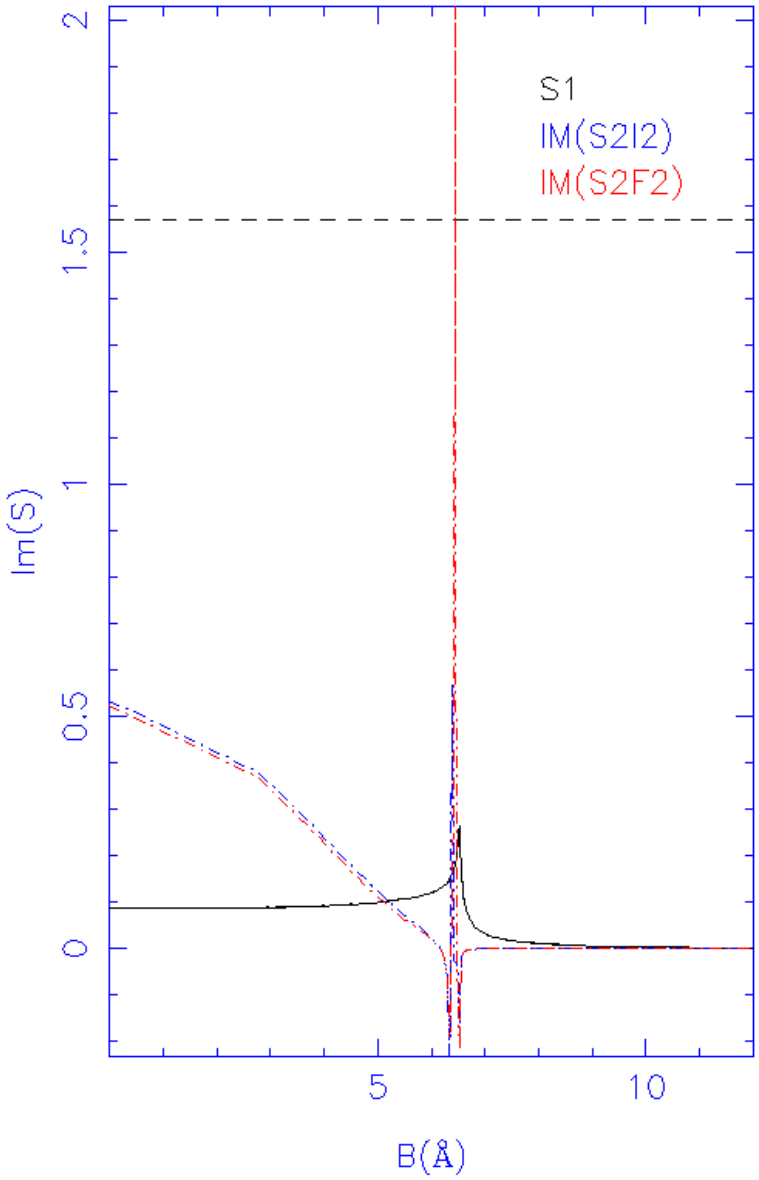
For many choices of the Lennard-Jones parameters solutions of the second order in time equations lead to imaginary v_c'. $\rightarrow$ integration of cross-section cannot be performed.

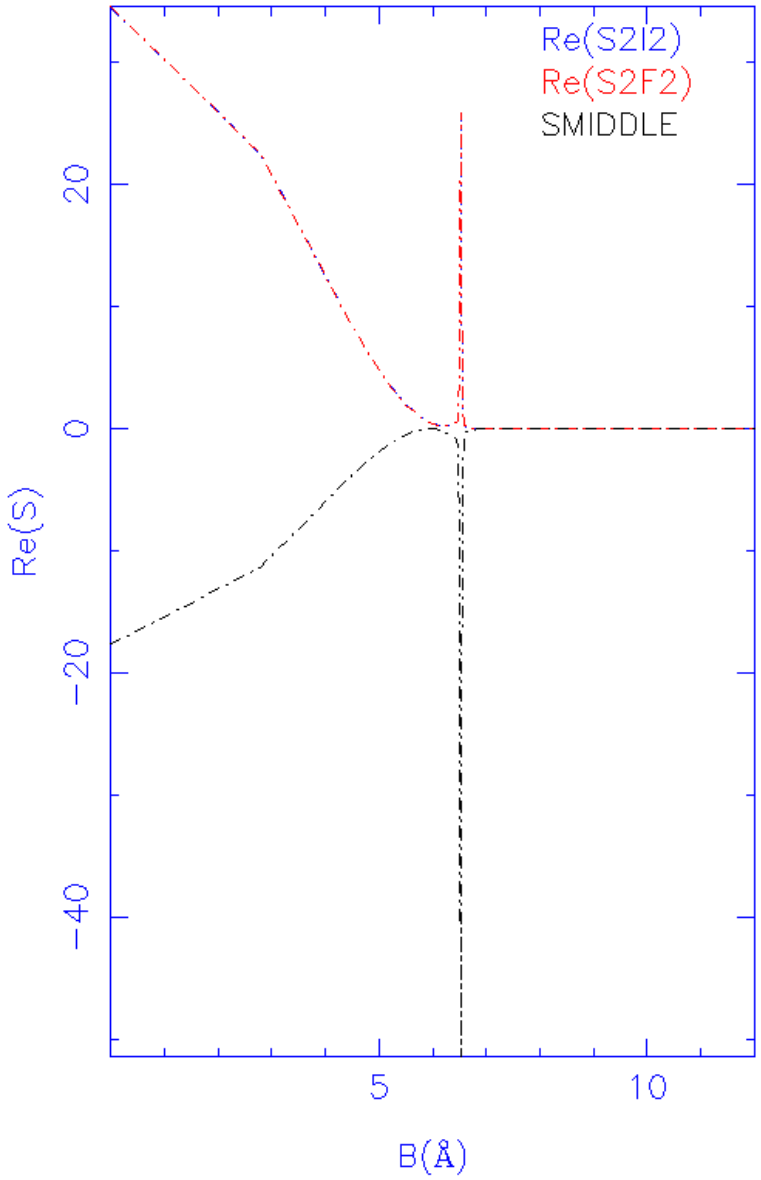
Very simple system

Initial results CO_2-N_2 at 296 K

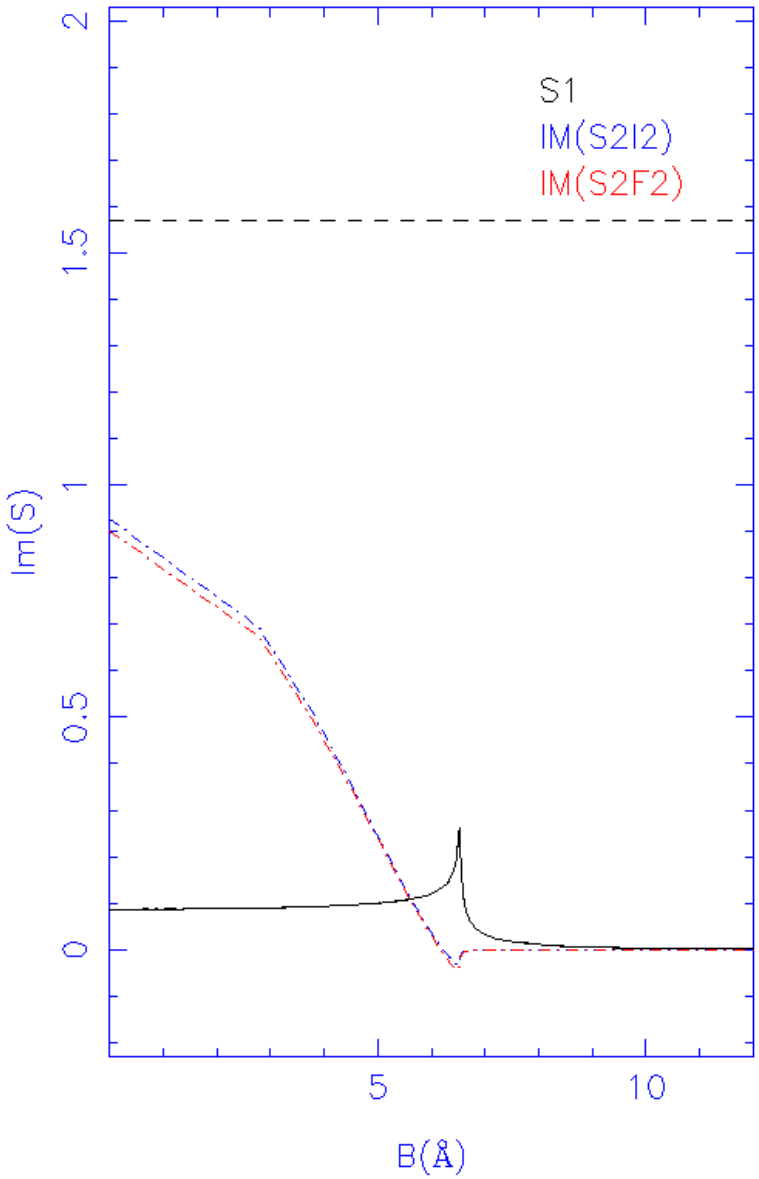
Transition	γ cm^{-1} atm^{-1}
$25 \leftarrow 24$	0.0457
$29 \leftarrow 28$	0.0289
$31 \leftarrow 30$	0.0176
$33 \leftarrow 32$	0.0022
$41 \leftarrow 40$	-0.1540
$45 \leftarrow 44$	-0.3868
$47 \leftarrow 46$	-0.6069

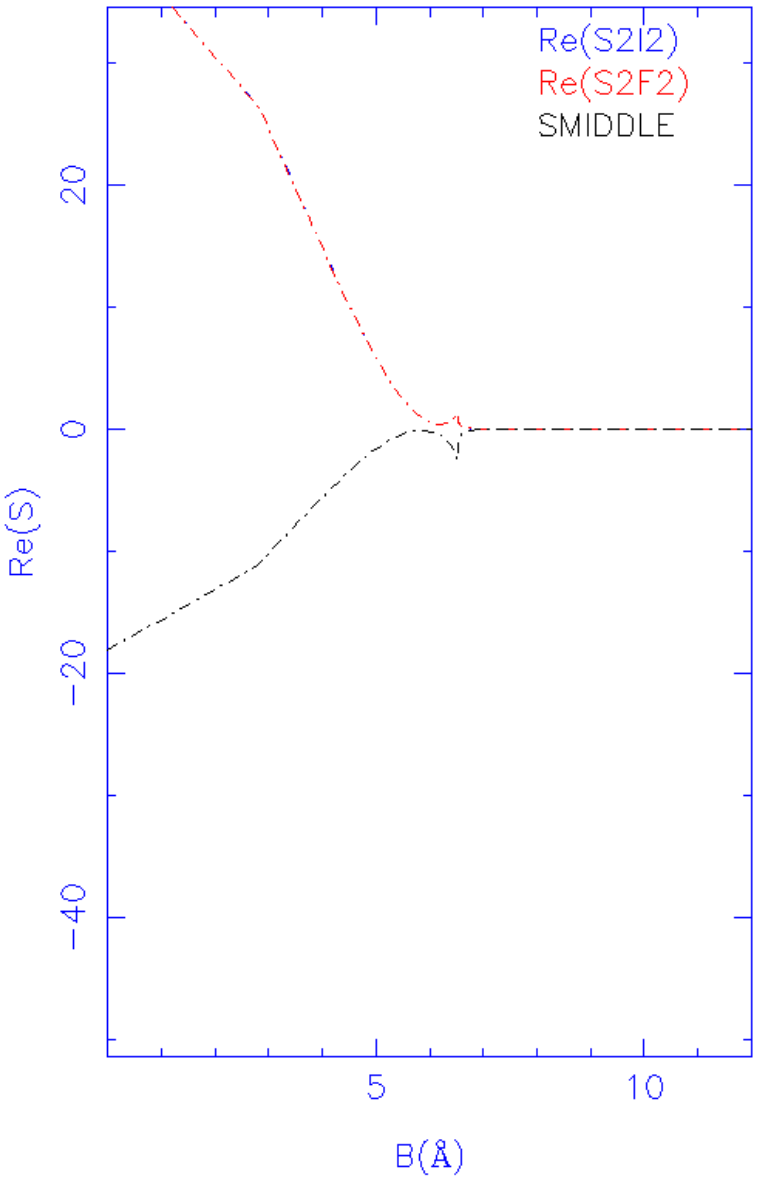
CO_2-N_2 ν_3 P20 transition, J_2=0, parabolic trajectories, T=100 K

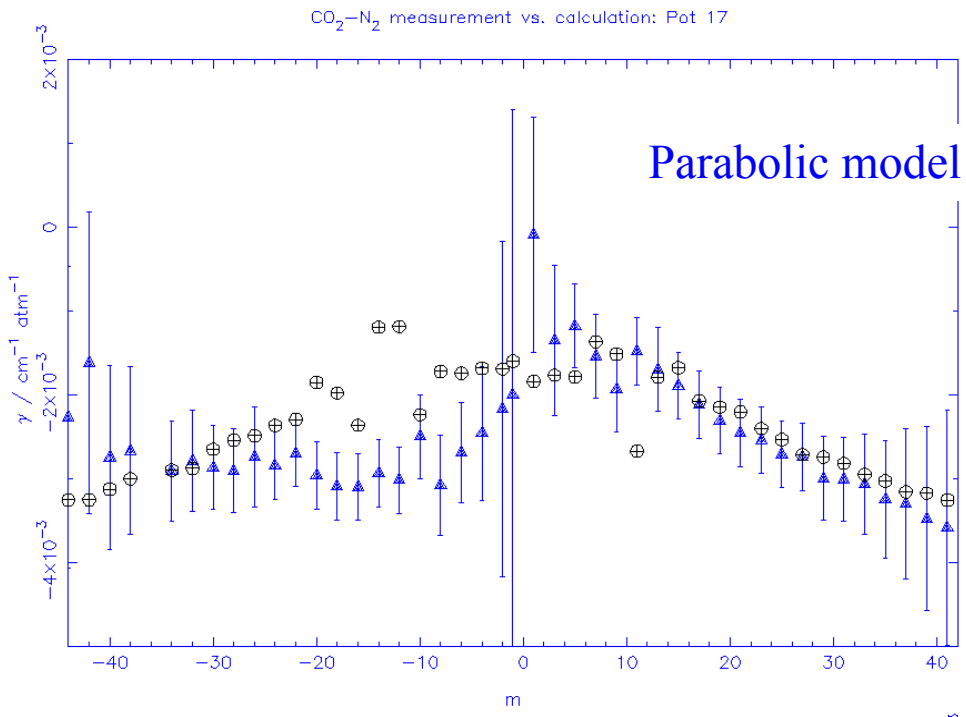




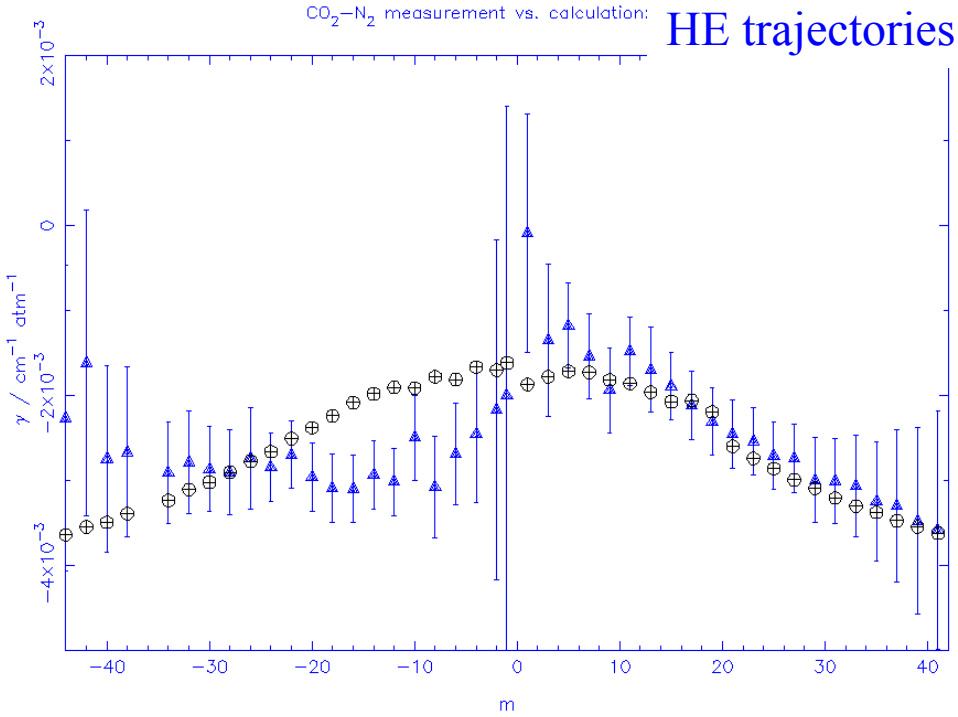
CO_2-N_2 ν_3 P20 transition, J_2=0, HE trajectories, T=100 K







Parabolic model trajectories



HE trajectories

Close collisions and the trajectory model.

See talk V7 by J. Lamouroux for details

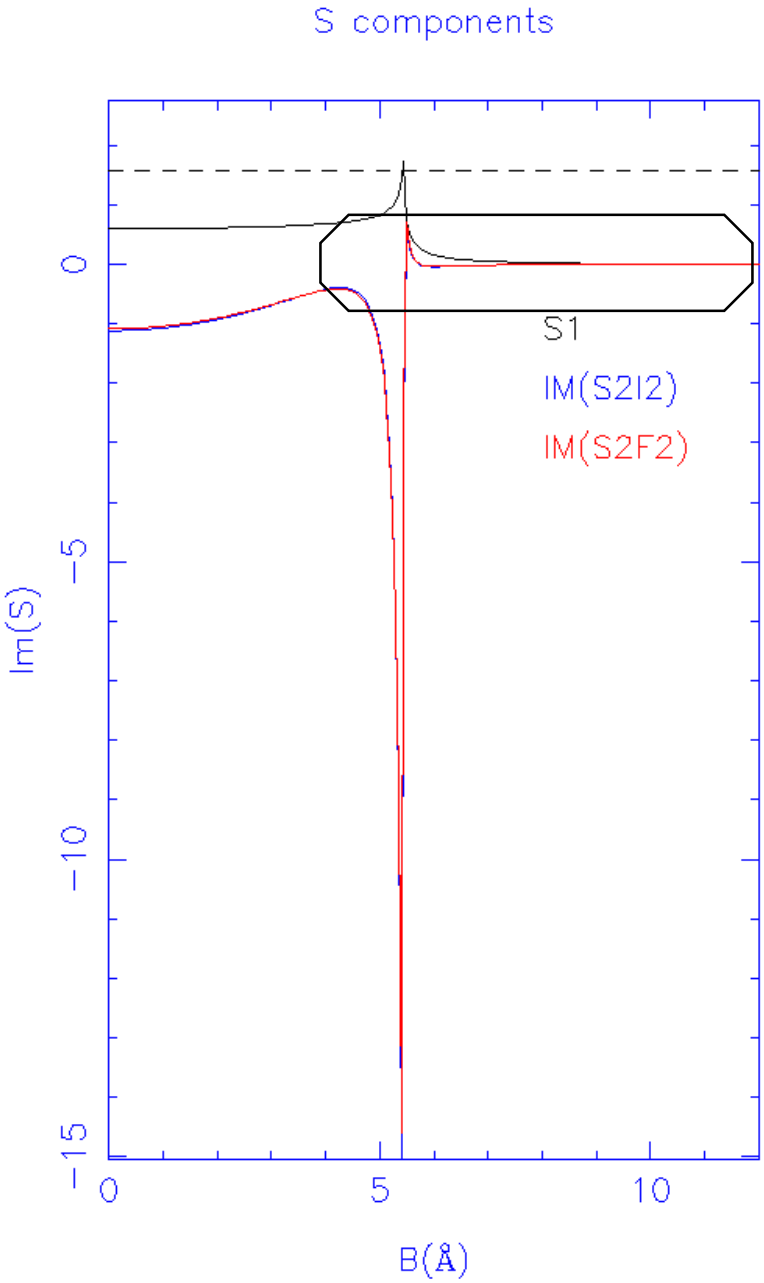
Integrand

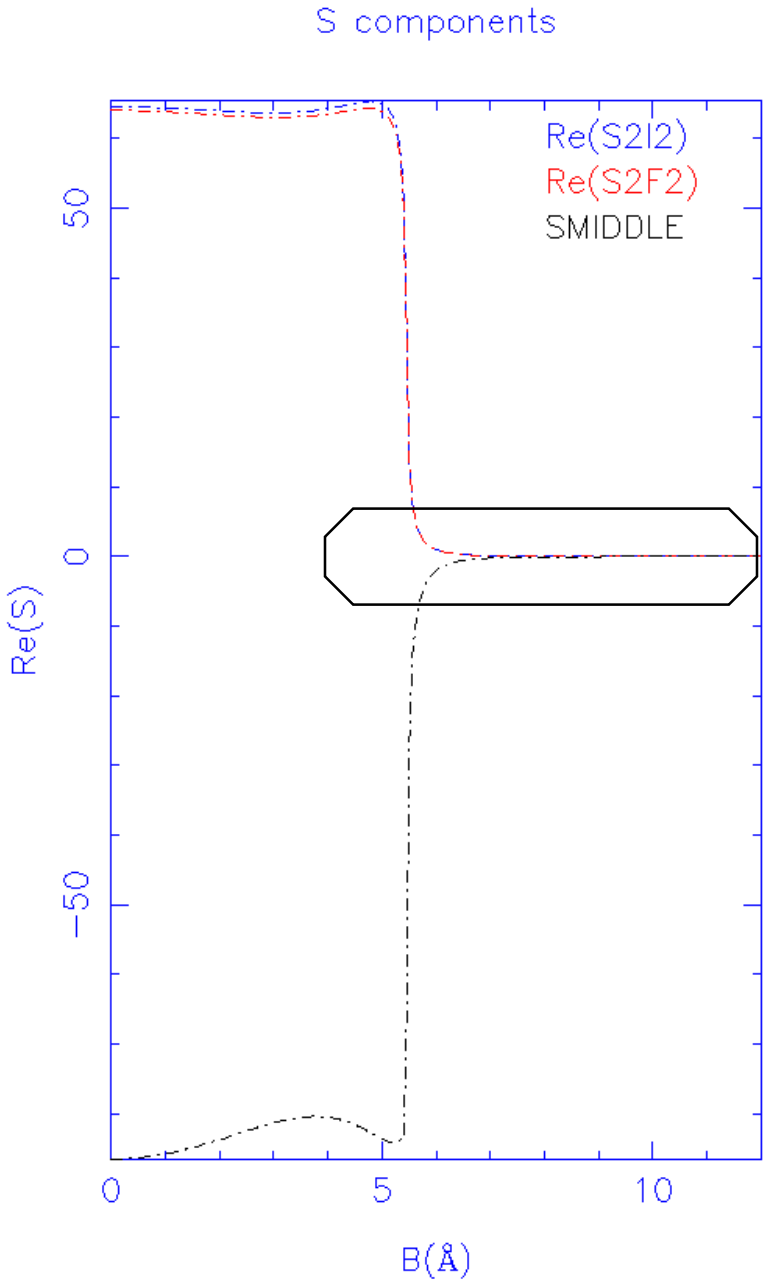
As $Re\{S_2\}$ gets large square bracket goes to one.

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

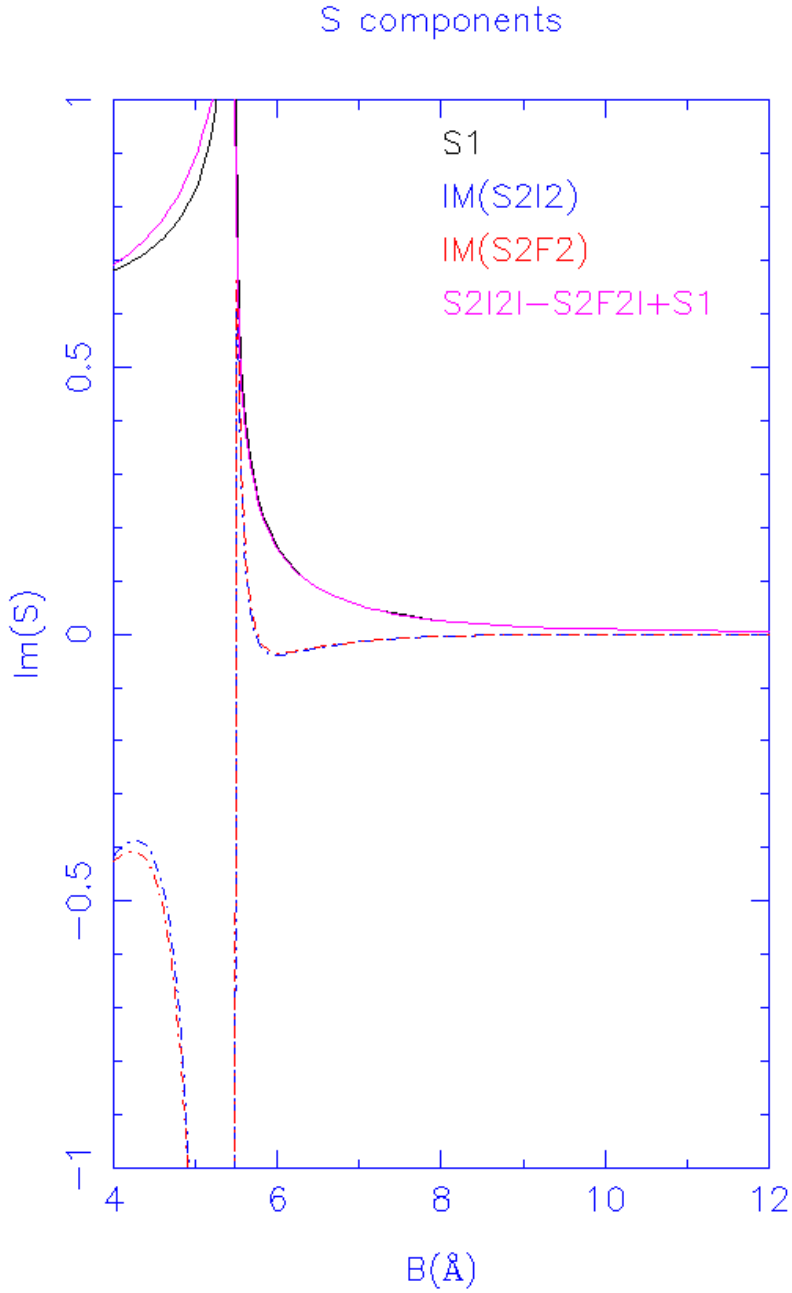
Test runs with electrostatic potential. We found cases where the square bracket is larger than one - unphysical.

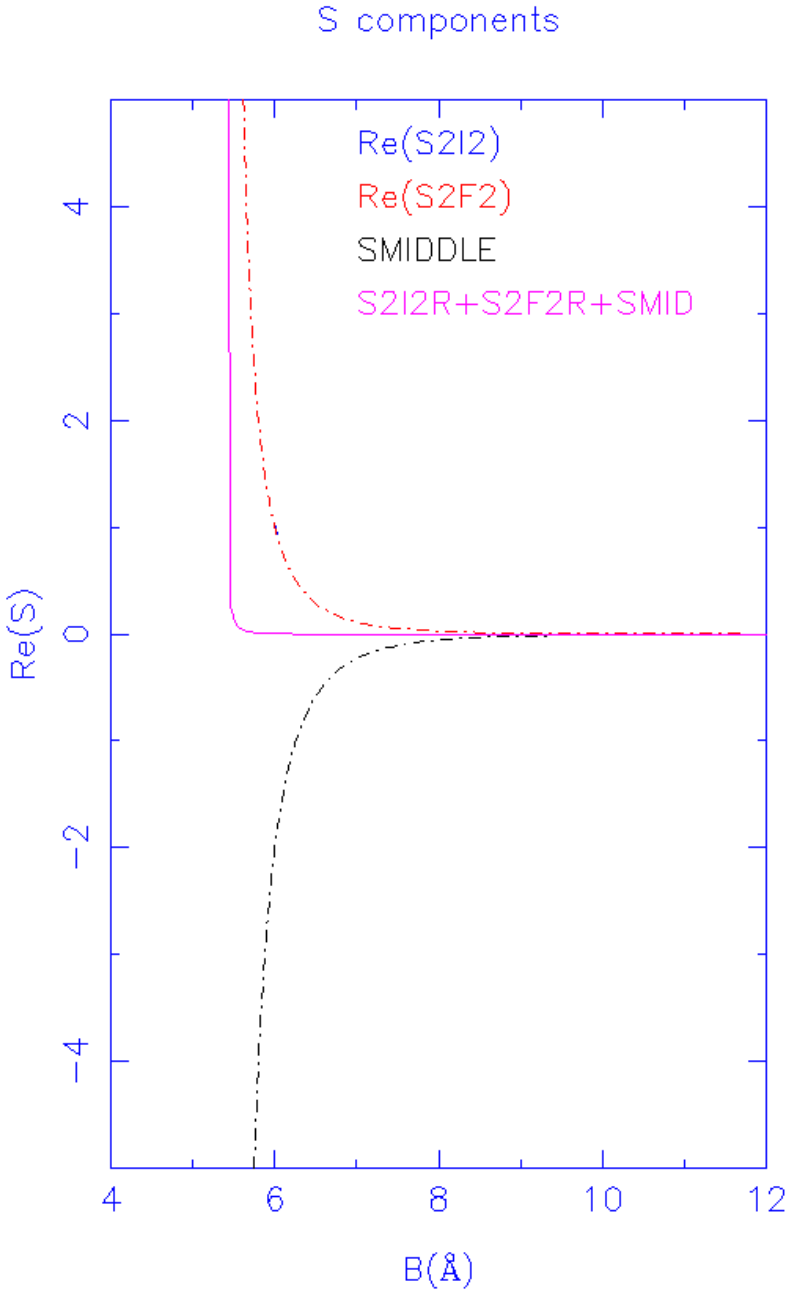
CO_2-CO_2 30012-00001 R50, J2=16, 296 K





CO_2-CO_2 30012-00001 R50, J2=16, 296 K





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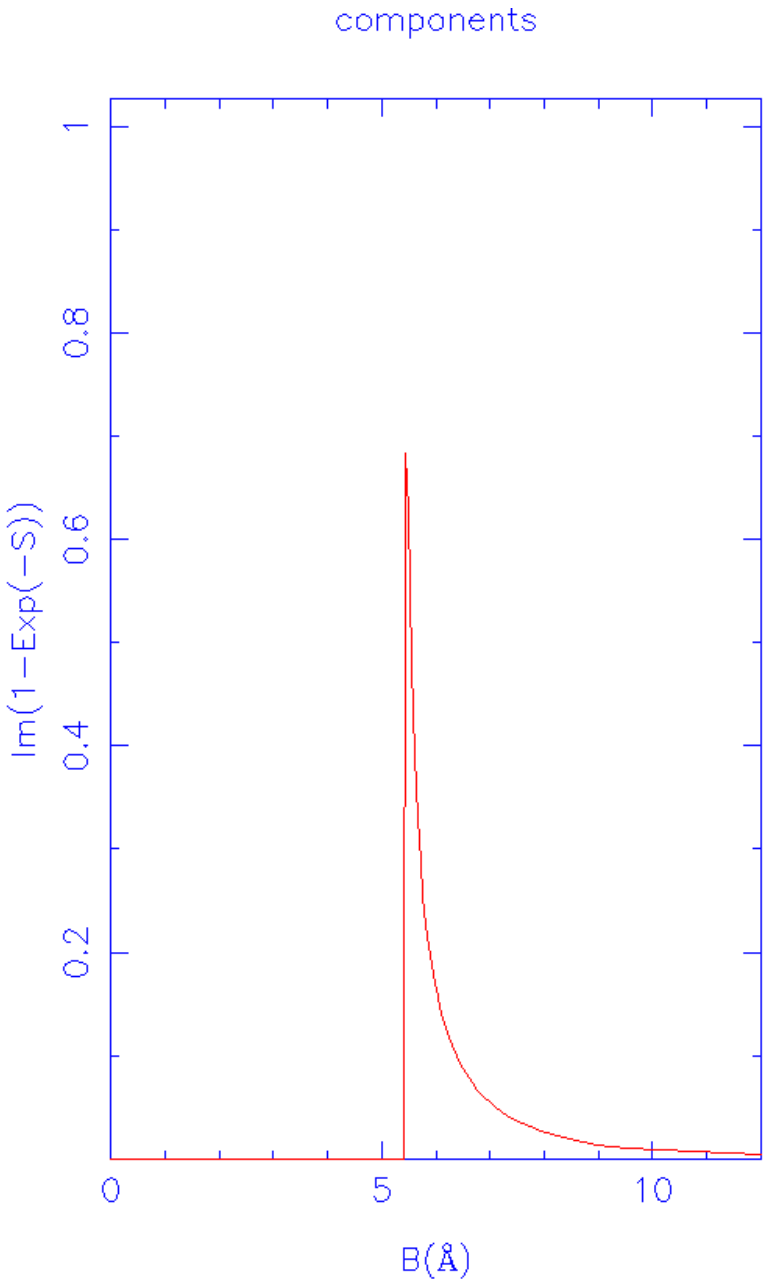
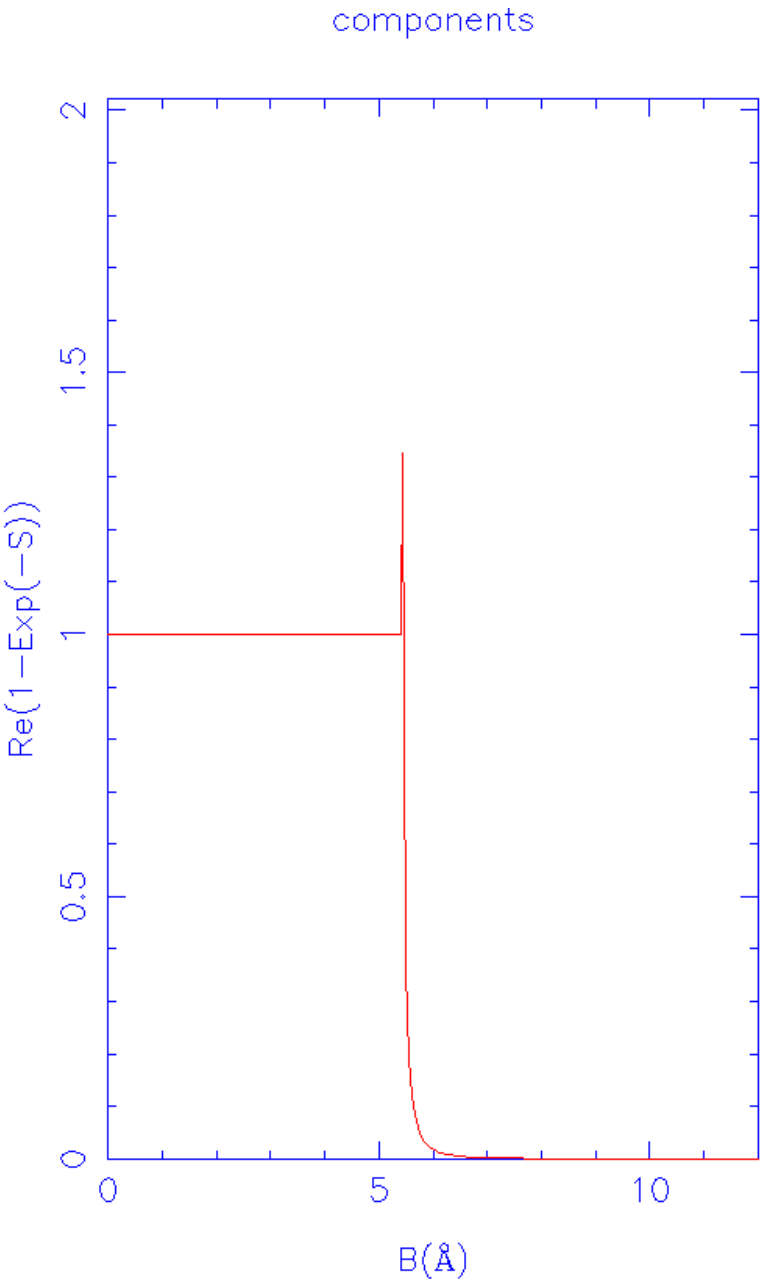
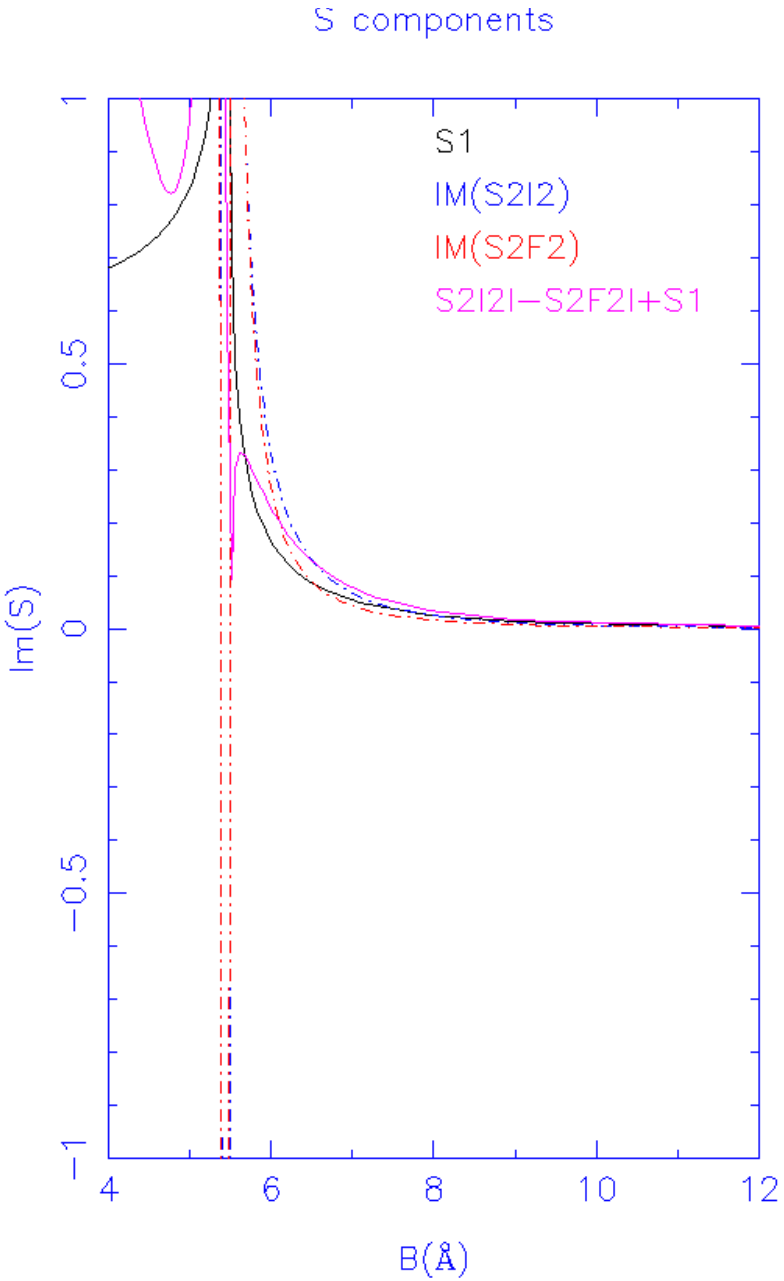
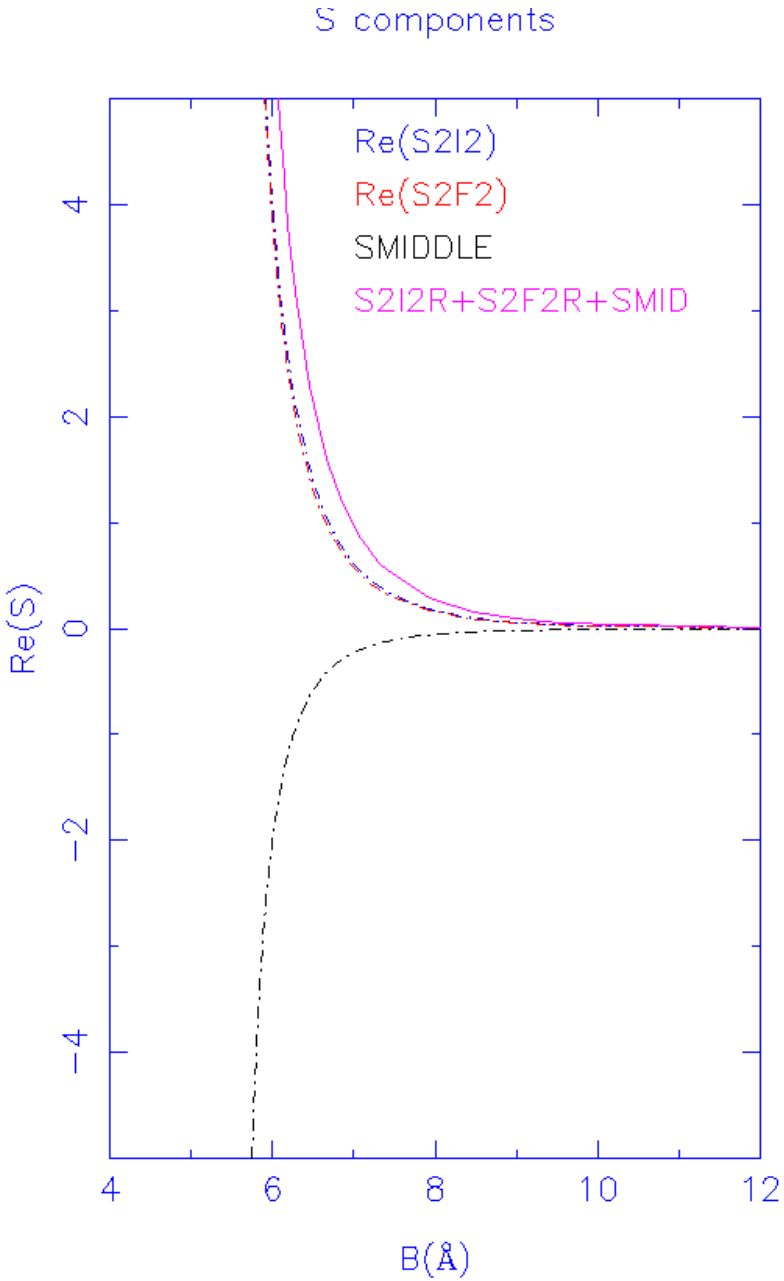


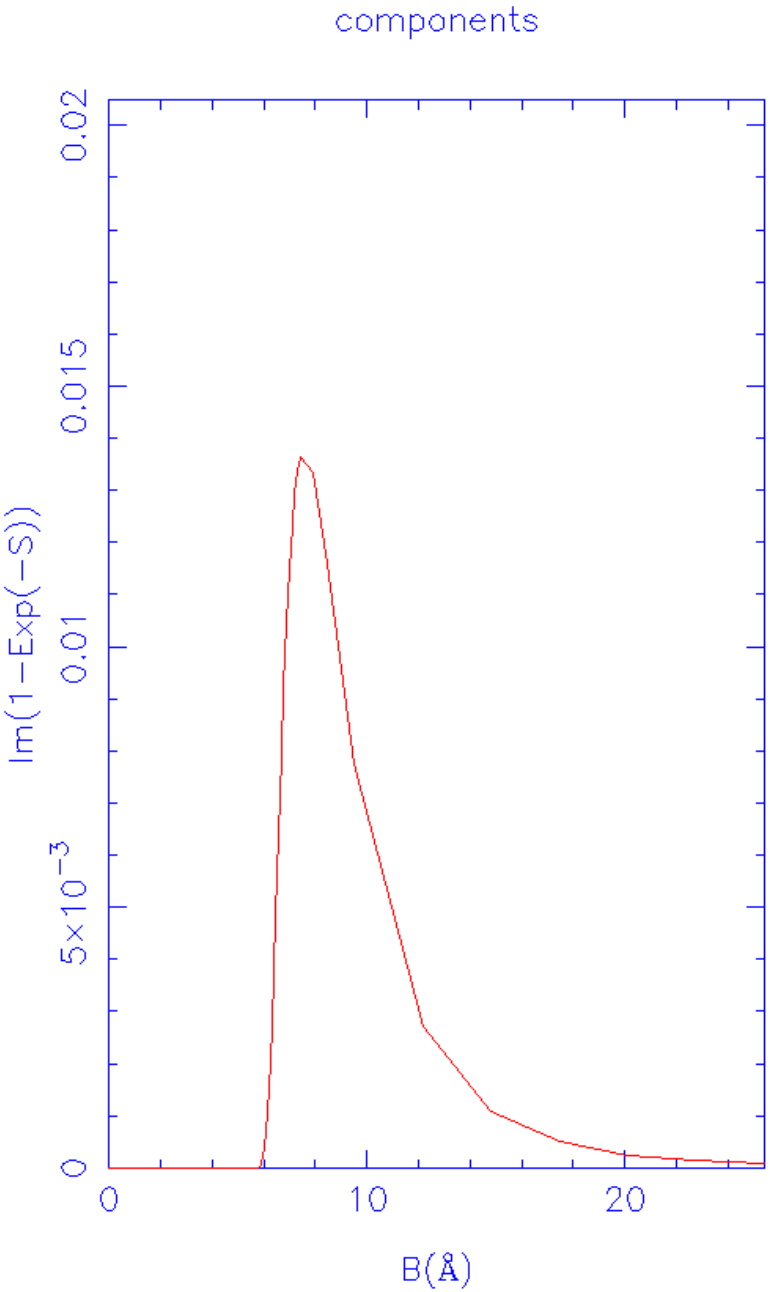


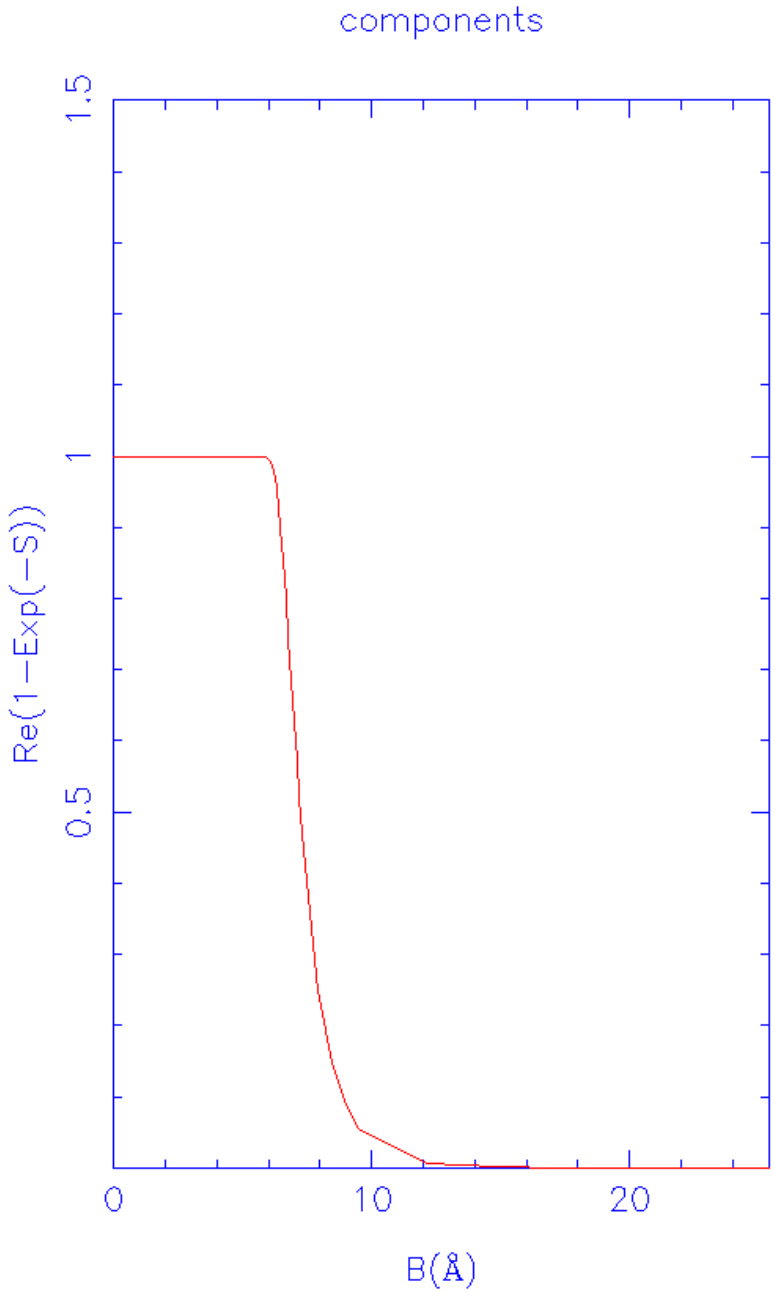
J dependent - CO_2-CO_2 30012-00001 R12, J2=16, 296 K





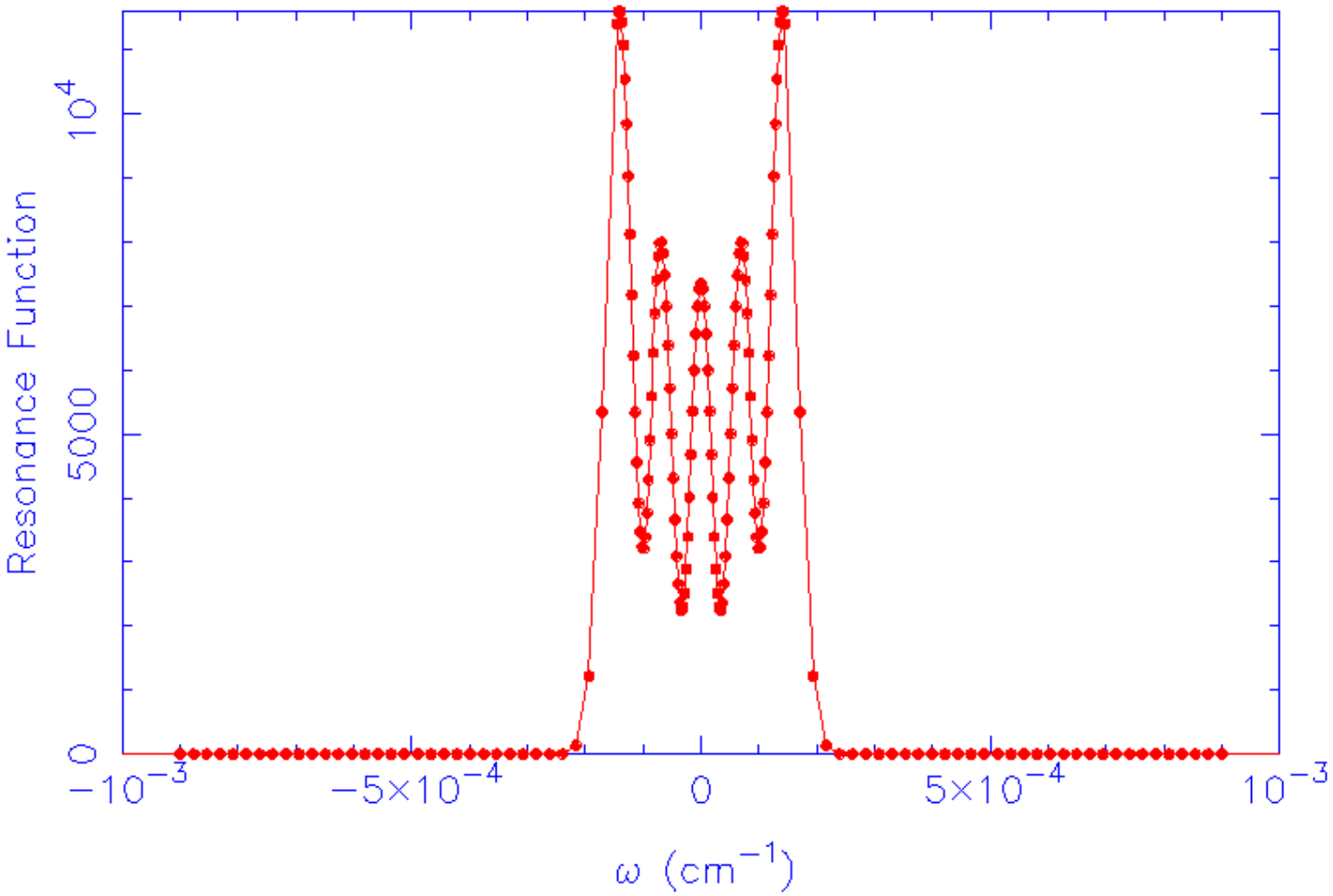
CO_2-CO_2 30012-00001 R12, J2=16, 296 K





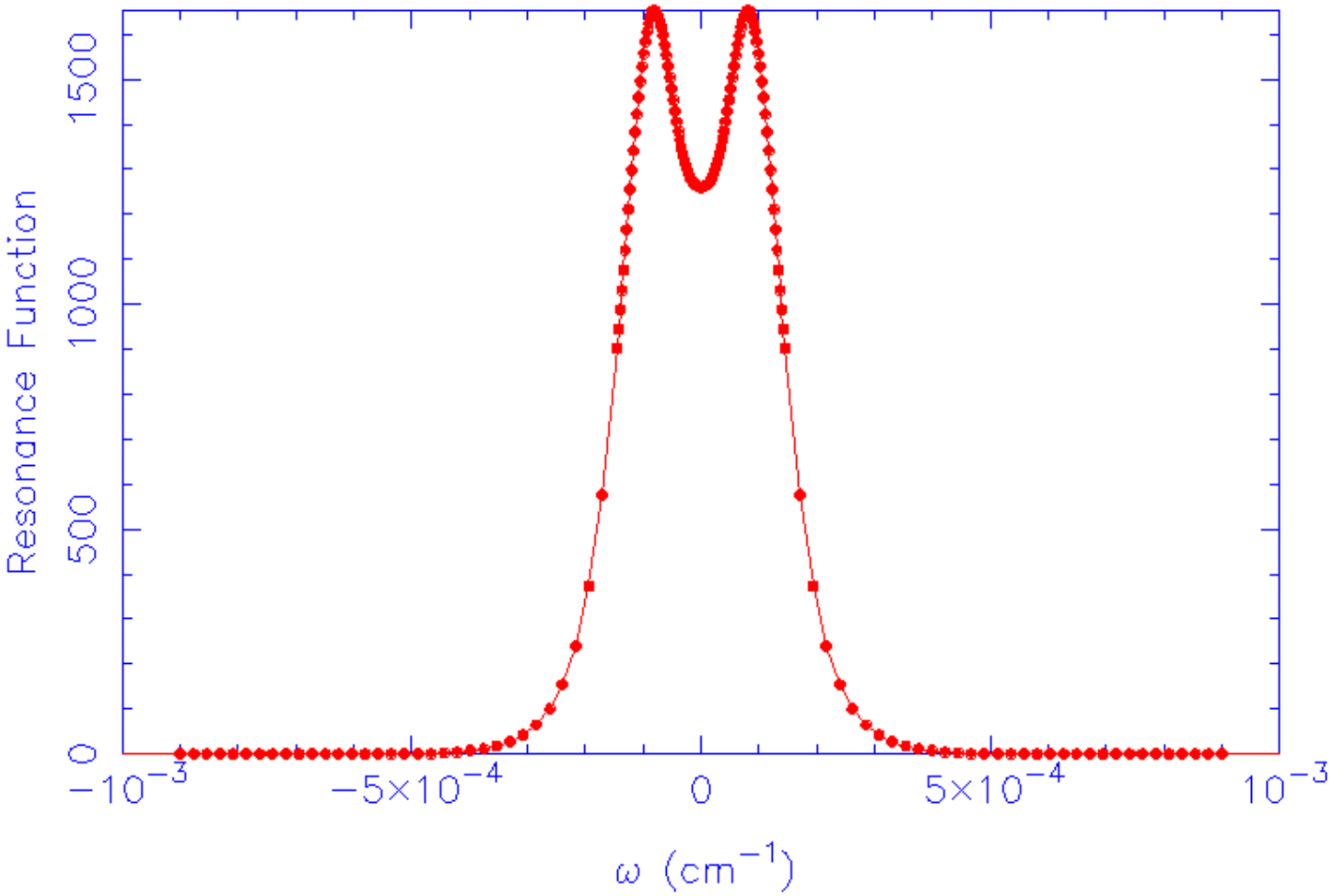
ℓ_1=2, ℓ_2=2 resonance function at 296 K, b = 5.45 Å

Electrostatic potential calculations giving ε/k_b=429.58 K and σ = 3.17 Å

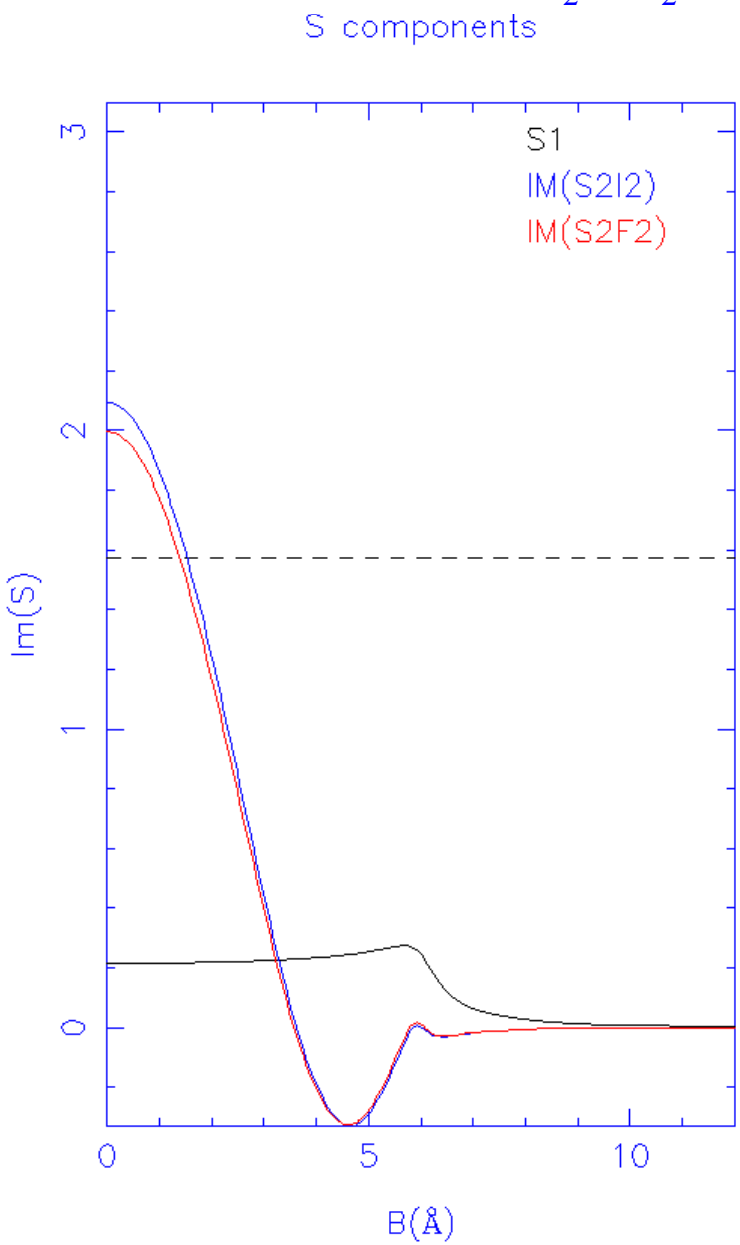


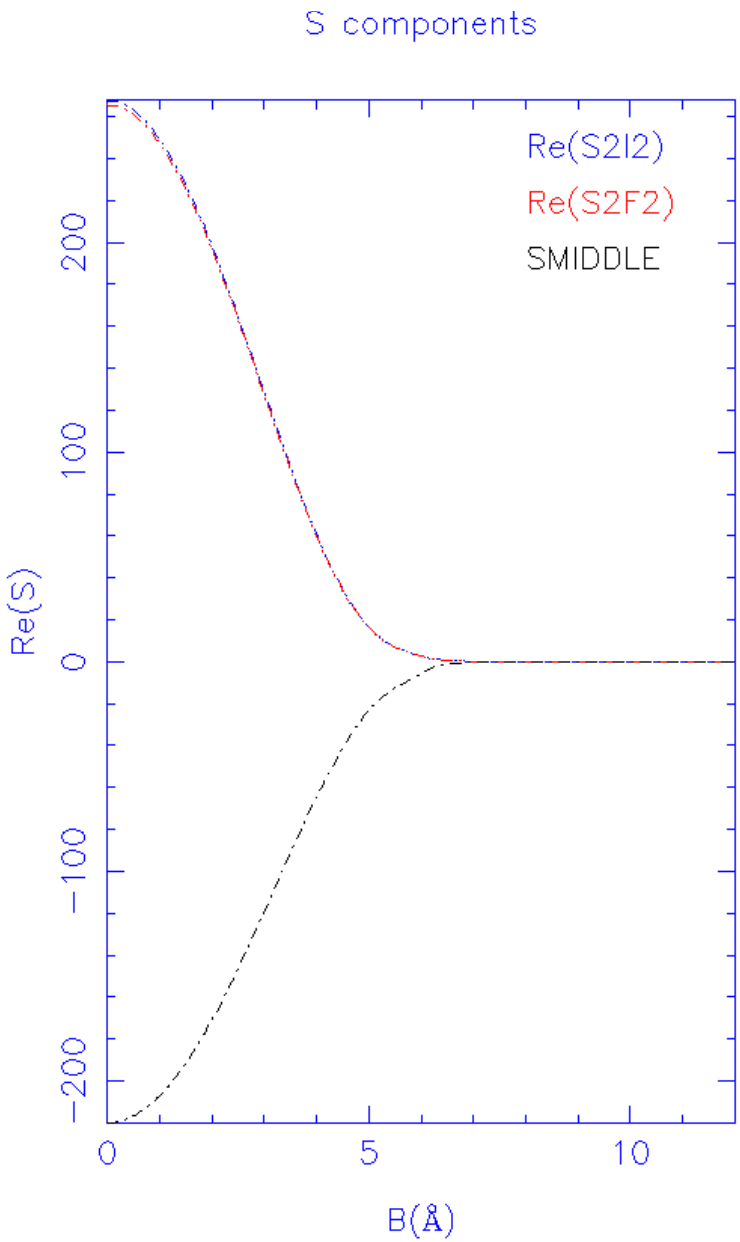
ℓ_1=2, ℓ_2=2 resonance function at 296 K, b = 5.45 Å

Atom-atom expansion → 8 2 2 giving ε/k_b=158.06 K and σ = 4.22 Å



CO_2-CO_2 30012-00001 R50, J2=16, 296 K





Line Shift

J-M Hartmann, JQSRT 110 (2009) 2019–2026

$$\delta\left[\left(\nu_1 + \Delta\nu_1, \nu_2 + \Delta\nu_2, \nu_3 + \Delta\nu_3, J_{f\,-\,J}\right) \leftarrow \left(\nu_1, \nu_2, \nu_3, J_i\right)\right] = \left(J_i - J_f\right)\,\delta_{Rot}\left(|m|\right) + \left(a_1\,\Delta\nu_1 + a_2\,\Delta\nu_2 + a_3\,\Delta\nu_3\right)\,\delta_{Vib}\left(|m|\right)$$

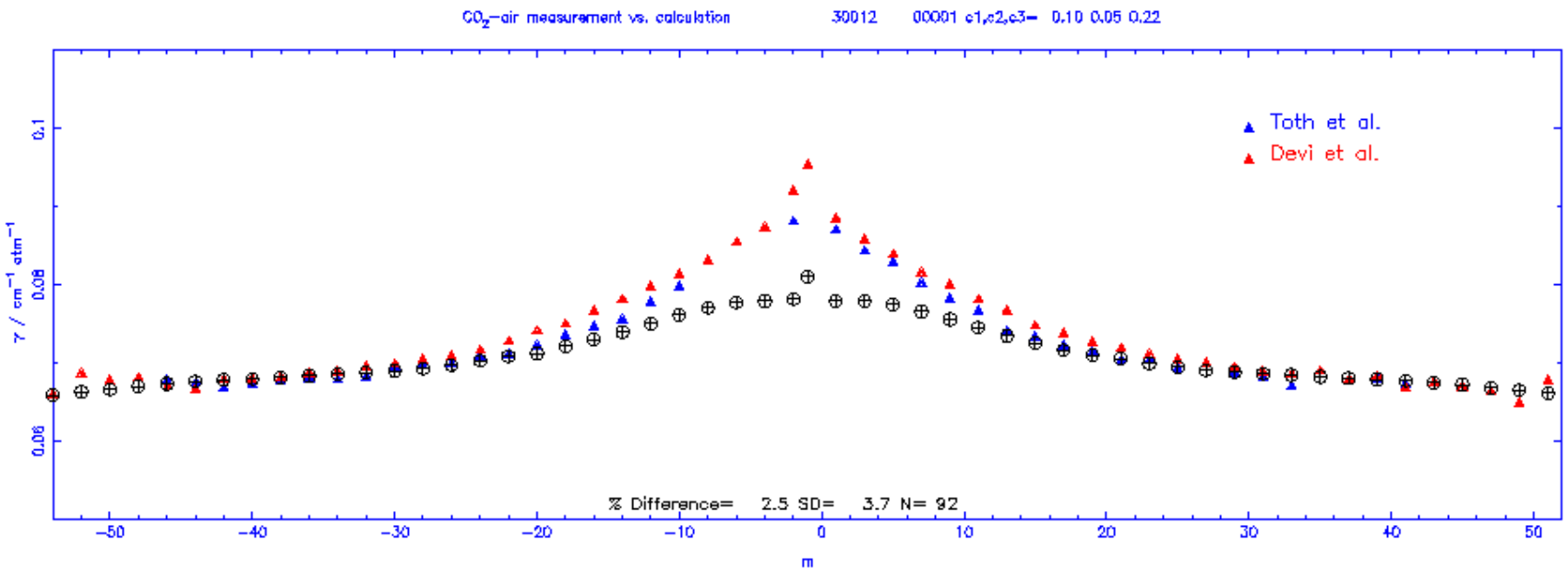
Using Hartmann's coefficients a_1, a_2, and a_3 we form the ratios

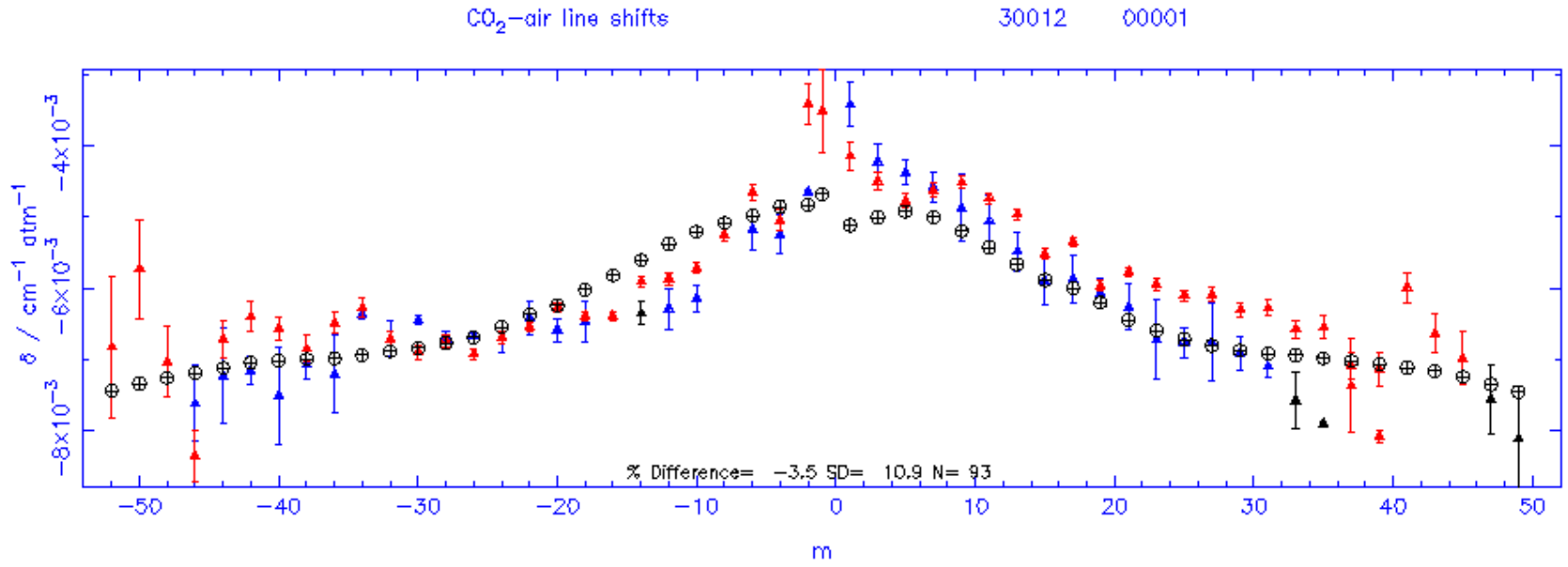
$$r_{12} = \frac{a_2}{a_1},\ r_{13} = \frac{a_3}{a_1},$$

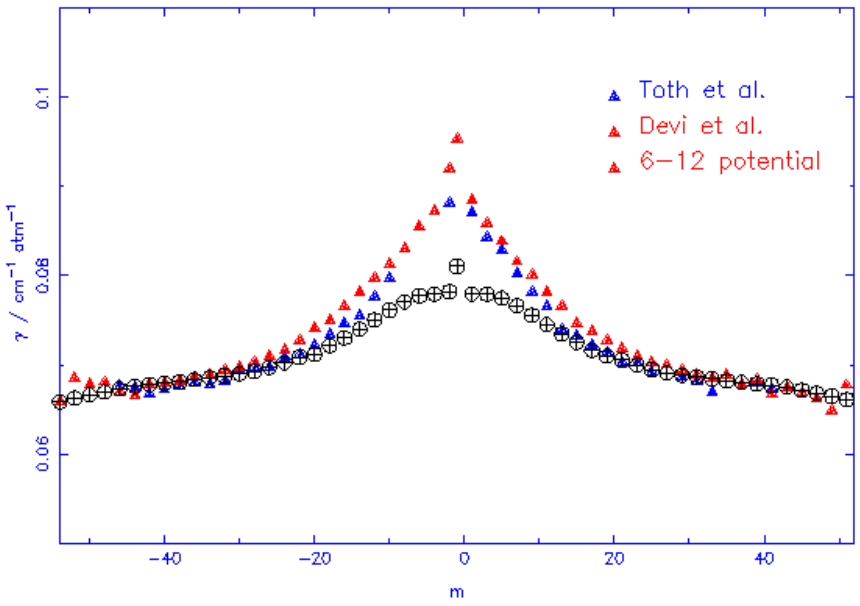
We adjust a_1 and set $a_2 = a_1 * r_{12}$ and $a_3 = a_1 * r_{13}$ by matching to the data of Toth *et al*. and Devi *et al*. for the 30012-00001 band transitions.

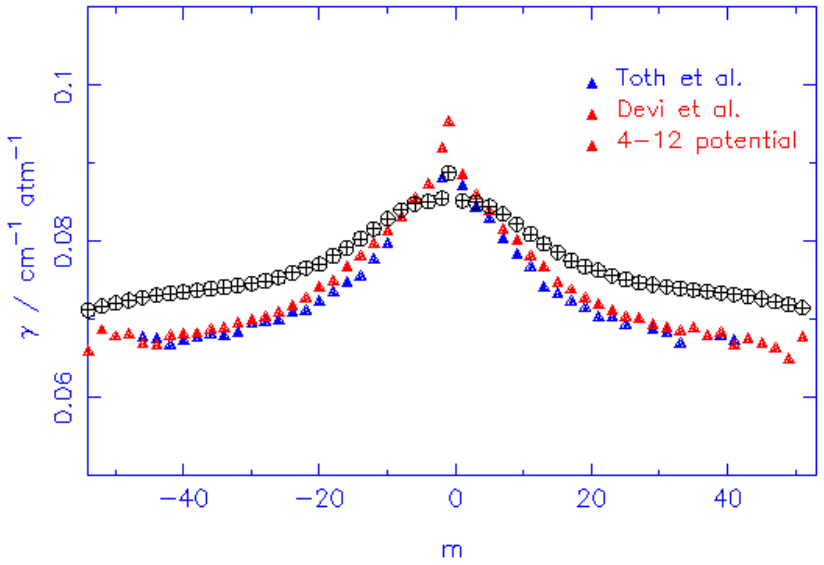
Current values

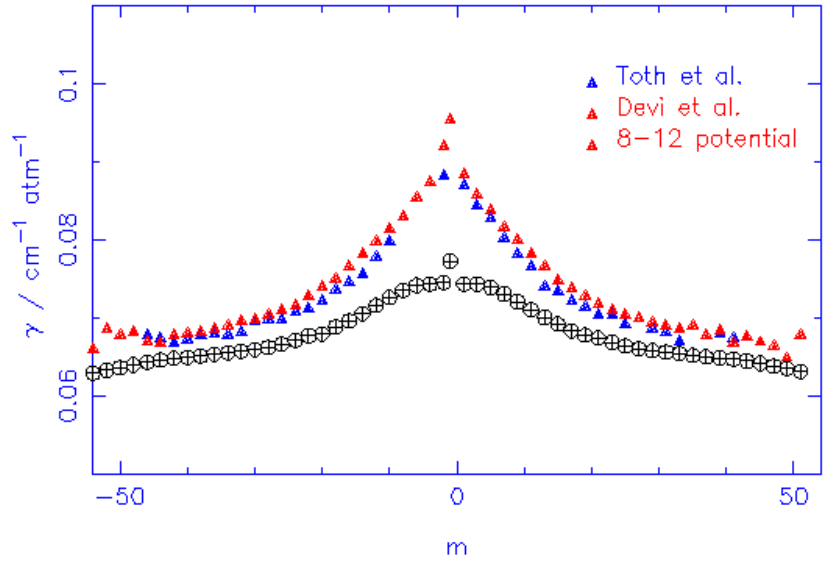
$a_1 = 0.1000$, $a_2 = 0.0516$, $a_3 = 0.2236$

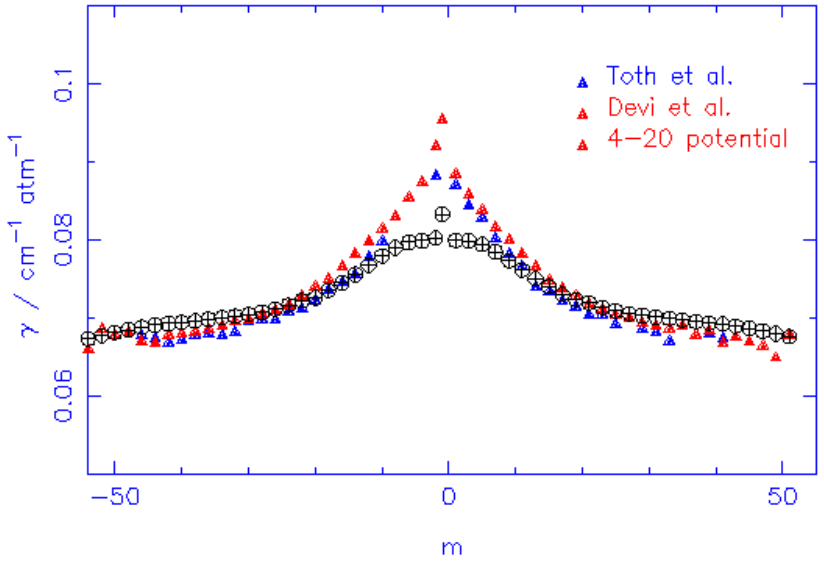

CO2–air measurement vs. calculation 30012 00001 c1,c2,c3= 0.10 0.05 0.22
Toth et al.
Devi et al.
γ / cm⁻¹ atm⁻¹
0.1
0.08
0.06
% Difference= 2.5 SD= 3.7 N= 92
−50 −40 −30 −20 −10 0 10 20 30 40 50
m

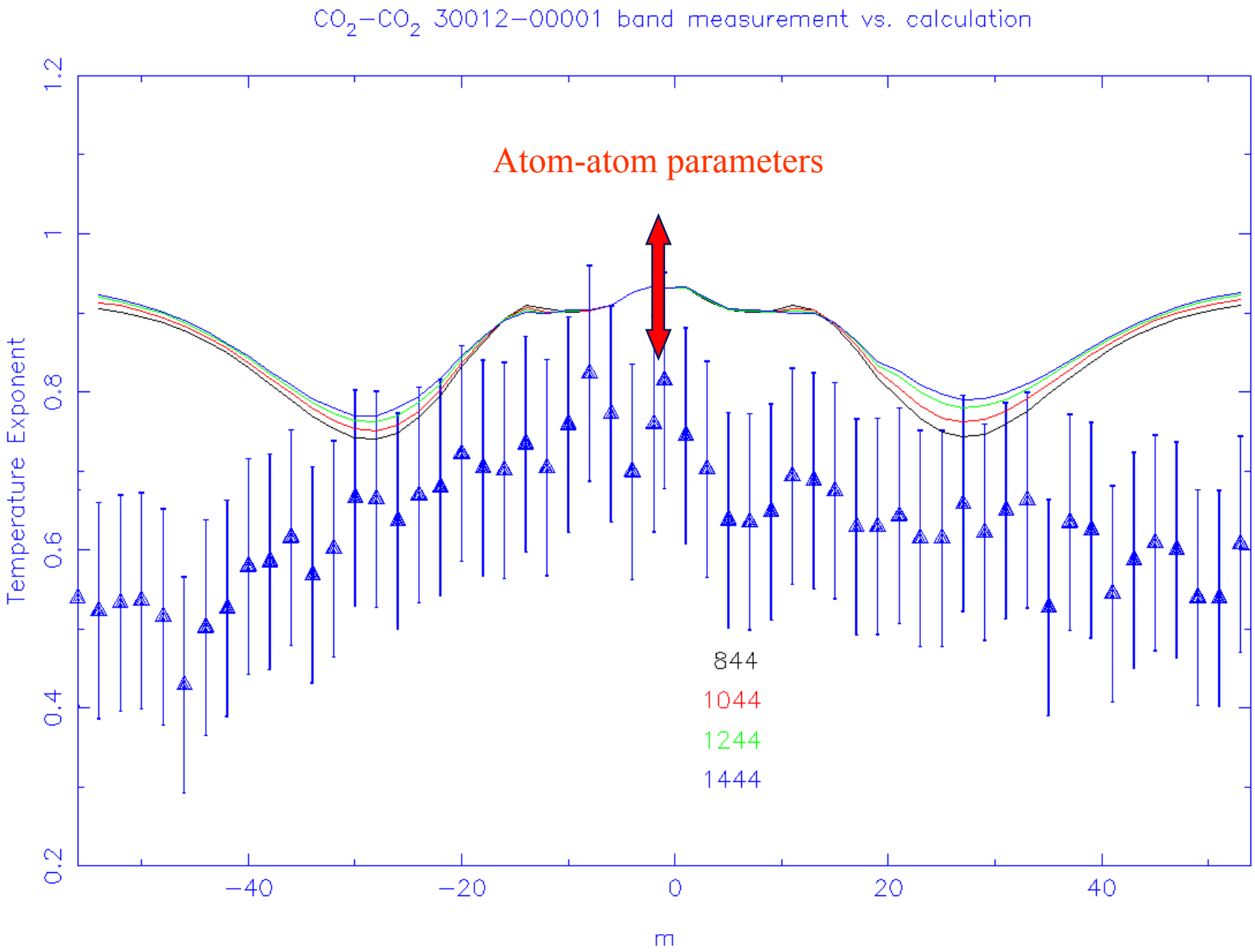

CO2–air line shifts 30012 00001
δ / cm⁻¹ atm⁻¹
−4x10⁻³
−6x10⁻³
−8x10⁻³
% Difference= −3.5 SD= 10.9 N= 93
−50 −40 −30 −20 −10 0 10 20 30 40 50
m


Toth et al.
Devi et al.
6−12 potential
γ / cm⁻¹ atm⁻¹
0.1
0.08
0.06
−40
−20
0
20
40
m


Toth et al.
Devi et al.
4−12 potential
γ / cm⁻¹ atm⁻¹
0.1
0.08
0.06
−40
−20
0
20
40
m


Toth et al.
Devi et al.
8−12 potential
γ / cm⁻¹ atm⁻¹
0.1
0.08
0.06
−50
0
50
m


Toth et al.
Devi et al.
4−20 potential
γ / cm⁻¹ atm⁻¹
0.1
0.08
0.06
−50
0
50
m


CO2–CO2 30012–00001 band measurement vs. calculation
Atom-atom parameters
Temperature Exponent
1.2
1
0.8
0.6
0.4
0.2
−40
−20
0
20
40
m
844
1044
1244
1444

Future work

Potential

powers, order, rank

→ Aim is that a single calculation will give the half-widths and their temperature dependence, the line shifts and their temperature dependence.

results are strongly dependent on the potential

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