The Collision-Broadened Line Shape of CO$_2$
via the Complex Robert-Bonamy Method:
*The Complexity of Simplicity*

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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

Bouanich and Brodbeck, JQSRT 14, 141 (1974)
Semiclassical complex Robert-Bonamy theory

The half-width and line shift are

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

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.
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

\[ V_{1,2}^{elec} = V_{\theta_1 \theta_2} \]
Atom-Atom Potential

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

Lennard-Jones (6-12) parameters

\( \text{CO}_2-N_2 \)

N-O \quad N-C

\( \sigma/\text{Å} \) \quad 2.55 \quad 2.77

\( \varepsilon/\text{k}_B(\text{K}) \) \quad 39.12 \quad 41.54
Spherical Tensor Expansion of the Potential

\[ V = \sum_{\ell_1, \ell_2} \sum_{n_1} \sum_{m_1 m_2} \sum_{w, q} \frac{U(\ell_1 \ell_2, n_1 w q)}{R^{q + \ell_1 + \ell_2 + 2w}} \]

\[ \otimes C(\ell_1 \ell_2 \ell, m_1 m_2 m) \ D_{m_1 n_1}^{\ell_1} (\Omega_1) \ D_{m_2 0}^{\ell_2} (\Omega_2) \ Y_{\ell m} (\omega) \]

- 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 \( \text{Order} = \ell_1 + \ell_2 + 2w \)
$\text{CO}_2$

Linear molecule - Quadrupole moment

$D_{-2}^2, D_0^2, D_2^2$

Wave functions - $D_J^{00}$
Reduced matrix elements - CO$_2$

\[ \int \Psi_{i'} V \Psi_i \, d\tau \propto \int D_{00}^{J_i} D_{k0}^{l_{1'}} D_{00}^{J_i} \, d\tau \]

\[ C(J_{i'}, \ell_{1'}, J_i; 0, k, 0) \]

Only potential term remaining is \[ D_{00}^2 \]
Trajectories

Parabolic Approximation

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

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**

<table>
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<tr>
<th>Transition</th>
<th>$\gamma$ cm$^{-1}$ atm$^{-1}$</th>
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<tr>
<td>25 $\leftarrow$ 24</td>
<td>0.0457</td>
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<tr>
<td>29 $\leftarrow$ 28</td>
<td>0.0289</td>
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<tr>
<td>31 $\leftarrow$ 30</td>
<td>0.0176</td>
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<td>33 $\leftarrow$ 32</td>
<td>0.0022</td>
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<tr>
<td>41 $\leftarrow$ 40</td>
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<tr>
<td>45 $\leftarrow$ 44</td>
<td>-0.3868</td>
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<tr>
<td>47 $\leftarrow$ 46</td>
<td>-0.6069</td>
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CO$_2$-N$_2$ $v_3$ P20 transition, $J_2=0$, parabolic trajectories, $T=100$ K
$CO_2-N_2 \nu_3$ P20 transition, $J_2=0$, HE trajectories, $T=100$ K
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.

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

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

S components

Re(S$_2$I$_2$)
Re(S$_2$F$_2$)
SMIDDLE

B(Å)

Im(S)

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B(Å)
$\text{CO}_2-\text{CO}_2$ 30012-00001 R50, J2=16, 296 K

$S$ components

- $S1$
- $\text{IM}(S2I2)$
- $\text{IM}(S2F2)$
- $S2I2I-S2F2I+S1$

$\text{Re}(S2I2)$
$\text{Re}(S2F2)$
$\text{SMIDDLE}$
$S2I2R+S2F2R+\text{SMID}$

Graphs showing $\text{Im}(S)$ and $\text{Re}(S)$ against $\mathcal{B}(\text{Å})$.
CO₂-CO₂ 30012-00001 R50, J2=16, 296 K

Components

\begin{align*}
\text{Im}(1-\exp(-S))
\end{align*}

\begin{align*}
\text{Re}(1-\exp(-S))
\end{align*}

\begin{align*}
B(\text{Å})
\end{align*}

\begin{align*}
\bar{B}(\text{Å})
\end{align*}
J dependent - CO$_2$-CO$_2$ 30012-00001 R12, J2=16, 296 K

S components

$\text{Re(}S\text{)}$
$\text{Re(}S\text{)}$
$\text{SMIDDE}
$\text{S}2\text{I2R}+\text{S}2\text{F2R}+\text{SMID}$

$\text{Im(}S\text{)}$
$\text{IM(}S\text{)}$
$\text{IM(}S\text{)}$
$S2I2I=S2F2I+S1$

B(Å)

B(Å)
\[ \ell_1 = 2, \ell_2 = 2 \text{ resonance function at } 296 \text{ K}, \ b = 5.45 \text{ Å} \]

Electrostatic potential calculations giving \( \varepsilon/k_b = 429.58 \text{ K} \) and \( \sigma = 3.17 \text{ Å} \)
\( \ell_1=2, \ell_2=2 \) resonance function at 296 K, \( b = 5.45 \, \text{Å} \)

Atom-atom expansion \( \rightarrow 8 \, 2 \, 2 \) giving \( \varepsilon/k_b = 158.06 \, \text{K} \) and \( \sigma = 4.22 \, \text{Å} \)
Line Shift

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

\[
\delta\left[(v_1 + \Delta v_1, v_2 + \Delta v_2, v_3 + \Delta v_3, J_f - J_i) \leftarrow (v_1, v_2, v_3, J_i)\right] = (J_i - J_f) \delta_{\text{rot}}(|m|) + (a_1 \Delta v_1 + a_2 \Delta v_2 + a_3 \Delta v_3) \delta_{\text{vib}}(|m|)
\]

Using Hartmann’s coefficients \(a_1\), \(a_2\), and \(a_3\) we form the ratios

\[
\begin{align*}
    r_{12} &= \frac{a_2}{a_1}, \quad r_{13} &= \frac{a_3}{a_1},
\end{align*}
\]

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

Current values

\[
a_1 = 0.1000, \quad a_2 = 0.0516, \quad a_3 = 0.2236
\]
Atom-atom parameters

CO₂–CO₂ 30012–00001 band measurement vs. calculation

Temperature Exponent

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
Acknowledgement

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