The Complex Robert-Bonamy Formalism

The theoretical model chosen is a complex implementation of the semiclassical formalism of Robert and Bonamy[1] (RB) for several reasons.

1) The formalism is based on the resolvent operator formalism of Baranger,[2] Kolb,[3] and Greim[4] (BKG). The application of linked-cluster techniques[5] to the BKG formalism leads to developments[1, 6-8] which eliminate the awkward cutoff procedure that characterized earlier theories.[9-11] Also, the cumulant[5] expansion, as incorporated in the RB formalism, provides a better description of the long term dynamics of the collisions.

2) The formalism is complex valued, yielding half-widths and line shifts from a single calculation.

3) The intermolecular dynamics are treated more realistically than in earlier theories, i.e. using curved rather than straight line trajectories. This has important consequences in the description of close intermolecular collisions (small impact parameters).

4) Connected to item (3) is the incorporation in the RB theory of a short range (Lennard-Jones 6-12[12]) atom-atom component to the intermolecular potential. This component has been shown to be essential for a proper description of pressure broadening, especially in systems where electrostatic interactions are weak.[13] (Here, the notion of strong and weak collisions adopts the definition of Oka.[14])

5) This formalism allows the removal of all "adjustable" parameters so as to arrive at a more predictive theory.

It should be noted that within the complex Robert-Bonamy formalism, the imaginary parts of the S matrix expansion affect both the calculation of the line shift and the halfwidth, an effect not achieved in Anderson-Tsao-Curnutte (ATC) theory.[9-11]

Calculations based on the complex Robert-Bonamy formalism indicate that the effect of the imaginary terms is very important in determining the half-width. [13, 15, 16, 17] The effect of the imaginary components on the half-widths varies from transition to transition and perturber to perturber but can be as much as 25%. The change is generally (almost always) in the direction of better agreement with experiment.

The halfwidth, γ, and line shift, δ, of a ro-vibrational transition f←i are given in the complex Robert-Bonamy (CRB) formalism by minus the imaginary part and the real part, respectively, of the diagonal elements of the complex relaxation matrix. In computational form, the halfwidth and line shift are usually expressed in terms of the Liouville scattering matrix[2,18]

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

$$\delta_{f \leftarrow i} = \frac{n_2 \, \overline{v}}{2 \, \pi \, c} \sum_{J_2} \left\langle J_2 \middle| \rho_2 \middle| J_2 \right\rangle \int_0^{\infty} 2\pi b \, \sin\{S_1 + \mathrm{Im}(S_2)\} \, e^{-\mathrm{Re}(S_2)} \, db \qquad (1)$$

where $\overline{v}$ is the mean relative thermal velocity, ρ_2 and n_2 are the density operator and number density of perturbers, and b is the impact parameter. S_1 and S_2 are the first and second order terms in the expansion of the Liouville scattering matrix and depend on the intermolecular potential.

The potential employed in the calculations consists of the leading electrostatic components for the A-X pair (i.e. the octupole moment of methane with the quadrupole

moment of N_2 or O_2), an atom-atom component[19,17] and isotropic induction and dispersion components. The isotropic component of the atom-atom potential is used to define the trajectory of the collision within the semiclassical model of Robert and Bonamy.[1]

Sarah has made several studies which focus on the wavefunctions of methane comparing three different sets of ν_3 wavefunctions and several ground state sets (all from the Université of Bourgogne, Dijon, France). She discovered sign errors in the second set of wavefunctions which led to half-widths in error by a factor of 2. We now have a set of reliable wavefunctions for states up to J=30 for the ground, ν_3, and ν_4 vibrational states. She has also begun to optimize the intermolecular potential for the CH_4-N_2 system by adjusting to data by Pine[20] and Benner et al.[21]

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