Modifications of the Robert-Bonamy Formalism and Further Refinement Challenges

Q. Ma, NASA/GISS

R. H. Tipping, Univ. of Alabama

C. Boulet, Univ. Paris-Sud, France

Statements

The presentation is not a review of the RB formalism.

Rather our focus is on some problems in the original derivation and extensions remaining to be solved.

There is no intention to underestimate its success.

The RB formalism

- The RB formalism has been widely and successfully used in calculating half-widths and shifts for years.

- In comparison with the Anderson-Tsao-Curnutte formalism, it contains two new features:

  - **To eliminate a cutoff by using the Linked-Cluster Theorem.**
  - **To replace straight lines by parabolic trajectories.**

- There have been some improvements since 1979 when the RB formalism was initially developed.
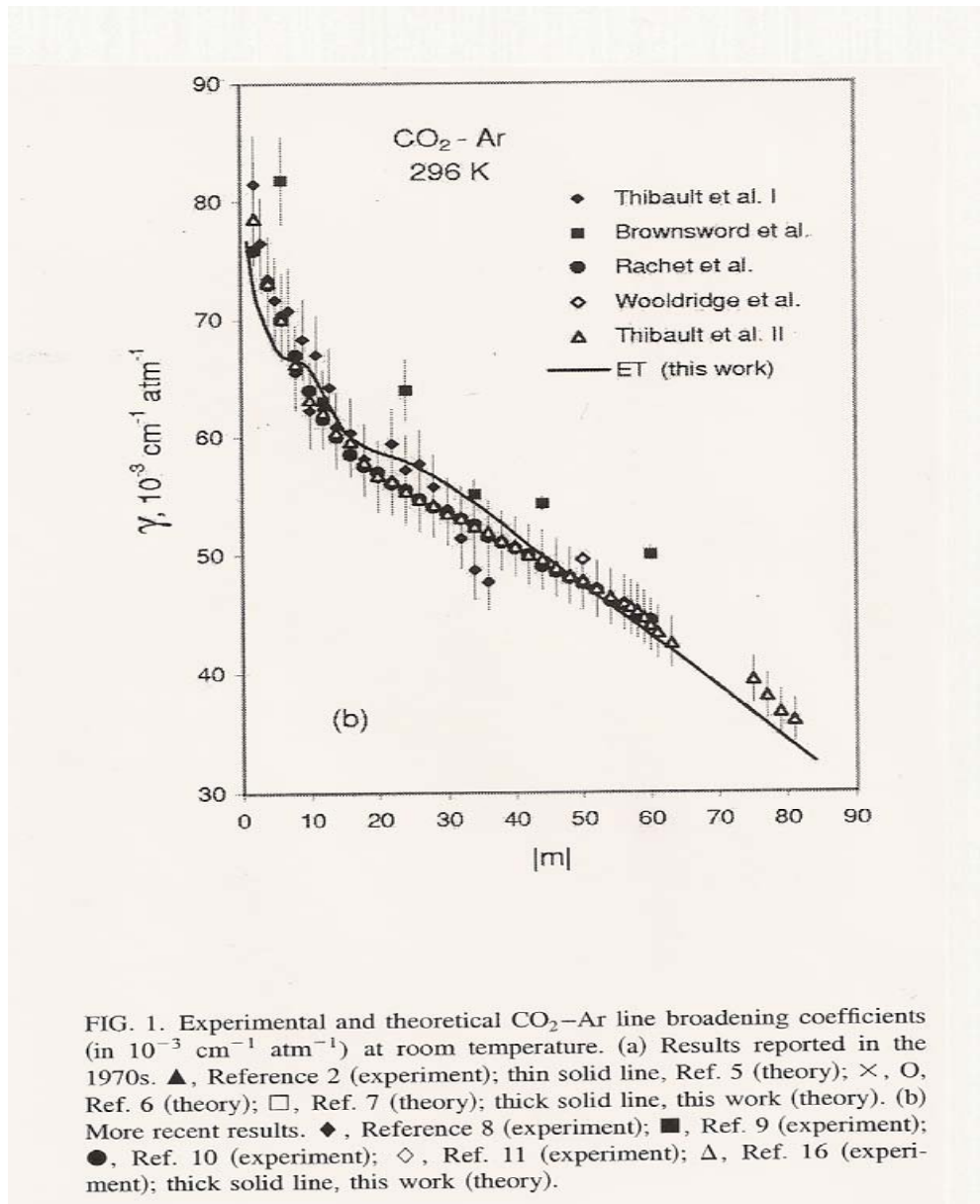
Improvements made previously

- To adopt more complicated potential models and to consider their vibrational dependence.

- To use "exact" trajectories and so on.

  However, the core part of the RB formalism has not been changed.

  There are several questionable assumptions remaining from the very beginning. Some of them are unjustified and some add limitations in its application.

  These cause main weakness of the RB formalism. See following examples.

Comparison between theories and measurements

FIG. 1. Experimental and theoretical CO_2-Ar line broadening coefficients (in 10^{-3} cm^{-1} atm^{-1}) at room temperature. (a) Results reported in the 1970s. ▲, Reference 2 (experiment); thin solid line, Ref. 5 (theory); ×, O, Ref. 6 (theory); □, Ref. 7 (theory); thick solid line, this work (theory). (b) More recent results. ◆, Reference 8 (experiment); ■, Ref. 9 (experiment); ●, Ref. 10 (experiment); ◇, Ref. 11 (experiment); △, Ref. 16 (experiment); thick solid line, this work (theory).

For $CO_2 - Ar$, based on a potential model (Parker et al. 1976), values of the width from RB represented by a solid line ⎯⎯ match data very well (J. Chem. Phys. 115, 7436(2001)).

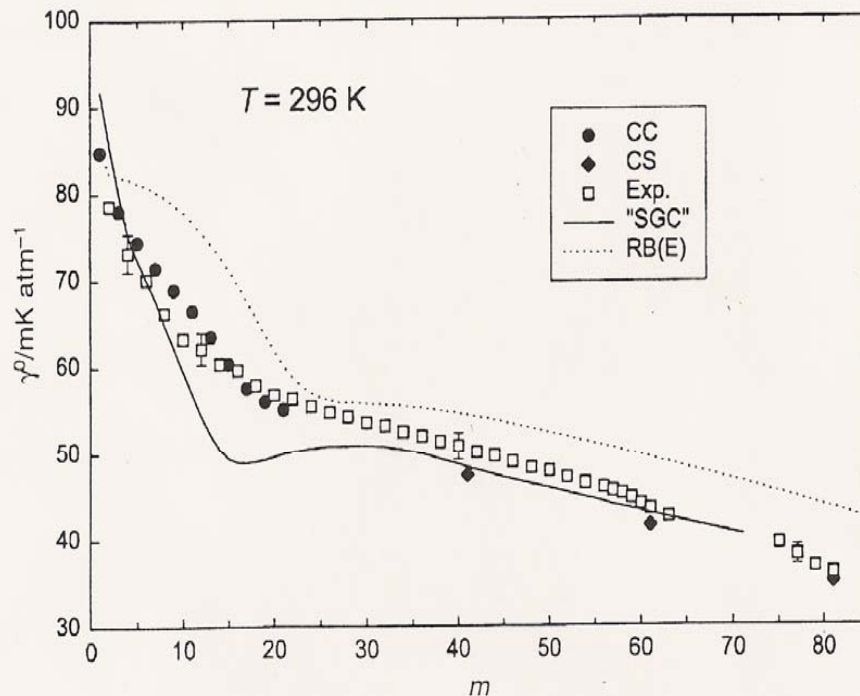Can one conclude that predicted widths from the RB formalism are reliable?

Fig. 6 Experimental and calculated broadening coefficients γ^0 vs. $|m|$ at 296 K. The vertical bars indicate a relative error of 3%.

- For CO_2 – Ar, based on an updated potential model (Hutson et al. 1996), results of the width from RB represented by ······ are in poor agreement with the measurements □. Meanwhile, values from the closed coupling method given by ● are good.
- **Because the agreement is not as good, can one claim adopting a more accurate potential model goes to a wrong direction?**

Convergence problem in the literature

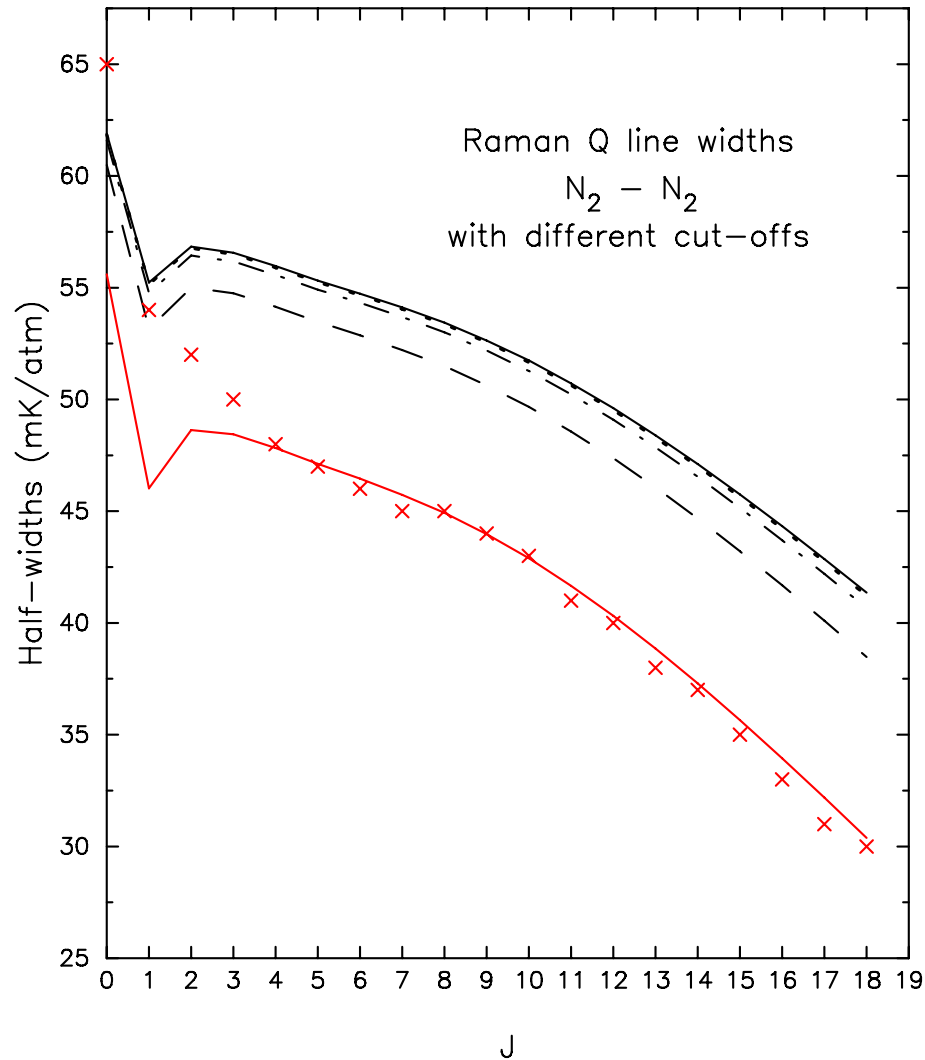
Raman Q line widths
N₂ − N₂
with different cut−offs

Fig. 3 Calculated Raman Q line widths of $N_2 - N_2$ at 296 K. Values derived from 4th, 6th, 8th, 10th, and 12th order cutoffs are presented by 5 curves from the bottom to the top. Experimental data are denoted by ×.

How fast the convergence goes depends on the molecular pairs. In general, it goes slowly.

The 4th order cutoff was used in many papers including the one (J. Chem. Phys. 95, 2379 (1991)) presented here.

Can one claim including more terms in the calculations goes to the wrong direction?

Modifications of the RB formalism

- The RB formalism is a theory, not empirical formulas. Every steps in the derivations must be sound.

- Recently, we have found two problems in their derivation process.

  – The first one is associated with how to apply the Linked-Cluster Theorem.

  – The second one results from how to determine trajectories.

- We have found some results published in the literature are not converged yet. As a result, some conclusions in these papers may not be valid.

First Modification

- The Linked-Cluster theorem was originally developed by Bloch, a nuclear scientist, in Hilbert space.

$$U(t) = U_L(t) <0|U(t)|0> = U_L(t)\, e^{<0|U(t)|0>^{(C)}},$$

where |0> is the non-degenerate ground state of the unperturbed Hamiltonian and U(t) is the time evolution operator.

- Its core part is to express the diagonal matrix element <0|U(t)|0> in an exponential form.

$$<0|U(t)|0> = e^{<0|U(t)|0>^{(C)}}.$$

- This is equivalent to applying Kubo's cumulant expansion by defining the diagonal matrix elements as the average.

What has happened in deriving the RB formalism?

These authors have assumed the diagonal matrix elements $<<J_f j_2 J_i j_2|\hat{S}|J_f j_2 J_i j_2>>$ in Liouville space can also be expressed as

$$<< J_f j_2 J_i j_2 \mid \hat{S} \mid J_f j_2 J_i j_2 >> = e^{-iS_1^{(C)} - S_2^{(C)}}.$$

At first sight, their applying the Linked-Cluster theorem appears to be correct because $<<J_f j_2 J_i j_2|\hat{S}|J_f j_2 J_i j_2>>$ is diagonal in the Liouville space. But, this assumption is not valid.

What's wrong in their derivation?

- Rules in the Liouville space could differ from those applicable in Hilbert space. A simple way to check is to rewrite everything back in Hilbert space.

- In Hilbert space, $|j_2 j_2 \rangle\rangle$ is defined as

$$| j_2 j_2 \rangle\rangle = \frac{(-1)^{j_2}}{\sqrt{2j_2+1}} \sum_{m_2} | j_2 m_2 \rangle |j_2 m_2 \rangle^\dagger .$$

- In Hilbert space, $\langle\langle J_f j_2 J_i j_2 | \hat{S} | J_f j_2 J_i j_2 \rangle\rangle$ is given by

$$\langle\langle J_f j_2 J_i j_2 | \hat{S} | J_f j_2 J_i j_2 \rangle\rangle = \frac{1}{2j_2+1}$$

$$\times \sum_{m_2, m_2'} \langle J_i ; j_2 m_2' | S_I | J_i ; j_2 m_2 \rangle \langle J_f ; j_2 m_2 | S_F^* | J_f ; j_2 m_2' \rangle .$$

- Conclusion: None of these matrix elements of S_I and S_F^* are diagonal. Thus, one can not apply the Linked-Cluster theorem at all.

A correction

- **The cumulant expansion is more general than the Linked-Cluster theorem.** It states that

$$< 1 - i \int_{-\infty}^{+\infty} L_1(t)dt - \int_{-\infty}^{+\infty} \int_{-\infty}^{t} L_1(t)L_1(t')dtdt' + \cdots >$$

$$= \exp\{ i \int_{-\infty}^{+\infty} < L_1(t) >_C dt - \int_{-\infty}^{+\infty} \int_{-\infty}^{t} < L_1(t)L_1(t') >_C dtdt' + \cdots \}, \quad where$$

$$< L_1(t) >_C = < L_1(t) >, < L_1(t)L_1(t') >_C = < L_1(t)L_1(t') > - < L_1(t) >< L_1(t') >, \cdots.$$

The average must satisfy the normalization condition <1> = 1.

- **We apply the cumulant expansion here** by defining the average as

$$< \hat{S} > = Tr_{internal}\{ \hat{S} \rho_b \} = \sum_{j_2, j_2'} << J_f j_2' J_i j_2' | \hat{S} | J_f j_2 J_i j_2 >> \rho_b(j_2).$$

Thus, we are able to express < Ŝ > in an exponential form

$$< \hat{S} > = e^{-i< S_1 >_{j2} - < S_2 >_{j2}},$$

where $< S_{1 or 2} >_{j_2}$ is given by

$$< S_{1 or 2} >_{j_2} = \sum_{j_2} (2 j_2 + 1) e^{-E(j_2)/kT} S_{1 or 2} / Q_b.$$

Expressions for the resolvent operator

- In the RB formalism,

$$<\hat{S}>_{bath} = <\{<e^{-iS_1-S_2}>_{j_2}\}>_{v,b},$$

- In the modified formalism,

$$<\hat{S}>_{bath} = <e^{-i<S_1>_{j_2}-<S_2>_{j_2}}>_{v,b},$$

where $<\cdots>_{v,b}$ means classical averages over the velocity v and the impact parameter b.

In the new expression, j_2 and j_2' are treated more equally which is consistent with a fact that the bath average of $\tilde{S}$ is carried out in a line space constructed by j_2 and j_2'.

Expressions for the half-width

- In the RB formalism

$$\gamma_{RB} = \frac{n_b}{2\pi c} \int\limits_0^{+\infty} vf(v)dv \int\limits_0^{+\infty} 2\pi b\,db <1-\cos(S_1+\mathrm{Im}(S_2))e^{-\mathrm{Re}(S_2)}>_{j_2},$$

where f(v) is the Maxwell-Boltzmann function.

- In the modified formalism

$$\gamma_{new} = \frac{n_b}{2\pi c} \int\limits_0^{+\infty} vf(v)dv \int\limits_0^{+\infty} 2\pi b\,db [1-\cos(<S_1>_{j_2}+\mathrm{Im}(<S_2>_{j_2}))e^{-\mathrm{Re}(<S_2>_{j_2})}].$$

Expressions for the shift

- In the RB formalism

$$\delta_{RB} = \frac{n_b}{2\pi c} \int\limits_0^{+\infty} vf(v)dv \int\limits_0^{+\infty} 2\pi b db < \sin(S_1 + \mathrm{Im}(S_2))e^{-\mathrm{Re}(S_2)} >_{j_2},$$

- In the modified formalism

$$\delta_{new} = \frac{n_b}{2\pi c} \int\limits_0^{+\infty} vf(v)dv \int\limits_0^{+\infty} 2\pi b db \, \sin(<S_1>_{j_2} + \mathrm{Im}(<S_2>_{j_2})) \, e^{-\mathrm{Re}(<S_2>_{j_2})}.$$

In the RB formulas, the summation over j_2 is outside of the cumulant expansion.

In the new ones, the summation over j_2 is inside.

Comments on the first modification

- Whether to adopt the modification or not is mainly determined by the following questions:
  - Is there a mistake or not? Is the modification correct or not?
  - Are effects from the modification significant or not?
  - Is extra work needed to make the modification?
  - Comparisons with data are helpful. But they are not the only factor to make a judgment.

- For weakly interacting pairs, results differ slightly. For strongly interacting pairs, differences are larger. Calculated shifts could differ dramatically.

- There is no extra work required.
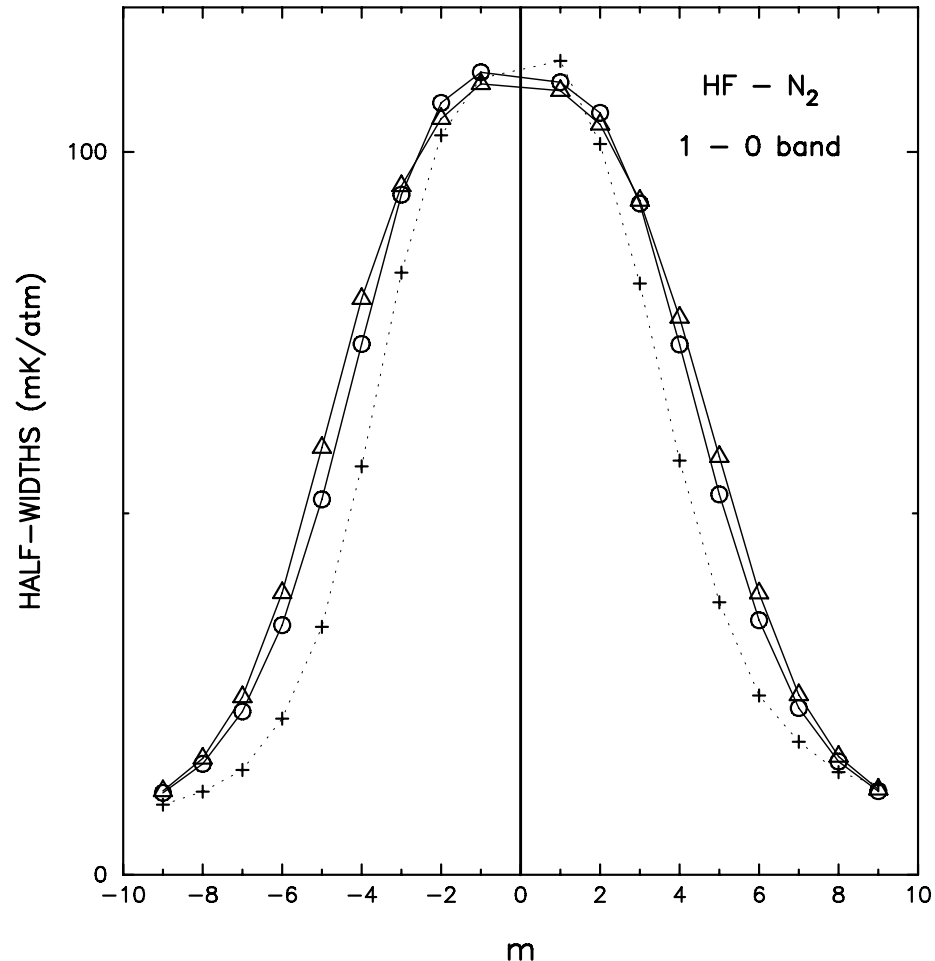
Numerical example for the widths

Fig. 4 Calculated half-widths of the 0-1 band of HF broadened by N$_2$ at 296 K. Values derived from the RB and the new formulas are denoted by ○ and △, respectively. Measurements at 295 K are given by +.
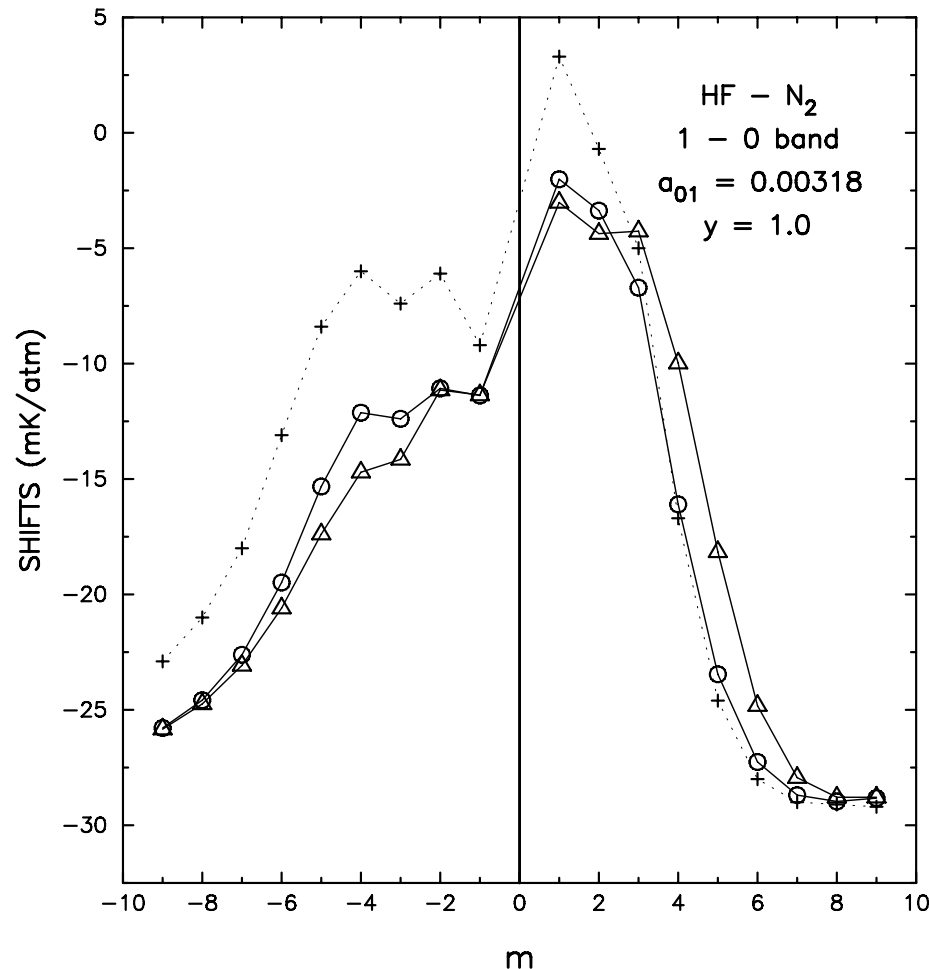
Numerical example for the shifts

Fig. 5 Calculated shifts of the 0-1 band of HF broadened by N_2 at 296 K. Values derived from the RB and the new formulas are denoted by ○ and △, respectively. Measurements at 295 K are given by +.
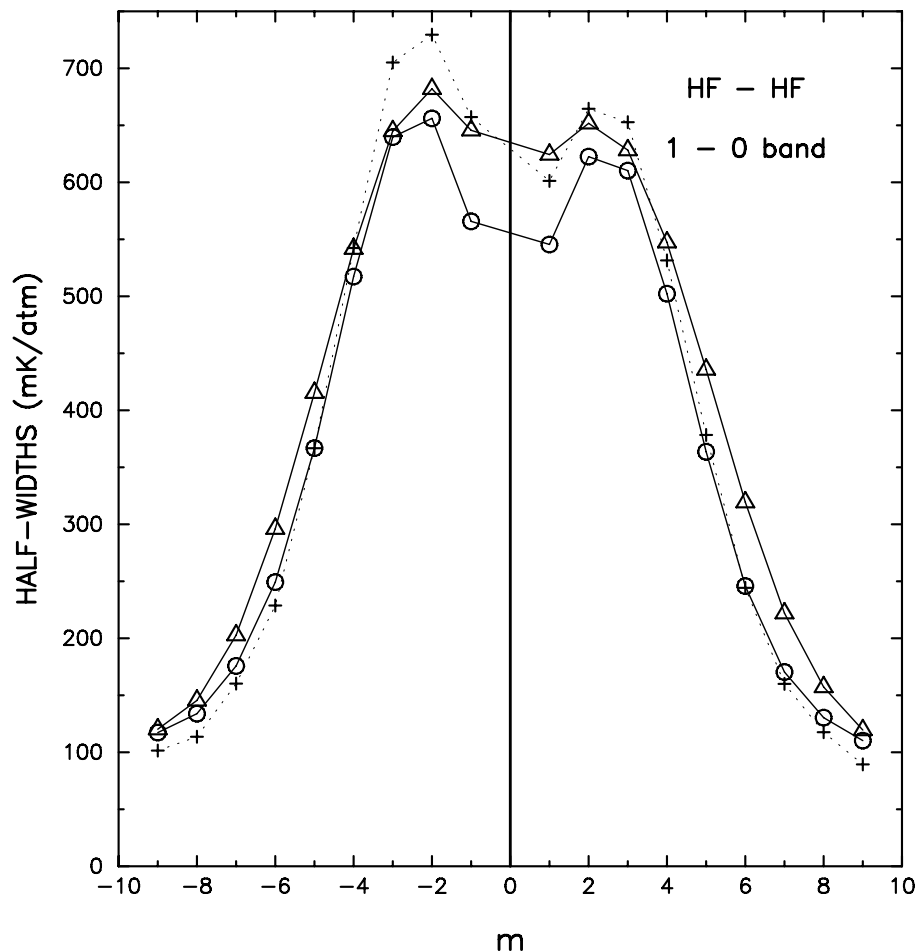
Numerical example for the widths

Fig. 6 Calculated widths of the 0-1 band of HF broadened by HF at 296 K. Values derived from the RB and the new formulas are denoted by ○ and △, respectively. Measurements at 295 K are given by +.
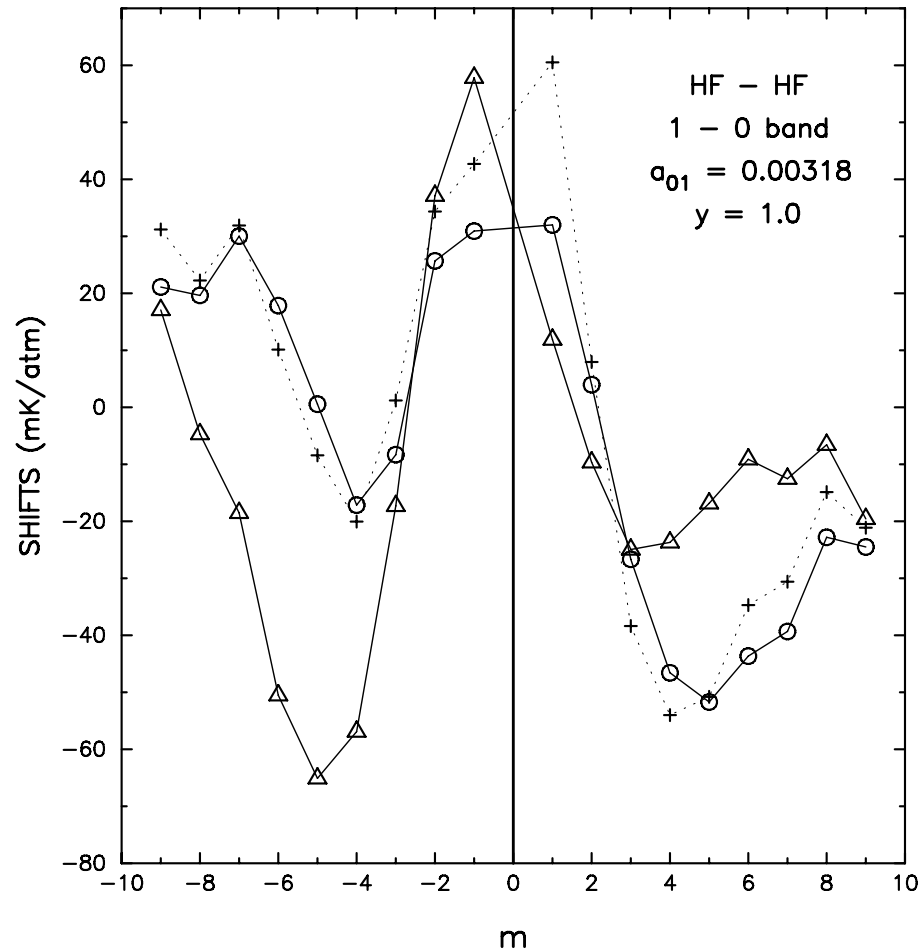
Numerical example for the shifts

Fig. 7 Calculated shifts of the 0-1 band of HF broadened by HF at 296 K. Values derived from the RB and the new formulas are denoted by ○ and △, respectively. Measurements at 295 K are given by +.

Where does the Second Modification come from?

- In the RB formalism, they assume that the trajectories are determined by $V_{iso}(R(t),\xi=0)$ where the normalized vibrational coordinate $\xi=(r-r_e)/r_e$.

  By setting $\xi=0$, the trajectories are vibrationally independent.

- This assumption is not correct, especially in calculating **vibrational dephasing** because the latter results from the vibration-dependent isotropic potential $V_{iso}(R(t),\xi)$ itself.

Physics basis of the second modification

- With the Born-Oppenheimer approximation, the translational motion R(t) is separated from the internal degrees α.

- R(t) is determined by potentials V_α

$$V_\alpha \approx <\alpha \mid V \mid \alpha>.$$

- Because V_α depends on the vibration quantum number, **the trajectories are vibration-dependent.**

- When one derives an expression for S_1 defined by

$$S_1 = \frac{1}{\hbar} \int_{-\infty}^{+\infty} dt \, [<f \mid V_{iso} \mid f> - <i \mid V_{iso} \mid i>],$$

  this modification becomes important.

Expression for S_1 in the RB formalism

When V_{iso} is given by the LJ model, the expression for S_1 is given by

$$S_1 = \frac{3\pi\varepsilon\sigma}{2\hbar v_c'} a_{01} \{ \frac{21}{32} y (\frac{\sigma}{b})^{11} - (\frac{\sigma}{b})^5 \},$$

where

$$v_c' = v\{1 + \frac{8\varepsilon}{mv^2}[5(\frac{\sigma}{r_c})^{12} - 2(\frac{\sigma}{r_c})^6]\}^{1/2},$$

$$y = \Delta_{fi}^{(1)}(\xi) / \Delta_{fi}^{(2)}(\xi),$$

$$a_{01} = \Delta_{fi}^{(2)}(\xi),$$

$$\Delta_{fi}^{(1)}(\xi) = s_1(< f | \xi | f > - < i | \xi | i >) + t_1(< f | \xi^2 | f > - < i | \xi^2 | i >),$$

$$\Delta_{fi}^{(2)}(\xi) = s_2(< f | \xi | f > - < i | \xi | i >) + t_2(< f | \xi^2 | f > - < i | \xi^2 | i >).$$

A new expression for S_1

- A new expression for S_1

$$S_1 = \frac{3\pi\varepsilon\sigma}{2\hbar v_c'} a_{01} \{ \frac{21}{32} \cdot (\frac{\sigma}{r_c})^{11} [y - W(y)] - (\frac{\sigma}{r_c})^5 [1 - W(y)] \},$$

$$W(y) = \frac{4\varepsilon}{m v_c'^2} [5(\frac{\sigma}{r_c})^{12} y - 2(\frac{\sigma}{r_c})^6].$$

- In comparison with the RB formalism, there are extra terms *W(y)* in S_1. These extra terms could be comparable with the original ones.

- How important the modification is depends on the molecular pairs. For those pairs with weak long-range interactions, effects could be significant. The shifts are more affected than the widths.

Numerical comparisons for the shift
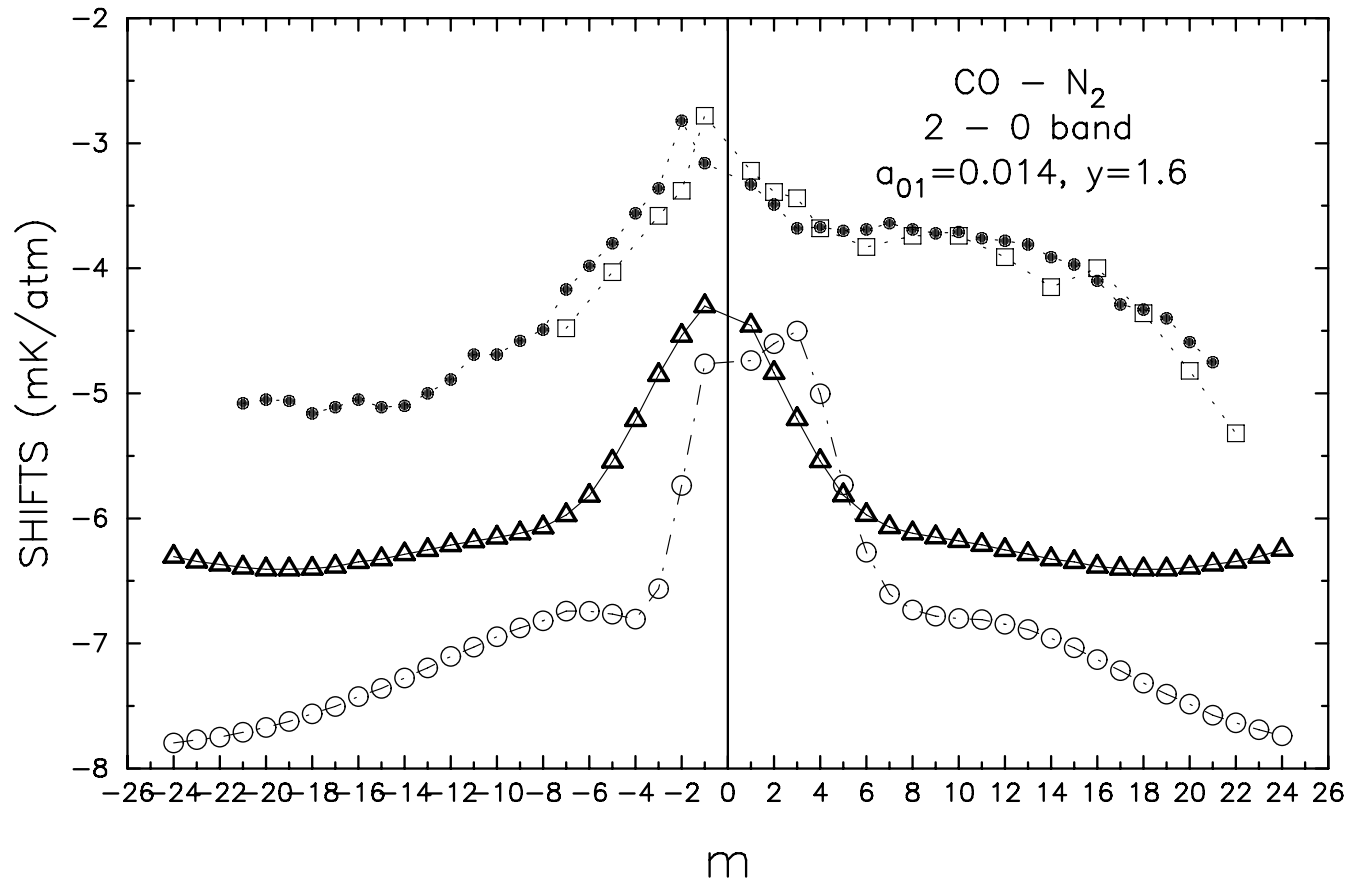
- Fig. 8 Calculated shifts in the 2 ← 0 band of CO broadened by N_2. Values derived from the RB formalism and the new one are represented by ○ and Δ. Measurements are represented by ● and □.

Numerical comparisons for the width
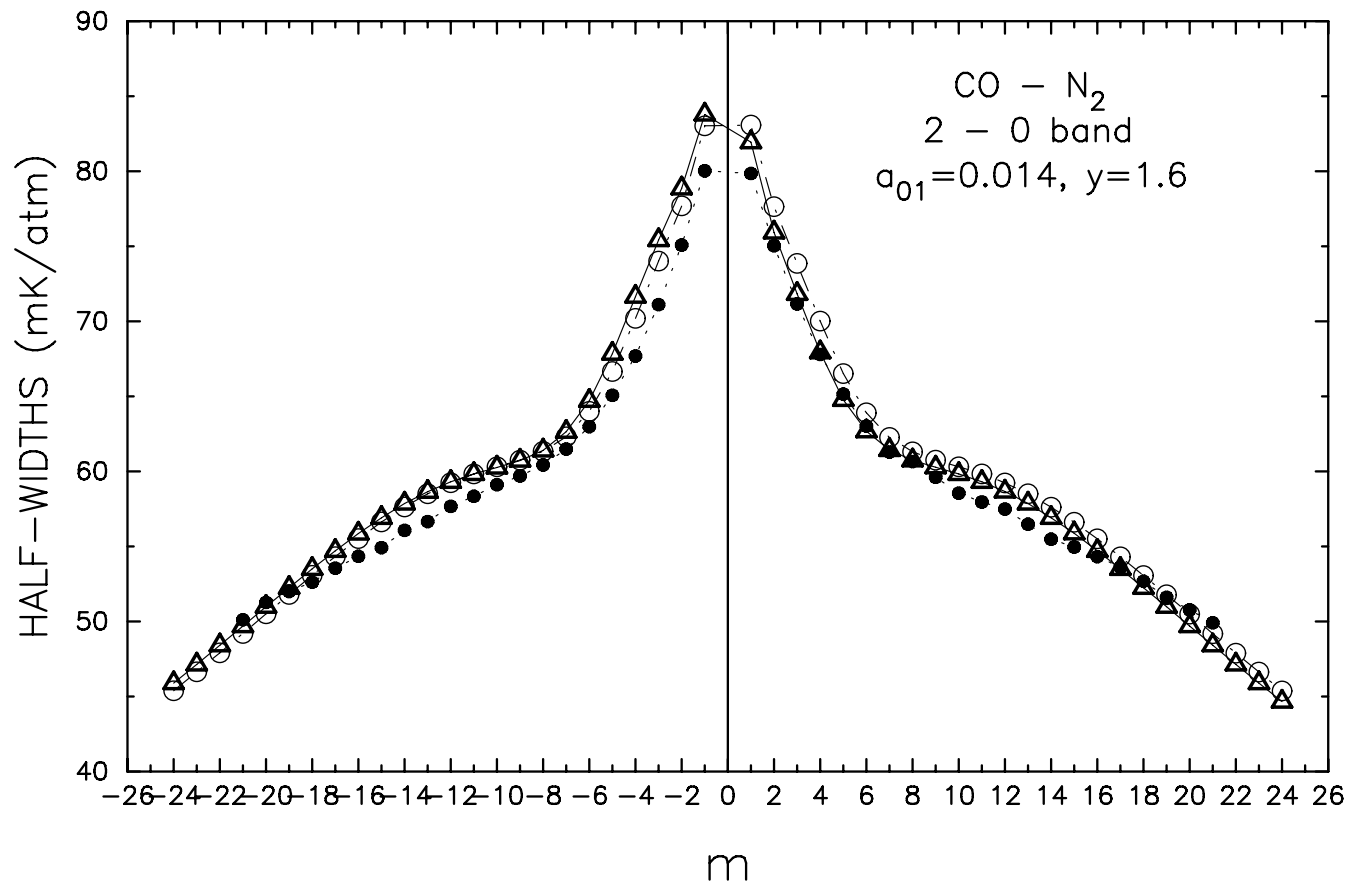
- Fig. 9 Calculated half-widths in the 2 ← 0 band of CO broadened by N_2. Values derived from the RB formalism and the new one are represented by ○ and Δ. Measurements are represented by ● and □.

Further refinement challenges

(1) To give up the assumption that the trajectories are only determined by the isotropic potentials.

  Benefit: Couplings between the translation and internal motions are taken into account.

  Challenge: It is a very difficult job because within the RB formalism the translational motion is treated classically, while the internal one is treated quantum mechanically.

(2) To give up the assumption that the resolvent operator is diagonal with respect to states of the absorber molecule.

  Benefit: Line couplings are taken into account.

  Challenge: One has to calculate a lot of off-diagonal matrix elements of the resolvent operator.

Further refinement challenges

(3) To consider contributions from the third-order expansion of the $\hat{S}$ matrix.

Benefit: one can get higher order contributions and make sure results are converged.

Challenge: One has to include many more terms in the calculations. We think that at least for pairs of two linear molecules, it is possible to solve this problem based on the coordinate representation.

We expect each of these refinements could significantly affect calculated widths and shifts.

Conclusions

- There is an urgent need to provide accurate theoretical results for line widths and shifts for many practical applications.

- It appears that one still needs to rely on the RB formalism to do calculations at present, because closed coupling calculations may not be possible for many collision pairs of interest.

- However, Unless the challenges mentioned above have been addressed, one can't conclude with certainty that theoretically predicted values from the RB formalism are really reliable.

- These problems have been ignored or avoided for two decades. It is the time to take actions right now.