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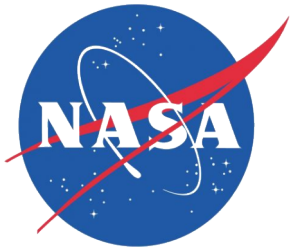
Complex Robert-Bonamy calculation of H_2O broadened by N_2, O_2 and air made with realistic trajectories

Julien Lamouroux, Anne L. Laraia, Robert R. Gamache,
University of Massachusetts Lowell, Lowell

Qiancheng Ma,
Columbia University, New York

Richard H. Tipping
University of Alabama, Tuscaloosa



Introduction

- Within the semi-classical theories, the relative radiator-perturber trajectories are described classically

- Several models are adopted to approximate the real trajectories : straight line, parabolic model

- More recently, more realistic trajectories can be obtained by numerical integration of the Hamilton's Equations

R.R Gamache and R.W. Davies, *JMS* **109** (1985), 283-299

Theoretical N_2-, O_2-, and Air-Broadened Halfwidths of $^{16}O_3$ Calculated by Quantum Fourier Transform Theory with Realistic Collision Dynamics

We have evaluated collision-broadened halfwidths of ozone with nitrogen and oxygen as the perturbing gases. Calculations using conventional Anderson theory or quantum Fourier transform theory are shown to be some 25 to 35% too low when compared to the experimental measurements. We show that it is important to consider more realistic collision dynamics in the calculations. By replacing the classical path trajectories by linear trajectories with constant velocities chosen to give the equations of motion exact to first order in time, we develop the interruption function in terms of the actual distance of closest approach determined by the intermolecular potential and the velocity at this point. This improvement to the theory results in N_2- and O_2-broadened halfwidths which are in good agreement with the experimental measurements. Air-broadened halfwidths have been evaluated from the nitrogen and oxygen results via the formula $\gamma_{air} = 0.79\gamma_{N_2} + 0.21\gamma_{O_2}$. The results agree with the air-broadened measurements to better than 5%.

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B.K. Antony, S. Neshyba, and R.R. Gamache, *JQSRT* **105**(2007), 148-163

Self-broadening of water vapor transitions via the complex Robert–Bonamy theory

4.2. Effects of the trajectories

It is known that for certain collision systems the effects of the trajectories can be important [91,92]. The current model uses the Robert and Bonamy parabolic model [66], which is correct to 2nd order in time. The method uses the isotropic part ($\ell_1 = \ell_2 = 0$) of the atom–atom potential to determine the distance, effective velocity, and force at closest approach. To simplify the trajectory calculations the isotropic part of the atom–atom expansion is fit to an isotropic Lennard–Jones 6–12 potential and the resulting parameters are used in the trajectory calculations. As the order of the expansion changes so do the resulting Lennard–Jones 6–12 potential parameters that define the trajectories. For a number of systems the change in the trajectories has a marked effect on the half-width [92–97].

Calculations were made using the isotropic part of the 8th order expansion of the atom–atom potential and solving Hamilton's equations for the exact trajectories. There are no significant differences in the half-width or line shift computed from the two models. These results imply the R–B trajectory model works well for this system. However, the above results for calculations for different orders of expansion of the atom–atom

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Why this study ?

- In a previous study, Neshyba and Gamache (unpublished data) compared half-widths of water vapor transitions determined via the parabolic model or by solving Hamilton's equations.

- Difference ~10% for some lines were found between the both model by Q. Ma

We need to re-investigate the Hamilton's Equations trajectory model

Complex Robert-Bonamy formalism

- Complex valued ;
- Short range atom-atom component to the intermolecular potential ;
- Improved treatment for close collisions

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

where n_2 is the number density of perturbers and $\langle\ \rangle_{b,v,J}$ represents an average over all trajectories (impact parameter b and initial relative velocity v) and initial rotational state J_2 of the collision partner.

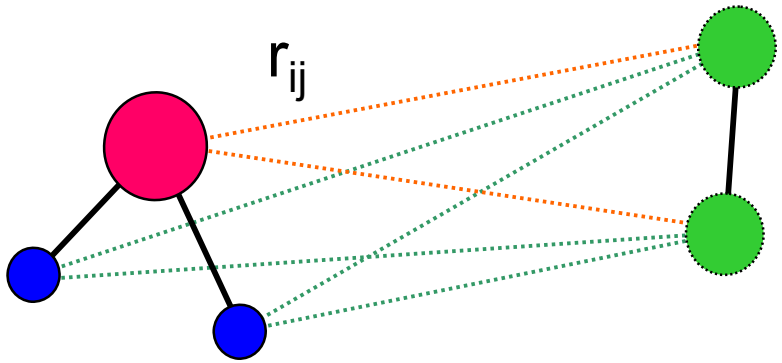
The potential

- Electrostatic components

$$V_{1,2}^{elec} = V_{\mu_1\mu_2} + V_{\mu_1\theta'_2} + V_{\theta'_1\mu_2} + V_{\theta''_1\mu_2} + V_{\theta'_1\theta'_2} + V_{\theta''_1\theta'_2} + \cdots$$

- Atom-atom potential

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



ε and σ have to be adjusted

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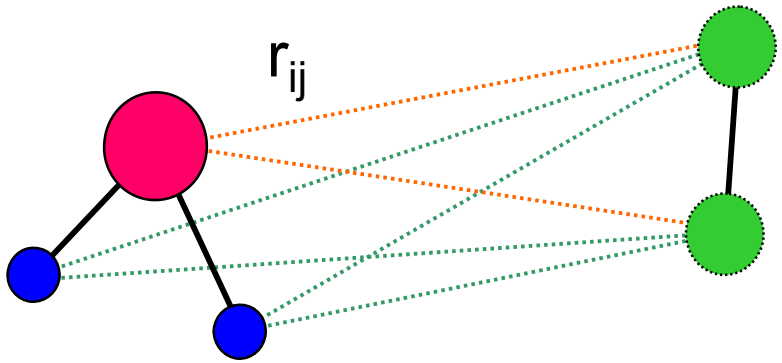


ε and σ have to be adjusted

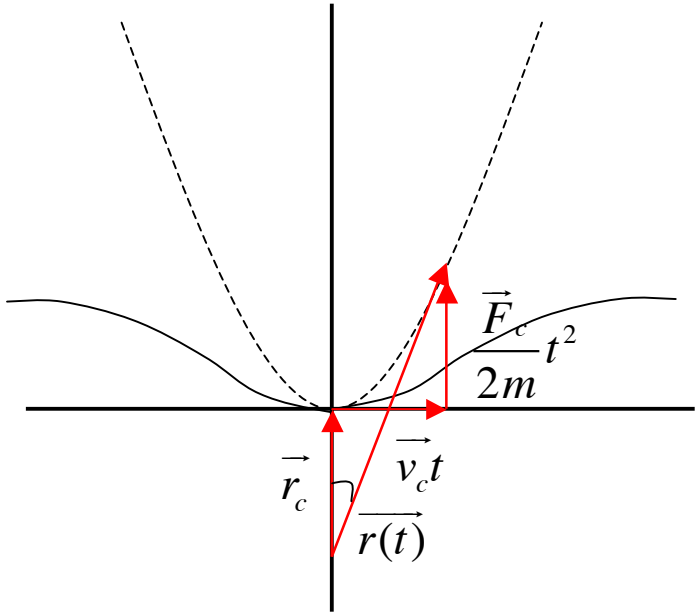
Trajectories : Parabolic model

The real trajectories are approximated by an analytical parabolic model correct at second order of time

$$R(t) = \sqrt{r_c^2 + v_c'^2 t^2} \ ;$$

$$\sin(\psi(t)) = \frac{v_c t}{\sqrt{r_c^2 + v_c'^2 t^2}}$$

$$\cos(\psi(t)) = \frac{r_c + \frac{\left|\vec{F}_c\right|}{2m} t^2}{\sqrt{r_c^2 + v_c'^2 t^2}}$$

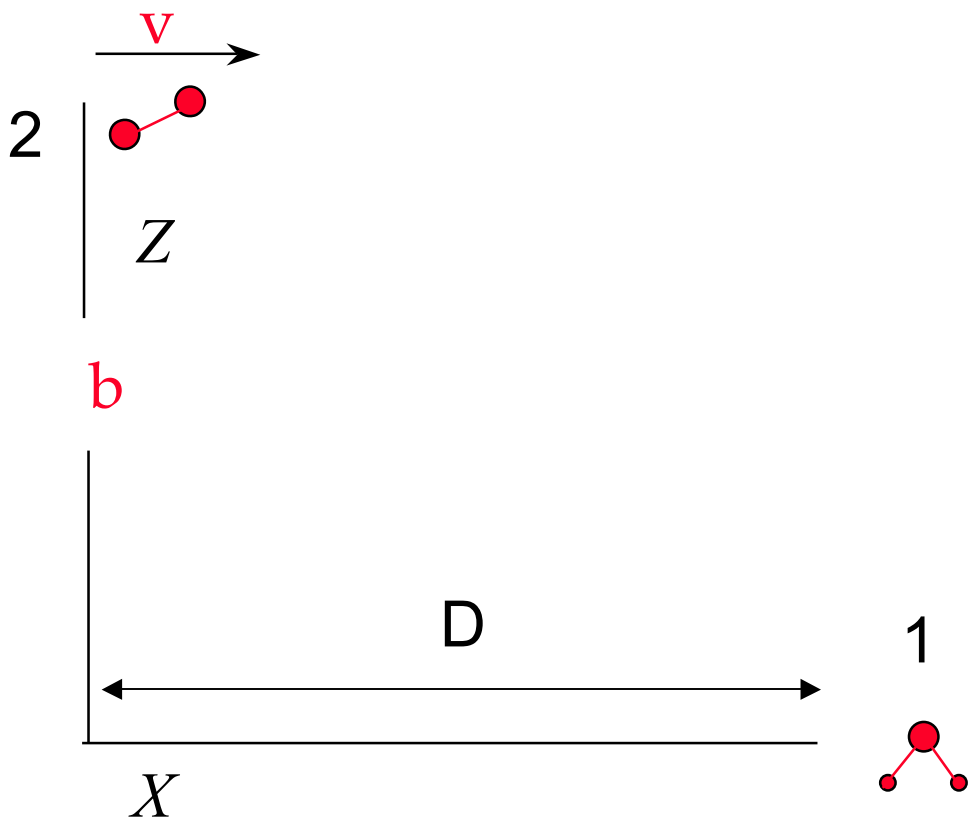


$$\vec{r(t)} \cong \vec{r}_c + \vec{v}_c t + \frac{\vec{F(r_c)}}{\mu} \frac{t^2}{2}$$

r_c, v_c, v_c' are determined from the isotropic part of the atom-atom potential

Trajectories : Hamilton's Equations

The trajectories are obtained by the numerical integration of the Hamilton's Equations



$$H = \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + V^{iso}$$

$$\begin{cases} \frac{d}{dt} X_i = \frac{\partial H}{\partial P_i} \\ \frac{d}{dt} P_i = -\frac{\partial H}{\partial X_i} \end{cases}$$

Trajectories : Hamilton's Equations

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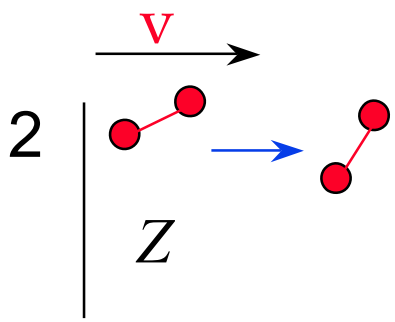

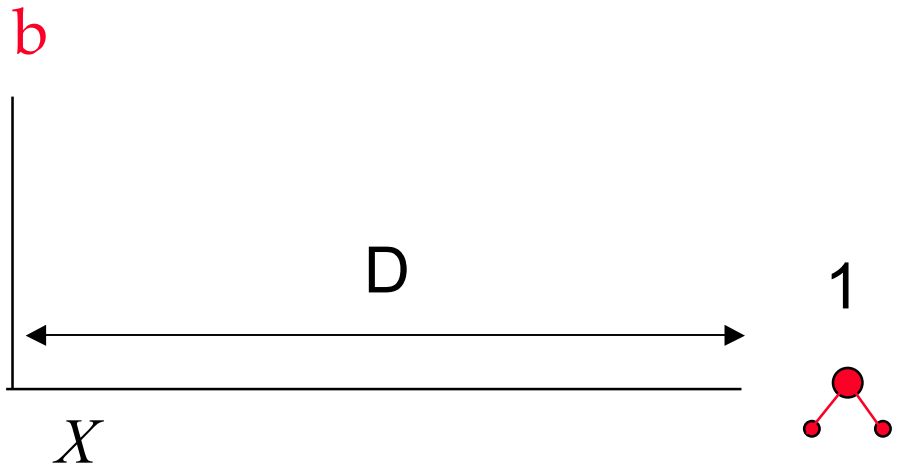

$$H = \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + V^{iso}$$

t=t+Δt

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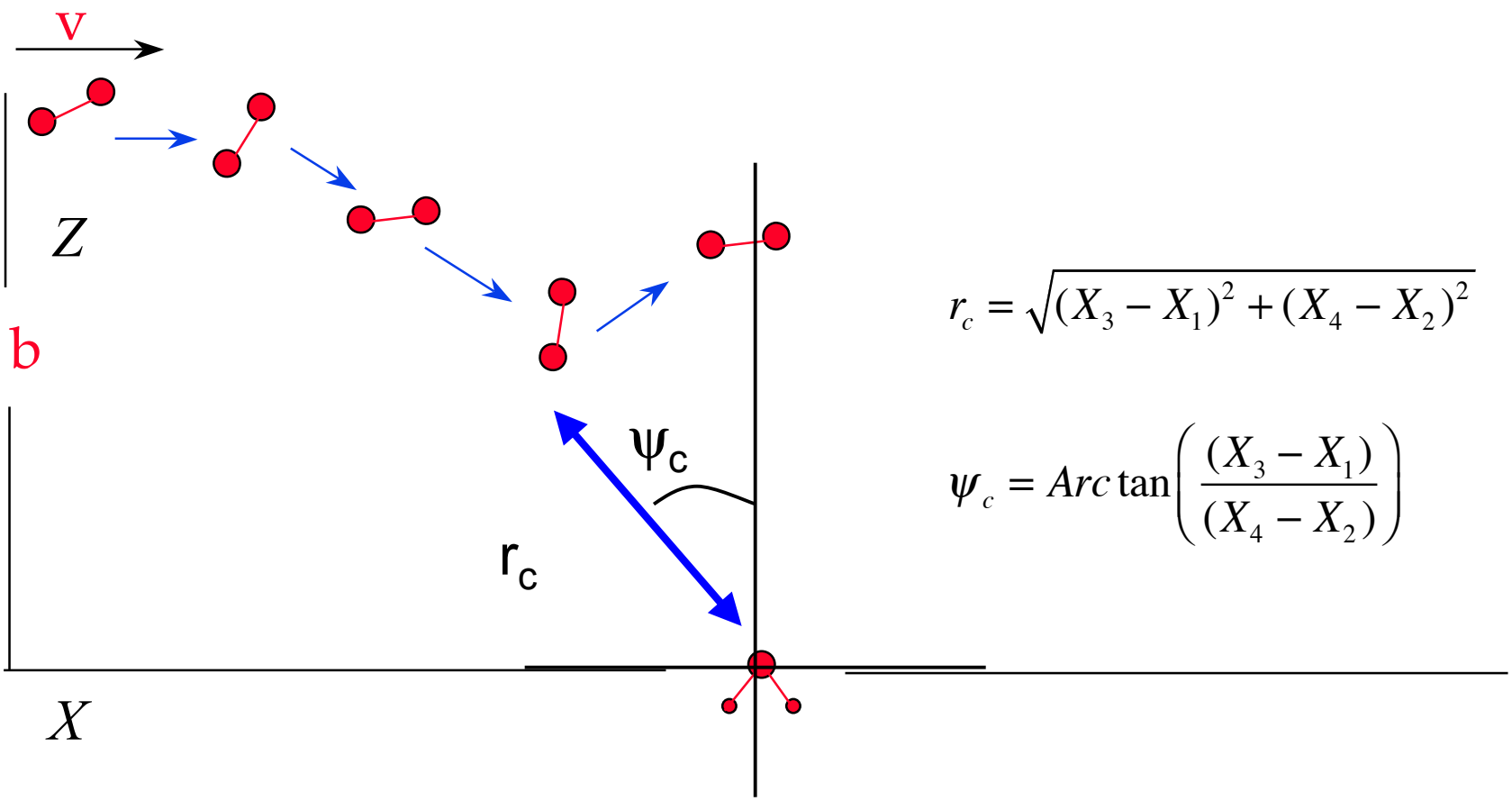
Trajectories : Hamilton's Equations

The closest approach parameters are determined numerically



$$r_c = \sqrt{(X_3 - X_1)^2 + (X_4 - X_2)^2}$$

$$\psi_c = Arc\tan\left(\frac{(X_3 - X_1)}{(X_4 - X_2)}\right)$$

Trajectories : Hamilton's Equations

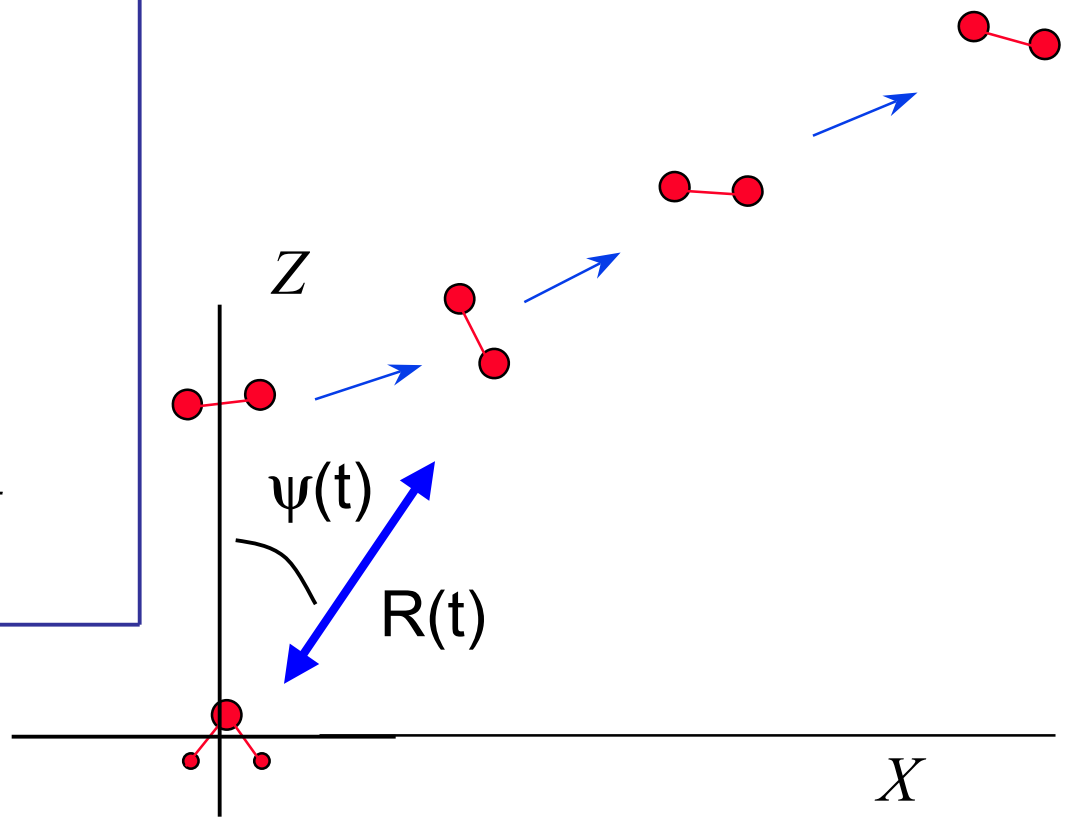
$$H = \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + V^{iso}$$

$$\begin{cases} \frac{d}{dt} X_i = \frac{\partial H}{\partial P_i} \\ \frac{d}{dt} P_i = -\frac{\partial H}{\partial X_i} \end{cases}$$

$$R(t) = \sqrt{(X_3 - X_1)^2 + (X_4 - X_2)^2}$$

$$\psi(t) = Arc\tan\left(\frac{(X_3 - X_1)}{(X_4 - X_2)}\right)$$

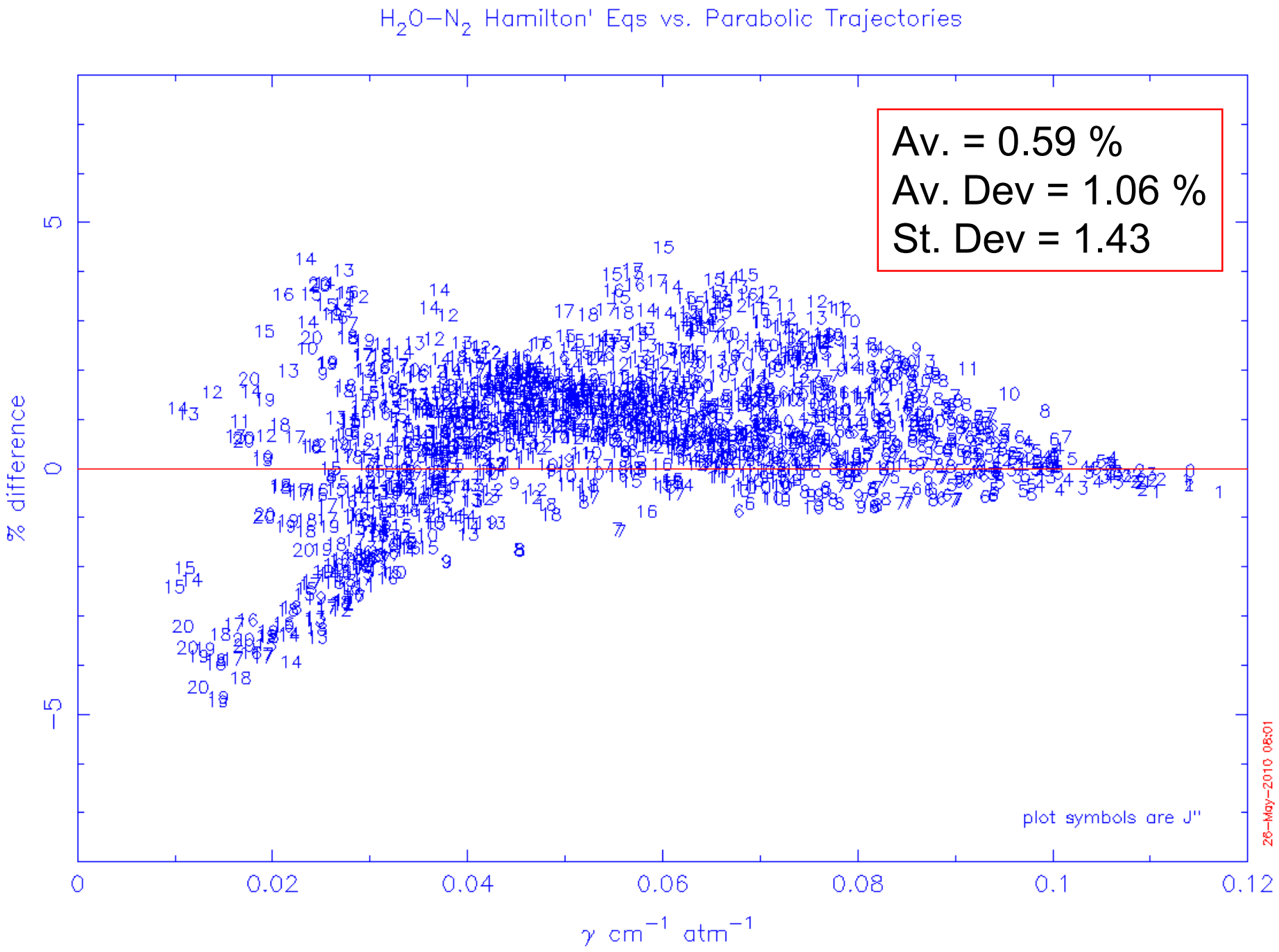
t=t+Δt

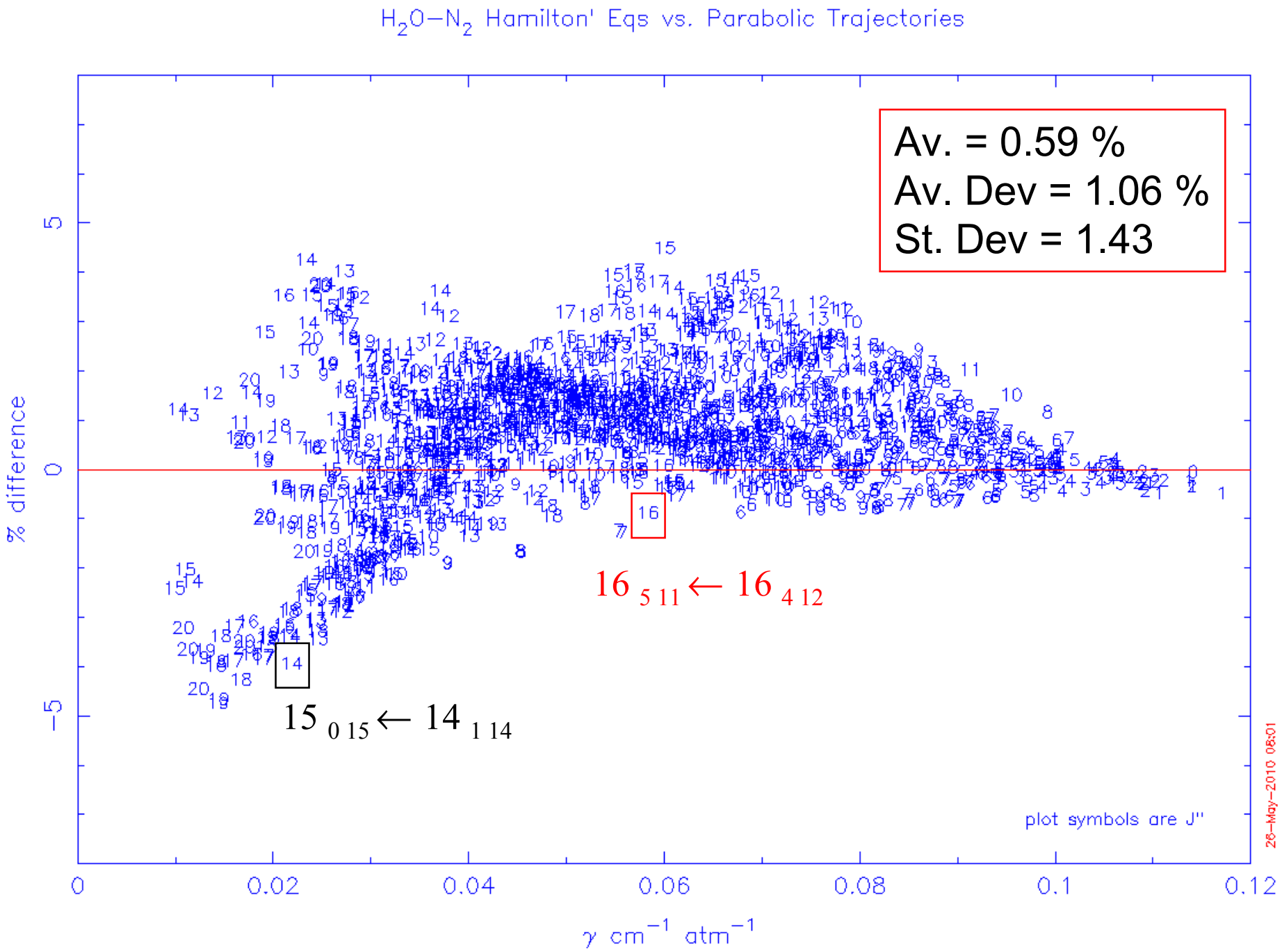


Initial calculations for water vapor

- CRB calculations for 1639 transitions for the (000)-(000) band for $H_2{}^{16}O$-N_2, $H_2{}^{16}O$-O_2 and $H_2{}^{16}O$-air
- Transitions selected from HITRAN2004 database
- Potential expanded at order=8 and rank=2
- The atom-atom parameters were adjusted to the Payne et al. recommended values for the 22-GHz and 183-GHz lines
- Average over the Maxwell-Boltzmann distributions of velocities (35 Temperatures)
- Parabolic trajectory model

R. R. Gamache and A. L. Laraia, J. Mol. Spectrosc. ***257****, 116-127 (2009).*


H2O–N2 Hamilton' Eqs vs. Parabolic Trajectories
Av. = 0.59 %
Av. Dev = 1.06 %
St. Dev = 1.43
% difference
5
0
-5
0
0.02
0.04
0.06
0.08
0.1
0.12
γ cm−1 atm−1
plot symbols are J''
26-May-2010 06:01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Av. = 0.59 %
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5
0
-5
0
0.02
0.04
0.06
0.08
0.1
0.12
γ cm−1 atm−1
16 5 11 ← 16 4 12
15 0 15 ← 14 1 14
plot symbols are J''
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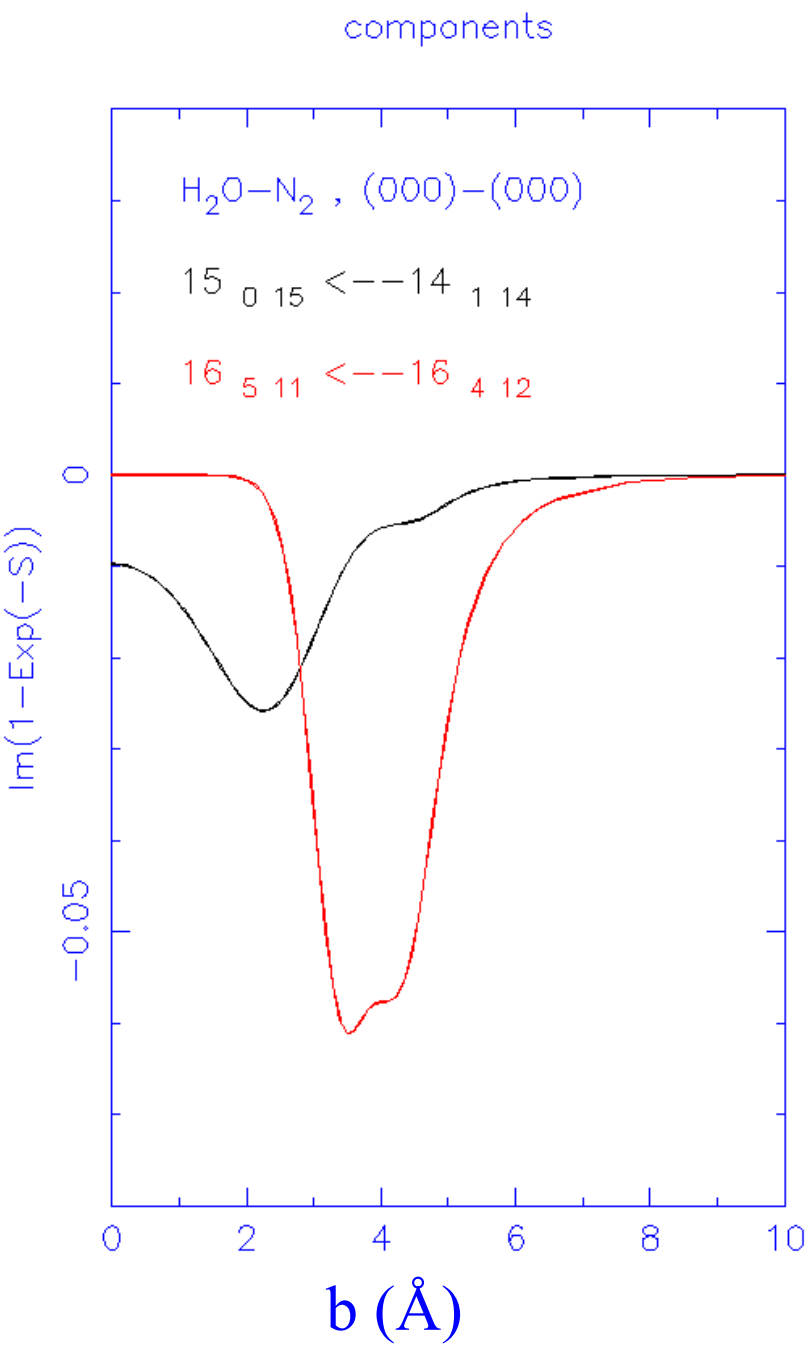
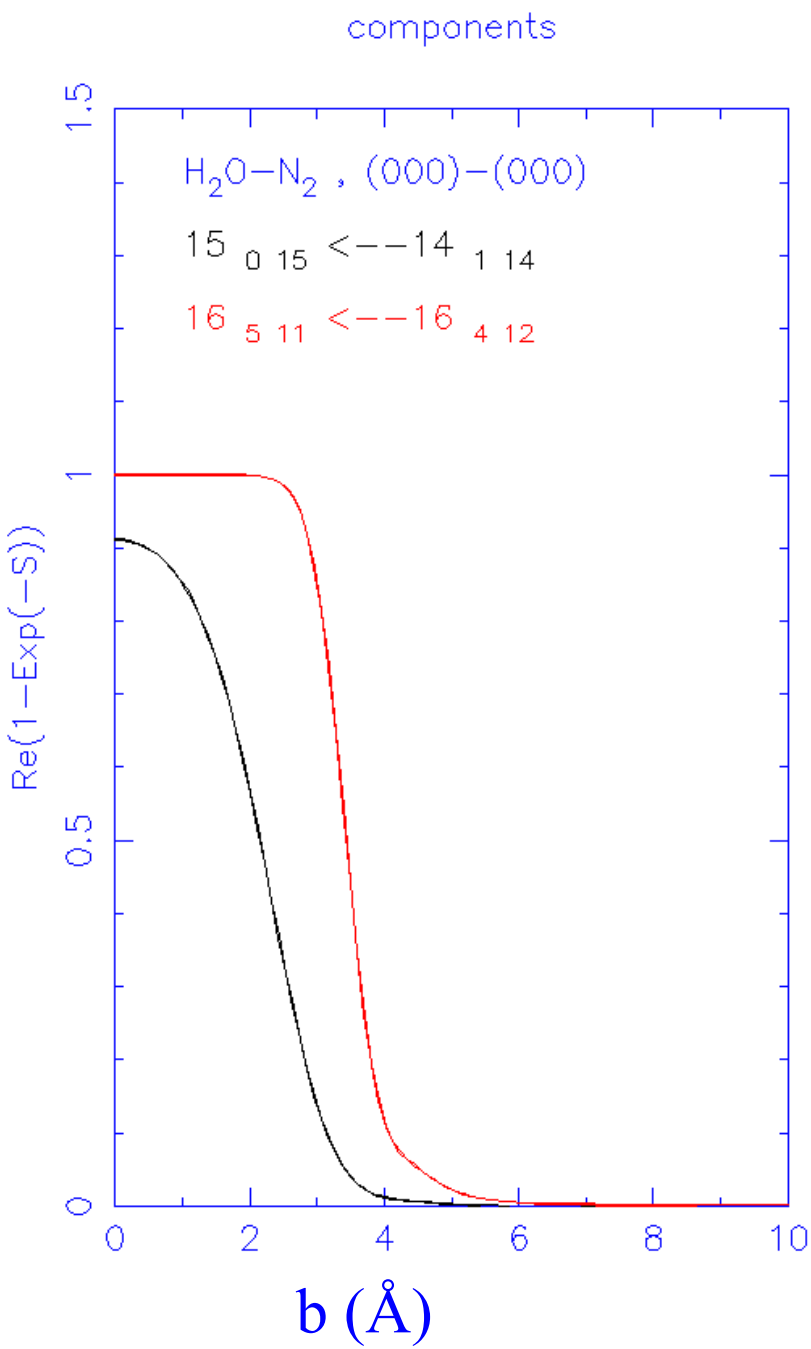
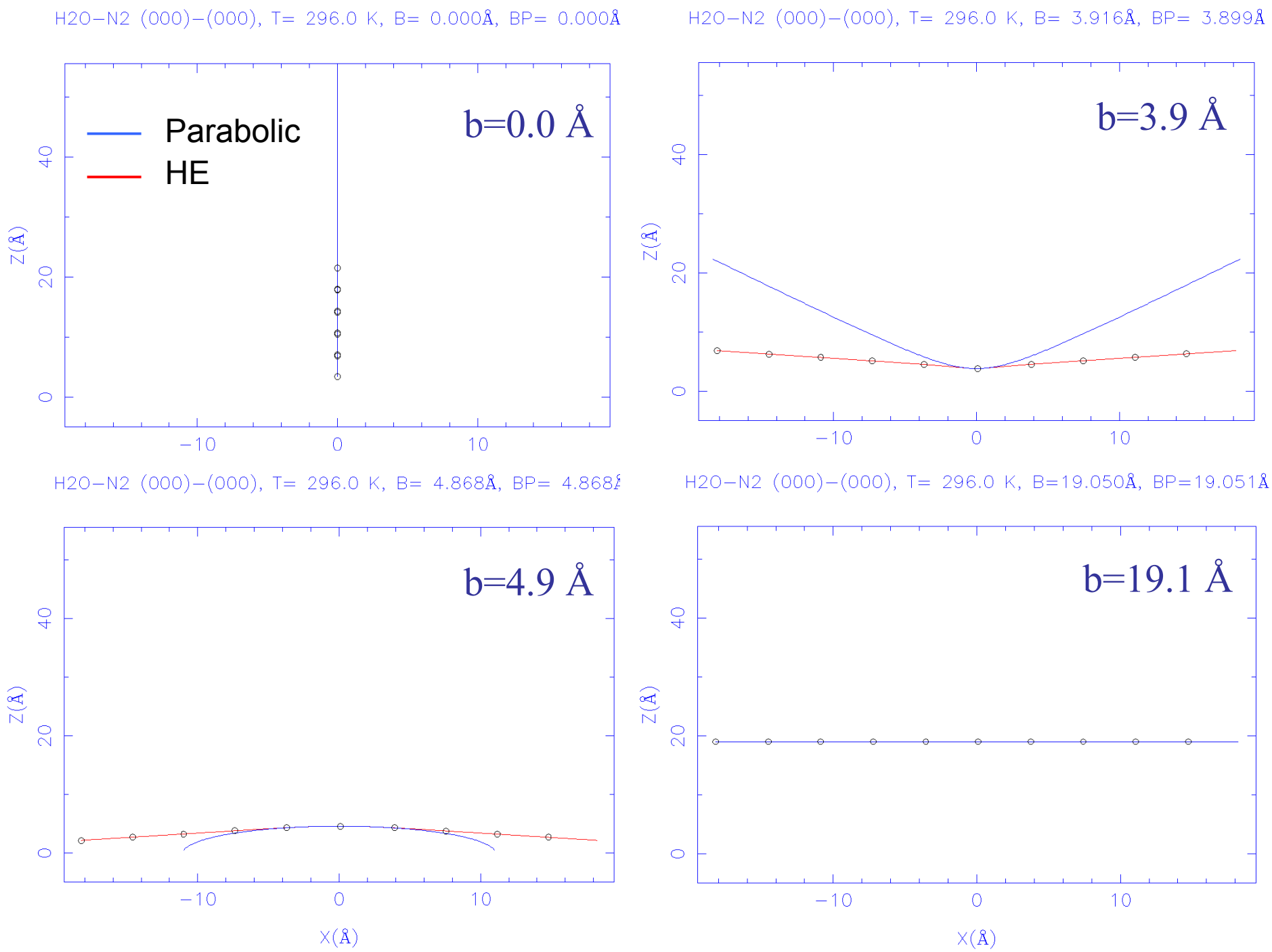
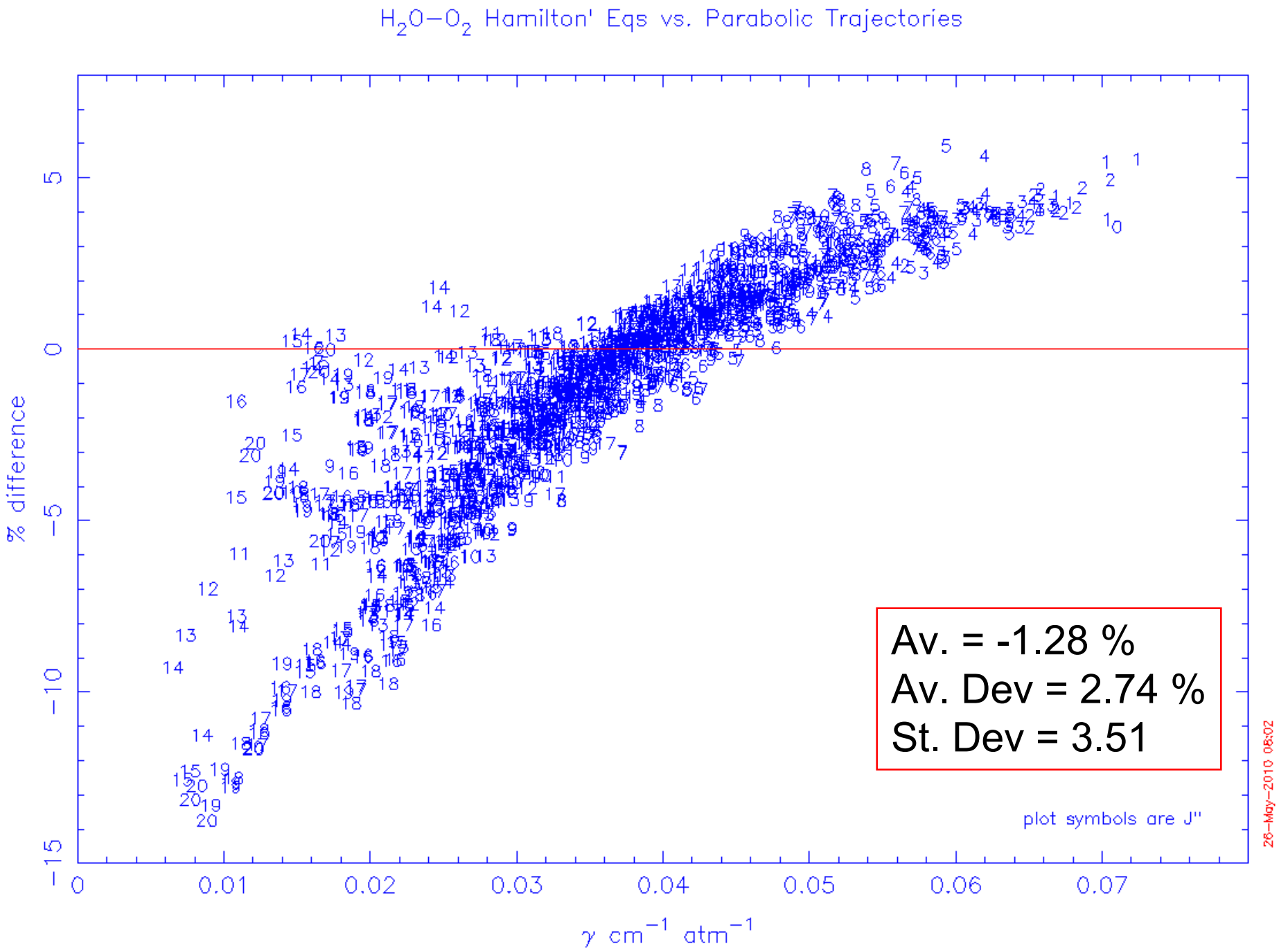

components
H2O–N2 , (000)–(000)
15 0 15 <--14 1 14
16 5 11 <--16 4 12
Im(1–Exp(–S))
0
–0.05
0
2
4
6
8
10
b (Å)


components
H2O–N2 , (000)–(000)
15 0 15 <--14 1 14
16 5 11 <--16 4 12
Re(1–Exp(–S))
1.5
1
0.5
0
0
2
4
6
8
10
b (Å)


H2O−N2 (000)−(000), T= 296.0 K, B= 0.000Å, BP= 0.000Å
Parabolic
HE
b=0.0 Å
H2O−N2 (000)−(000), T= 296.0 K, B= 3.916Å, BP= 3.899Å
b=3.9 Å
H2O−N2 (000)−(000), T= 296.0 K, B= 4.868Å, BP= 4.868Å
b=4.9 Å
H2O−N2 (000)−(000), T= 296.0 K, B=19.050Å, BP=19.051Å
b=19.1 Å
Z(Å)
X(Å)
0
20
40
−10
0
10

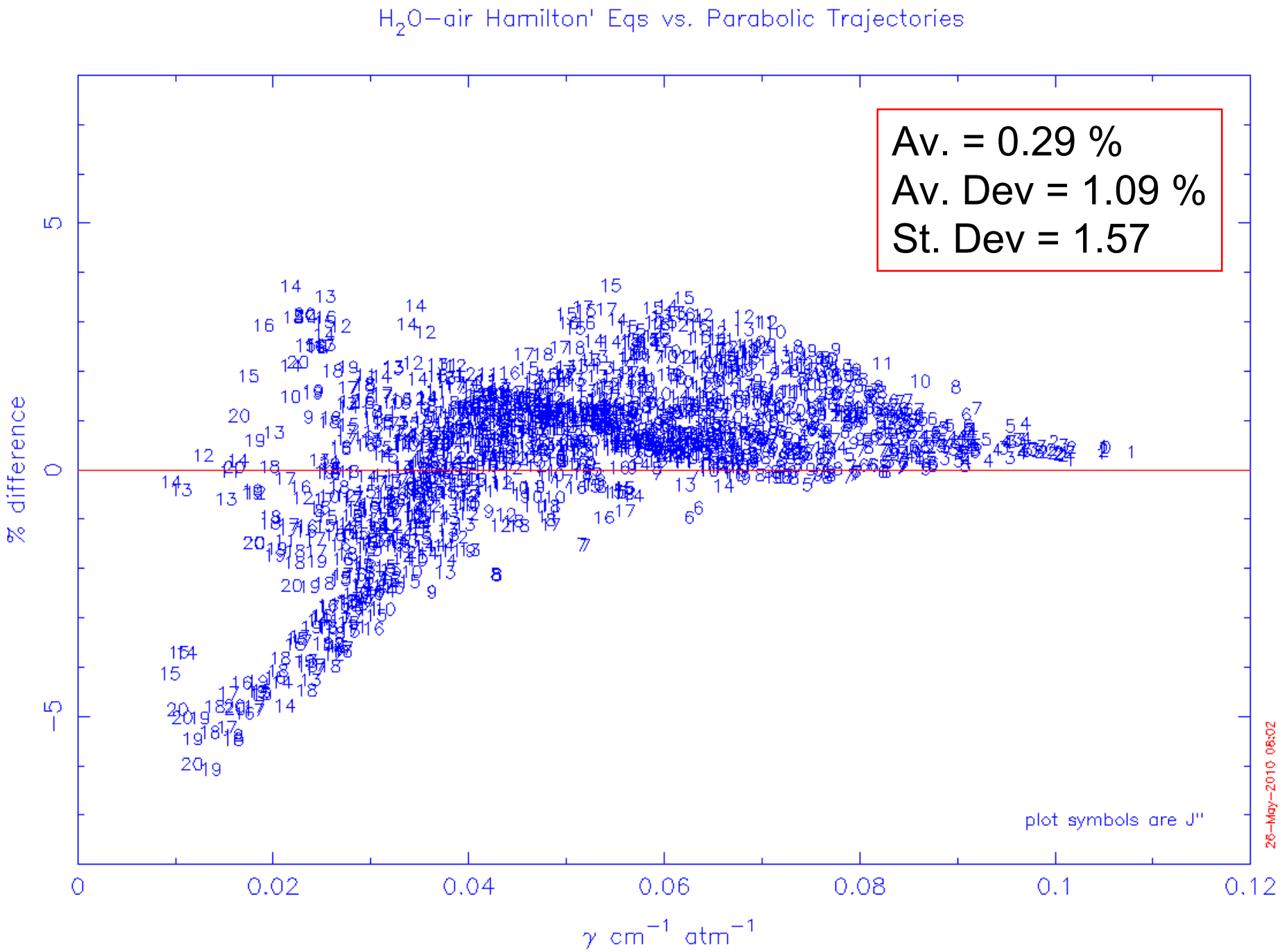

H2O–O2 Hamilton' Eqs vs. Parabolic Trajectories
% difference
5
0
-5
-10
-15
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
γ cm−1 atm−1
Av. = -1.28 %
Av. Dev = 2.74 %
St. Dev = 3.51
plot symbols are J''
26-May-2010 08:02

$H_2{}^{16}O$-Air calculations

For each transition at each temperature the air-broadened half-widths are determined by

$$\gamma_{air}^{HE} = 0.79\ \gamma_{N_2}^{HE} + 0.21\ \gamma_{O_2}^{HE}$$

$$\gamma_{air}^{P} = 0.79\ \gamma_{N_2}^{P} + 0.21\ \gamma_{O_2}^{P}$$


H2O–air Hamilton' Eqs vs. Parabolic Trajectories
Av. = 0.29 %
Av. Dev = 1.09 %
St. Dev = 1.57
% difference
5
0
-5
0
0.02
0.04
0.06
0.08
0.1
0.12
γ cm−1 atm−1
plot symbols are J''
26-May-2010 08:02

Conclusion

- While the percent difference between the two methods of calculation is small, it is greater than the uncertainty desired by the remote sensing community.

- We now use the HE trajectory model in our code

- The convergence of the calculations relatively to the order and the rank need to be investigated (Ma *et al.*, *Mol. Phys.*, submitted 2010)

Acknowledgement

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