THEORETICAL CALCULATION OF THE N_2 BROADENED HALF-WIDTHS OF H_2O

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For many applications, in addition to accurate spectral line frequencies and intensities one needs accurate Lorentzian parameters (half-widths, pressure shifts, and their temperature dependencies). Because of the importance of H_2O in the Earth's atmosphere, extensive compilations of these data are available in the HITRAN database. Recently, ab initio calculations have been carried out and databases containing tens of millions of line frequencies and intensities are available. Obviously, it is not possible to measure their Lorentzian parameters, and one must rely on theoretical calculations. For many years researchers have used the Robert-Bonamy (RB) formalism; however, we recently discovered a subtle error was made in their original derivation, and this modification is not negligible for certain systems. In this theory the internal motions are treated quantum mechanically, while the translational motion is treated classically. In order to achieve the desired accuracy, one needs to use a realistic interaction potential, and a realistic trajectory model for the translational motion. Because of the large number of potential matrix elements appearing in the standard application of the RB theory, one is forced to introduce cut-offs that may limit the accuracy attainable. To obviate the necessity of low-order cut-offs and achieve results for half-widths to the accuracy of the interaction potential, we recently reformulated the theory using the coordinate representation[a]. In the present paper, we present results to study the effects of using different experimental half-width data to obtain the parameters in several models for the interaction potential, and the effects of different trajectory models for treating the relative motion. From our detailed analysis, we are able to draw several conclusions that should help theorists to make choices in order to achieve realistic theoretical half-widths and to assess their accuracy.

[a] Q. Ma, R. H. Tipping, and C. Boulet, J. Chem. Phys. **124**, 014109 (2006).