A THEORETICAL MODEL
FOR WIDE-BAND IR-ABSORPTION MOLECULAR SPECTRA AT ANY PRESSURE:

FICTION OR REALITY?

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Outline of the needs

Mars

Earth

Venus

∀ T, P, chemical compositions

Outline of the needs

- Absorption coefficient as a function of frequency for each spectroscopically active molecule
- Atmospheric radiative transfer codes
  - Retrieval of geophysical parameters (temperature, humidity, ...)
  - Weather/climate models
  - Optimization of solar photovoltaic systems
  - ...

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Absorption coefficients as functions of frequency

Region of molecular resonances:
- low pressures
  - / -
- high pressures
  + / -

Spectral wings:
- near
- far

Contributions from Collision-Induced Absorption

Contributions from dimers and higher-order clusters
STANDARD APPROACH for allowed absorption

\[
\alpha(\sigma) = \frac{8\pi^3}{3hc} \sigma n_1 (1 - e^{-\frac{hc\sigma}{kT}}) \frac{1}{\pi} \text{Re} \sum_{k,k'} \rho_k d_k d_{k'} [i(\sigma - \sigma_k)] + n_2 W_{kk'}^{-1}
\]

- \(\alpha(\sigma)\): absorption coefficient at wavenumber \(\sigma\)
- \(\sigma n_1 (1 - e^{-\frac{hc\sigma}{kT}})\): Active-gas density
- \(\text{Re} \sum_{k,k'} \rho_k d_k d_{k'} [i(\sigma - \sigma_k)]\): Rotational population
- \(n_2 W_{kk'}^{-1}\): Dipole matrix element
- \(\text{Im} W_{kk'}\): Isolated-line positions
- \(\text{Re} W_{kk}\): Bath-gas density

Modelled by the Energy-Corrected Sudden approach for «downward» transitions + detailed-balance relation \(\text{Re} W_{kk'} \rho_k = \text{Re} W_{kk'} \rho_{k'}\) for «upward» ones

One-parameter empirical modelling using the detailed balance

Calculated by sum rules \(W_{kk} = -\sum_{k'} \frac{d_{k'}}{d_k} W_{kk'}\)

Niro et al., JQSRT 88, 483 (2004)
Outline of the needs

STANDARD APPROACH: PROBLEMS

1. ECS parameters fitted to experimental LW
   Sum rules for calculation of diag. elements
   \[ \rightarrow \text{Recalculated LW} \neq \text{experimental LW} \]

2. Empirical modeling of Im W

3. Far spectral wings: break down of the impact approximation

4. Far spectral wings: violation of the detailed balance
   \[ \Phi(-\omega) = \Phi(\omega) \exp(-\beta \hbar \omega) \]
   Filippov & Tonkov, JCP 108, 3608 (1998)

5. One-sided sum rules → asymptotic behavior $\sigma^{-3}$ in the far wing
   → negative intensities in low-frequency wing

General sum rules hold ONLY in the non-Markovian case

Bulanin et al., JQSRT 31, 521 (1984)
Symmetrized spectral density:

\[
S^{(r)}(\sigma) = \frac{1}{\pi} \text{Re} \sum_{k, k'} A_k^{(r)} \left[ i(\sigma - \sigma_k) + n_2 \Gamma^{(r)}(\sigma) \right]^{-1} A_{k'}^{(r)}
\]

- \( r \) - rank of the coupling tensor
- \( \sigma_k \) - proper frequencies of the free active molecule
- \( n_2 \) - gas density
- \( A_k^{(r)} \) - intensities of separate lines

General form of the off-diagonal relaxation matrix elements:

\[
\Gamma_{i f, i' f'}^{(r)}(\sigma) = -\left[ 1 + \exp(-hc\sigma / kT) \right] / 2n_{if}n_{i'f'} \\
\times \sum_L (2L + 1) F_{i f, i' f'}^{Lr} \left[ \rho_i \Phi_L(\sigma - \sigma_{f' i}) + \rho_{i'} \Phi_L(\sigma - \sigma_{f' i'}) \right]
\]

Kouzov, PRA 60, 2931 (1999)
Properties of the non-Markovian relaxation matrix

Symmetry (detailed balance):
\[ \Gamma_{if,i'f'}^{(r)}(\sigma) = \Gamma_{i'f',if}^{(r)}(\sigma) \]

Time-reversal symmetry:
\[ \Gamma_{if,i'f'}^{(r)}(\sigma) = \Gamma_{fi,f'i'}^{(r)*}(-\sigma) \]

Double-sided sum rules:
\[ \sum_{i'f' \neq if} \Gamma_{if,i'f'}^{(r)}(\sigma) A_{i'f'}^{(r)} = \sum_{i'f' \neq if} A_{i'f'}^{(r)} \Gamma_{i'f',if}^{(r)}(\sigma) = -\Gamma_{if,if}^{(r)}(\sigma) A_{if}^{(r)} \]

Positive definition:
\[ \sum_{if,i'f'} B_{if,i'f'}^{(r)} \Gamma_{if,i'f'}^{(r)}(\sigma) B_{i'f'}^{(r)} \geq 0, \quad \forall B^{(r)} \]
ECS modeling of the correlation function

\[ \text{Re } \Phi_L(\sigma) = \frac{2}{1 + \exp(-hc\sigma/kT)} \Phi^{\text{class}}_L(\sigma) \]

\[ \Phi^{\text{class}}_L(\sigma) = Q'_L \Omega(\sigma) \]

\[ \Omega(\sigma) = \left(1 + \frac{(2\pi\alpha b_c \sigma)^2}{12 \negthinspace n \bar{v}^2}\right)^{-n}, \quad n = 1 \text{ or } 2 \]

\[ Q_L = \frac{A(T)}{L(L+1)}^\alpha \exp\left[-\gamma \frac{B}{kT} L(L+1)\right] \]

**Standard ECS parameters**

- **ECS-EP**: \( A(T), \alpha, \gamma, b_c \)
- **ECS-P**: \( A(T), \alpha, b_c \)
- **ECS-E**: \( A(T), \gamma, b_c \)

**Spectroscopy-independent**
Modifications for IR absorption bands

Linear molecule with a bending mode \((v_1 v_2 v_3)\)
can be considered as a symmetric top with \(K \equiv l\)

(I) Isolated-line intensities

\[
A_k^{(r)} = (-1)^{J_i+l_f} \sqrt{(2J_i+1)(2J_f+1)} \begin{pmatrix} J_i & r & J_f \\ l_i & l_f - l_i & -l_f \end{pmatrix} \sqrt{\frac{\rho_i + \rho_f}{2}}
\]

(II) Relaxation matrix

\[
F_{if,i'f'}^{Lr} = (-1)^{r+l_i+l_f} \begin{pmatrix} J_i' & L & J_i \\ -l_i & 0 & l_i \end{pmatrix} \begin{pmatrix} J_f & L & J_f' \\ l_f & 0 & -l_f \end{pmatrix} \begin{pmatrix} J_i & J_f & r \\ J_i' & J_f' & L \end{pmatrix}
\]
(III) Vibration-rotation interactions:

(A) Isolated-line intensities: Correction via Herman-Wallis factors

\[ F(m) = (1 + a_1 m + a_2 m^2 + a_3 m^3)^2 \quad P- \ & R- \]
\[ F(m) = (1 + b_2 m^2)^2 \quad Q- \]
\[ m = -J \quad (P); \quad m = J \quad (Q); \quad m = J + 1 \quad (R) \]

\[ A_k^{(1)} \rightarrow A_k^{(1)HW} = A_k^{(1)} \sqrt{F(m)} \]

Coriolis interactions between vibrational levels:

- If sum rules are restricted to one band, unperturbed dipole elements should be used
- Modifications of rel. matr. for Coriolis effects have no influence on the absorption shape

(B) Relaxation matrix modeling:

\[ A_k^{(1)} \]

\[ \text{CO}_2: \text{Effective correction allowed for diagonal elements} \]
Applications to high-density IR spectra

OCS-He $2\nu_3$

Buldyreva et al., JCP 138, 164117 (2013)
Applications to high-density IR spectra

OCS-He $\nu_2$

- 20 atm
  - 298 K

- 70 atm
  - 298 K

Expt
- Sum of Lorentzians
- ECS-P2
- ECS-E2

Buldyreva et al., JCP 138, 164117 (2013)
Applications to high-density IR spectra

\[
\text{CO}_2-\text{CO}_2 \quad 2\nu_1 + \nu_3
\]

\[a_1 = -0.00009, \quad a_2 = -0.47 \times 10^{-5}\]

No empirical correction

Filippov et al., PCCP 15, 13826 (2013)

HW factors: Rothman et al., JQSRT 48, 537 (1992)
Empirical correction
\[ \gamma'_{\nu} = 0.040 \text{ cm}^{-1} \text{ amagat}^{-1} \]

\[ a_1 = -0.000215 \]

HW factors: Rothman et al., JQSRT 48, 537 (1992)

Filippov et al., PCCP 15, 13826 (2013)
Applications to high-density IR spectra

\[ \text{CO}_2 - \text{CO}_2 \ (\nu_1 + \nu_2)_I \]

\[ a_1 = -0.3772, \ a_2 = 0.52 \times 10^{-5}, \ b_2 = -0.58 \times 10^{-5} \]

HW factors: Rothman et al., JQSRT 48, 537 (1992)

\[ \gamma'_\nu = 0.020 \text{ cm}^{-1} \text{ amagat}^{-1} \]

\[ \gamma'_\nu = 0.016 \text{ cm}^{-1} \text{ amagat}^{-1} \]

\[ \gamma'_\nu = 0.013 \text{ cm}^{-1} \text{ amagat}^{-1} \]

Filippov et al., PCCP 15, 13826 (2013)
Applications to high-density IR spectra

$\text{CO}_2$-$\text{CO}_2$ $\nu_3$ wing

Absorption, cm$^{-1}$ amagat$^{-2}$

Wavenumber, cm$^{-1}$

296 K


Buldyreva & Daneshvar, JCP 139, 164107 (2013)
Applications to $\text{CO}_2$ IR spectra at low densities

SOIR spectra of the atmosphere of Venus (Venus Express)

Wavenumber (cm$^{-1}$)

Transmitance

Courtesy: A.C. Vandaele (IASB)
Applications to CO$_2$ IR spectra at low densities

10 FTS spectra recorded (55 m, 293 K)

Resolution = 0.005 – 0.05 cm$^{-1}$

2.8 – 903 hPa

Daneshvar et al., JQSRT 2014 (under revision)
Applications to CO$_2$ IR spectra at low densities

Daneshvar et al., JQSRT 2014 (under revision)
Applications to CO$_2$ IR spectra at low densities

Daneshvar et al., JQSRT 2014 (under revision)
Applications to CO$_2$ IR spectra at low densities

0.029 atm  Q-branch zoom

Transmittance

Wavenumber, cm$^{-1}$
Conclusions & perspectives

Main results

• Immediate good agreement with expt OCS-He spectra up to 300 atm without any additional fitting parameter

• Satisfactory agreement for CO$_2$ up to nearly liquid phase (+ 1 fitting parameter)

• Excellent agreement with low-density expt CO$_2$ spectra down to 0.03 atm

• The model has a universal character (IR, Raman iso, aniso)

Further improvements/tests/applications

• Studies of extremely low pressures (narrowing effects)
• Modeling of Im $\Gamma$
• Studies of far wings (non-Markovian effects)
• Modeling of temperature dependences
• Calculations of correlation functions from ab initio PES
• Studies of other bands and other molecular systems

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