Journal of Quantitative Spectroscopy & Radiative Transfer 167 (2015) 126–134

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

High-resolution absorption measurements of NH_3 at high temperatures: 500–2100 cm^{-1}

Emma J. Barton [a], Sergei N. Yurchenko [a], Jonathan Tennyson [a,*], Sønnik Clausen [b], Alexander Fateev [b]

[a] Department of Physics and Astronomy, University College London, London WC1E 6BT, UK
[b] Technical University of Denmark, Department of Chemical and Biochemical Engineering, Frederiksborgvej 399, 4000 Roskilde, Denmark

ARTICLE INFO

Article history:
Received 20 June 2015
Accepted 28 July 2015
Available online 7 August 2015

Keywords:
High temperature
Ammonia
Absorption
FTIR spectroscopy
High-temperature flow gas cell
Line assignments

ABSTRACT

High-resolution absorption spectra of NH_3 in the region 500–2100 cm^{-1} at temperatures up to 1027 °C and approximately atmospheric pressure (1013 ± 20 mbar) are measured. NH_3 concentrations of 1000 ppm, 0.5% and 1% in volume fraction were used in the measurements. Spectra are recorded in high temperature gas flow cells using a Fourier Transform Infrared (FTIR) spectrometer at a nominal resolution of 0.09 cm^{-1}. Measurements at 22.7 °C are compared to high-resolution cross sections available from the Pacific Northwest National Laboratory (PNNL). The higher temperature spectra are analysed by comparison to a variational line list, BYTe, and experimental energy levels determined using the MARVEL procedure. Approximately 2000 lines have been assigned, of which 851 are newly assigned to mainly hot bands involving vibrational states as high as $v_2=5$.

1. Introduction

Hot planets, cool stars and high temperature industrial processes have molecules (and temperatures) of interest in common. NH_3 is one such molecule.

In smoke stacks NH_3 is used post-combustion to convert highly reactive nitrogen oxides (NOx) into free nitrogen and water vapour through selective catalytic and non-catalytic reduction (SCR and SNCR) [1]. This process must be monitored closely as any un-reacted NH_3, referred to as 'ammonia slip' [2], can cause fouling and corrosion of downstream components and contamination of fly ash [3]. NH_3 is also used throughout the chemical industry, its most important use being for the production of nitric acid [4].

From an astronomical perspective NH_3 has been detected in multiple environments. Cool environments include nearby molecular cloud MBM 12 [5], the comae of comet 10P/Tempel 2 [6], and solar system planets [7]. The presence of NH_3 in the atmospheres of Neptune and Jupiter suggests that it is also likely to be present in the atmospheres of extrasolar giant planets [8]. Hot environments include brown dwarfs (see for example [9]). NH_3 is a significant source of opacity in the infrared spectra of late type T dwarfs, see for example [10], and is expected to be even more important in recently discovered Y dwarfs [11,12]. In fact NH_3 features identified in the near-infrared spectrum of a T dwarf played a significant role in the justification of the Y spectral class [10,11].

The conditions, chemical reactions and gas mixing in industrial processes involving combustion can be monitored by in situ measurements of gas temperature and composition. This can be done spectroscopically, though the result is highly dependent on the quality of reference data [13]. Analysis of brown dwarfs and other such objects using model atmospheres also requires reliable line lists [10].

A hot variational line list for NH_3 called BYTe is available [14] and has been proven to be an effective tool

* Corresponding author.
E-mail address: j.tennyson@ucl.ac.uk (J. Tennyson).

http://dx.doi.org/10.1016/j.jqsrt.2015.07.020
0022-4073/

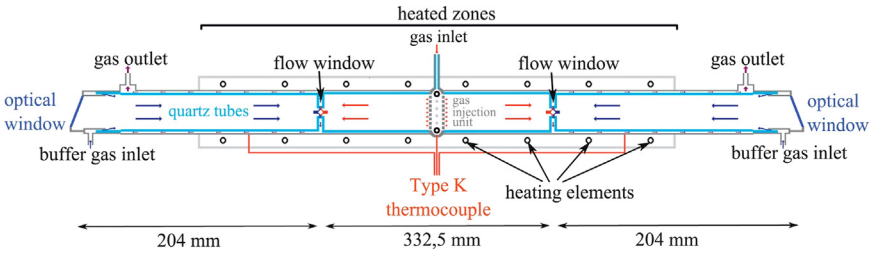

Fig. 1. High temperature quartz gas flow cell (q-HGC) used in the experiments. The red arrows indicate the hot reactive gases, while the blue arrows show the colder buffer gas. Reproduced from [35]. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this paper.)

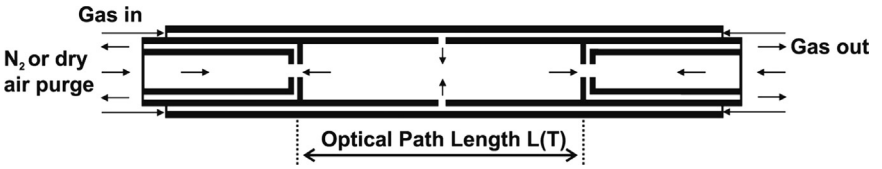

Fig. 2. High temperature ceramic gas flow cell (c-HGC) used in the experiments. Black arrows indicate flow direction. Reproduced from [38].

for the analysis of the tetraatomic molecules' spectrum [15]. BYTe is a variationally computed line list for hot NH_3 that covers the range 0–12,000 cm^{-1} and is expected to be fairly accurate for all temperatures up to 1500 K (1226 °C). It comprises 1,138,323,251 transitions constructed from 1,373,897 energy levels lying below 18,000 cm^{-1}. It was computed using the NH3-2010 potential energy surface [16], the TROVE ro-vibrational computer program [17] and an *ab initio* dipole moment surface [18].

However there is motivation to improve the present line list, which in particular is known to be less accurate for higher frequency transitions [19–21]. During the data analysis presented below we note some frequency shifts and some systematic underestimation of intensities for strong lines in the BYTe lines in comparison to experiment (see Section 4.2). Assigned high resolution laboratory spectra are needed to refine and validate theoretical line positions and intensities.

Numerous studies have endeavoured to assign cold (for example [22–24]) and hot (for example [25,26,15]) NH_3 spectra, many of which are collected in the HITRAN database [27,28]. This has proven to be a challenge due to the congested and complicated nature of the spectrum. A comprehensive compilation of all measured NH_3 rotational and ro-vibrational spectra can be found in a recent MARVEL study [29]. The MARVEL (measured active rotation–vibration energy levels) algorithm [30,31] simultaneously analyses all available assigned and labelled experimental lines, thus yielding the associated energy levels. The recent study for NH_3 analysed 29,450 measured transitions and yielded 4961 accurately-determined energy levels which mostly lie below 7000 cm^{-1} [29].

High resolution emission spectra of NH_3 up to 1300 °C in the regions 740–2100 cm^{-1} and 1650–4000 cm^{-1} were recorded by Hargreaves et al. [32,33]. Zobov et al. [15] analysed the first region and presented assignments for strong lines whose upper levels belong to vibrational states with band origins up to 2100 cm^{-1}. The present work is complementary to these previous works, providing high resolution absorption spectra of NH_3 up to 1027 °C in the region 500–2100 cm^{-1} including assignments. A proportion of these line assignments are new, of which some lines are also present but unassigned in the emission spectra. The notable advantage of our measurements is the absolute intensity scale, as emission intensities are notoriously difficult to calibrate [32–34].

This paper has the following structure. Section 2 describes the experimental setup used for the measurements. Section 3 gives an overview of the method used to calculate experimental and theoretical absorbance spectra and the assignment procedure. Section 4 comes in three parts. The experimental spectrum at 22.7 °C is compared to high resolution PNNL spectra to verify the performance of the whole experimental setup in Section 4.1. The accuracy of BYTe is assessed in Section 4.2 by a direct comparison with the experimental spectra. A summary of all assignments is presented in Section 4.3. Finally Section 5 gives our conclusions and discusses avenues for further work.

2. Experimental details

Measurements up to 500 °C were performed using a quartz high-temperature gas-flow cell (q-HGC) (see Fig. 1) validated for high resolution measurements at temperatures up to 500 °C in the ultra-violet (UV) and infrared (IR) regions [35]. This q-HGC has previously been used to measure absorption cross-sections of various gases (e.g. SO_2) up to 773 K (500 °C) [35]. Measurements above 500 °C were performed using a ceramic high-temperature gas-flow cell (c-HGC) (see Fig. 2) that has also been used by the DTU group [36–38] to study e.g. hot CO and to validate HITEMP2010 [39] for CO_2 and H_2O respectively. This cell operates at temperatures up to 1873 K (1600 °C) [40].

Both cells have the same basic design, three sections separated by flow windows, a fully heated central part and two partially heated buffer parts with interchangeable optical windows at the ends. The buffer parts compensate for heat losses at the ends of the sample cell so as to obtain