Journal of Molecular Spectroscopy xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

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

Near-global distribution of CO isotopic fractionation in the Earth's atmosphere

C.A. Beale [a,*], E.M. Buzan [b], C.D. Boone [c], P.F. Bernath [b,c]

[a] Department of Ocean, Earth and Atmospheric Sciences, Old Dominion University, Norfolk, VA 23529, United States
[b] Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, United States
[c] Department of Chemistry, University of Waterloo, Waterloo, ON N2L 3G1, Canada

ARTICLE INFO

Article history:
Received 10 July 2015
In revised form 6 November 2015
Accepted 14 December 2015
Available online xxxx

Keywords:
Carbon monoxide
Isotopic fractionation
Atmospheric modeling
Satellite measurements
FTIR

ABSTRACT

The first near-global (−85° to 85°) measurements of the isotopic fractionation of ^{13}CO relative to ^{12}CO have been obtained from 5 to 90 km using the ACE-FTS (Atmospheric Chemistry Experiment-Fourier Transform Spectrometer). These observations have been compared to predictions from WACCM (Whole Atmosphere Community Climate Model). The highest positive fractionation (i.e. relatively more ^{13}CO) values of over 100‰ are observed in the lower thermosphere during winter in both hemispheres, whereas the highest negative fractionation (i.e. relatively more ^{12}CO) is observed in the mesosphere in the summer at high latitudes (due to the highly fractionating effect that UV light has on CO_2) and year round in the tropics. Agreement between measurements and model results is generally good at high altitude, although ACE shows a stronger fractionation effect from CO_2 photolysis than predicted by WACCM. In the lower atmosphere, agreement is qualitatively good, although there is a distinct discrepancy at 40 km in all seasons, which is likely a retrieval artifact.

1. Introduction

Carbon monoxide (CO) is an important molecule in atmospheric chemistry. Although it has a small direct global warming potential, it acts as an indirect greenhouse gas as a result of the formation of carbon dioxide (CO_2) through the reaction with the hydroxyl radical (OH). The reaction between CO and OH also leads to the formation of tropospheric ozone (O_3) [1] which acts as both a pollutant and a greenhouse gas [2]. The lifetime of CO (~2 months) makes it an excellent tracer of atmospheric dynamics, in particular vertical transport at high latitudes [3]. Both CO and O_3 are considered major pollutants in the troposphere [4] and have detrimental effects on human health, including lung disease and cancer [5].

CO has four major sources in the troposphere: fossil fuel combustion, biomass burning, methane oxidation and non-methane hydrocarbon oxidation. The major sink throughout the atmosphere is the reaction with OH. Since the concentration of OH is strongly dependent on the actinic flux, and therefore the time of year, the tropospheric lifetime of CO is seasonally variant (1–6 months). The spatial distribution is also varied given the relatively short lifetime and the disparity of fossil fuel production between the Northern and Southern Hemispheres. In the troposphere CO is a precursor (through production of HO_2) to the formation of ozone under high NO_x conditions [1,6,7]. In the stratosphere and mesosphere the main sources of CO are from formaldehyde (CH_2O), which is formed through hydrocarbon oxidation [8–10], and photodissociation of CO_2, respectively. The volume mixing ratio and lifetime of CO in the mesosphere is much higher than in the troposphere or stratosphere and it can be used as an atmospheric tracer of vertical transport and other dynamical effects in the upper atmosphere.

CO exists predominantly as the $^{12}C^{16}O$ isotopologue, but there are appreciable amounts of $^{13}C^{16}O$ in the atmosphere and to a lesser extent $^{12}C^{17}O$ and $^{12}C^{18}O$. The various CO sources have different isotopic signatures [11–13] because of the different isotopic compositions of the reactants and the different fractionation processes that they undergo during CO formation. Indeed removal by OH oxidation also has considerable isotopic fractionation [8]. Measurements of the isotopic makeup of CO can therefore lead to a determination of the various sources and sinks [7,12,14,15]. The variation of the isotopic composition of a sample from the standard isotopic abundance is given in δ notation and expressed as 'per mil' (‰) changes. For ^{13}C, this would be expressed as

$$\delta^{13}\mathrm{C} = \left[\frac{[^{13}\mathrm{C_S}]/[^{12}\mathrm{C_S}]}{[^{13}\mathrm{C_R}]/[^{12}\mathrm{C_R}]} - 1\right] \times 1000‰,$$

* Corresponding author.
E-mail address: cbeale@odu.edu (C.A. Beale).

http://dx.doi.org/10.1016/j.jms.2015.12.005
0022-2852/

In which the S and R subscripts refer to the concentrations for the sample and reference, respectively. For ^{13}C, this reference is the Vienna Pee Dee Belemnite (V-PDB) which has a $[^{13}C]/[^{12}C]$ value of 0.0112372.

A number of previous studies have used CO isotopologues to quantify the relative contributions of the various sources and sinks. In situ collection and measurement of suitable samples can be difficult due to the small volume mixing ratio of CO and generally sophisticated cryogenic traps are used [12] to isolate the sample. This technique is clearly spatially limited, although analysis with mass spectrometry techniques provides highly precise values for the isotopic composition of a sample. Samples from the high latitude northern hemisphere [7], Japan [16], Barbados [14], a transect along the Trans-Siberian railroad [17] and other locales have been analyzed and modeling efforts have included a two dimensional model employed by Manning et al. [15] to predict CO concentrations and $\delta^{13}C$ values in the extra tropical southern hemisphere. The CARIBIC project has provided isotopic fractionation values for CO in the upper troposphere and lower stratosphere [18], although the sampling method suffered from contamination. However, all of these results are relatively local and cover a limited altitude range. Given the seasonal and spatial variability of CO, as well as the different contributions of sources and sinks, a more comprehensive study is needed. Nadir sounding instruments such SCIAMACHY [19] and MOPITT [20] and limb sounders such as MIPAS [6], IASI [21] and ACE [22] have successfully measured CO from satellite platforms, although this has not yet been extended to isotopic measurements.

2. Experimental

SCISAT is a Canadian-led satellite mission that was launched in 2003. The primary instrument on board is the Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS) which is a high resolution (0.02 cm^{-1}) spectrometer covering the spectral region 750–4400 cm^{-1}. The instrument records solar occultation spectra, recording transmission spectra through the limb of the Earth's atmosphere at sunrise and sunset over a latitudinal range of about 85°S to 85°N. The satellite's orbital inclination of 74° provides near global coverage with a strong weighting toward occultations at higher latitudes (Fig. 1). Profiles of over 30 trace gas species are obtained from ACE-FTS spectra, at a vertical resolution of around 3–4 km [23].

Retrievals of ACE-FTS data were obtained using version 3.5 of the ACE-FTS software [24]. Pressure and temperature profiles are first derived from the ACE-FTS spectra through the analysis of CO_2 lines, and then volume mixing ratio (VMR) profiles are retrieved for the various atmospheric constituents of interest using a forward model in which the target molecule's concentration is adjusted until the calculated spectrum matches observations. Spectroscopic parameters for the forward model calculations were taken from the HITRAN 2004 database [25].

The subsidiary isotopologues from a number of molecules are routinely retrieved from ACE-FTS measurements, including H_2O, CO_2, O_3, N_2O, CH_4, OCS, and CO (http://www.ace.uwaterloo.ca/). For carbon monoxide, in addition to the main isotopologue ($^{12}C^{16}O$), VMR profiles are retrieved for $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{12}C^{17}O$.

The high altitude portion (above ~95 km) of the retrieval for main isotopologue CO in version 3.5 differs significantly from version 3.0, the previous processing version. In version 3.0, the CO VMR profile in the thermosphere was assumed to be increasing rapidly with altitude, which yielded an overestimation of the contribution to the calculated spectrum from the altitude region above the highest analyzed measurement (~110 km). In version 3.5, a constant VMR was assumed above the highest analyzed measurement.

The spectral microwindows employed in the CO and ^{13}CO retrievals are presented in Tables 2 and 3, respectively. The ACE-FTS measurements cover the 1–0 and 2–0 CO vibration–rotation bands, both of which are included in the ^{12}CO microwindow set, with the weaker 2–0 band used for low altitudes where many of the lines in the 1–0 band are saturated. The microwindow set for the ^{13}CO isotopologue only contains lines from the fundamental band. Unlike the main isotopologue, lines in the 1–0 band for ^{13}CO do not saturate in the low-altitude ACE-FTS spectra thanks to the lower atmospheric abundance compared to ^{12}CO.

In general, the infrared is well-suited for isotopic studies, containing a wealth of narrow, isolated lines that allows ready

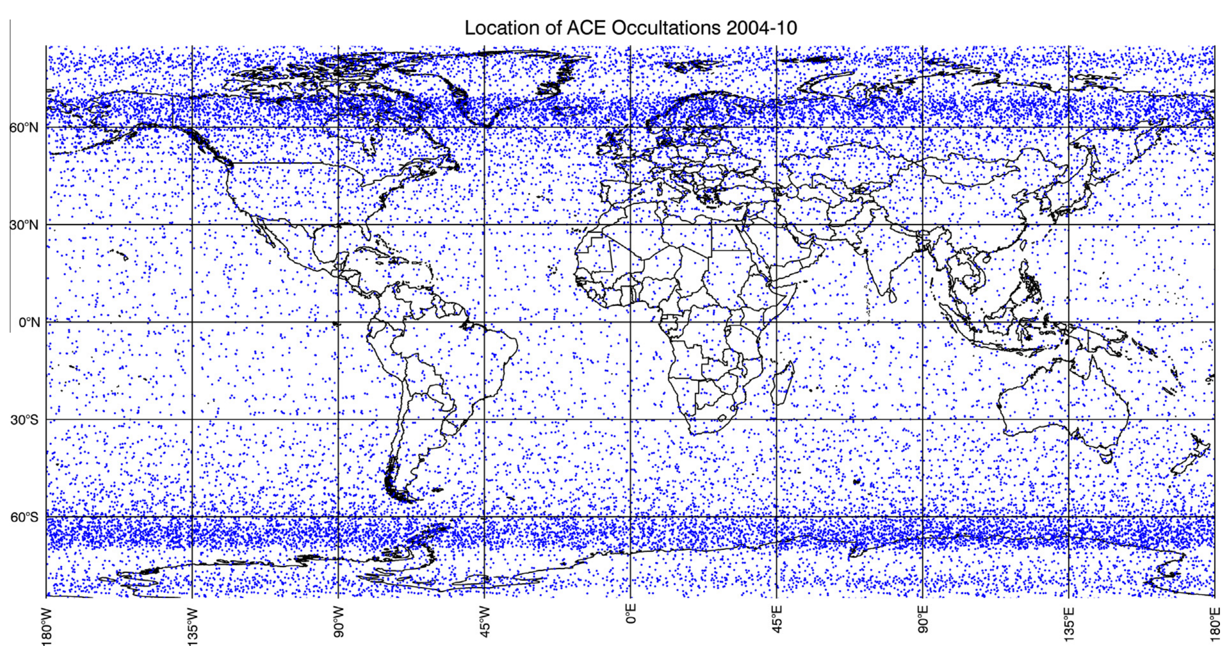

Fig. 1. Locations of 25,855 ACE-FTS occultations between March 2004 and October 2010 showing the global coverage of the instrument with a particularly large number of measurements at high latitudes.