On the Feasibility of Retrieving $^{16}O^{18}O^{16}O$ Ozone From High Resolution Ground-Based FTIR Spectra

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Abstract-We present evidence of the $^{16}O^{18}O^{16}O$ ozone isotope in the 5 μ region from FTIR solar occultation spectra obtained from the Jungfraujoch Solar Observatory (47°N, 8°E, 3580 m) in Switzerland at a spectral resolution of 0.0025 cm^{-1} (Res. = 1/2L). These spectra clearly show numerous unblended lines of the $^{16}O^{18}O^{16}O$ ozone isotope. Laboratory spectra in the 5 μ region of $^{16}O^{18}O^{16}O$ have been measured and have yielded line positions of the $\nu_1 + \nu_3$ isotopic bands which can eventually lead to their retrieval from measured ground-based solar occultation spectra.

Over the past decade the enrichment of heavy ozone isotopes in stratosphere has been well documented (Ref. 1-8, and references therein). Various laboratory experiments (Ref. 9-13) have noted a significant isotopic enrichment for $^{50}O_3$ as well (13% for 16-16-18 + 16-18-16), but with much more consistency than the field measurements, which have varied over a wide range of magnitude. A main reason for the large variation is the strong altitude dependence of the enrichment, with a maximum of up to 40% at an altitude typically between 25 and 37 km as observed by ballon-borne measurements. Since ground-based retrievals are averaged through the entire atmosphere, they will yield on average lower isotopic enrichments (ca. 0 to 10%). In spite of this, these spectra can be evaluated on a routine, low cost day-to-day basis, which may then assist in the explanation of the stratospheric ozone anomaly.

We present the first identification of this isotope made in the 5 μ region (2030 - 2040 cm^{-1}). We find this region more favorable than the 10 μ region due to the fact that greater Signal/Noise ratios can be achieved owing to better detector sensitivity, and interferences from other atmospheric constituents are much lower.

For the example shown in this report, a high resolution (0.0025 cm^{-1}) spectrum was collected on 29 January 1989 at a solar zenith angle of 75.66°, with a high resolution Fourier Transform Infrared Spectrometer (2.0 mm Aperture, 700 mm Focal Length, total scan time of 23 min., S/N=1667) developed in the Department of Astrophysics at the University of Liege, Belgium.

Line positions of the 16-18-16 ozone isotopes as observed in the solar spectra are listed below with their respective lower state energies (E"). Actual line strengths will be reported at a later date pending further calculations which will include higher J and K_a values.

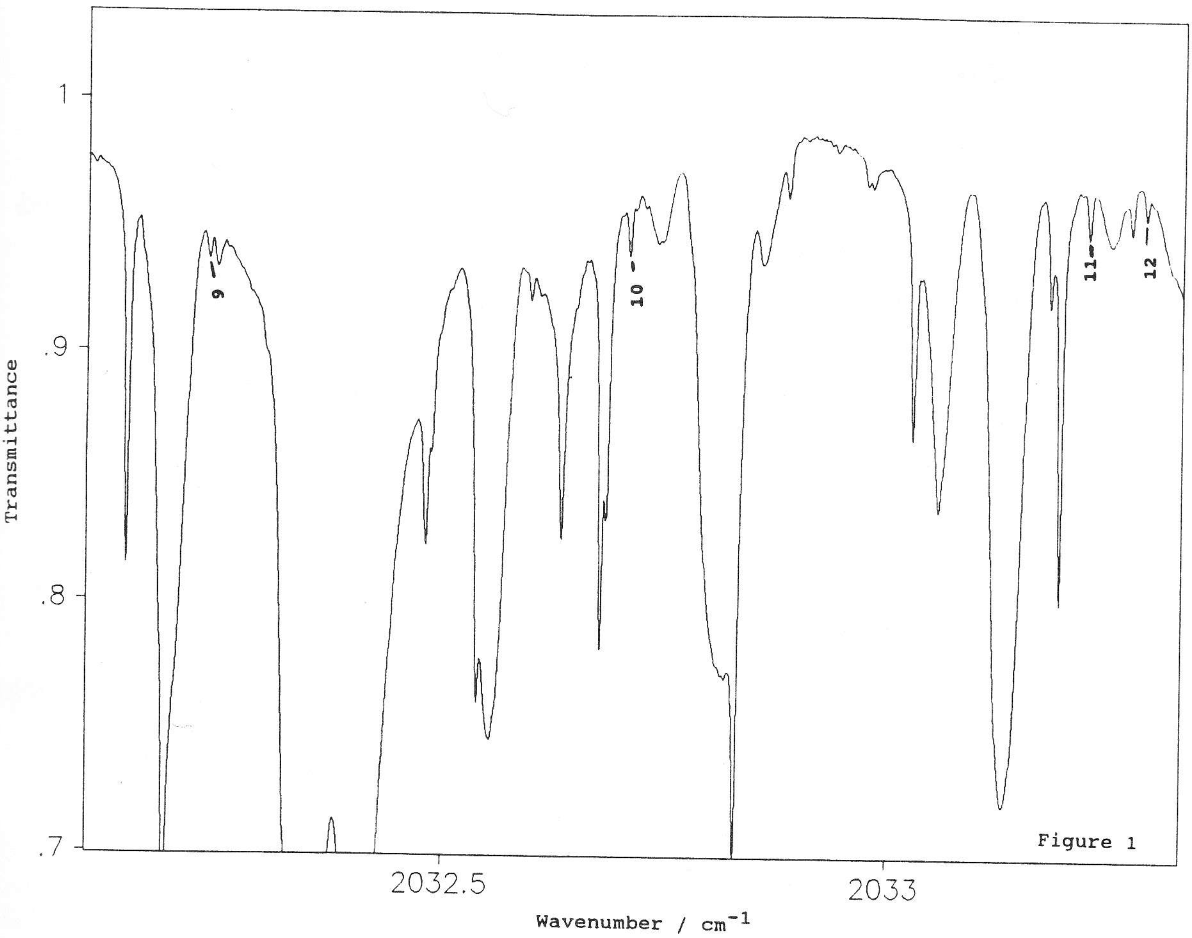
Preliminary calculations show that the line strengths typically range between 1.00E-21 and 4.00E-21 $cm^{-1}/molecule \cdot cm^{-2}$. All vibrational transitions are 000-101.

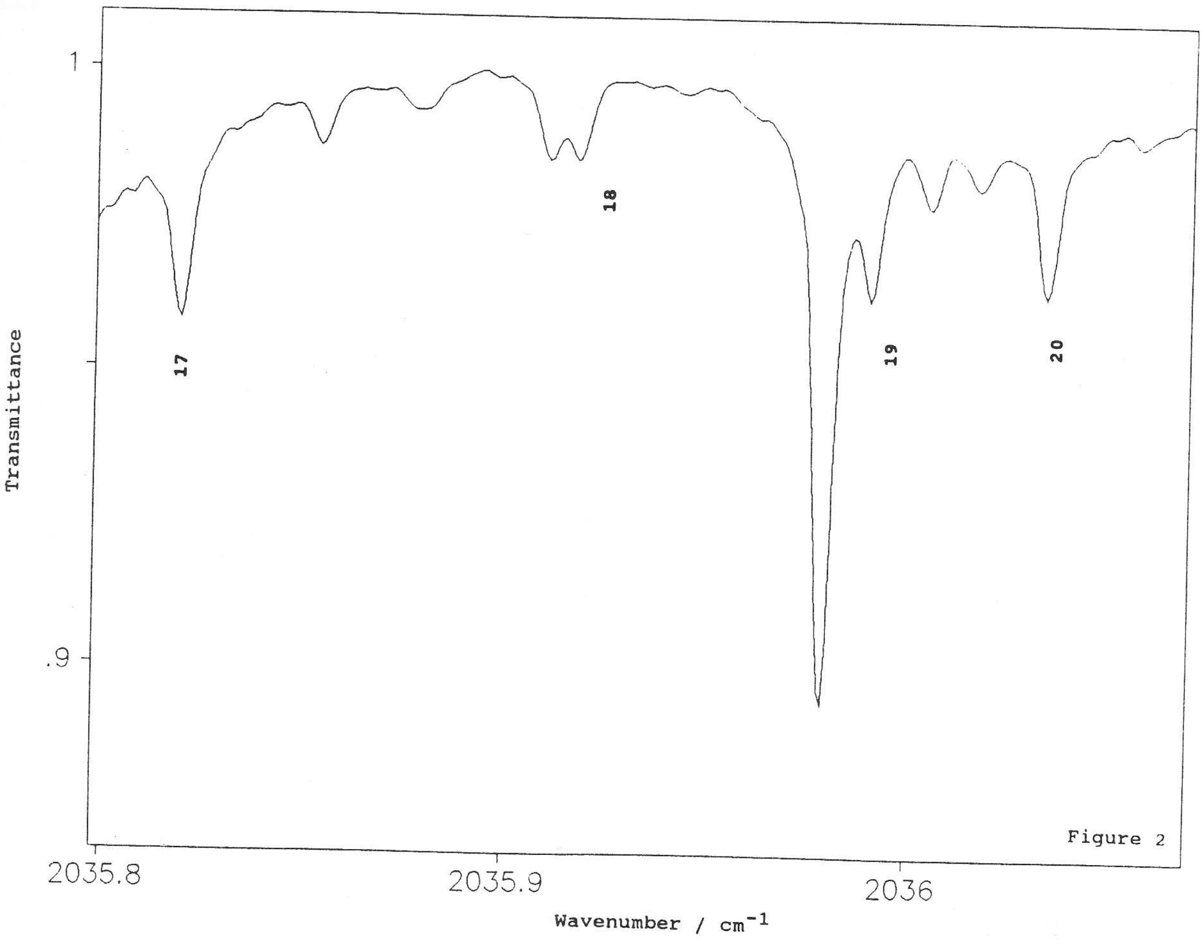
Peak Nr.	Line Position (cm^{-1})	E" (cm^{-1})
1.	2030.0836	230.8299
2.	2030.4423	205.1483
3.	2030.7169	246.3322
4.	2030.7370	185.1266
5.	2031.1663	214.9047
6.	2031.7124	156.9273
7.	2031.7354	169.5318
8.	2031.7429	155.7660
9.	2032.2356	199.8193
10.	2032.7090	140.0241
11.	2033.2258	139.0045
12.	2033.2910	185.5746
13.	2033.6541	159.8517
14.	2033.8059	126.1186
15.	2035.2903	111.5890
16.	2035.7292	133.8556
17.	2035.8195	99.6320
18.	2035.9183	179.3377
19.	2035.9907	113.9036
20.	2036.0347	100.3727
21.	2036.3745	205.5885
22.	2036.3755	147.8772
23.	2036.6937	86.5734
24.	2037.7837	76.3172

Several absorption lines of the 16-18-16 isotope listed above are shown according to peak number in Figures 1 and 2.

In this preliminary study we have identified the presence of the 16-18-16 ozone isotope from high resolution ground-based spectra. Continuation of this study will include searching for more absorption lines of the 16-18-16 isotope in the attempt to optimize the retrieval procedures. A long-trend database of isotopic ratios can then be compiled to be compared and correlated with prevailing tropospheric and stratospheric meteorological conditions. This may lend to further information leading to the sources of the stratospheric ozone isotope anomaly, as well as increase our knowledge of the basic processes which control the cycle of stratospheric ozone.

Future work will also include the retrievals of the 16-18-16 and 16-16-18 isotopes in the 2030 to 2040 cm^{-1} and 2060 to 2085 cm^{-1} regions, respectively. Because the 16-16-18 isotope is not symmetric (no nuclear spin restriction) twice as many energy levels, or absorption lines can occur. Also, since the molecule can be arranged either as 16-16-18 or as 18-16-16, the abundance of this isotope is twice that of the 16-18-16 isotope. However, because the number of transitions is doubled, the intensity of each line is reduced by a factor of 2.


Transmittance
1
.9
.8
.7
9
10
11
12
2032.5
2033
Wavenumber / cm^{-1}
Figure 1


Transmittance
1
.9
17
18
19
20
2035.8
2035.9
2036
Wavenumber / cm^{-1}
Figure 2

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