

Theoretical Studies of Spectroscopic Line Mixing in Remote Sensing Applications

*Qiancheng Ma¹, Christian Boulet², Richard Tipping³

1. Columbia University of New York City, USA, 2. Institut des Sciences Moléculaires Orsay (ISMO), CNRS (UMR8214) and Université Paris-Sud Bat 350, Campus d'Orsay F-91405, FRANCE, 3. Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL 35487-0324, USA

The phenomenon of collisional transfer of intensity due to line mixing has an increasing importance for atmospheric monitoring. From a theoretical point of view, all relevant information about the collisional effect on line shapes is contained in the relaxation matrix whose diagonal elements are the half-widths and shifts of individual lines while the off-diagonal elements correspond to line interferences. For simple systems such as those consisting of diatom-atom or diatom-diatom, accurate fully quantum calculations based on sophisticated and realistic interaction potentials are feasible. However, fully quantum calculations become unrealistic for more complex systems. Meanwhile, due to relying on the isolated line approximation, the semi-classical Robert-Bonamy formalism, which has been widely used to calculate half-widths and shifts for decades, fails in calculating the off-diagonal matrix elements. As a result, in order to simulate atmospheric spectra where effects from line mixing are important, semi-empirical fitting or scaling laws such as the energy corrected sudden (ECS) and infinite order sudden (IOS) models are commonly used. Recently, we have found that in developing semi-classical line shape theories, to rely on the isolated line approximation is not necessary [1]. By eliminating this assumption, we have developed a more capable formalism that enables one not only to reduce uncertainties of calculated half-widths and shifts, but also to calculate the whole relaxation matrix. Thanks to this progress, one can address the line mixing based on interaction potentials between two interacting molecules. We have applied this formalism for Raman and infrared spectra of linear molecules [1-4], asymmetric-top molecule [5], and symmetric tops with inversion symmetry such as the NH₃ molecule [6-8]. Our calculated half-widths of NH₃ lines in the parallel and perpendicular bands match measurements very well. Furthermore, the method has been applied to the calculation of the shape of the Q branch and of some R manifolds in the ν_1 band of NH₃, for which an obvious signature of line mixing effects has been experimentally demonstrated. Similarly, the formalism very well reproduces off diagonal elements measured in some of ¹³C doublets in the ν_4 band. In summary, comparisons with measurements show that predictions from the new formalism accurately match the experimental line shapes.

References

- [1] Q. Ma, C. Boulet and R.H. Tipping, J. Chem. Phys. **139**, 034305 (2013).
- [2] C. Boulet, Q. Ma and F. Thibault, J. Chem. Phys. **140**, 084310 (2014).
- [3] Q. Ma, C. Boulet and R.H. Tipping, J. Chem. Phys. **140**, 104304 (2014).
- [4] C. Boulet, Q. Ma and R.H. Tipping, J. Chem. Phys. **143**, 124313 (2015).
- [5] Q. Ma, C. Boulet and R.H. Tipping, J. Chem. Phys. **140**, 244301 (2014).
- [6] Q. Ma and C. Boulet, J. Chem. Phys. **144**, 224303 (2016).
- [7] C. Boulet and Q. Ma, J. Chem. Phys. **144**, 224303 (2016).
- [8] Q. Ma, C. Boulet and R.H. Tipping, JQSRT. <http://dx.doi.org/10.1016/j.jqsrt.2017.01.010> (2017).

Keywords: Line mixing, relaxation matrix, line shape parameters, pressure broadened half-widths and shifts