

The Roles of the S_1 and S_2 Scattering Matrix Terms on Half-Widths and Their Temperature Dependence for the Water Vapor-Nitrogen System

R. R. Gamache^{*}, B. K. Antony^{*} and P. R. Gamache^{*} and Jean-Michel Hartmann[†]

^{*}Department of Environmental, Earth & Atmospheric Sciences,
Intercampus Graduate School of Marine Sciences and Technology
University of Massachusetts Lowell, 265 Riverside Street, Lowell, MA 01854-5045
USA

[†]Laboratoire Inter-Universitaire des Systèmes Atmosphériques (LISA)
CNRS, Université Paris 12 et Paris 7,
61 ave Général de Gaulle
94010 Créteil Cédex France

Abstract. The effect of the first (S_1) and second (S_2) order successive approximations to the S matrix on the half-width and the temperature dependence of the half-width are studied for the water vapor-nitrogen system. The calculations are done via the Robert-Bonamy semi-classical formalism. It is found that the influence of the S_1 and S_2 terms depends on the rotational states of the transition. For the H_2O-N_2 system, half-widths for H_2O transitions with low J quantum numbers are dominated by the S_2 terms. Transitions with high J values the half-width is determined largely by the S_1 term. For transitions with intermediate values of J both the S_1 and S_2 terms contribute. The temperature dependence of the half-width also depends on whether it is the S_2 , S_1 or S_2+S_1 that are contributing to the half-width. It is found that the standard power law temperature dependence of the half-width is only valid for transitions where $Re(S_2)$ dominates. When S_1 dominates the temperature dependence is negative and when both terms contribute the temperature dependence is not modeled by the power law.

Keywords: half-width, temperature dependence of the half-width, H_2O-N_2 .

PACS: 30

INTRODUCTION

The complex the Robert-Bonamy (CRB) formalism [1] to calculate the half-width and line shift for a ro-vibrational transition is a semi-classical method based on a second order successive expansion of the S matrix. This approach yields a first order term that is purely isotropic and imaginary, S_1 , and a complex second order term, S_2 . Depending on the collision interaction system each term can contribute more or less. In this work it is found that for the H_2O-N_2 collision system the contributions of the S_1 and S_2 terms changes from transition to transition. The mechanism for this is detailed below. The CRB calculations used a potential which consists of the leading

electrostatic components for the H₂O-N₂ (the dipole and quadrupole moments of H₂O with the quadrupole moment of N₂), atom-atom interactions, and isotropic induction and London dispersion interactions in the S_1 term. Here the atom-atom part of the potential is expanded to 8th order to insure convergence of this part of the potential [2]. The isotropic component of the atom-atom potential are fit to an effective isotropic (or "hetero-molecular") Lennard-Jones 6-12 potential which is used to define the trajectory of the collisions within the semi-classical model of Robert and Bonamy [1]. All parameters used in the calculations are the best available from the literature and can be found in Ref. [3].

RESULTS AND DISCUSSION

The calculation of the half-width and line shift for a ro-vibrational transition $f \leftarrow i$ is made by averaging over all collisionally induced transitions. In the collision the absorbing molecule is driven from state i to state i' (or f to state f') with an energy gap $\Delta E_{i \rightarrow i'}$. In the same collision the perturbing molecule goes from state J_2 to J_2' with an energy gap $\Delta E_{J_2 \rightarrow J_2'}$. If the energy gaps match each other the collision is said to be on resonance and the collisional contribution to the half-width will be large. These components are in the $Re(S_2)$ term. For conditions where the energy gaps do not match the collision is said to be off resonance and the collisional contribution is small. In such cases it is the S_1 term and the $Im(S_2)$ term that contribute to the half-width. What is observed for the H₂O-N₂ system is that for low J states of water the collisions are on resonance and the half-width is determined mostly from collisional contributions, the $Re(S_2)$ term. For high J states most of the collisions are off resonance. In such cases the half-width is determined from vibrational contributions (S_1 and $Im(S_2)$). These tend to be narrow lines.

The temperature dependence of the half-width was worked out by Birnbaum [4] assuming on resonance collisions and a single term in the intermolecular potential. The result is the standard power law seen in the literature, for example see Wagner et al. [5]. We have observed that for low J lines, which are determined mostly by the real part of S_2 , the power law model works well. (Note, all figures are for the ν_2 band of water.) Figure 1a shows the fit for the $2_{0,2} \leftarrow 3_{1,3}$ transition. The slope (temperature exponent) is 0.74 and the correlation coefficient is 1 to four significant figures indicating the power law model is nearly perfect for this line. For the high J lines, where the S_1 and $Re(S_2)$ terms determine the half-width, the temperature exponents can be negative and the power law is approximate, see Fig. 1b. What is interesting is the intermediate J region where both the S_1 and S_2 parts contribute to the half-width. Figure 1c is a plot for the $9_{0,9} \leftarrow 8_{1,8}$ transition. The temperature dependence of these lines is not modeled by the power law.

Caution should be used when modeling the temperature dependence of the half-width of N₂-broadened water vapor transitions. When the collisions are on resonance the usual power law model correctly describes the temperature dependence. For high J lines where the collisions are far off resonance the power law approximately models the temperature behavior. However for intermediate J transitions the power law fails to model the observed temperature dependence of the half-width. Similar results are found for O₂- and air-broadening of water vapor transitions. This could have large

effects in modeling radiative transfer in mediums where the temperature is changing, i.e. Earth's atmosphere, combustion media, etc. For such cases a more sophisticated model is needed.

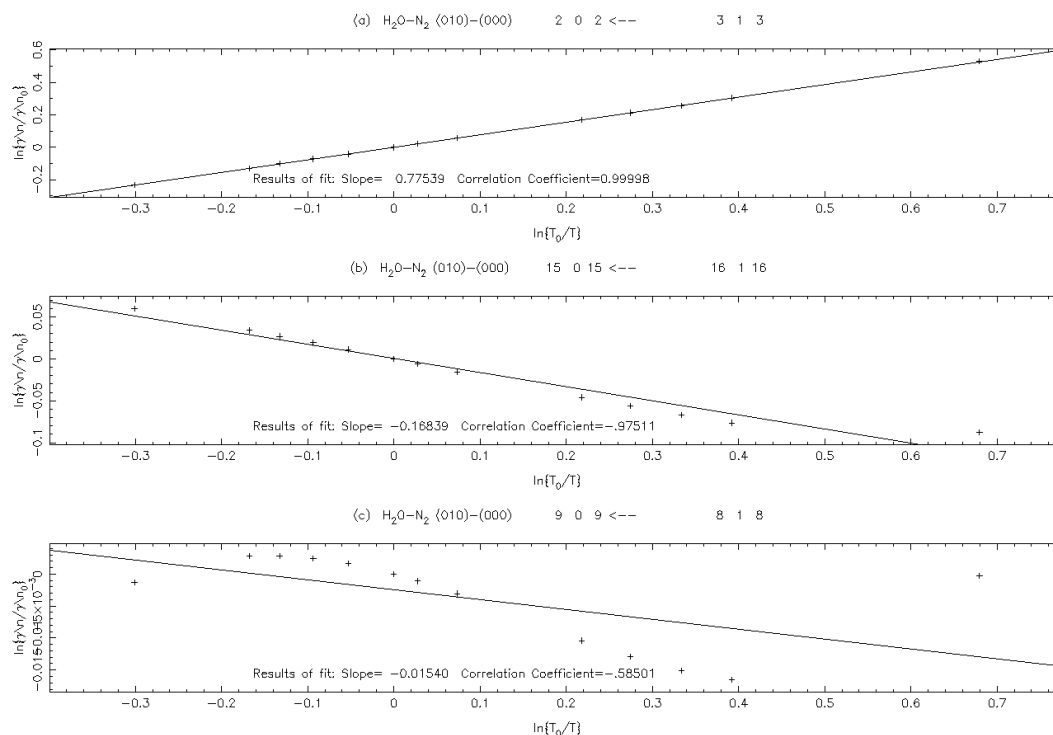


FIGURE 1. Plots of $\ln\{\gamma(T)/\gamma(T_0)\}$ versus $\ln\{T_0/T\}$ to determine the temperature exponent in the temperature range 150-400 K. (a) $2\ 0\ 2 \leftarrow 3\ 1\ 3$ v_2 band transition, (b) $15\ 0\ 15 \leftarrow 16\ 1\ 16$ v_2 band transition, (c) $9\ 0\ 9 \leftarrow 8\ 1\ 8$ v_2 band transition.

ACKNOWLEDGMENTS

The authors are pleased to acknowledge support of this research by the National Aeronautics and Space Administration (NASA) through Grant No. NAG5-11064 and by the National Science Foundation (NSF) through Grant No. ATM-0242537.

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of NASA or NSF.

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