Complex Robert-Bonamy calculation of H\textsubscript{2}O broadened by N\textsubscript{2}, O\textsubscript{2} and air made with realistic trajectories

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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.
We show that it is important to consider more realistic collision dynamics in the calculations.
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. The results agree with the air-broadened measurements to better than 5%.
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...
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- In a previous study, Neshyba and Gamache (unpublished data) compared half-widths of water vapor transitions determined via the parabolic model or by solving Hamilton’s equations.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.

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

where \( n_2 \) is the number density of perturbers and \( \left\langle \right\rangle_{b,v,J} \) 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**

\[ V_{1,2}^{elec} = V_{\mu_1\mu_2} + V_{\mu_1\theta_2} + V_{\theta_1\mu_2} + V_{\theta_1\mu_2} + V_{\theta_1\theta_2} + V_{\theta_1\theta_2} + \ldots \]

- **Atom-atom potential**

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

\(\varepsilon\) and \(\sigma\) have to be adjusted
The potential

- **Electrostatic components**

\[ V_{1,2}^{\text{elec}} = V_{\mu_1\mu_2} + V_{\mu_1\theta'_2} + V_{\theta'_1\mu_2} + V_{\theta''_1\mu_2} + V_{\theta'_1\theta'_2} + V_{\theta''_1\theta'_2} + \ldots \]

- **Atom-atom potential**

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

\( \varepsilon \) and \( \sigma \) have to be adjusted
The real trajectories are approximated by an analytical parabolic model correct at second order of time

\[ R(t) = \sqrt{r_c^2 + v_c'^2 t^2} \]

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

\[ \cos(\psi(t)) = \frac{r_c + \frac{|F_c|}{2m} t^2}{\sqrt{r_c^2 + v_c'^2 t^2}} \]

\[ r(t) \equiv r_c + v_c t + \frac{F(r_c) t^2}{\mu} \]

\( r_c, v_c, v_c' \) 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

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

\[
\begin{align*}
\frac{d}{dt} X_i &= \frac{\partial H}{\partial P_i} \\
\frac{d}{dt} P_i &= -\frac{\partial H}{\partial X_i}
\end{align*}
\]
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\[ \frac{d}{dt} X_i = \frac{\partial H}{\partial P_i} \]

\[ \frac{d}{dt} P_i = -\frac{\partial H}{\partial X_i} \]
Trajectories : Hamilton’s Equations

The closest approach parameters are determined numerically

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

\[ \psi_c = \arctan\left(\frac{(X_3 - X_1)}{(X_4 - X_2)}\right) \]
Trajectories: Hamilton’s Equations

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

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\begin{align*}
\frac{d}{dt} X_i &= \frac{\partial H}{\partial P_i} \\
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\end{align*}
\]

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

\[ \psi(t) = \arctan \left( \frac{(X_3 - X_1)}{(X_4 - X_2)} \right) \]
Initial calculations for water vapor

- CRB calculations for 1639 transitions for the (000)-(000) band for $\text{H}_2^{16}\text{O-N}_2$, $\text{H}_2^{16}\text{O-O}_2$ and $\text{H}_2^{16}\text{O-air}$
- 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

H$_2$O–N$_2$ Hamilton' Eqs vs. Parabolic Trajectories

Av. = 0.59 %
Av. Dev = 1.06 %
St. Dev = 1.43
$\text{H}_2\text{O-N}_2$ Hamilton' Eqs vs. Parabolic Trajectories

$\text{Av.} = 0.59 \%$

$\text{Av. Dev} = 1.06 \%$

$\text{St. Dev} = 1.43$

plot symbols are $J''$
Parabolic HE

\[ b = 0.0 \text{ Å} \]  \[ b = 3.9 \text{ Å} \]  \[ b = 4.9 \text{ Å} \]  \[ b = 19.1 \text{ Å} \]
Av. = -1.28 %
Av. Dev = 2.74 %
St. Dev = 3.51
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

plot symbols are J''
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).
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