

Self-broadening of water vapor transitions via the complex Robert–Bonamy theory

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Abstract

Calculations of self-broadened half-widths and self-induced pressure shifts are made using the complex Robert–Bonamy formalism. The results of calculations using different approximations of the intermolecular potential indicate that this is a strong collision system. The effects of the imaginary components on the half-widths are studied. The temperature, vibrational, and rotational state dependence of the half-width are investigated. Results are compared with measurements from the database of self-broadening of water vapor [Gamache RR, Hartmann J-M. An intercomparison of measured pressure-broadening and pressure-shifting parameters of water vapor. *Can J Chem* 2004; 82: 1013–27].

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1. Introduction

Water vapor is the strongest atmospheric absorber of infrared radiation and is therefore the most important gas controlling Earth's surface temperature. There are about 50 000 significant atmospheric spectral transitions for H₂O ranging from microwave to the visible range of the spectrum. The transitions can be described in terms of spectral parameters, which are cataloged in databases such as HITRAN [1] or GEISA [2]. The interpretation of remote sensing measurements and study of the radiative properties of atmosphere depends on knowledge of these spectral parameters. Of the parameters needed for inverting remotely sensed data, the air-broadened half-width is the least well known for atmospheric applications [3]. The effect of uncertainty in half-widths on the accuracy of retrieved concentration profiles depends on molecule and altitude [4–7] and is a major source of the uncertainty on the resulting concentration profile, especially in the lower atmosphere. It is now known that the effect of the line shift on reducing data from remote sensing measurements can be significant [8–10]. The spectroscopic and remote sensing communities [3,11–13] have

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determined that for accurate retrievals the half-width and its temperature dependence should be known with an uncertainty of 3% for strong lines and 10% for weak lines. However, the self-broadening contribution in typical air-broadened spectra can be as large as 5% and if omitted will result in values with uncertainty greater than that desired for the inversion process. Thus, the self-broadening correction must be accounted for in retrievals.

There have been a fair number of measurements of self-broadening of water vapor transitions from the microwave to visible region of the spectrum [14–63] and a lesser number of measurements of the self-induced line shift [26,34,42,47,50,56,58]. Together these studies yield data for 10 596 self-broadened half-widths and 1543 self-induced line shifts. An intercomparison of these data, i.e. comparing measured values for the same ro-vibrational transition, has recently been done [64]. From this data set it is possible to make 440 intercomparisons of half-widths. Only four intercomparisons are possible for more than three measured data points; three 4-point and one 5-point intercomparisons. The estimated uncertainty (see Ref. [64] for details) for these intercomparisons is greater than 10%. The 5-point intercomparison for the $3_{13} \leftarrow 2_{20}$ transition of the rotational band is shown in Fig. 1 demonstrating typical spread in the measurements. The intercomparison of pairs of points contains 92% of the self-broadening intercomparisons of which 61% have estimated uncertainties greater than 10%. There are no intercomparisons of the line shifts.

Theory can contribute to the spectroscopic picture in uniquely useful ways. Although laboratory measurements can and do supply pressure-broadened half-widths and line shifts, it is difficult to exhaustively cover the vast spectral range and diversity of environmental conditions encountered in the actual atmosphere. Theoretical calculations are in principle an attractive alternative, depending on the accuracy requirements of the radiative transfer application one has in mind, and of course the credibility of the theory. Even when laboratory measurements are available, however, certain effects (such as line mixing [65]) may still require a sophisticated theoretical model in order to unravel observed spectra.

The complex Robert–Bonamy (CRB) formalism has been successful in predicting the half-width and line shift for self- and foreign-broadened spectral lines of many molecular systems. With the increased computational capacity over the past decade, there have been many improvements in the potential and wavefunctions yielding more accurate results. In this article, we report the self-broadening of water vapor transitions using the CRB formalism. The effects of the expansion of the atom–atom potential and the imaginary components were studied. Dependence of the half-width on temperature, vibrational state, and rotational state was also investigated. The results were compared with measurements from the self-broadening of water vapor database [64].

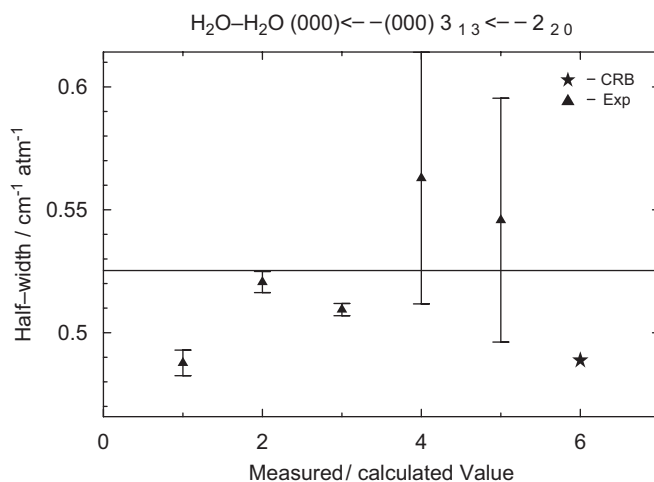


Fig. 1. The 5-point intercomparison of measured half-widths for the $3_{13} \leftarrow 2_{20}$ transition of the rotational band demonstrating typical spread in the measurements.

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