Improvements, Corrections and New Developments in Semiclassical Theories of Collisional Line Broadening

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Summary

❶ **Introduction**

❷ **Line profile models**

❸ **Collisional widths & shifts**

- **Semiclassical methods**
- **Semiempirical method**
- **Classical method**

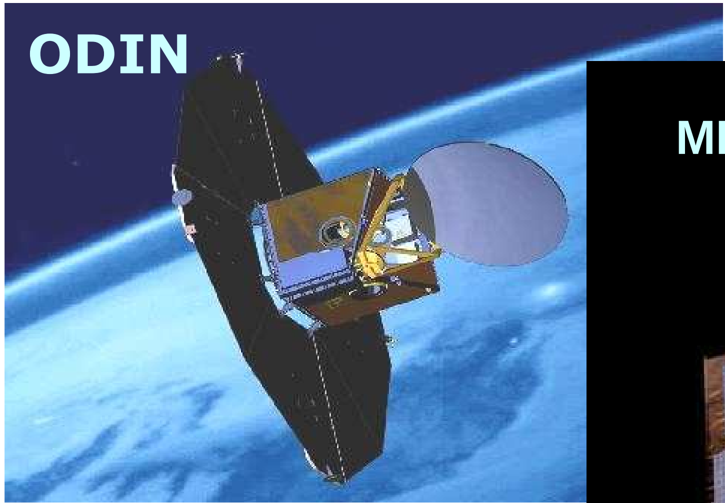
❹ **Conclusions**

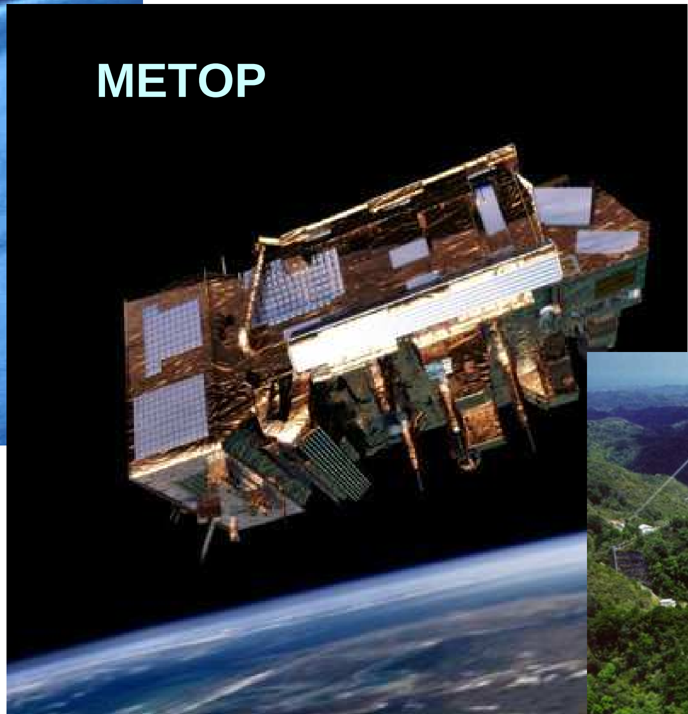
❶

INTRODUCTION

PLANETARY ATMOSPHERES

(relatively) low temperatures, low pressures
IR/(sub)millimeter absorption spectroscopy





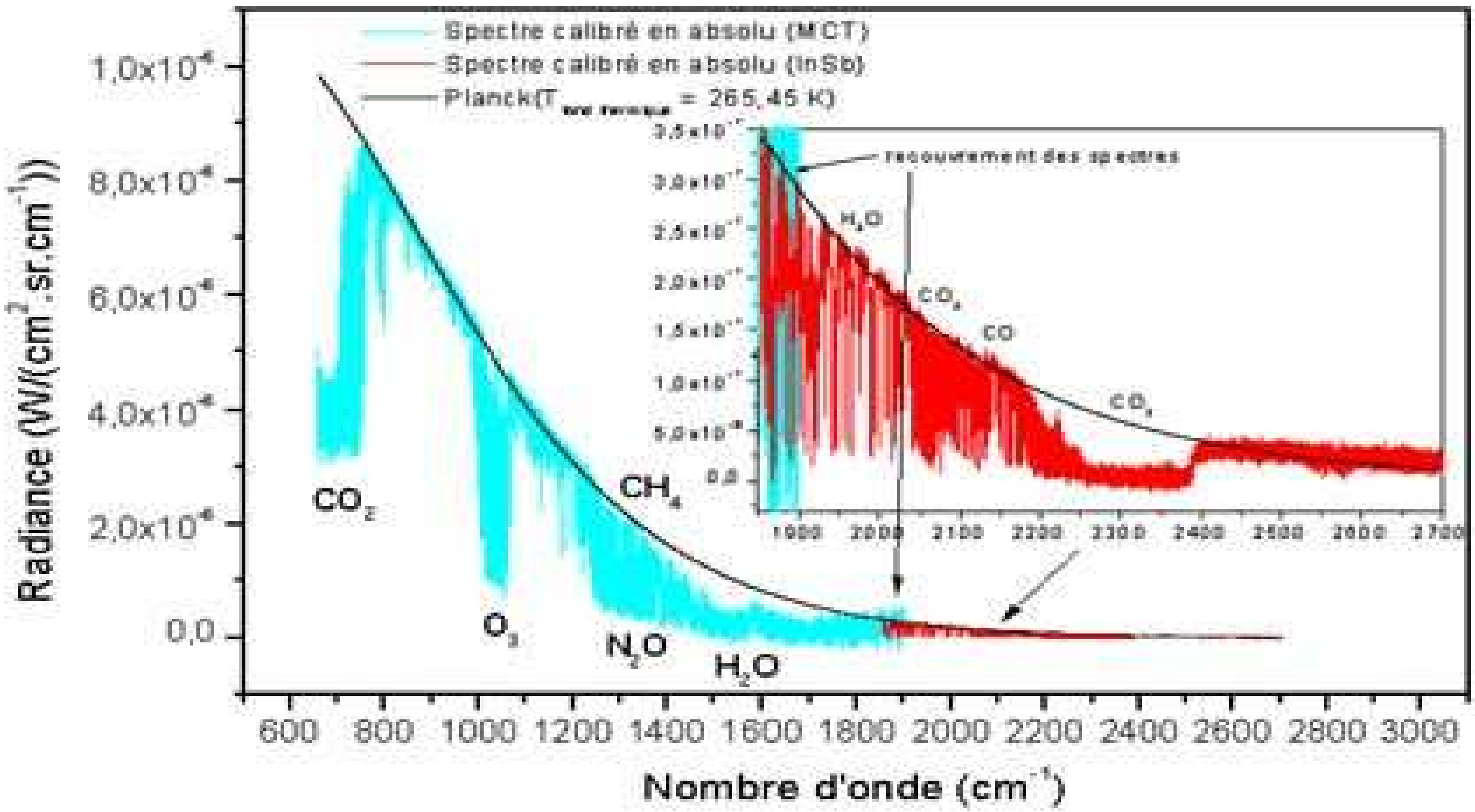
H_2O, CO_2, O_3, N_2O,
NO, CO, C_2H_2, C_2H_4, HNO_3

/N_2, O_2, CH_4, …

❶

INTRODUCTION

IR/millimeter absorption spectra



Analysis ⇦ Laboratory measurements / calculations

➋

LINE SHAPE MODELS

Information about the medium – via collisions of the active molecule with the bath molecules

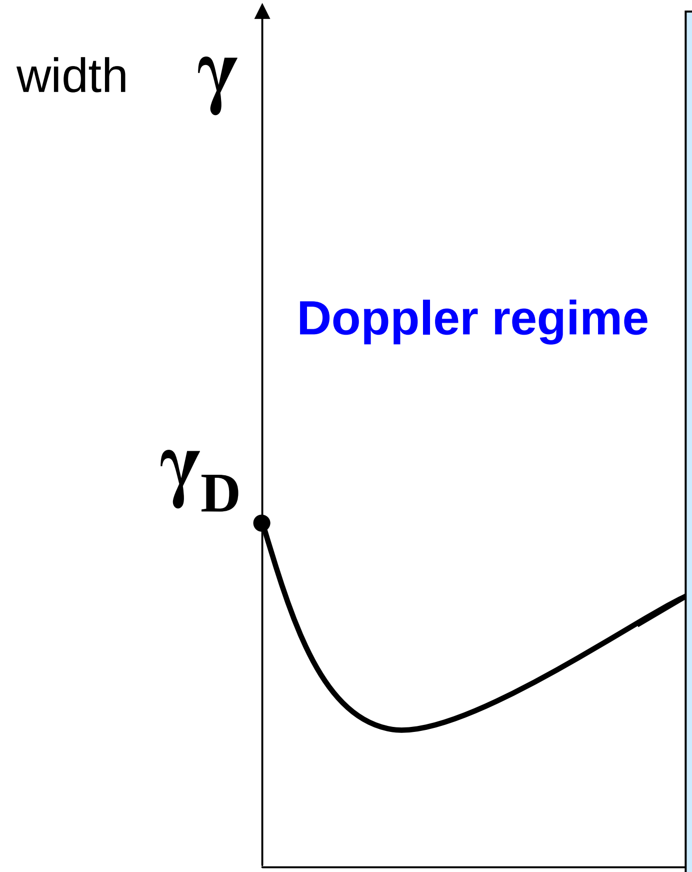
⇧

Describe the effect of the collisions on the spectrum: shape (profile), width, shift, intensity,…

⇧

Dependence on pressure

❷ LINE SHAPE MODELS



Gauss Profile

$$G(\nu-\nu_0)=\frac{1}{\gamma_D}\sqrt{\frac{\ln 2}{\pi}}\,e^{-\ln 2\left(\frac{\nu-\nu_0}{\gamma_D}\right)^2}$$

ν – frequency

ν_0 – position of the line center

$$\gamma_D = 3.581\cdot 10^{-7}\nu_0\sqrt{\frac{T}{m_a}}\quad [\mathrm{cm}^{-1}]$$

IR: $\gamma_D \approx 10^{-3}$ cm^{-1} >> $\gamma_n \approx 10^{-8}$ cm^{-1}

❷ LINE SHAPE MODELS

Lorentz profile

$$L(\nu-\nu_0)=\frac{1}{\pi}\frac{\gamma_c}{(\nu-\nu_0-\delta_c)^2+\gamma_c^2}$$

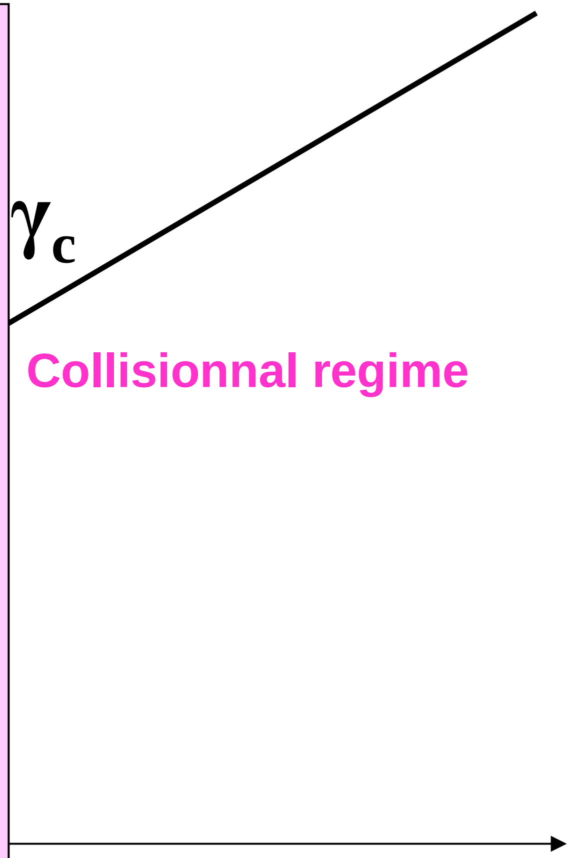
γ_c – **half-width at half-height (cm^{-1})**
δ_c – **shift of the line center (cm^{-1})**

$$\gamma_c = p\gamma \qquad\qquad \delta_c = p\delta$$

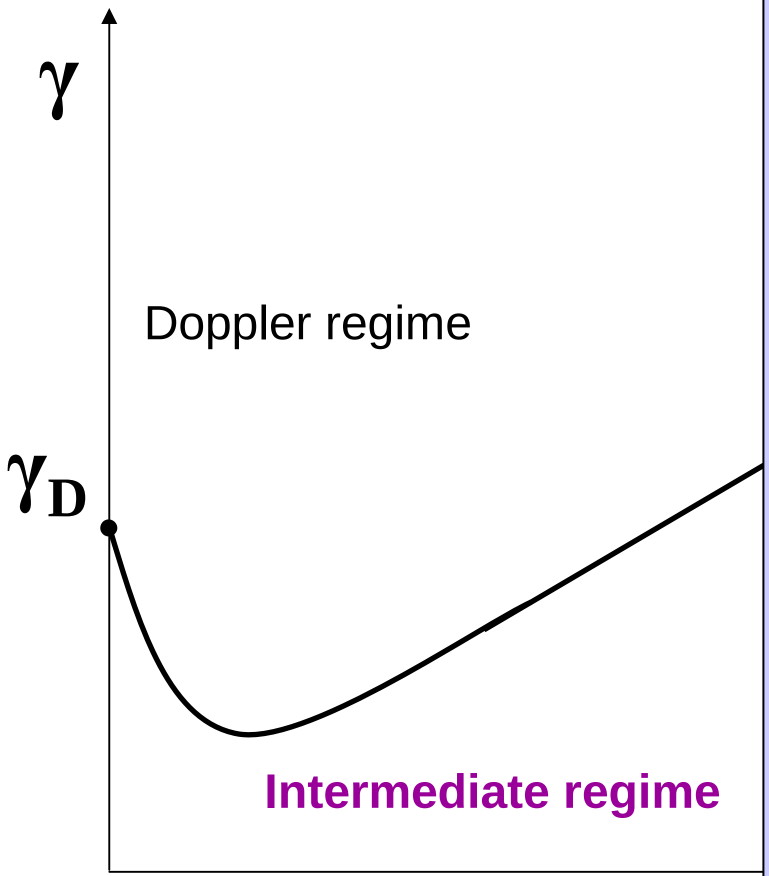
broadening coefficient

shifting coefficient

Gas mixtures: $$\gamma_c = p\gamma + \sum_i p_i \gamma_i$$



❷ LINE SHAPE MODELS



1. Statistical independence – Voigt Profile

(no velocity changing during collisions)

$$V(\nu - \nu_0) = \frac{1}{\gamma_D}\sqrt{\frac{\ln 2}{\pi}}\, u(x, y) \quad ,$$

$$u(x, y) = \frac{y}{\pi}\int_{-\infty}^{+\infty} \frac{e^{-t^2}}{y^2 + (x - t)^2}\, dt$$

$$x = \frac{\nu - \nu_0}{\gamma_D}\sqrt{\ln 2} \qquad y = \frac{\gamma_c}{\gamma_D}\sqrt{\ln 2}$$

$\gamma_D \gg \gamma_c$: $V(\nu - \nu_0) \rightarrow G(\nu - \nu_0)$

$\gamma_c \gg \gamma_D$: $V(\nu - \nu_0) \rightarrow L(\nu - \nu_0)$

Importance: 1st estimation of the width

❷ LINE SHAPE MODELS

2. Dicke effect – corrections to Gauss profile

(non correlated collisional perturbations)

Rautian profile

(hard collision model
for velocity-changing collisions)

[S.G. Rautian and I.I. Sobelman,
Sov. Phys. Uspekhi **9**, 701 (1967)]

Galatry Profile

(soft collision model
for velocity-changing collisions)

[L. Galatry, Phys. Rev. **122**, 1218 (1967)]

3. Dicke effect – corrections to Voigt profile

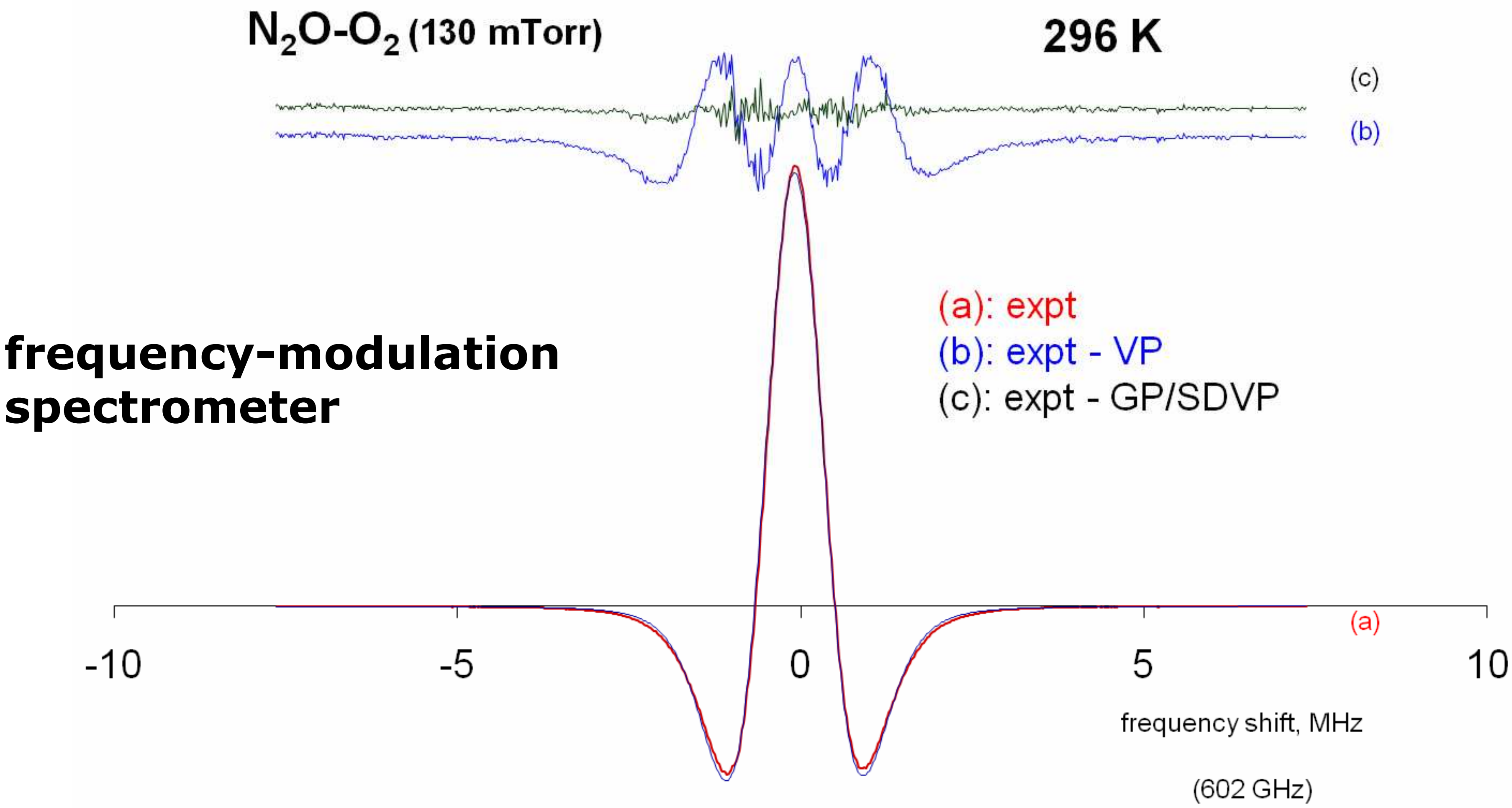
Speed-dependent Voigt profile

(relaxation rates depend on
the absolute velocity of the active molecule)

$$\Gamma(v_a) = \Gamma_0 + \Gamma_2\left[\left(\frac{v_a}{v_{a0}}\right)^2 - \frac{3}{2}\right]$$

4. Dicke effect – other profiles…
generalized theory of Ciurylo, Pine, Szudy [JQSRT 68, 257 (2001)]

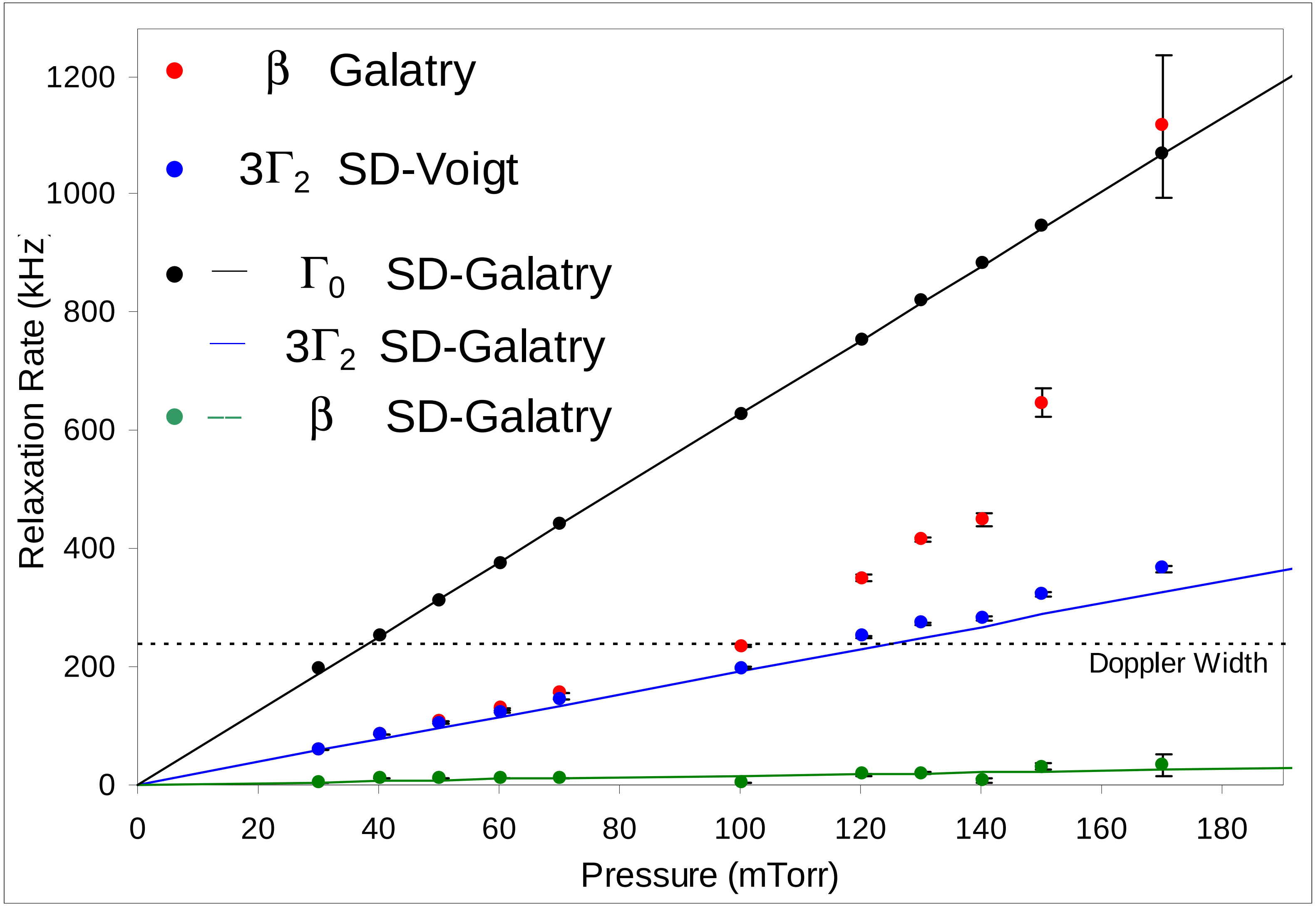
❷ LINE SHAPE MODELS



L. Nguyen et al., Mol.Phys. 104, 2701 (2006)

❷ # LINE SHAPE MODELS

172 GHz line of $HCN\text{-}N_2$



F. Rohart et al., J. Mol. Spectrosc. 246, 213 (2007)

Why do we need THEORETICAL collisional parameters?

1) Experimental collisional widths/shifts are deduced by model profiles
   $\Rightarrow$ can be distorted by the imperfections of these models

2) For some lines/frequency domains the measurements are impossible

3) Sometimes the measurements by different authors differ (significantly)

$\Rightarrow$ an independent approach is necessary

THEORETICAL METHODES

for calculation of collisional parameters (isolated lines)

	+	−
Calculations by quantum mechanics (CC & CS)	• rigorous & precise	• very expensive (CPU) • PES ab initio • simple systems • T not too high
Calculations by classical mechanics (Gordon)	• simple & clear	• quite expensive (CPU) • correspondence principle with quant. mechanics • limited systems
Semiclassical calculations	• internal motions-quantum description • classical translation • analytical formulae • simple potentials • (∀) systems • (∀) T	• inapplicable at too low temperatures • inapplicable to light systems • inapplicable to very anisotropic molecules

SEMICLASSICAL METHODS

"Numerical" Approaches

Neilsen—Gordon ⇔ CC

⇓

Peaking approximation ⇔ CS

⇓

Smith—Giraud—Couper

"Semi-analytical" (perturbation) approaches

Anderson—Tsao—Curnutte

Murphy—Boggs

Cattani

Cherkasov

Korff—Leavitt

Salesky—Korff

Robert—Bonamy

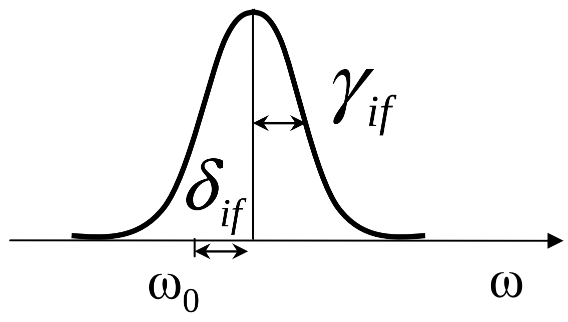
❸ COLLISIONAL WIDTHS & SHIFTS

Semiclassical methods

❸ ...\ SEMICLASSICAL METHODS

Collisional line width & shift

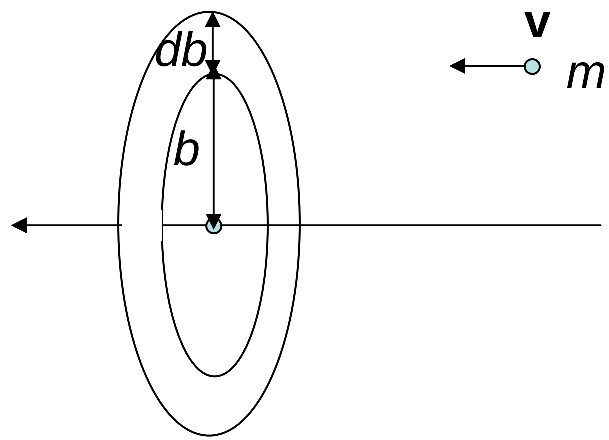
$$\gamma_{if} - i\,\delta_{if} = \frac{nv}{2\pi c} \sum_{j_2} \rho_{j_2}\, \sigma_{j_2}$$



ρ_{j_2} - **population of the j_2 level of the perturbing molecule**

σ_{j_2} - **differential cross-section:**

$$\sigma_{j_2} = 2\pi \int_0^{\infty} b\,db\,S(b)$$



with $S(b)$ **- «interruption function ».**

❸ …\ SEMICLASSICAL METHODS

Anderson-Tsao-Curnutte (ATC) theory

W. Anderson, Phys. Rev 76, 647 (1949); C.J. Tsao, B. Curnutte, JQSRT 2, 41 (1962)

- **molecular interaction described by long-range forces**
- **interruption function in series of perturbation powers**

$$S(b) = S_1(b) + S_2(b) + \ldots$$

limited to the 2d order ($S_2 \leq 1$),

- **straight-line trajectories at constant velocity**

Robert-Bonamy (RB) formalism

D. Robert, J. Bonamy, J. Phys. 40, 923 (1979)

- **accounting for short-range interactions**
- **exponential form of the interruption function:**

$$S(b) = 1 - \exp\left[-S_1(b) - S_2(b)\right],$$

- **parabolic trajectories governed by the isotropic potential**

❸ # ...\ SEMICLASSICAL METHODS

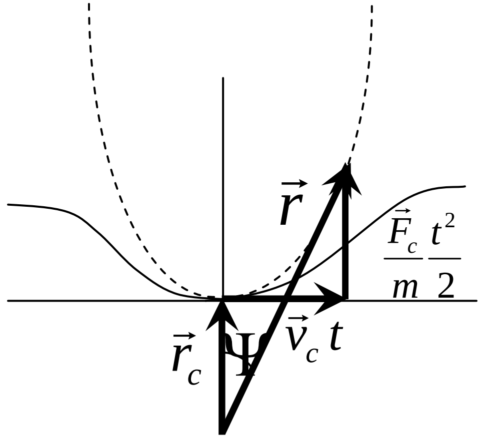
RB half-widths:

$$\mathrm{Re}\,S = 1 - \exp\left[-\left(\mathrm{Re}\,S_{2f} + \mathrm{Re}\,S_{2i} + S_{2fi}\right)\right]$$

Wave functions

$$S_{2i} \propto \left| \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \langle i2 | V_{aniso}\left[r(t)\right] | i'2' \rangle \right|^2$$

potential trajectory



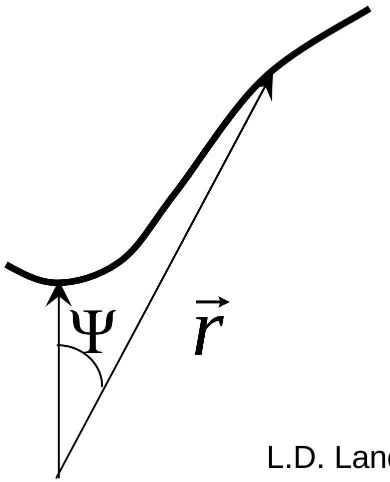
Fully Complex RB formalism (CRB)

R.R. Gamache, R. Lynch, S.P. Neshyba, JQSRT 59, 319 (1998)

❸ ...\ SEMICLASSICAL METHODS

RB formalism with exact trajectories (RBE)

J. Buldyreva, J. Bonamy, D. Robert, JQSRT 62, 321 (1999)
J. Buldyreva, S. Benec'h, M. Chrysos, Phys. Rev. A 63, 0123708 (2001)
J. Buldyreva, L. Nguyen, Phys. Rev. A 77, 042720 (2008)



$$t(r)=\int_{r_c}^{r}\frac{dr'}{\sqrt{2\left[E-V_{iso}(r')\right]/m-M^2/m^2r'^2}} ,$$

$$\Psi(r)=\int_{r_c}^{r}\frac{M/mr'^2dr'}{\sqrt{2\left[E-V_{iso}(r')\right]/m-M^2/m^2r'^2}} .$$

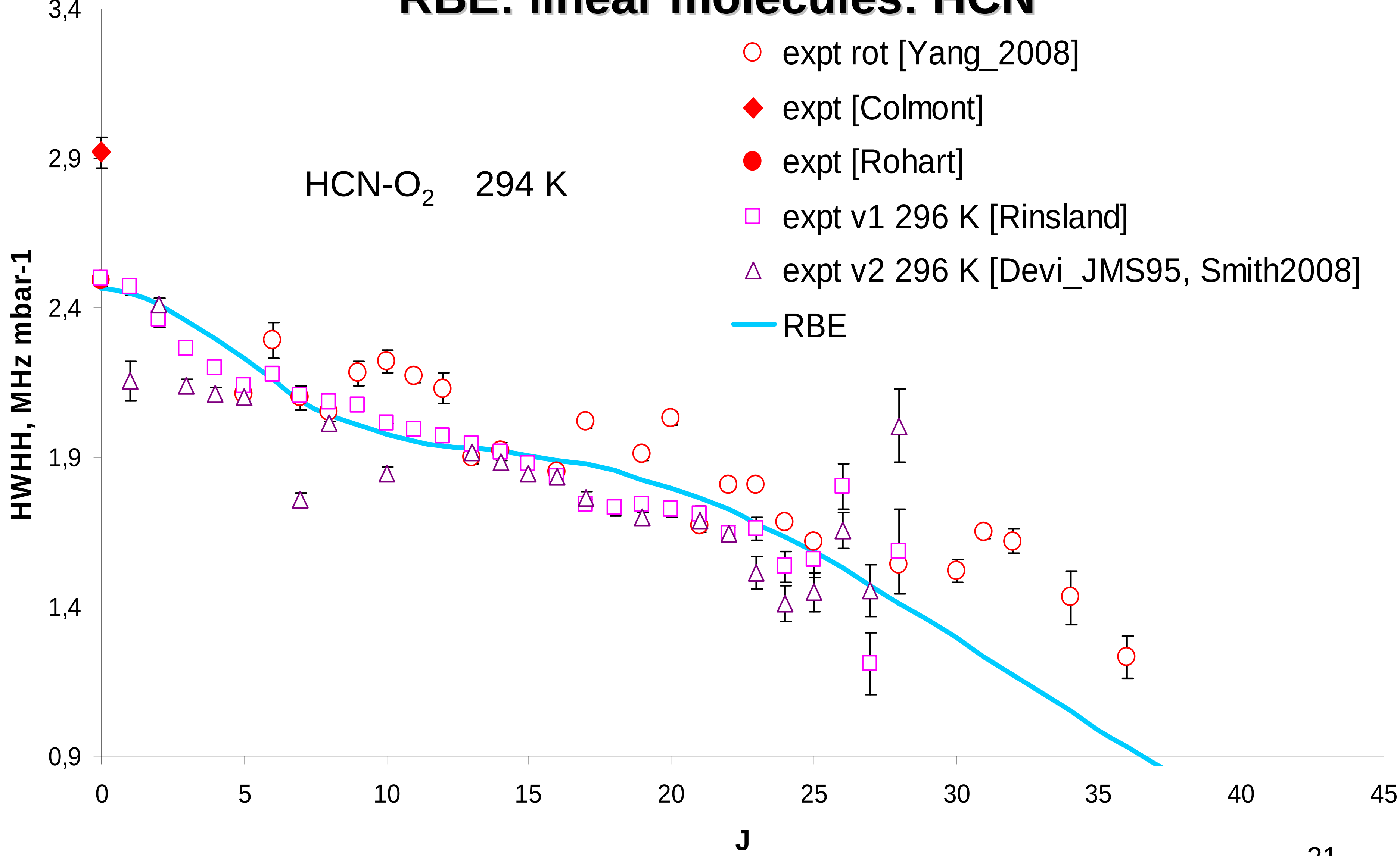
L.D. Landau, E.M. Lifshits, Cource of Theoretical Physics v.1, Pergamon, Oxford 1976
A. D. Bykov and N. N. Lavrentieva, and L. N. Sinitsa, Atmos. Oceanic Opt. 5, 587-594 (1992)

$$V_{aniso}(r)=\sum_{\substack{l_1 l_2 l\\ k_1 k_2}}V_{l_1 l_2 l}^{k_1 k_2}(r)\sum_{m_1 m_2 m}C_{l_1 m_1 l_2 m_2}^{lm}D_{m_1 k_1}^{l_1 *}(1)D_{m_2 k_2}^{l_2 *}(2)Y_{lm}^{*}(\theta,\Psi)$$

$$\left|J\tau m\right\rangle=\sum_K a_K^{(J\tau)}\left|JKm\right\rangle$$

➌ …\ SEMICLASSICAL METHODS

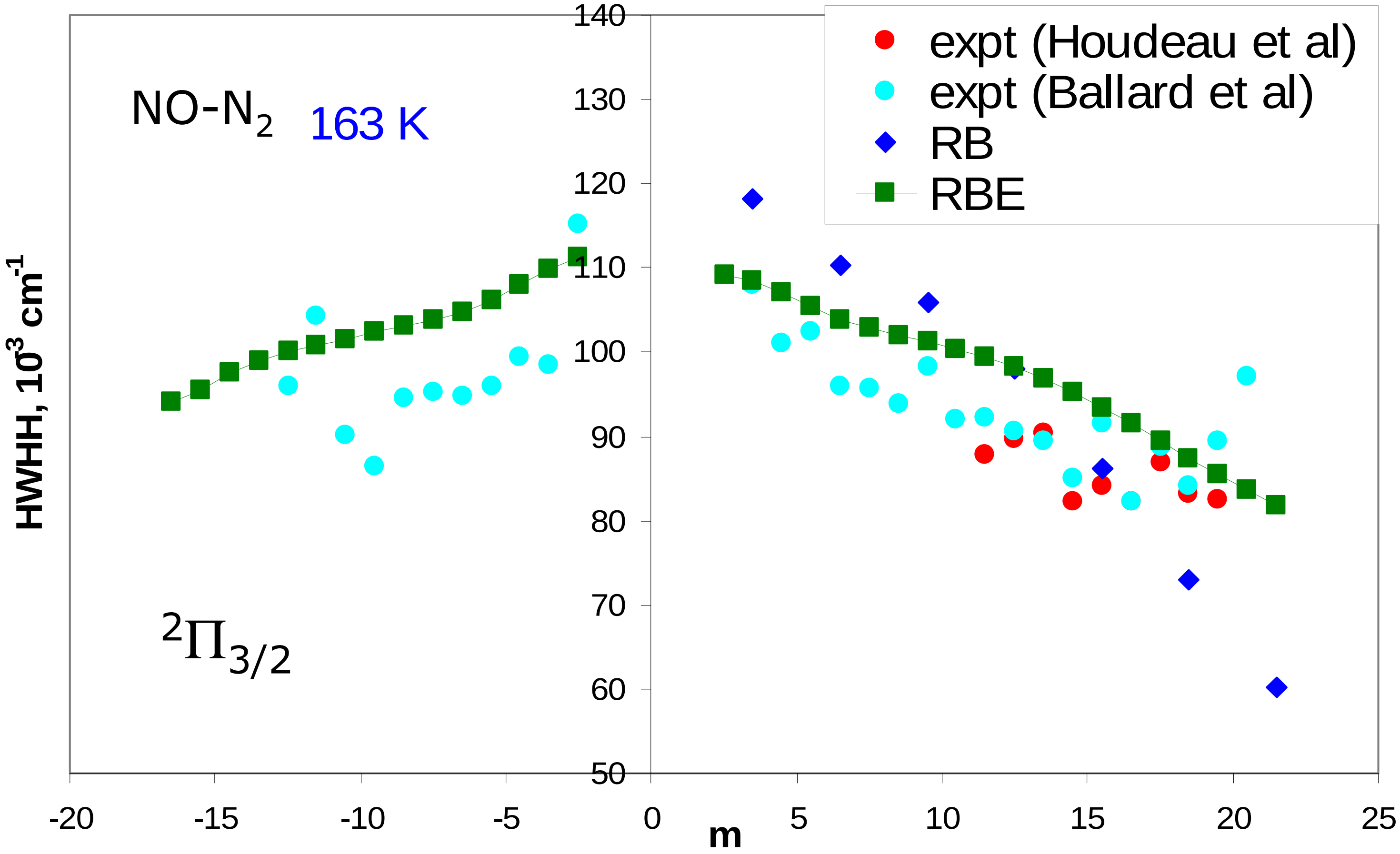
RBE: linear molecules: HCN



C.Yang et al., JQSRT 109, 2857 (2008)

❸ …\ SEMICLASSICAL METHODS

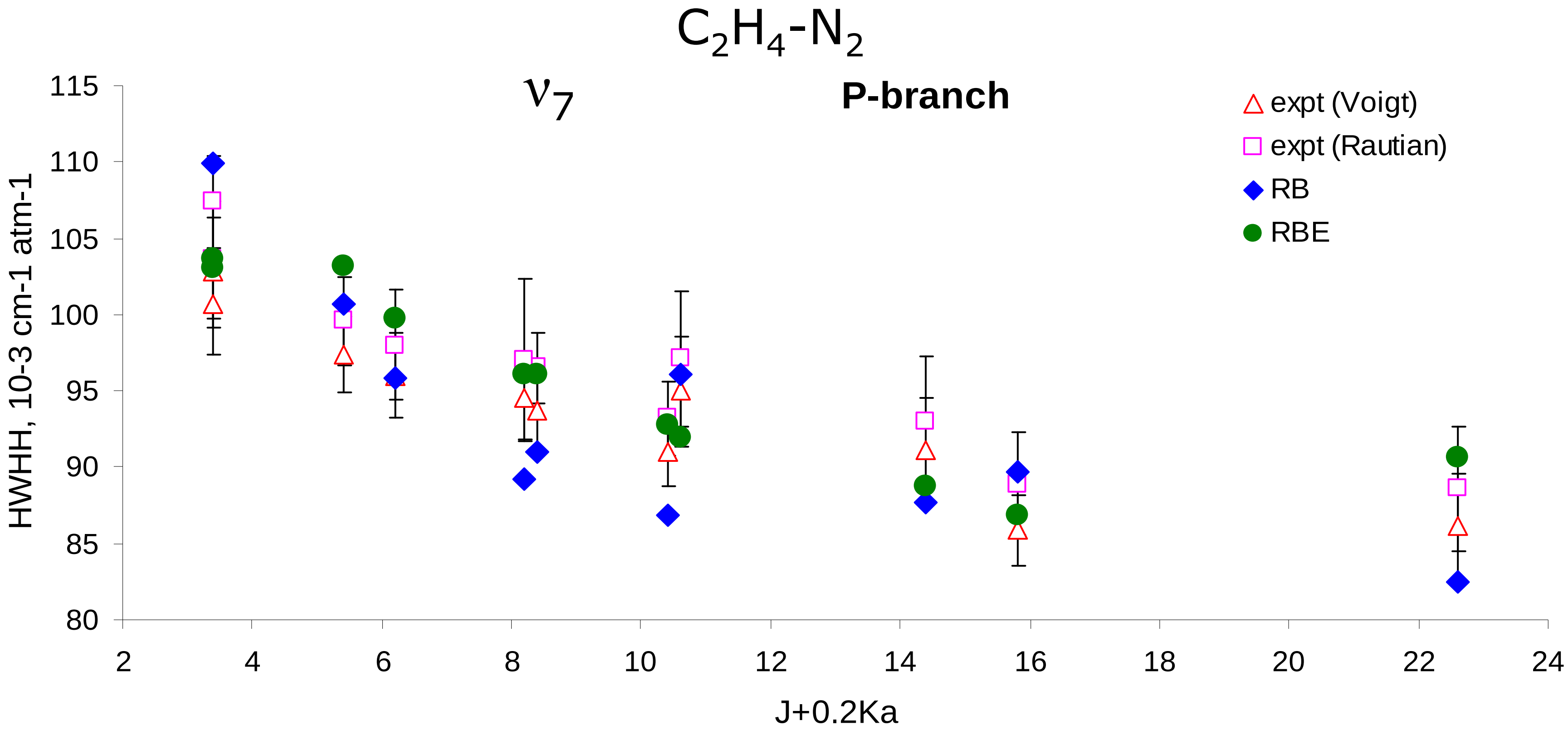
RBE: symmetric tops: NO



RBE: J. Buldyreva, S. Benec'h, M. Chrysos, Phys. Rev. A 63, 0123708 (2001)
RB: J. Bonamy, A. Khayar, D. Robert, Chem. Phys. Lett. 83, 539 (1981)

❸ # …\ SEMICLASSICAL METHODS

RBE: asymmetric tops : C_2H_4



RBE: J. Buldyreva, L. Nguyen, Phys. Rev. A 77, 042720 (2008)

RB: J. Walrand et al., J. Mol. Spectrosc. 229, 198 (2005)

❸ …\ SEMICLASSICAL METHODS

Modified Robert-Bonamy (RB) formalism

Q. Ma, R.H. Tipping, C. Boulet, JQSRT 103, 588 (2007)

an invalid assumption of the RB formalism:
cumulant expansion to evaluate the Liouville matrix element $\left\langle\left\langle f2i2\middle|\hat{S}\middle|f2i2\right\rangle\right\rangle$

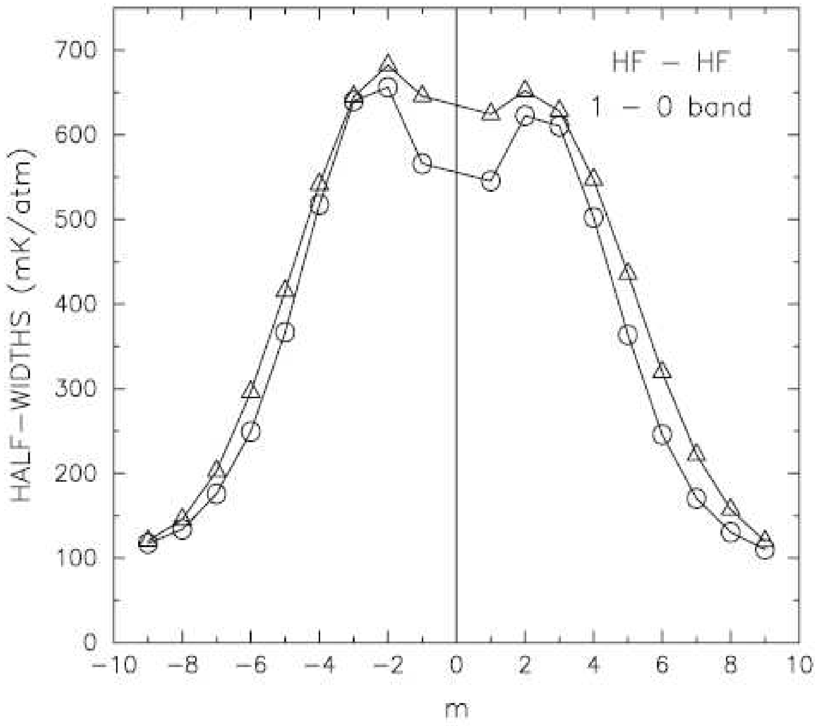
$$\gamma_{RB} = \frac{n_b}{2\pi c}\int_0^\infty vf(v)dv\int_0^\infty 2\pi b db \left\langle 1-\cos(S_1+\mathrm{Im}\,S_2)\mathrm{e}^{-\mathrm{Re}\,S_2}\right\rangle_{J_2}$$

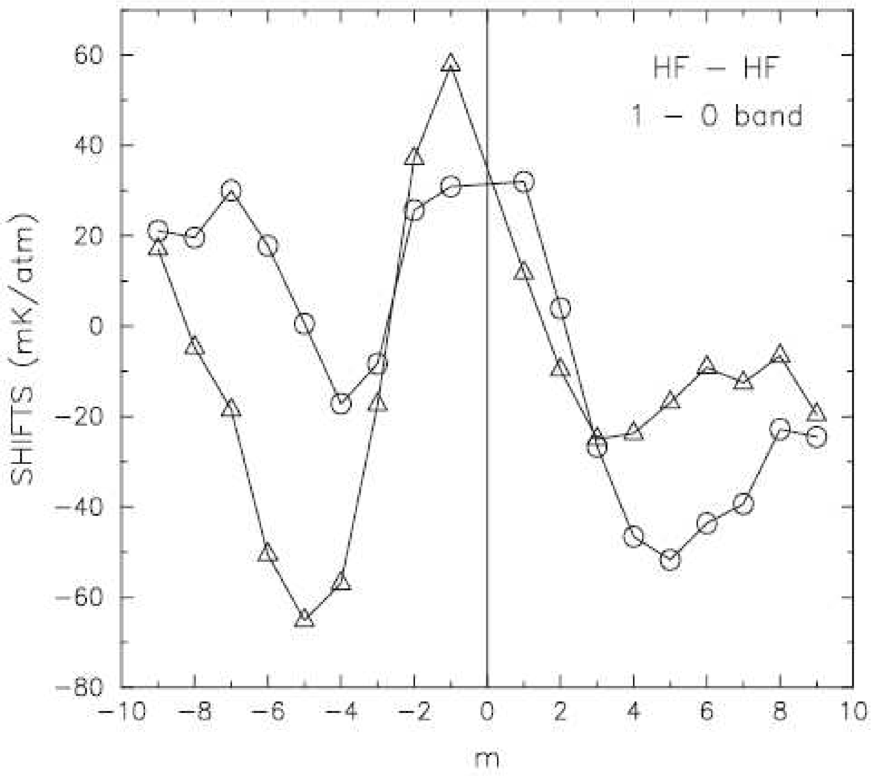
$$\gamma_{MRB} = \frac{n_b}{2\pi c}\int_0^\infty vf(v)dv\int_0^\infty 2\pi b db \left[1-\cos(\langle S_1\rangle_{J_2}+\mathrm{Im}\langle S_2\rangle_{J_2})\mathrm{e}^{-\mathrm{Re}\langle S_2\rangle_{J_2}}\right]$$

❸ …\ SEMICLASSICAL METHODS

Modified Robert-Bonamy (RB) formalism

Q. Ma, R.H. Tipping, C. Boulet, JQSRT 103, 588 (2007)





In comparison with the RB calculations,
the agreement of the MRB results with experiment is worse!

❸ …\ SEMICLASSICAL METHODS

Modified CRB formalism

B.K. Antony et al., Mol. Phys. 104, 2791 (2006)

Representative systems with strong to weak interactions:
H2O–H2O, H2O–N2, H2O–O2, O3–N2, O3–O2, and CH4–N2

Table 6. Comparison of CRB and MCRB half-widths with measurement for H_2O–H_2O and H_2O–N_2.

	H_2O–H_2O		H_2O–N_2	
	322 transitions		182 transitions	
	CRB	MCRB	CRB	MCRB
Percentage difference	1.4	−1.7	0.66	−2.5
|Percentage difference|	6.0	6.6	5.4	6.4
Standard deviation	8.4	9.0	9.3	10.4

« In all cases the CRB calculations agreed with measurement better, on average, than the MCRB calculations. »

« For HF–HF MCRB method often gave shifts with the wrong sign and demonstrated poor agreement with measurement. »

❸ ...\ SEMICLASSICAL METHODS

Vibration-dependent trajectories

Q. Ma et al., JMS 243, 105 (2007)

$$S_1(b)=\frac{1}{\hbar}\int_{-\infty}^{+\infty}dt\left\langle f\left|V_{iso}(r(t),\xi)\right|f\right\rangle-\frac{1}{\hbar}\int_{-\infty}^{+\infty}dt\left\langle i\left|V_{iso}(r(t),\xi)\right|i\right\rangle$$

$$V_{iso}(r(t),\xi)=V_0(r(t))+\Delta V_{iso}(r(t),\xi)$$

❸ …\ SEMICLASSICAL METHODS

Vibration-dependent trajectories

Q. Ma, JMS 243, 105 (2007)

H_2-He

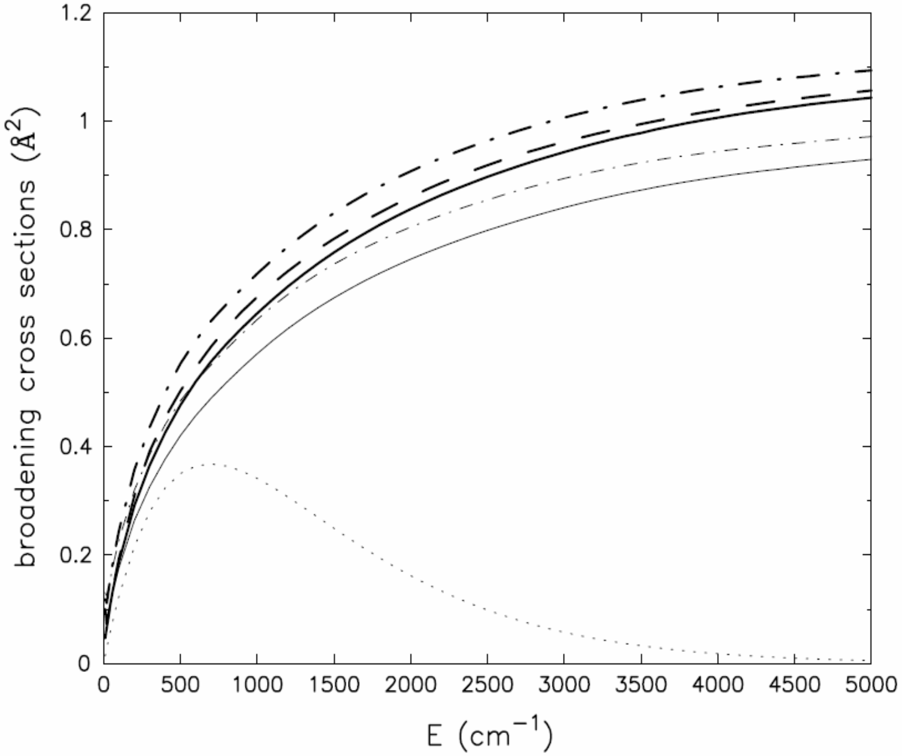


Fig. 1. Calculated broadening cross sections for the Q(1) line of $v = 1 \leftarrow v = 0$ band of H_2 broadened by He as function of the initial kinetic energy E. Values derived from the RB formalism are plotted by two dot-dashed lines: the bold one comes from the "exact" trajectory model and the thin one from the "parabolic" trajectory model. Similarly, results derived from the new formula with these two trajectory models are represented by two solid curves. In addition, values calculated from the MOLSCAT code are given by a bold dashed line. In order to be consistent, there is only the isotropic part of the potential surface used in the MOLSCAT calculations. For a reference, one (i.e., $T = 1000$ K) of the weighting functions introduced later in calculating the line parameters is plotted by a thin dotted line with arbitrary units.

Calculation of the S1 term in the RB approach must contain vibrational dependence (for particular systems)

❸ **...\ SEMICLASSICAL METHODS**

Coordinate representation and S-matrix in terms of autocorrelation functions

Q. Ma, R.H. Tipping, C. Boulet, JCP 124, 014109 (2006)

$$\mathrm{Re}\, S_{2i} = \sqrt{\frac{\pi}{2}} \sum_{l_1 l_2} \left\{ \sum_{j_i'} (2j_i'+1)\left(C^{l_1\,0}_{j_i\,0\;j_i'\,0}\right)^2 \right.$$

$$\left. \sum_{j_2 j_2'} (2j_2+1)(2j_2'+1)\rho_{j_2}\left(C^{l_2\,0}_{j_2\,0\;j_2'\,0}\right)^2 H_{l_1 l_2}(\omega_{j_i j_i'} - \omega_{j_2 j_2'}) \right\}$$

$$H_{l_1 l_2}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt\, e^{i\omega t} F_{l_1 l_2}(t)$$

- Fourier transform of the CF

$$F_{l_1 l_2}(t) = \int_{-\infty}^{\infty} dt' G_{l_1 l_2}\left(t' + \frac{t}{2}, t' - \frac{t}{2}\right)$$

(overlapping between $V(\vec{r}(t))$ and $V(\vec{r}(t'))$

❸ COLLISIONAL WIDTHS & SHIFTS

Semiempirical method

❸ …\ SEMIEMPIRICAL METHOD

A. Bykov, N. Lavrentieva, L. Sinitsa, Mol. Phys. 102, 1706 (2004)

Reducing of the CPU time without loss of precision via

- simplification of the RB equations to Anderson-type forms

- additional adjustable parameters
(trajectory curvature, vibrational effects, corrections to the scattering matrix)

- extensive use of experimental data

❸ # …\ SEMIEMPIRICAL METHOD

Transition strengths (active molecule)

$$\gamma_{if} = A(if) + \sum_l D^2(ii'|l)P_l(\omega_{ii'}) + \sum_l D^2(ff'|l)P_l(\omega_{ff'}) + \cdots$$

$$\delta_{if} = B(if) + \sum_l D^2(ii'|l)P_l(\omega_{ii'}) + \sum_l D^2(ff'|l)P_l(\omega_{ff'}) + \cdots$$

Interaction (potential, trajectory), perturbing molecule

Cutoff

$$A(if) = \frac{n}{c}\sum_{J_2}\rho_{J_2}\int_0^\infty v\,dv\, b_0^2(if, J_2, v)$$

$$B(if) = \frac{n}{c}(\alpha_i - \alpha_f)\sum_{J_2}\rho_{J_2}\int_0^\infty v\,dv\, b_0^{-3}(if, J_2, v)$$

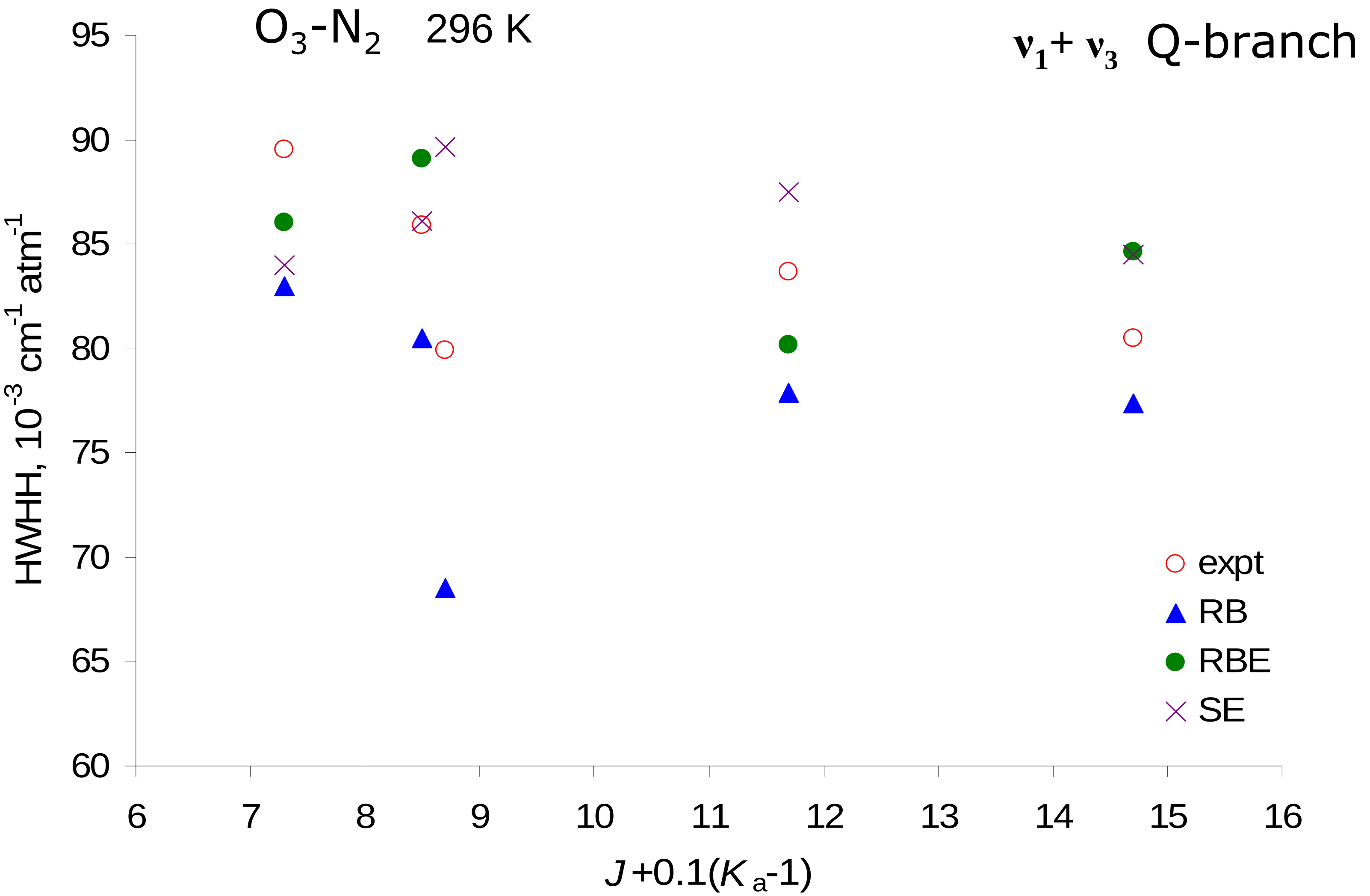
V_{iso}

$$P_l(\omega_{ii'}) = P_l^{Anderson}(\omega_{ii'})C_l(\omega_{ii'})$$

$$C_l = \frac{c_1}{c_2\sqrt{j_i} + 1}$$

Adjustable correction factor

❸ ...\ SEMIEMPIRICAL METHOD

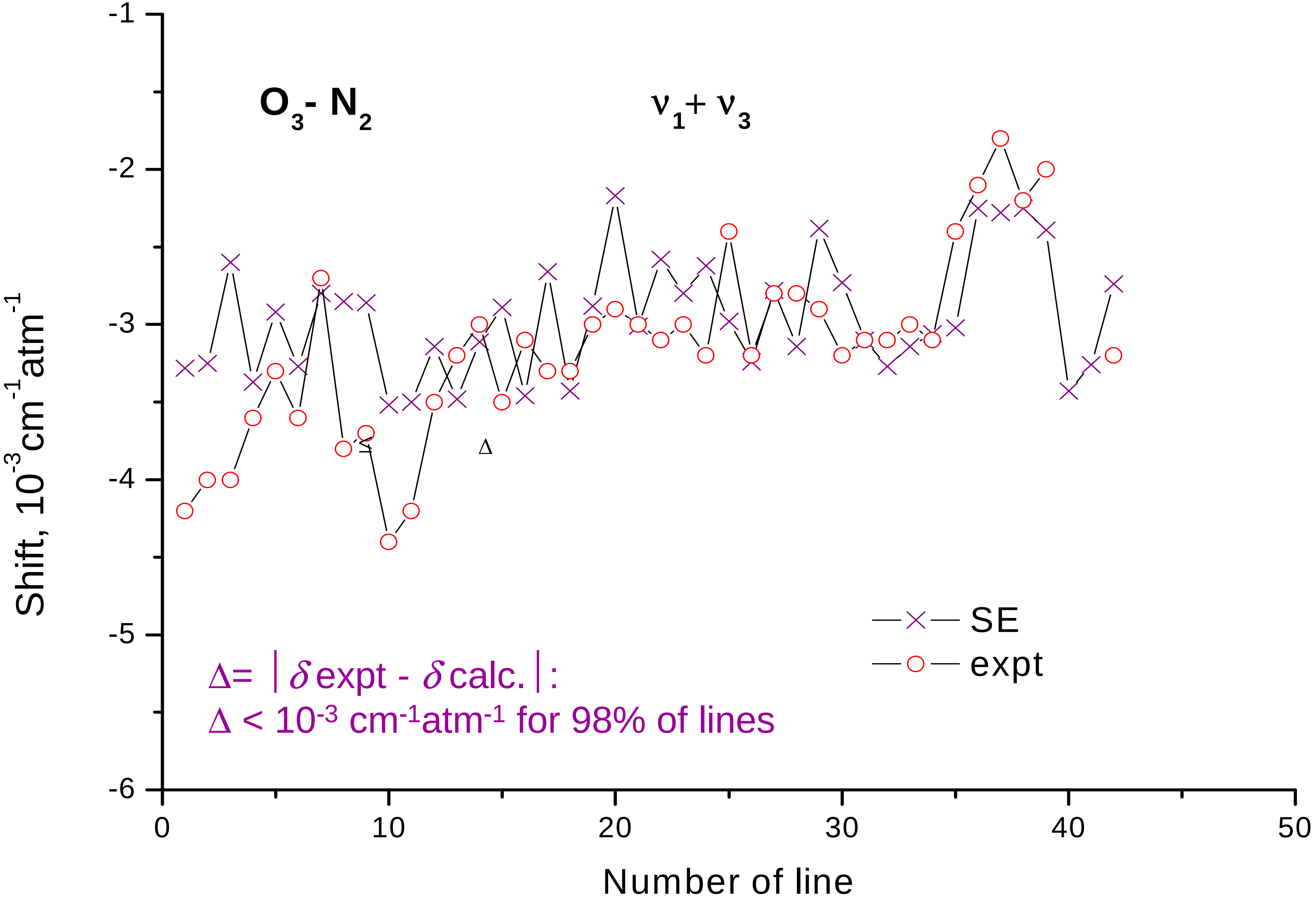


expt: S. Bouazza et al., JMS 157, 271 (1993); Barbe et al. JMS 180, 175 (1996)

RB: S. Bouazza et al., J. Mol. Spectrosc. 157, 271 (1993)

RBE/SE: J. Buldyreva, N. Lavrentieva, Mol. Phys.107, 1527 (2009)

❸ ...\ SEMIEMPIRICAL METHOD



Expt: A. Barbe, S. Bouazza, J.J. Plateaux, Appl. Opt. 30, 2431-2436 (1991)

SE: N. Lavrentieva, A. Osipova, J. Buldyreva, Mol. Phys. 107, 2045 (2009)

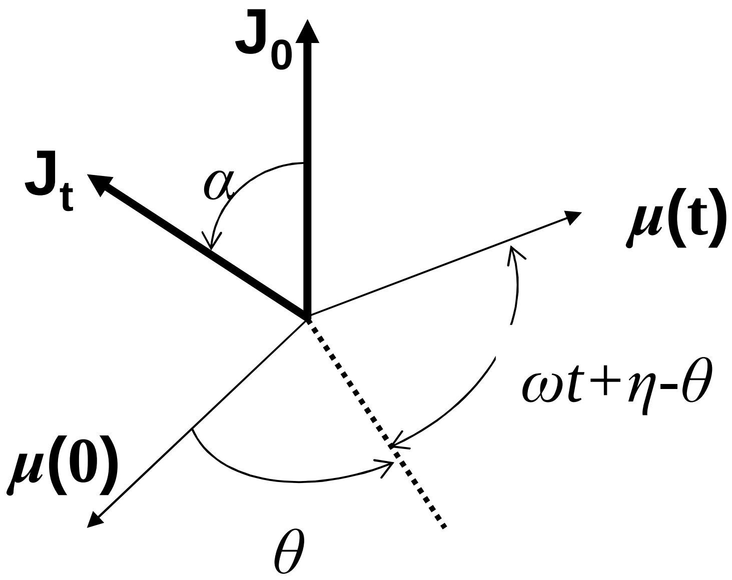
❸ COLLISIONAL WIDTHS & SHIFTS

Classical method

❸ …\ CLASSICAL METHOD

R.G. Gordon, JCP 44, 3083 (1966); M.D. Pattengill, JCP 66, 5042 (1977)

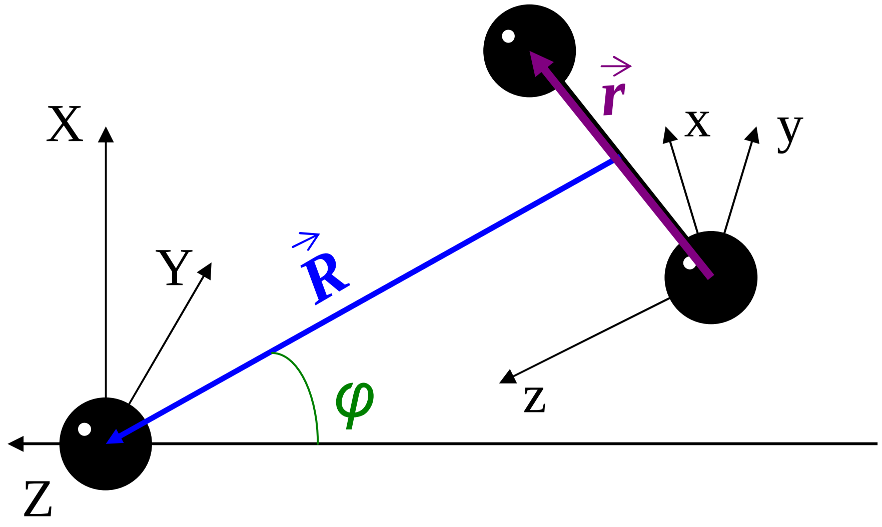
$$I(\omega) = \frac{1}{\pi}\int_0^\infty \mathrm{e}^{-i\omega t}\langle \mu(t)\mu(0)\rangle\, dt = \frac{\mathrm{I}}{\pi}\int_0^\infty \mathrm{e}^{-i\omega t}\langle u(t)u(0)\rangle\, dt$$



$$\gamma = n\left\langle v\left(1 - P_{el}\cos\eta\cos^2\frac{\alpha}{2}\right)\right\rangle_{b,v,0}$$

$$P_{el} = \exp\left[-\pi(2\hbar)^{-2}(\Delta M_{cl})^2\right]$$

❸ …\ CLASSICAL METHOD



$$\dot{R} = \frac{p_R}{\mu}; \quad \dot{\theta} = \frac{p_\theta + \mathrm{A}}{\mu \mathrm{R}^2 \sin^2\varphi}; \quad \dot{\varphi} = \frac{p_\varphi - J_y}{\mu \mathrm{R}^2}$$

$$\dot{p}_R = \frac{p_\theta^2 + \mathrm{A}(\mathrm{A} + 2p_\theta)}{\mu \mathrm{R}^3 \sin^2\varphi} + \frac{p_\varphi^2 + J_y(J_y - 2p_\varphi)}{\mu R^3} - \frac{\partial V}{\partial R}$$

$$\dot{p}_\varphi = \frac{\cos\varphi\left(p_\theta^2 + \mathrm{A}(\mathrm{A} + 2p_\theta)\right)}{\mu R^2 \sin^3\varphi} - \frac{\mathrm{B}(\mathrm{A} + p_\theta)}{\mu R^2 \sin^2\varphi}$$

$$\dot{x} = \frac{p_x}{m} + \frac{y\cos\varphi(\mathrm{A} + p_\theta)}{\mu \mathrm{R}^2 \sin^2\varphi} + \frac{z(J_y - p_\varphi)}{\mu R^2}$$

$$\dot{y} = \frac{p_y}{m} - \frac{(x\cos\varphi + z\sin\varphi)(\mathrm{A} + p_\theta)}{\mu \mathrm{R}^2 \sin^2\varphi}$$

$$\dot{x} = \frac{p_z}{m} + \frac{y\sin\varphi(\mathrm{A} + p_\theta)}{\mu \mathrm{R}^2 \sin^2\varphi} - \frac{x(J_y - p_\varphi)}{\mu R^2}$$

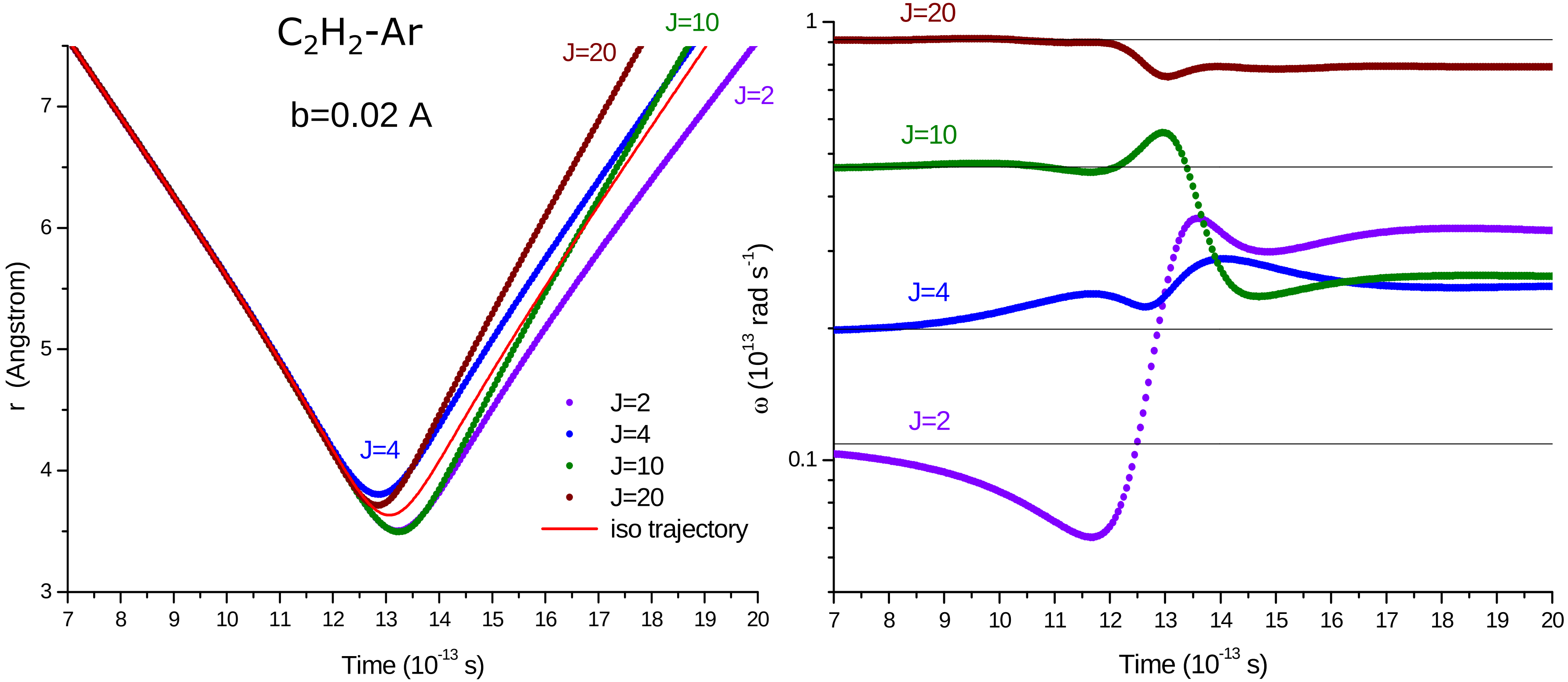
$$\dot{p}_x = \frac{p_y\cos\varphi(\mathrm{A} + p_\theta)}{\mu \mathrm{R}^2 \sin^2\varphi} + \frac{p_z(J_y - p_\varphi)}{\mu R^2} - \frac{\partial V}{\partial x}$$

$$\dot{p}_y = -\frac{(p_x\cos\varphi + p_z\sin\varphi)(\mathrm{A} + p_\theta)}{\mu R^2 \sin^2\varphi} - \frac{\partial V}{\partial y}$$

$$\dot{p}_z = \frac{p_y\sin\varphi(\mathrm{A} + p_\theta)}{\mu \mathrm{R}^2 \sin^2\varphi} - \frac{p_x(J_y - p_\varphi)}{\mu R^2} - \frac{\partial V}{\partial z}$$

$$\mathrm{A} = J_x\sin\varphi - J_z\cos\varphi; \quad \mathrm{B} = J_x\cos\varphi + J_z\sin\varphi; \quad \vec{\mathrm{J}} = \vec{r} \times \vec{p}; \quad r^2 = x^2 + y^2 + z^2$$

❸ ...\ CLASSICAL METHOD



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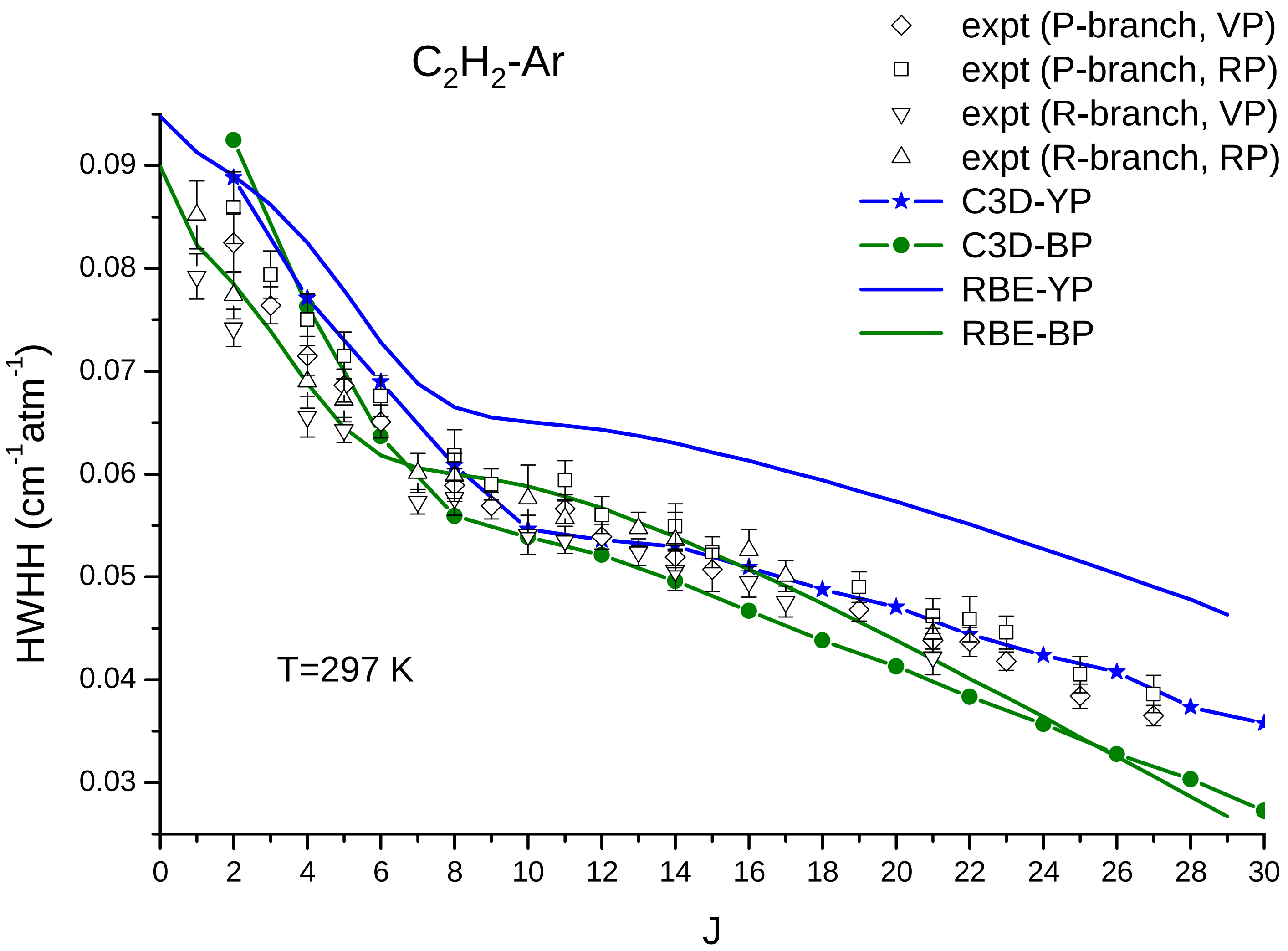
❸ ...\ CLASSICAL METHOD



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❹ **CONCLUSIONS**

1) **To have reliable experimental values of collisional parameters: appropriate profile model (L, SDVP, …)**

2) **To have reliable theoretical values for line widths/shifts: {CC, CS}, …, {NG, PA, SGC, (M)RBE, SE} (in function of molecular system and CPU cost)**

PERSPECTIVES

► **Importance of line shifts in spectra modeling**

► **Interpretation of the asymmetry of rotational lines (profile models)**

► **K-dependences of widths & shifts (terahertz region)**

► **Temperature dependence of collisional parameters**

► **Line interference**

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