THEORETICAL STUDIES OF THE RELAXATION MATRIX FOR MOLECULAR SYSTEMS

QIANCHENG MA, *Applied Physis and Applied Mathematics, Columbia University, New York, NY, USA*; C. BOULET, *Institut des Sciences Moléculaires d'Orsay, Université Paris-Sud, Orsay, France*.

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 processes is contained in the relaxation matrix where the diagonal elements give half-widths and shifts, and 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 interaction potentials are feasible. However, fully quantum calculations become unrealistic for more complex systems. On the other hand, 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 resulting from applying the isolated line approximation. As a result, in order to simulate atmospheric spectra where the effects from line mixing are important, semi-empirical fitting or scaling laws such as the energy corrected sudden (ECS) and the infinite order sudden (IOS) models are commonly used. Recently, we have found that in developing this semi-classical line shape theory, to rely on the isolated line approximation is not necessary. By eliminating this unjustified assumption, and accurately evaluating matrix elements of the exponential operators, we have developed a more capable formalism that enables one not only to reduce uncertainties for calculated half-widths and shifts, but also to calculate the whole relaxation matrix. This implies that we can address the line mixing with the semi-classical theory based on interaction potentials between molecular absorber and molecular perturber. We have applied this formalism for Raman and infrared spectra of linear and asymmetric-top molecules. Recently, the method has been extended into symmetric-tops with inverse symmetry such as the NH_3 molecule. Our calculated half-widths of NH_3 lines in the ν_1 and the pure rotational bands match measurements very well. Then, the model has been applied to the calculation of the shape of the Q branch and of some R manifolds, for which an obvious signature of line mixing effects has been experimentally demonstrated. Comparisons with measurements show that the present formalism leads to an accurate prediction of the available experimental lineshapes.