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Comparison between theoretical calculations and high-resolution measurements of pressure broadening for near-infrared water spectra

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ABSTRACT

We report N_2 and air foreign pressure broadening coefficients of more than twenty rovibrational transitions of water vapor in the 935-nm spectral region, and these measurements are compared to new theoretical calculations. The data were obtained using the frequency-stabilized cavity ring-down spectroscopy method, yielding relative uncertainties for the broadening parameters in the range 0.4–2.2%. The sensitivity of measured broadening parameters to the choice of line shape functions is discussed, and systematic differences between experimentally determined collisional broadening coefficients are shown for the cases when the observed line narrowing is interpreted in terms of Dicke-narrowing or the speed-dependence of the collisional broadening and shifting. Theoretical models of pressure broadening for these transitions agree with the measurements to within 4% for most transitions with an average relative difference of 0.63%.

1. Introduction

A quantitative understanding of molecular-transition line shapes is essential in many practical spectroscopic applications, including the remote sensing of gas temperature and pressure as well as retrievals of gas mixture composition. For such applications, databases of line parameters (assignments, intensities, width and shift parameters, etc.) exist for molecules contained in atmospheres of the Earth and other planets. See for example HITRAN 2004 [1] or others given in Refs. [2–4]. These databases are continuously improved to fulfill the increasingly demanding requirements of the newest remote sensing instruments, and line parameters with sub-1% accuracy are sometimes required [5]. This level of accuracy is often difficult to achieve in laboratory measurements because of complications associated with preparing samples of known concentration and uncertainties in spectroscopic measurements. Here we consider the spectroscopy of water, one of the most abundant and important molecules in the atmosphere. From an experimental perspective, the accurate measurement of water vapor's spectroscopic parameters (in particular the line intensity S) poses a unique challenge because H_2O has a tendency to stick to and desorb from bounding surfaces, making it difficult to prepare gas mixtures with known and stable concentrations. Moreover, as was shown before [6], the measurement of line intensities as well as collisional broadening coefficients at sub-1%-levels of accuracy may be achieved only by taking subtle line shape effects into account. The most important of the line shape effects are the collisional narrowing [7] and dependence of collisional broadening and shifting on molecular speed (the so-called speed-dependent effects) [8]. When these effects are sufficiently important, fitting the commonly used Voigt profile to experimental spectra causes systematic errors in the retrieval of line shape parameters. Such biases can affect measurement of S which is typically determined from the fitted spectral area.

The speed-dependent effects are particularly difficult to treat because for many molecular systems there is no simple analytical model that can adequately represent the speed-dependence of both pressure broadening and pressure shifting. In this case, line shapes of individual transitions must be modeled individually, making it difficult to incorporate speed-dependent effects into standardized spectral databases. Although theoretical calculations of pressure broadening parameters usually cannot achieve accuracies better than 1%, they can provide critical information on the speed-dependence of collisional parameters needed for analysis of the most precise experimental data and for predictions in situations where data is lacking.

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In the remainder of this paper we investigate collisional broadening parameters for H_2O broadened by N_2 and by air, and we specifically consider 21 transitions from the ground vibrational state to the $(\nu_1 \nu_2 \nu_3) = (2 0 1)$ vibrational band of H_2O occurring in the wave number region 10603–10732 cm^{-1}. We present line shapes measured at room temperature using the frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) technique, and we report relative standard uncertainties less than 1%. We also discuss systematic effects associated with the dependence of the collisional broadening coefficient on the fitted line shape function. Finally, we present two sets of predictions for the observed line broadening and compare them to our measurements. Both sets of predictions used the corrected Anderson, Tsao, Curnutte (ATC) model of line broadening [9], the difference being that the H_2O energy levels and dipole transition moments were derived either from an effective Hamiltonian (EH) or a discrete variable representation (DVR) [10] for the nuclear motion. The EH approach is accurate when corrections arising from anharmonicity, Coriolis coupling or centrifugal distortion are small. This occurs when considering transitions to low-lying vibrational states for which the vibrational amplitudes are small in comparison with equilibrium distances between atoms, so that molecular properties such as multipole moments and polarizabilities can be accurately represented by a Taylor series expansion about equilibrium. In the case of transitions to highly-excited states, the Taylor series expansions are slowly convergent or even divergent because the vibrational motion cannot be considered to be of small amplitude, and consequently the DVR method gives more accurate wave functions than the EH method.

2. Experiment

2.1. Measurement technique

Water vapor line shapes were measured by the FS-CRDS method using a spectrometer built and operated at the National Institute of Standards and Technology (NIST). Detailed descriptions of this technique and the NIST FS-CRDS spectrometer can be found in Refs. [11,12]. The ring-down cavity consisted of two mirrors separated by about 73 cm and having high-reflectivity $R = 0.9997$ at the probe wavelength $\lambda_p = 931.9–943.1$ nm, and lower reflectivity $R = 0.97$ at the reference laser wavelength $\lambda_r = 633$ nm. The probe laser was a continuous wave external cavity diode laser (ECDL) having a Littrow cavity configuration and providing about 2 mW of power incident on the ring-down cavity. The reference laser was a frequency-stabilized HeNe laser (long-term stability of 1 MHz) that provided a stable optical frequency required for active control of the ring-down cavity mirror-to-mirror distance. Fluctuations in the HeNe laser were monitored by measuring the heterodyne beat note produced by interference of the reference laser and a separate I_2-stabilized HeNe laser having an absolute frequency stability of 10 kHz. Stabilization of the cavity length constrained the ring-down cavity resonant frequencies to a well-defined frequency comb of constant spacing which we used to calibrate the detuning axis of our spectral scans. The length-stabilization servo involved imposing a 20 kHz modulation (with a modulation depth of 2 MHz) on the HeNe frequency using a double-passed acousto-optic modulator (AOM), phase sensitive detection of the transmitted beam at the modulation frequency, and proportional and integral feedback of the error signal to the cavity length via a pzt-actuated mirror. The frequency stability of the comb of ring-down cavity modes was approximately 100 kHz using this stabilization scheme and was limited by our ability to compensate for the observed fluctuations in the HeNe laser frequency. By stepwise locking of the ECDL probe laser to successive longitudinal modes of the TEM_{00}, spectra of water vapor were probed by measuring the ring-down decay time constants $\tau(\nu)$ at each step. The intensity of light exiting the cavity was measured with a Si-PIN photoreceiver (10 MHz bandwidth) that was digitized by a 12-bit board mounted in a desktop computer. The absorption coefficient $\alpha(\nu)$ was calculated from $\alpha(\nu) + \alpha_{bg}(\nu) = 1/(c\tau)$, where $\alpha_{bg} \cong 4 \times 10^{-6}$ cm^{-1} corresponds to the baseline of spectrum and is associated with base losses of the ring-down cavity mirrors, c is the speed of light and ν is the radiation frequency. For a single isolated transition, the absorption coefficient is modeled by $\alpha(\nu) = n_a c\, S\, g(\nu - \nu_0)$, where the line shape function g is normalized to unity area $\int d\nu g(\nu - \nu_0) = 1$, and hence the line area $\mathcal{A} = \int d\nu \alpha(\nu) = n_a cS$. Here n_a denotes the absorber concentration, c is the speed of light and ν_0 is the transition frequency.

Note that the frequency difference between longitudinal modes is equal to the free-spectral-range (FSR) of the cavity (202.812(22) MHz). However, we were able to realize frequency steps much smaller than the FSR by precisely frequency shifting (50 kHz resolution see Ref. [13]) the reference HeNe laser with the AOM. We emphasize that since the ring-down cavity length was servoed to the frequency of the reference laser, this technique shifted the entire comb of resonant frequencies of the ring-down cavity in a controlled way. For the line shape measurements discussed in this article, we used steps in the range 50–100 MHz, which gave several 100 points per line profile. At each frequency step 300 ring-down signals were acquired, individual signals were fit using an exponential function and the fitted time constants were averaged. This method yielded measured spectra with signal-to-noise ratios of about 1000:1. Excellent linearity and low uncertainty for both the spectrum frequency and absorption axes of our spectrometer was demonstrated earlier [6,13,14], and using the FS-CRDS method to measure transitions of the O_2 A-band, we have recently demonstrated signal-to-noise ratios in excess of 6000:1 [15].

We carefully prepared and monitored the water vapor concentration in the ring-down cavity gas sampling system in order to optimize the quality of the experimental results. This effort was critical to the experiment because of well-known difficulties arising from persistent adsorption and desorption of water from bounding surfaces. We used a continuous flow of the gas mixture through the ring-down cell to mitigate these confounding effects. To further suppress these effects, all-metal seals and electro-polished stainless steel internal surfaces were used throughout the flow system and dead volumes were minimized. For generating the sample streams, purified N_2 carrier gas was metered through two mass flow controllers operated in parallel. The first stream (flow rate = 0.025 std. L min^{-1}) passed through the head-space of a temperature-regulated water-filled saturator, and the second stream (flow rate = 1.2 std. L min^{-1}) bypassed the saturator. Downstream of the saturator the two streams were recombined, and a portion (0.5 std. L min^{-1}) was diverted to a reference-grade chilled-mirror hygrometer (CMH) which measured the molar fraction of water vapor in the mixture. The combined stability of the saturator and CMH was approximately 0.4% in terms of water vapor molar fraction. The water vapor molar fraction ranged from about 10^{-4}–2.5×10^{-4} and was adjusted for each transition so that the peak absorption loss was approximately equal to the base loss of the ring-down cavity. The gas pressure, p, was measured with two NIST-calibrated capacitance diaphragm gauges having full scale responses of 13.3 kPa and a 133 kPa, respectively. Each pressure gauge had a relative combined standard uncertainty of 0.02%. The gas mixture passed through the ring-down cell with a constant flow rate of about 0.5 std. L min^{-1} and the total gas pressure in the ring-down cell was actively stabilized to within 0.1%. A calibrated 100-Ω platinum resistance thermometer (PRT) measured the exterior temperature, T, of the ring-down cell with a standard