Journal of Quantitative Spectroscopy & Radiative Transfer 186 (2017) 139–149

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

New and improved infra-red absorption cross sections and ACE-FTS retrievals of carbon tetrachloride (CCl_4)

Jeremy J. Harrison [a,b,*], Christopher D. Boone [c], Peter F. Bernath [c,d]

[a] Department of Physics and Astronomy, University of Leicester, Leicester LE1 7RH, United Kingdom
[b] National Centre for Earth Observation, University of Leicester, Leicester LE1 7RH, United Kingdom
[c] Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1
[d] Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, Virginia 23529, United States of America

ARTICLE INFO

Article history:
Received 17 February 2016
Received in revised form
28 April 2016
Accepted 28 April 2016
Available online 6 May 2016

Keywords:
CCl_4
Carbon tetrachloride
High-resolution Fourier transform spectroscopy
Infra-red absorption cross sections
Remote sensing
Atmospheric chemistry

ABSTRACT

Carbon tetrachloride (CCl_4) is one of the species regulated by the Montreal Protocol on account of its ability to deplete stratospheric ozone. As such, the inconsistency between observations of its abundance and estimated sources and sinks is an important problem requiring urgent attention (Carpenter et al., 2014) [5]. Satellite remote-sensing has a role to play, particularly limb sounders which can provide vertical profiles into the stratosphere and therefore validate stratospheric loss rates in atmospheric models.

This work is in two parts. The first describes new and improved high-resolution infra-red absorption cross sections of carbon tetrachloride/dry synthetic air over the spectral range 700–860 cm^{-1} for a range of temperatures and pressures (7.5–760 Torr and 208–296 K) appropriate for atmospheric conditions. This new cross-section dataset improves upon the one currently available in the HITRAN and GEISA databases. The second describes a new, preliminary ACE-FTS carbon tetrachloride retrieval that improves upon the v3.0/v3.5 data products, which are biased high by up to ~20–30% relative to ground measurements. Making use of the new spectroscopic data, this retrieval also improves the microwindow selection, contains additional interfering species, and utilises a new instrumental lineshape; it will form the basis for the upcoming v4.0 CCl_4 data product.

1. Introduction

A clear, colourless, sweet-smelling liquid at room temperature, carbon tetrachloride (CCl_4; also known as tetrachloromethane or CFC-10) was first synthesised in 1839 from chloroform and chlorine gas by Henry Victor Regnault [1]. As carbon tetrachloride does not occur naturally in the Earth system, its presence in the atmosphere, soil and ocean arises through its anthropogenic uses.

In the early twentieth century, carbon tetrachloride found many uses, for example in dry cleaning (excellent solvent properties), fire extinguishers, postage stamp collecting (to reveal watermarks without damaging the paper), lava lamps, and even as a refrigerant in early refrigerators. The discovery that carbon tetrachloride is harmful to human health – a potential human carcinogen, it has been shown to depress the central nervous system, inhibit liver and kidney function, and even kill – led to a decline in these uses. However, this had no effect on the largest industrial application of carbon tetrachloride in the twentieth century, its use as a feedstock in the production of trichlorofluoromethane (CFC-11) and dichlorodifluoromethane (CFC-12), which were commercialised in the 1930s as nonflammable and non-toxic refrigerants [2].

---

[*] Corresponding author at: Department of Physics and Astronomy, University of Leicester, University Road, Leicester LE1 7RH, United Kingdom.
E-mail address: jh592@leicester.ac.uk (J.J. Harrison).

http://dx.doi.org/10.1016/j.jqsrt.2016.04.025
0022-4073/

It was not until the realisation that long-lived chlorine-containing species such as CCl_4 and the CFCs (chlorofluorocarbons) could destroy stratospheric ozone that the use of CCl_4 in industry began to decline, as regulated by the 1987 Montreal Protocol (and its later amendments). Under the terms of the Protocol production and consumption of CCl_4 were eliminated for developed countries in 1996 and for developing countries in 2010 [3]. There are no limits on the use of CCl_4 as a feedstock, however, so it is still used, for example, in the production of hydrofluorocarbons. Although an ozone-depleting substance, with an ozone depletion potential of 0.72 [4], CCl_4 is also a very strong greenhouse gas with a 100-year global warming potential of 1730 [4].

As one of the species controlled by the Montreal Protocol, there is much work carried out in monitoring CCl_4 atmospheric concentrations by global networks such as AGAGE (Advanced Global Atmospheric Gases Experiment), NOAA (National Oceanic and Atmospheric Administration), and UCI (University of California, Irvine). The latest ozone assessment report from 2014 [5] indicates that the global surface mean mole fraction of CCl_4 has continued to decline between 2008 and 2012, with the AGAGE and UCI networks reporting a rate of decline of 1.2–1.3% from 2011 to 2012, and 1.6% reported by the NOAA network. These rates of decline are comparable with those determined by remote sensing instruments of 1.1–1.2% yr^{-1}, from the Atmospheric Chemistry Experiment-Fourier transform spectrometer (ACE-FTS) on SCISAT and the ground-based FTS at Jungfraujoch [6].

Recently there has been particular interest in carbon tetrachloride, on account of the inconsistency between observations of its abundance and estimated sources and sinks [3]. A recent study [3] has suggested that the observed inter-hemispheric gradient for CCl_4 (1.5 ± 0.2 ppt for 2000–2012) is primarily caused by ongoing emissions, however the 2007–2012 emissions estimate based on the UNEP reported production and feedstock usage is near-zero. Additionally, the decline of atmospheric concentrations is slower than can be accounted for by our current best estimates of the total CCl_4 lifetime and its uncertainties.

In addition to the ground-based networks of CCl_4 measurements, remote-sensing measurements which provide vertical profiles into the stratosphere are particularly useful in validating stratospheric loss rates in atmospheric models (the atmospheric loss of CCl_4 is essentially all due to photolysis in the stratosphere). The literature reports a number of remote-sensing instruments capable of measuring CCl_4 in the Earth's atmosphere: ATMOS (Atmospheric Trace MOlecule Spectroscopy) [7] and CIRRIS 1A (Cryogenic Infra-Red Radiance Instrumentation for Shuttle) [8], both deployed on the space shuttle, the JPL balloon-borne MkIV interferometer [1], MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) on ENVISAT (ENVIronmental SATellite) (e.g. [9]), and the ACE-FTS [1,10].

In the literature, the only global distribution of CCl_4 extending up to the mid-stratosphere is derived from ACE-FTS measurements. Covering the spectral region 750–4400 cm^{-1} with a resolution of 0.02 cm^{-1}, the ACE-FTS instrument uses the sun as a light source to record limb transmission through the Earth's atmosphere (~300 km effective length) during sunrise and sunset ('solar occultation'). The measured spectra, with high signal-to-noise ratios and through long atmospheric path lengths, provide a low detection threshold for retrieving the profiles of trace species. In fact, the ACE-FTS can detect more of these species than any other satellite instrument, although it only records spectra for at most 30 occultation events per day [11,12 (this issue)]. Unfortunately, the ACE-FTS v3.0/v3.5 CCl_4 retrieval is biased high by up to ~20–30% relative to ground measurements; the reasons for this have been attributed to errors in the CCl_4 spectroscopy, bad line parameters from other absorbing species in the microwindow, and several absorbing species missing from the forward model. The aim of the present work was to improve the ACE-FTS CCl_4 retrieval and minimise this high bias. This problem has been attacked on two fronts: (1) through the utilisation of new laboratory spectroscopic measurements of air-broadened CCl_4 samples over a range of atmospheric pressure-temperature (PT) combinations and; (2) through improvements in the retrieval itself, in particular improved microwindow selection (the avoidance of spectral regions associated with poor or inadequate line parameters of interfering species), the inclusion of new interfering species, and a new instrumental lineshape (ILS). This new scheme will form the basis for the upcoming processing version 4.0 of ACE-FTS data. Section 2 of this manuscript presents some spectroscopic background to CCl_4, and a discussion of previous infra-red (IR) absorption cross section datasets. Section 3 provides details on the new measurements, the derivation of cross sections, and a discussion of the results and comparison with previous measurements. Section 4 provides details of the new ACE-FTS CCl_4 retrieval scheme.

2. Infra-red spectroscopy of carbon tetrachloride

2.1. Spectroscopic background

Since carbon and chlorine each have two stable isotopes, there are ten stable isotopologues of carbon tetrachloride, namely ${}^{12/13}C^{35}Cl_4$, ${}^{12/13}C^{35}Cl_3^{37}Cl$, ${}^{12/13}C^{35}Cl_2^{37}Cl_2$, ${}^{12/13}C^{35}Cl^{37}Cl_3$, and ${}^{12/13}C^{37}Cl_4$; these belong to the point groups T_d, C_{3v}, C_{2v}, C_{3v} and T_d, respectively. With natural abundances of ~99% and ~1% for ${}^{12}C$ and ${}^{13}C$, and ~76% and ~24% for ${}^{35}Cl$ and ${}^{37}Cl$, it turns out that the four isotopologues ${}^{12}C^{35}Cl_4$, ${}^{12}C^{35}Cl_3^{37}Cl$, ${}^{12}C^{35}Cl_2^{37}Cl_2$, and ${}^{12/13}C^{35}Cl^{37}Cl_3$ account for ~99% of the isotopologues found, that is 33%, 42%, 20% and 4%, respectively [13].

CCl_4 has nine normal vibrational modes; in the T_d point group these are labelled ν_1 (non-degenerate, A_1), ν_2 (doubly-degenerate, E), ν_3 (triply degenerate, T_2), and ν_4 (triply degenerate, T_2). For the lower-symmetry isotopologues, the degeneracy can be lifted; ν_2 splits into A_1 and A_2 for C_{2v}, and ν_3 and ν_4 split into A_1 and E under C_{3v}, and A_1, B_1 and B_2 under C_{2v}. In the literature, however, it is more common to label bands under the assumption of T_d symmetry, as the splittings are likely small to a first approximation.