ANALYTICAL EVALUATION OF THE MAXWELL-BOLTZMAN VELOCITY AVERAGE IN PRESSURE-BROADENED HALFWIDTH CALCULATIONS: APPLICATION TO OZONE

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For the first time the halfwidth within the Complex Robert-Bonamy (CRB) formalism is calculated without making the mean-relative thermal velocity approximation. The application is to nitrogen-broadened halfwidth of the 500.4 GHz transition (34 ₂₃₂ j- 34 ₁₃₃) of the ground vibrational state of ozone. For each states of the perturber, the optical cross-sections are determined at a number of velocities with the intermolecular potential taken as a sum of electrostatic contributions and Lennard-Jones (6-12) atom-atom components. The dynamics of the collision process are correct to second order in time. Using a non-linear least-squares fitting method, the optical cross-sections are fit to a double power law, which allows the velocity integral for the halfwidth to be done analytically. The results are compared with the mean-relative thermal velocity Complex Robert-Bonamy calculations and with measurement. The temperature dependence of the halfwidth, which is necessary for reduction of remotely sensed data, is determined from both methods and compared with experiment.