

Current Status of Quantitative Rotational Spectroscopy for Atmospheric Research

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Abstract

Remote sensing of rotational transitions in the Earth's atmosphere has become an important method for the retrieval of geophysical temperatures, pressures and chemical composition profiles that requires accurate spectral information. Both HITRAN and the JPL spectral line catalog are repositories of this spectral information and contain extensive frequency and intensity listings of rotational transitions of atmospheric species. This paper highlights the current status of rotational data that are useful for atmospheric measurements, with a discussion of the types the rotational lineshape measurements that are not generally available in either online repository.

This synopsis describes general considerations for inclusion of rotational lineshape data for atmospheric studies in the context of the HITRAN database[1]. Air-broadened spectral halfwidth and lineshift parameters are not listed in the Jet Propulsion Laboratory's Spectral Line Catalog[2] (JPL SLC), and HITRAN values are primarily based on ro-vibrational measurements. Generally, the rotational transition halfwidth parameters that are available are scattered throughout the literature. As a prelude to a database that could include critically evaluated rotational lineshape data, this synopsis highlights the literature search and particular caveats associated with important species.

Ozone and water represent two very different, and yet equally critical problems for atmospheric measurements in the rotational bands. Water, although sparse in resonant transitions in the longer wavelengths, has considerable non-resonant absorption and emission. This drastically affects the sensitivity of instrumentation in the wet atmosphere. On the other hand, ozone has a denser

spectrum that often causes issues with spectral congestion. In both cases, rotational lineshapes of these species are required prior to remote measurements of other trace species. For both ozone and water, future updates of frequency and/or intensity are expected to be small. Recent improvement of the water frequency database has come with robust measurements and analysis of the higher quanta. Similar work on water isotopes could establish integrity within the isotopic data sets. However, even with further measurements, water refuses to fit into the generic categories (semi-rigid rotor, isotopic invariants, etc.) that allow further extrapolation. On the other hand, ozone has a highly accurate (and extrapolative) frequency listing for all abundant isotopomers. Rotational linewidth investigations for water and ozone are becoming more common as remote sensing missions expand into new frequency ranges. For water, inter-comparisons of the rotational linewidth data are difficult due to minimal overlap of the data sets. However, with ozone most of the rotational linewidth data inter-compare well with ν_1 linewidth data. In light of these facts, rotational transition halfwidths that have not been explicitly measured could be assumed as the corresponding values from the lower energy state of the ν_1 band. In consideration of the previous discussion it is clear that pressure broadening parameters for the ozone database will benefit greatly from combined analyses, whereas a corresponding analysis for water may be problematic.

In many ways the caveats regarding atmospheric parameters for ozone and water are exacerbated with most other chemical species. Generally, resonant frequencies are well known, but precise lineshape parameters are rare. In decreasing order of air-broadened lineshape measurements these species are: CO, O₂, HCl, OH, NO, HBr, HI, ClO, BrO and the linear species: N₂O, OCS and HCN. Among these species, only CO and O₂ have more than two inter-comparable air-broadened rotational transition measurements of the lineshape.

There is good reason to believe that the more prevalent ro-vibrational halfwidth data are well correlated to the rotational halfwidths. The current listing in HITRAN of ro-vibrational halfwidth parameters for light, linear species is therefore a reasonable source for the rotational halfwidths as well. The heavier (except hydrogen halides) species have under-developed data sets in both the rotational and ro-vibrational bands and therefore such a statement remains speculative. Furthermore, it remains unclear at this point whether or not lineshift parameters can be extrapolated from vibrational data into the rotational bands.

In the non-linear polyatomic regime, even the frequency listings become factors influencing the quality of the rotational and ro-vibrational data. Many of the species, SO₂, HNO₃, H₂CO, H₂S, ClONO₂) have divergent frequency listings in HITRAN and/or JPL SLC and still more have available data not currently

listed in the databases. Furthermore, there remain species that have been detected in the atmosphere which remain unlisted (HClCO, Cl₂CO, (ClO)₂ to name a few).

Recent discussions[3] about needs for atmospheric remote sensing have focussed on the precision, accuracy and need for critical evaluation of necessary spectral parameters. In the ro-vibrational spectral region there are often multiple measurements of the spectral parameters, thus necessitating a critical evaluation and subsequent recommendation of the 'best' parameters. In contrast, the rotational bands have very few re-measurements on parameters. Consequently there are few comparisons to evaluate/recommend prior to database entry.

The creation of a dedicated rotational/ro-vibrational database or inclusion of available rotational data in the existing HITRAN database will facilitate the advancement of these two fields that are slowly merging. Such an effort will not only solidify remote sensing needs in both spectral regions, but also prove invaluable to laboratories that support these missions.

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