RELAXATION MATRICES OF THE NH$_3$ MOLECULE IN PARALLEL AND PERPENDICULAR BANDS

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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 W where the diagonal elements give half-widths and shifts, and the off-diagonal elements correspond to line interferences. For simple systems such as diatom-atom and diatom-diatom, fully quantum calculations are feasible, but become unrealistic for more complex systems. Meanwhile, the semi-classical Robert-Bonamy (RB) formalism widely used to calculate half-widths and shifts completely fails in calculating the off-diagonal elements of W resulting from applying the isolated line approximation. Recently, we have developed a new semi-classical formalism without this approximation that enables one not only to reduce uncertainties for calculated half-widths and shifts, but also to calculate the off-diagonal elements. This implies that we can address line mixing based on interaction potentials between molecular absorber and molecular perturber. In the present study, we have applied this method to calculate the relaxation matrices for self-broadened NH$_3$ lines in the parallel pure-rotational, $\nu_1$, $\nu_2$, and $2\nu_2$ bands and also in the perpendicular $\nu_4$ band. Our studies have exhibited a significant off-diagonality of W in the pure-rotational, $\nu_1$, and $\nu_4$ bands. For the $\nu_2$ and $2\nu_2$ bands, the off-diagonality is much less and even becomes completely absent. Given the fact that the inversion doublet splitting is the main source responsible for the off-diagonality of W and its value in these bands dramatically increases from less than 1 cm$^{-1}$, to 36 cm$^{-1}$, and further to 284 cm$^{-1}$, it is easy to understand these results. By comparing with half-widths derived from the RB formalism, our values in the pure-rotational, $\nu_1$, and $\nu_4$ bands are significantly reduced and match measurements very well. We have also compare calculated off-diagonal elements of W and Rosenkranz line mixing coefficients with measured results. In addition, we have compared the calculated profiles, including line mixing effects with the observed ones in various cases: a good agreement is obtained in the $^2$P doublets of the $\nu_4$ band as well as in the Q branch and the R(3,k) manifold in the $\nu_1$ band. For some other measurements reported in literature, very large discrepancies (up to two orders) have been found and our comments on these measurements are presented.