Validation of Ozone Infrared Line Intensities

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1 Introduction

Measurements of infrared absorption or emission are used to determine the concentrations and distributions of atmospheric gases on global, regional, and local scales. The accuracy of these remote measurements depends significantly on the accuracy of our knowledge of the molecular spectra of ozone and other infrared-active atmospheric species. Several recent high-resolution spectroscopic studies [1, 2, 3, 4] have determined absolute intensities of ozone infrared absorption lines in the 9-11 μm region, using as a reference standard the UV absorption cross-section of ozone at 254 nm. This paper reviews the various measurements and compares them to each other and to the current HITRAN line parameters compilation [5].

2 Review of Measurements

The first study reporting measurements of ozone 10- μm line intensities referenced to a 254-nm UV absorption standard was that of Pickett et al. [1]. They used a high-resolution Fourier transform spectrometer (FTS) to measure intensities of 47 lines in the P branch of the ν_3 fundamental band. Ozone partial pressures in the sample cell were determined through measurements of UV absorption at 254 nm, using as a reference standard the cross-section measurements of Hearn [6]. The results are based on individual measurements in two spectra fitted separately. Taking an arithmetic average of all the intensity measurements, the mean difference from HITRAN is +8.3 %. However, if the most well-determined intensities are given greater weight, the mean difference from HITRAN is +5.1 %. The reported absolute accuracy of these measurements is 1 %; however, we note that the reference UV standard [6] has an accuracy of only 2 %.

Measurements of the intensity of the single (10 5 6)$\leftarrow$(9 5 5) ν_3 line at 1048.6736 cm^{-1}, made using both tunable diode laser (TDL) and laser heterodyne spectrometers, were reported by DeBacker et al. [2]. Ozone concentrations in these experiments were determined by continuously monitoring the total pressure in a closed system. The accuracy of this technique has been verified [7] by measuring the UV absorption at 254 nm, using the more recent reference standard of Mauersberger et al. [8]. The line intensity resulting from the TDL measurements agrees exactly with the HITRAN value, while the laser heterodyne result is approximately 1 % larger. These small differences are consistent with the 1 % precision reported for the measurements.

In addition to the (10 5 6)$\leftarrow$(9 5 5) line, DeBacker-Barilly and Courtois [3] used their TDL system to measure intensities of 46 other lines in the R branch of the ν_3 band. The reported accuracy of the intensities for these lines is 4 % and their weighted-mean difference from HITRAN is -5 %. However, there is considerable scatter among the individual differences from HITRAN, and their arithmetic average is -7.5 %.

Recently Smith et al. [4] have determined absolute intensities of numerous $^{16}O_3$ lines in the 9-11 μm region from spectra recorded using the 1-m FTS at Kitt Peak. Ozone concentrations in the sample cell were determined using a 254 nm UV-absorption monitor of the same design as Pickett et al. [1]. However, the more accurate ($\pm$0.5 %) UV cross-section value of Mauersberger et al. [8] was used as the reference standard for these measurements. Four spectra for which the ozone partial pressure varied by $<$ 1.0 % during the recording were fit simultaneously using a multispectrum nonlinear least-squares procedure [9]. Line positions and intensities were determined for over 270 lines in the P, Q, and R branches of the ν_3 fundamental band and 10 lines in the R branch of the ν_1 band. Absolute accuracies of these intensity values range from 2 % for the strongest, most well-isolated lines to over 4 % for the weakest lines measured. For both arithmetic and weighted averages, the mean difference from HITRAN is +1 % in the ν_3 band and $-$0.2 % in the ν_1 band.

3 Intercomparison

On average, taking all the measurements [1, 2, 3, 4] together, the line intensities are about 1 % larger than the values on the current HITRAN compilation [5]. However, a few individual measured intensities differ from the HITRAN values by as much as 9 to 15 %. Only 44 lines were measured in more than one experimental study, and only one of these lines has more than two independent measurements. Comparison of the various intensity measurements shows excellent agreement for a few lines but considerable discrepancies (greater than the stated uncertainties) for others.

The (10 5 6)$\leftarrow$(9 5 5) line at 1048.6736 cm^{-1} was measured by three different techniques: TDL [2, 3], laser heterodyne spectrometer [2], and FTS [4]; all three intensities are within 1.1 % of the HITRAN value. For the 44 ν_3 band transitions with at least two measurements, the intensities of Smith et al. [4], obtained for both $P-$ and $R-$branch transitions, average 1.4 % larger than the values on the HITRAN compilation [5]. This result appears to split the difference between the FTS measurements of Pickett et al. [1] in the P branch and the tunable diode laser (TDL) results reported by DeBacker-Barilly and Courtois [3] in the R branch. However, for these two earlier sets of measurements [1, 3] the intensity differences from HITRAN appear to become larger for increasing rotational quantum number J''. There may be a contribution to these trends from experimental temperature uncertainties; further investigation is needed to determine the exact cause. The study of Smith et al. [4], which covered a wide range of rotational quantum numbers in the P, Q, and R branches of the ν_3 band, found no obvious J''-dependence of the intensity differences from the HITRAN compilation.

In summary, the recent experimental studies in the 9-11 μm region appear to have verified that the intensities of $^{16}O_3$ transitions given in the HITRAN line parameters compilation [5] in this region have an absolute accuracy of 2 % at best. The HITRAN ozone intensities in the infrared also are quite consistent (1 % precision) with the ultraviolet absorption cross-section standard at 254 nm [8].

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