MODIFICATIONS OF THE ROBERT-BONAMY FORMALISM AND FURTHER REFINEMENT CHALLENGES

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We present two modifications of the Robert-Bonamy (RB) formalism that has been widely used for calculating Lorentzian half-widths and shifts for decades. The first one comes from a correction of their derivation when they assumed the cumulant expansion can be used to evaluate the diagonal Liouville matrix elements $<< j2i2|S|j2i2 >>$[a]. Unfortunately, their assumption is invalid and as a result, their expressions for the half-width and shift are not correct. By choosing an average over the internal degrees of the bath molecules as the average in the cumulant expansion, one is able to apply this expansion properly and obtain the correct expressions. The second correction is to the expression for the vibrational dephasing that is essential in calculating the shifts. This is not given correctly in the RB formalism[b] because they made an inconsistent assumption that the trajectories of interest are vibrationally independent. Based on vibration-dependent trajectories, we derive the correct expression. Beside these two corrections, we point it out that there are several drawbacks in the RB formalism which could significantly affect the reliability of calculated width and shift values. One must address these problems in refining the RB formalism further.

[a] D. Robert and J. Bonamy *J. Phys.* **40**, 923 1979.
[b] D. Robert, J. Bonamy, J. P. Sala, G. Levi, and F. Marsault-Herail *Chem. Phys.* **99**, 303 1985.