

Lineshape parameters for water vapor in the 3.2–17.76 μm region for atmospheric applications

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Abstract

Several NASA EOS instruments, the atmospheric infrared sounder (AIRS) on Aqua, and the tropospheric emission spectrometer (TES) and the high-resolution dynamics limb sounder (HIRDLS) on AURA, will be measuring water vapor in the Earth's atmosphere in the 3.2–17.76 μm spectral region. In order to do retrievals of temperature and concentration profiles, the spectral parameters for many thousands of water vapor transitions must be known. Currently the largest uncertainty in these data is associated with the pressure-broadened half-width. To help ameliorate this situation, complex Robert–Bonamy calculations were made to determine N_2 -, O_2 -, and air-broadened half-widths and line shifts for 5442 transitions of the principal isotopologue of water vapor for the 11 vibrational bands in this region. The intermolecular potential is a sum of electrostatic terms (dipole–quadrupole and quadrupole–quadrupole), isotropic induction and London dispersion terms, and the atom–atom potential expanded to eighth order. The parameters are adjusted as described in Gamache and Hartmann [J. Quant. Spectrosc. Radiat. Transfer 83 (2004) 119]. Calculations were made at 225 and 296 K in order to determine the temperature dependence of the half-widths. When possible the data are compared with measurements. The average percent difference between the measured and calculated half-widths is -1.97 , 2.6 , and -1.55 for N_2 -, O_2 -, and air-broadening of water vapor, respectively. The agreement for the line shifts is less satisfactory. It is clear from this work that the calculations will benefit from a comprehensive adjustment of the intermolecular potential.

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1. Introduction

The scientific evidence that human activities are increasing the rates of global changes is growing [1]. For example, carbon dioxide levels have risen 25% since the industrial revolution and continue to rise. The Earth system is complex and the cause-and-effect relationships among lands, oceans, and atmosphere are not known well enough to predict accurately the impacts these anthropogenic forcings will have on future climate. To help address these questions, measurements must be made over the entire globe for long periods of time.

These data can then be used to construct accurate computer models that will enable a forecast of the causes and effects of climate change. The only feasible way to measure such data is from satellites with “remote” sensors. This approach is one of the principal components of NASA's Earth Observing System. A number of satellites with a variety of instrumentation are either in orbit or will be launched into orbit to collect remote sensed data to use as input to climate models.

The translation of remotely measured data (including ground based, balloon-borne, rocket, and satellite observations) to an understanding of the Earth system is based on the use of physical models. The reduction of these remote sensed data into concentration or temperature profiles, wind velocities, pollutant concentrations,

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or atmospheric heating rates requires additional modeling. Key to these models is the absorption coefficients of atmospheric gases. The absorption coefficient can be described by the molecular spectroscopic parameters given, for example, in the HITRAN or GEISA databases [2,3], i.e., the vacuum wavenumber of a molecular quantum transition, the corresponding transition intensity, the half-width and line shift of the transition, and the lower state energy. These parameters and their temperature dependence, are at the root of our understanding of the atmosphere. All improvements in these data lead to a better understanding of the Earth system, to better tests of the models, and to developing improved models. Of the parameters needed for inverting remotely sensed data, the collision-broadened half-width is the least well known for atmospheric applications [4]. The effects of uncertainty in half-widths on the accuracy of retrieved parameters are well understood [5,6]. In addition, the importance of the line shift has recently come to light [7,8].

Several NASA EOS instruments will be measuring water vapor in the Earth's atmosphere. In particular, the atmospheric infrared sounder (AIRS) on Aqua, and the tropospheric emission spectrometer (TES) and the high-resolution dynamics limb sounder (HIRDLS) on AURA will measure H₂O in addition to a number of other molecules. AIRS consists of an array grating spectrometer that provides coverage in the infrared and will provide clear-column air temperature profiles and surface temperatures. TES is a high-resolution infrared imaging Fourier transform spectrometer with a spectral coverage from 3.2 to 15.4 μm at a spectral resolution of 0.1 cm^{-1} in the low-resolution mode and 0.025 cm^{-1} in the high-resolution mode. HIRDLS is an infrared limb-scanning radiometer designed to sound the upper troposphere, stratosphere, and mesosphere to determine temperature, the concentration of O₃, H₂O, CH₄, N₂O, NO₂, HNO₃, N₂O₅, CFC11, CFC12, and aerosols. The instrument measures infrared emission in 21 channels ranging from 6.12 to 17.76 μm . (More information on the Aqua and Aura missions can be obtained at http://eospsso.gsfc.nasa.gov/eos_homepage/mission_profiles/index.php).

Water is the principle absorber of longwave radiation in the terrestrial atmosphere, responsible for some 80% of "greenhouse" warming of the Earth's surface [9]. In this process, water in its vapor phase plays an important and unique role, distinguishable from liquid or ice phases (clouds) in terms of spectral properties, geographic location, etc. A good understanding of the spectroscopy underlying the greenhouse warming, especially pressure broadening of water vapor, is important for two identifiable reasons. First, as peak absorptivity is redistributed to line wings, higher concentrations are required to saturate pressure-broadened lines. This redistribution causes an increase in the radiative forcing, a

fact that could have important consequences in radiatively unsaturated conditions such as prevail in the polar winter sky. A second motivation, closely related to the first, derives from the fact that a good understanding of the spectroscopy is essential for a proper interpretation of remote sensing measurements of the atmosphere.

Theory can contribute to the spectroscopic picture in uniquely useful ways. Atmospheric radiative transfer models, which are used both to model natural radiative processes and to interpret remote sensing data, require high-precision parameters describing line positions, intensities, pressure-broadened half-widths and line shifts. Although laboratory measurements can and do supply such parameters, 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, and of course the credibility of the theory. Even when laboratory measurements are available, however, certain effects (such as line mixing [10]) may still require a sophisticated theoretical model in order to unravel observed spectra.

In this work, calculations of the half-width and line shift for water vapor transitions in the 3.2–17.76 μm region are made for nitrogen and oxygen as perturbing gases at temperatures of 225 and 296 K. The results of these calculations are used to determine the air-broadened half-widths and line shifts for H₂O. The temperature dependence of the half-width was determined for the transitions studied in this work.

2. Theory

The calculations are based on the complex Robert–Bonamy (CRB) theory [11]. A full description of the formalism can be found in [12–14]; here only the salient features are presented. The method is complex valued so that the half-width and line shift are obtained from a single calculation. By the use of linked-cluster techniques [15] the awkward cutoff procedure that characterized earlier theories [16–18] is eliminated. The dynamics are developed to second order in time giving curved trajectories based on the isotropic part of the intermolecular potential [11]. This has important consequences in the description of close intermolecular collisions (small impact parameters). Also important for close collision systems is the incorporation in the RB theory of a short range (Lennard-Jones 6-12 [19]) atom–atom component to the intermolecular potential. This component has been shown to be essential for a proper description of pressure broadening, especially in systems where electrostatic interactions are weak [20]. (Here, the notion of strong and weak collisions adopts the definition of Oka [21]).

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