Modified Complex Robert-Bonamy (MCRB) calculations of H$_2$O transitions broadened by H$_2$ for applications to planetary and exoplanet atmospheres

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Abstract. Line shape parameters for hydrogen broadening of water vapor are needed to understand remote sensing measurements of planetary and exoplanet atmospheres. In order to address these needs, semiclassical calculations based on the Modified Complex Robert-Bonamy (MCRB) formalism were made. The intermolecular potential for the calculation is comprised of electrostatic, atom-atom (expanded to order 16 and rank 4), induction, and London dispersion terms. The trajectories were determined by numerical integration of the Hamilton’s equations. The average over the Maxwell–Boltzmann distribution of velocities was performed by integration over 35 velocities corresponding to the temperature range 75K – 27000K. The formalism is complex valued yielding the half-width and line shift from a single calculation. The calculations are reported at 7 temperatures from 200 to 700 K. The half-width temperature dependence coefficient $n$ was determined using the relation $\gamma(T) = \gamma(T_0) \left(\frac{T}{T_0}\right)^n$ with $T_0=296$K. The calculations are compared with the measurements of Brown and Plymate [JQSRT 56, 263, 1996]. Future plans for further refinement of the intermolecular potential are discussed.

1. Introduction

Atmospheres surrounding planets in our solar system have been known and studied since the 19th century$^1$. Some early studies of planetary atmospheres were the spectroscopic identification of methane in the atmospheres of the giant planets$^2$, carbon dioxide on the terrestrial planets$^3$, and the spectroscopic detection of an atmosphere on Titan$^4$. Starting from these early observations, the basic physics and chemistry of planetary atmospheres have been established.

In the mid 1990s exoplanets orbiting sun-like stars were first observed using radial velocity detection. Because of this detection technique many of the exoplanets discovered in the first few years orbited exceedingly close to the host star. Astronomers tell us that statistically every star in the Milky Way Galaxy should have at least one planet$^4$ and that small rocky planets are extremely common$^5$. The Milky Way Galaxy has 100 billion stars, and our Universe has upwards of 100 billion galaxies. Thus, based on sheer probability the chance for life elsewhere seems inevitable. Currently there are over 3000 known exoplanets; see http://exoplanet.eu/catalog.php for details.

A variety of methods$^8$ were developed in the past two decades to discover and characterize exoplanets. Part of the development are techniques to study exoplanet atmospheres. Spectra have
been measured for a handful of exoplanets and broadband spectrophotometry has been used to study dozens more. For many researchers the ultimate goal is the search for habitable exoplanets. The exoplanet atmosphere is the only way to infer whether or not a planet is habitable or likely inhabited.

Over fifty years ago it was realized that signs of life could be recognized on a distant planet by remotely sensing gases in the planet’s atmosphere. Gases produced by life, called biosignature gases, can accumulate in a planet atmosphere to detectable levels. These gases provide a means by which we can deduce the possible existence of life on an exoplanet. Thus, the planetary atmosphere is our window into temperatures, habitability indicators, and biosignature gases.

The list of possible biosignature gases is growing and there is a need to determine which molecules provide the best opportunities for detection. This task is accomplished by modeling using the radiative transfer equations. As light travels from the parent star through the atmosphere of the exoplanet, it acquires molecular features from the exoplanet due to the composition, temperature, and pressure structure of the atmosphere.

Currently measurements are being made by space borne satellites, e.g. the Hubble Space Telescope (HST) and the Spitzer Space Telescope (SST), and by ground based telescopes, such as the Keck II 10-m telescope, the Cerro Tololo Inter-American Observatory, or the 10.4 m Gran Telescopio Canarias. These platforms have instruments that operate at low to moderate resolution. For example on the HST the Near Infrared Camera and Multi-Object Spectrometer (NICMOS) has resolving power (R=\(\Delta \lambda / \lambda\)) ~ 15~11, the Space Telescope Imaging Spectrograph (STIS) has R=500~12, and the Wide Field Camera 3 (WFC3) has R=130~12. The Infrared Spectrograph on the Spitzer Space Telescope comprises four separate spectrograph modules covering the wavelength range from 5.3 to 38 \(\mu\)m with spectral resolutions, R = 90 and 600~13.

In 2018 the James Webb Space Telescope (JWST) will be launched. JWST (jwst.stsci.edu) instruments include the Near-Infrared Spectrograph (NIRSpec) and the Mid Infrared Instrument (MIRI), which will measure the infrared line emission by gaseous molecules such as H\(_2\)O, CO, CO\(_2\), OH and a growing list of organics. These instruments have a much improved resolving power (R~2700) that will separate individual lines in complex molecular bands and allow for accurate measurements of weak lines critical for constraining chemical models, including those of rare isotopologues.

While the current measurements are of moderate resolution, it is important to note that the interpretation of these spectra are and have been done using line by line radiative transfer models, hence all spectroscopic parameters are needed. Madhusudhan and Seager\(^{14}\) developed a temperature and abundance retrieval method for exoplanet atmospheres based on parametric pressure–temperature (P-T) profile coupled with line-by-line radiative transfer, hydrostatic equilibrium, and energy balance, along with prescriptions for non-equilibrium molecular composition and energy redistribution. This method has become the standard and has been used by many to model exoplanet atmosphere spectra\(^{15-20}\). However, in the line by line model much of the line shape data are poorly estimated.

In order to understand the measured spectra, the spectral parameters for the gases in the atmosphere must be known. Of the spectroscopic parameters the line shape is the least well known. Here we address the line shape of water vapor broadened by hydrogen as determined via semi-classical calculations.

2. Modified Complex Robert-Bonamy formalism

Semi-classical line shape calculations using the MCRB\(^{21}\) formalism were made for 274 \(\nu_2\) transitions to compare with the measurements of Brown and Plymate\(^{22}\). The intermolecular potential is comprised of electrostatic components, an atom-atom potential, and the vibrational dependence of the isotropic potential, which uses the induction and London dispersion potentials. Water is a light asymmetric rotor with typical energy gaps for collisionally induced transitions in the range of 0 to 500 cm\(^{-1}\). Hydrogen is a diatomic molecule with a B value of 61.264895 cm\(^{-1}\). Figure 1 shows the average energy gaps as a function of J. The figure suggests that the H\(_2\)O and H\(_2\) energy gaps will seldom
match leading to mostly off-resonance collisions. This fact hints that the atom-atom potential will play a large role in the determination of the line-shape parameters.

The initial atom-atom potential (pot 00) used combination rules to determine the atom-atom coefficients. Four additional runs were made increasing each atom-atom coefficient by 10%, pot 01-04, to determine the effect of the atom-atom coefficients on the half-widths. Figure 2 shows the difference between the pot 01-04 calculations and pot 00 versus an energy ordered Index.

Figure 1 Average energy gaps for collisionally induced transitions for H$_2$O (blue) and H$_2$ (red)  
Figure 2 difference between the pot 01-04 calculations and pot 00 versus an energy ordered index.

The fact that there is structure in Figure 2 suggest adjusting the atom-atom coefficients will affect the computed half-widths differently for each transition. Ten iterations were made. In the final potential, the epsilon values were not changed; $\sigma_{HH}$ is 8.36% lower and $\sigma_{OH}$ is 10.1% higher than the pot 00 values. Figures 3 and 4 show the comparison of the half-width measurements of Brown and Plymate$^{12}$ with the pot 00 and pot 10 calculations, respectively. The pot 00 comparison has an average percent difference of -59.75 and a standard deviation of 23.3%. The pot 10 comparison has an average percent difference of -0.11 and a standard deviation of 8.2%.

Figure 3 H$_2$O-H$_2$ B&P data versus MCRB pot 0 
Figure 4 H$_2$O-H$_2$ B&P data versus MCRB pot 10
The intermolecular potential will be further refined using results of an intercomparison of all measurements of H$_2$O-H$_2$ broadening, the family of transitions idea of Brown and Plymate$^{11}$, and the partner transition and smooth variation rules of Ma et al.$^{23}$.

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References

[1] Chalis J 1863 MNRAS 23, 231
[2] Adel A, Slipher VM 1934 Phys. Rev. 46 902
[3] Adel A 1937 ApJ. 85 345
[4] Kuiper G 1944 ApJ. 100 378
[5] Cassan A, et al. 2012 Nature 481(7380) 167
[6] Fressin F, et al. 2013 Astrophys J 766 81
[7] Marcy G W, et al. 2014 Proc Natl Acad Sci USA 111 12655
[8] Seager S 2011 Exoplanets, ed Seager S (Univ of Arizona Press, Tucson, AZ)
[9] Lederberg J 1965 Nature 207(992) 9
[10] Lovelock JE, Nature 207(997), 568, 1965
[11] Sivaramakrishnan R M 2000 Proc. SPIE, UV, Optical, and IR Space Telescopes and Instruments 4013 386
[12] Huitson C M 2013 MNRAS; 434 3252
[13] Houck J R , 2004 The Astrophysical Journal Supplement Series; 154 18
[14] Madhusudhan N, Seager S. 2009 The Astrophysical Journal 707 24
[15] Antígona L K, Subhanjoy S 2011 The Astrophysical Journal 733 35
[16] Ranjan S, et al. 2014 Ap. J. 785 148
[17] Stevenson K B, et al. 2014 Astronomical Journal 147 161
[18] Swain M R, Vasisht G, Tinett G 2008 Nature 452 329
[19] Swain M R, et al. 2009 The Astrophysical Journal 704 1616
[20] Swain M R, et al. 2009 Ap. J. 690 L114
[21] Ma Q, Tipping R H, Boulet C 2007 JQSRT 103 588
[22] Brown L R, Plymate C 1996 JQSRT 56 263
[23] Ma Q, Tipping R H, Lavrentieva N N 2011 Mol. Phys. 109 1925