

Identification of enhanced absorption by $^{16}\text{O}_3$ lines around $5\ \mu\text{m}$ in high-resolution FTIR solar spectra

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Abstract

A set of previously unpredicted $^{16}\text{O}_3$ strong absorption lines in the $5\ \mu\text{m}$ region are identified for the first time in balloon-borne high-resolution ($0.003\ \text{cm}^{-1}$) solar spectra. These spectral features are consistent with recent ozone laboratory spectra, and are interpreted by accidental resonance effects. Some of the lines are also observed in high-resolution ground-based spectra.

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1. Introduction

Analysis of high-resolution balloon-borne and ground-based infrared solar absorption spectra continues to reveal previously unknown features of the atmospheric spectrum. In particular, studies in the $5\ \mu\text{m}$ region at $0.003\ \text{cm}^{-1}$ resolution led to the first identification of stratospheric ozone lines of the isotopic species $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ [1], $^{16}\text{O}^{16}\text{O}^{17}\text{O}$ and $^{16}\text{O}^{17}\text{O}^{16}\text{O}$ [2]

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and isotopic and hot band OCS lines [3]. These studies originated from the ongoing work on the University of Denver (DU) Stratospheric Infrared Atlas [4], with corresponding analysis of laboratory spectra obtained at the Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA) laboratory at Reims in collaboration with the Laboratory of Theoretical Spectroscopy, Tomsk, Russia, and at the DU Atmospheric Spectroscopy Laboratory, in collaboration with the Laboratoire de Photophysique Moléculaire (LPPM), Orsay, France.

In the present study we report the observation and interpretation of unusually strong $^{16}\text{O}_3$ lines in the $5\ \mu\text{m}$ region, which have not been accounted for previously and are not in the HITRAN spectroscopic database, either the HITRAN 2000/2001 or 2004 editions [5–7]. Recent studies of enhanced intensities of ozone lines due to accidental vibration-rotation resonances [8] were extended here for the interpretation of the newly observed lines, and provide complete explanation of positions and intensities. The identification and interpretation of these lines contribute to a more complete understanding of the atmospheric infrared spectrum.

2. Data and analysis

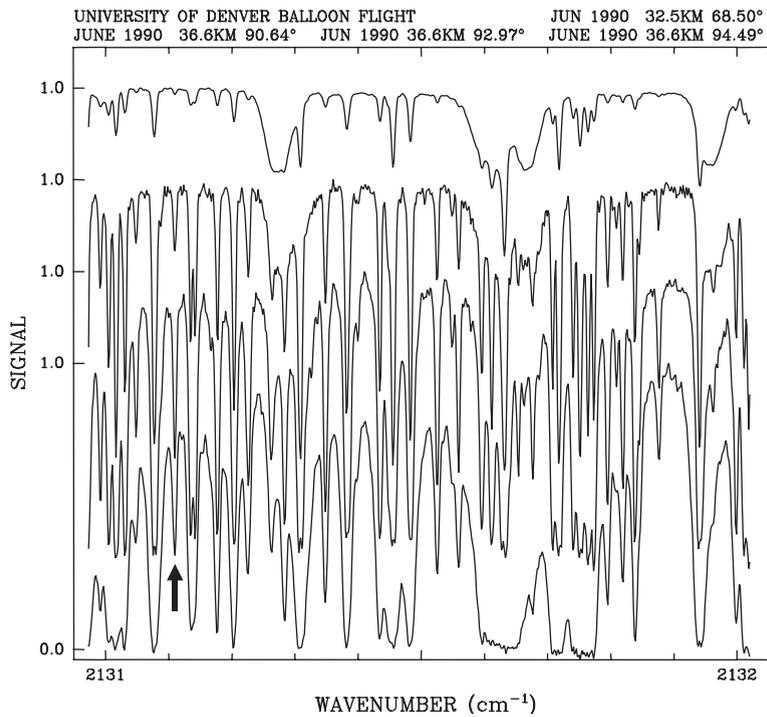
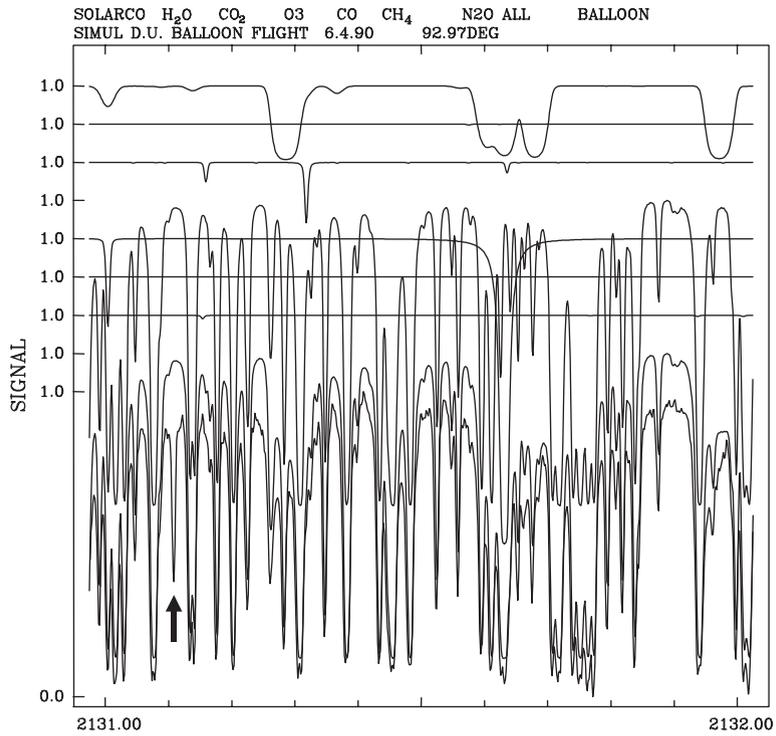
The balloon-borne solar spectra ($0.003\ \text{cm}^{-1}$ resolution) were obtained by the University of Denver during a June 4, 1990 flight, covering the $1600\text{--}2300\ \text{cm}^{-1}$ region, from float altitude near 37 km. During the continuing atlas work [4] we have identified two unexpectedly strong line features, observed at 2131.1098 and $2066.1857\ \text{cm}^{-1}$. By comparisons to ^{17}O and ^{18}O enriched ozone DU laboratory spectra of the type discussed by Perrin et al. [9] and on the basis of the behavior of the features in the balloon-borne spectra as a function of the optical path through the stratospheric ozone layer, it was concluded that these are $^{16}\text{O}_3$ lines. This conclusion was confirmed using measurements and analysis of ^{18}O enriched ozone spectra performed by the Reims team [10], which led to the quantum mechanical interpretation of the line transitions.

Typical observed spectra in the $2131\text{--}2132$ and $2066\text{--}2067\ \text{cm}^{-1}$ are shown in the bottom parts of Figs. 1 and 2, respectively, with solar zenith angles near 68.5° , 90.5° , 93° and 94.5° . The tangent altitudes for the two low sun scans are near 28 and 18 km, respectively.

Figs. 1 and 2 also show (top parts) the corresponding molecule-by-molecule simulated spectra in comparison with the 93° scan (lowest trace), for which the stratospheric ozone absorption is largest in the observed spectra. These simulations were prepared using the HITRAN 2004 line parameters [7].

The $2131.1098\ \text{cm}^{-1}$ line is completely isolated, with its immediate neighborhood dominated by “normal” $^{16}\text{O}_3$ lines, some solar CO lines, and a few weak CO_2 and N_2O lines. Simulation for the same interval with the HITRAN 2001 database [5] show no observable differences in the spectral features.

Fig. 1. Bottom: Selected scans from the DU June 4, 1990 balloon flight in the $2131\text{--}2132\ \text{cm}^{-1}$, where the enhanced $^{16}\text{O}_3$ line at $2131.1098\ \text{cm}^{-1}$ occurs (marked with an arrow). The spectra were obtained from balloon altitudes and solar zenith angles listed at the top of the figure. The upper trace is a coadded set of high sun spectra. Top: Spectral simulations for the $2131\text{--}2132\ \text{cm}^{-1}$ for 92.97° scan, using the HITRAN 2004 [7] database. The simulated molecular components, listed at the top line of the frame from left to right, are plotted from top to bottom. The last two traces are the combined simulation of all the molecular species and the observed spectrum, respectively.



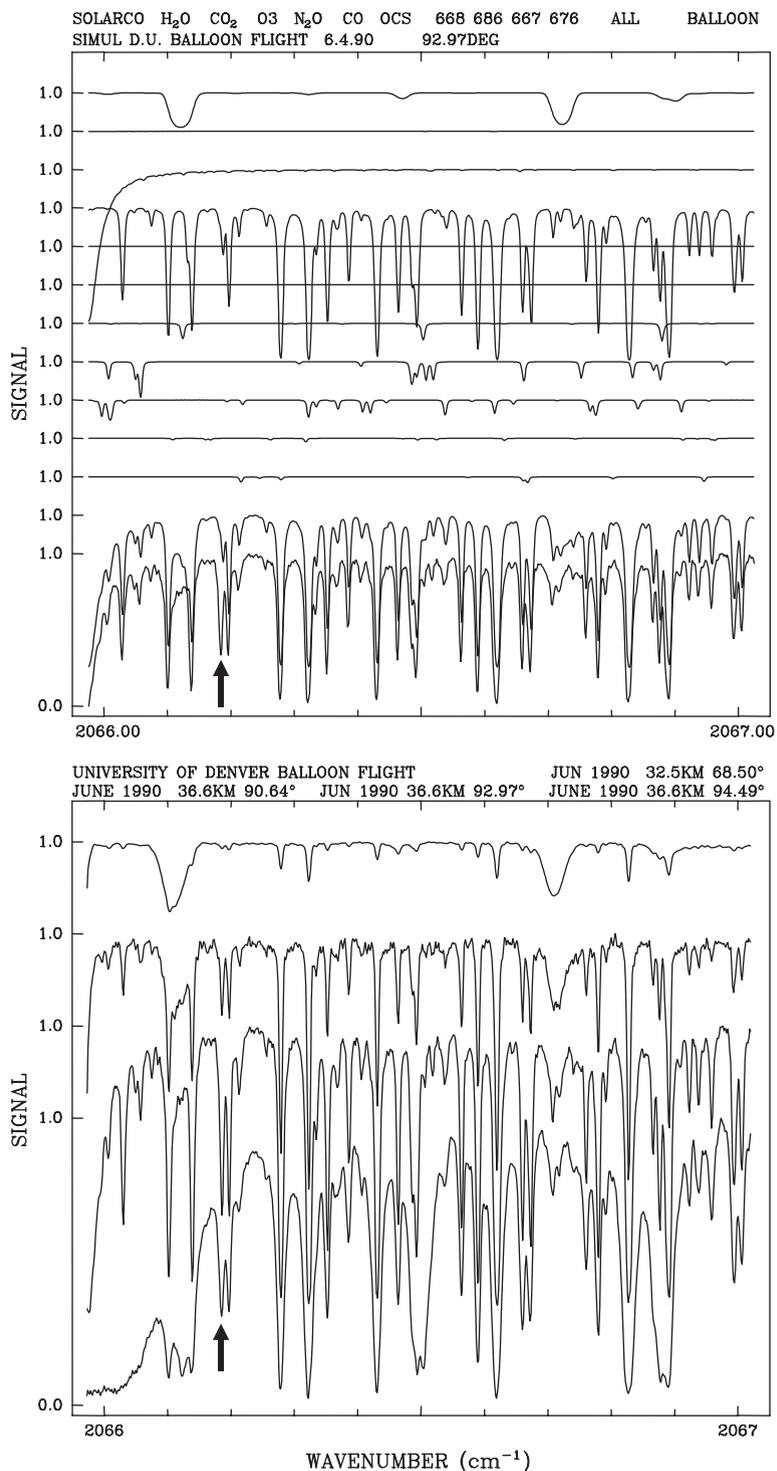


Fig. 2. Similar to Fig. 1, but for the 2066–2067 cm⁻¹ region where the 2066.1857 cm⁻¹ enhanced ¹⁶O₃ line occurs (marked with an arrow).

The 2066.1857 cm^{-1} line is also well resolved, but occurs in a more complicated interval, with nearby lines of “normal” $^{16}\text{O}_3$ lines, solar CO, CO_2 , OCS, and isotopic ozone lines of $^{16}\text{O}^{16}\text{O}^{18}\text{O}$, $^{16}\text{O}^{18}\text{O}^{16}\text{O}$, $^{16}\text{O}^{16}\text{O}^{17}\text{O}$, and $^{16}\text{O}^{17}\text{O}^{16}\text{O}$ (similar to the spectra and simulations shown in the OCS study by Goldman et al. [3]). The HITRAN 2000/2001 database [5] did not include the above isotopic ozone lines, but preliminary versions of these lines were used in Refs. [1,2]. The HITRAN 2004 compilation includes a newer version of these isotopic lines which show some differences in the simulations for this region compared with the new Reims lines for $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}^{18}\text{O}^{16}\text{O}$. For example, see Fig. 2, top, and Fig. 3, bottom, near 2066.00 cm^{-1} .

In the present study, it was established, by extending the analysis used for the Spectral and Molecular Properties of Ozone (S&MPO, available at <http://ozone.univ-reims.fr> or <http://ozone.iao.ru>) [11,12] to higher ΔK_a values, that the lines in question are $2\nu_1$ $^{16}\text{O}_3$ lines with $\Delta K_a = 5$ (in previous calculations ΔK_a max was 4). The line at 2131.1098 cm^{-1} is due to the R transition 38 0 38 (200) \leftarrow 37 5 33 (000). Lines with such a large change of the K_a quantum number would normally be extremely weak for the ozone molecule and not observable, but in this particular case, due to accidental resonance between the energy levels 38 0 8 (200) at 2801.1188 cm^{-1} and 38 5 34 (101) at 2801.2125 cm^{-1} , there is a large mixing between the two corresponding wavefunctions, leading to significantly enhanced intensity. The line observed at 2066.1857 cm^{-1} is the corresponding P transition 38 0 8 (200) \leftarrow 39 5 35 (000) and the normally weak (but observable) intensity is enhanced significantly. The calculated intensities of these two lines are, respectively, 6.76×10^{-23} and $5.43 \times 10^{-23} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$ at 296 K.

It is important to note that this accidental resonance was implicitly taken into account by the theoretical modeling of Reims laboratory spectra [13], and no additional term had to be added to the Hamiltonian for precise reproduction of positions and intensities of the corresponding transitions. It should be noted that it is only in this spectral region that lines due to $\Delta K_a > 4$ appear.

Several other enhanced $^{16}\text{O}_3$ lines were predicted [13] and observed, which are due to completely different types of resonances. Standing out is an isolated, medium intensity, $^{16}\text{O}_3$ line observed at 2134.0723 cm^{-1} , where previous simulations predicted no lines. A line at 2124.3634 cm^{-1} is observed with significantly enhanced intensity compared to previous predictions. These lines are due to the $3\nu_2$ band, and are in accidental Coriolis resonance with $\nu_1 + \nu_3$. The 2124.3634 “line” is actually an unresolved overlap of a “normal”, weaker line and the newly calculated line.

The Reims–Tomsk ozone database (S&MPO) is thus currently being extended¹ to include such lines, and incorporated in our new modeling of the observed spectra. Fig. 3 shows simulated spectra in the 2131–2132 and 2066–2067 cm^{-1} using the HITRAN 2004 database with the $^{16}\text{O}_3$, $^{16}\text{O}^{16}\text{O}^{18}\text{O}$, and $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ lines replaced by the Reims ozone database. The newly calculated Reims lines agree well with the observed atmospheric lines, showing the appropriate intensities for all the enhanced 5 μm lines observed in the atmospheric spectra, as well as for other lines in the wider region of 1900–2300 cm^{-1} of the laboratory spectra [13].

Some of the enhanced $^{16}\text{O}_3$ lines can also be observed in ground-based high-resolution FTIR solar spectra with sufficiently large solar zenith angles. Thus, spectra taken at Mauna Loa, Hawaii, USA, at zenith angles of $\sim 70^\circ$ show weak absorption of the isolated 2131.1098 cm^{-1} line.

¹A new release of the S&MPO will be available for public access via Internet by the end of 2004.

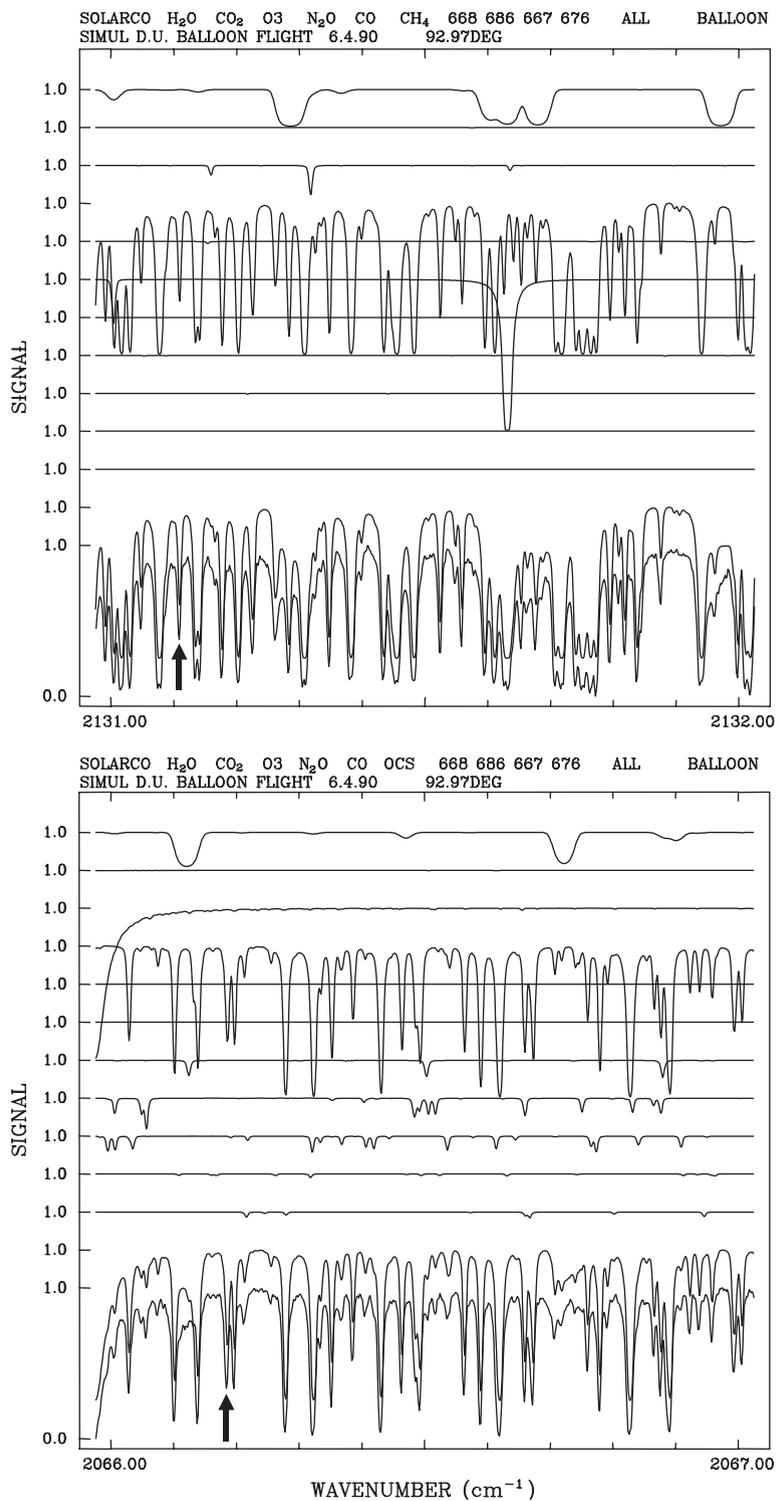


Fig. 3. Repeat of the simulations from Figs. 1 and 2, now with the ozone-revised database (this work).

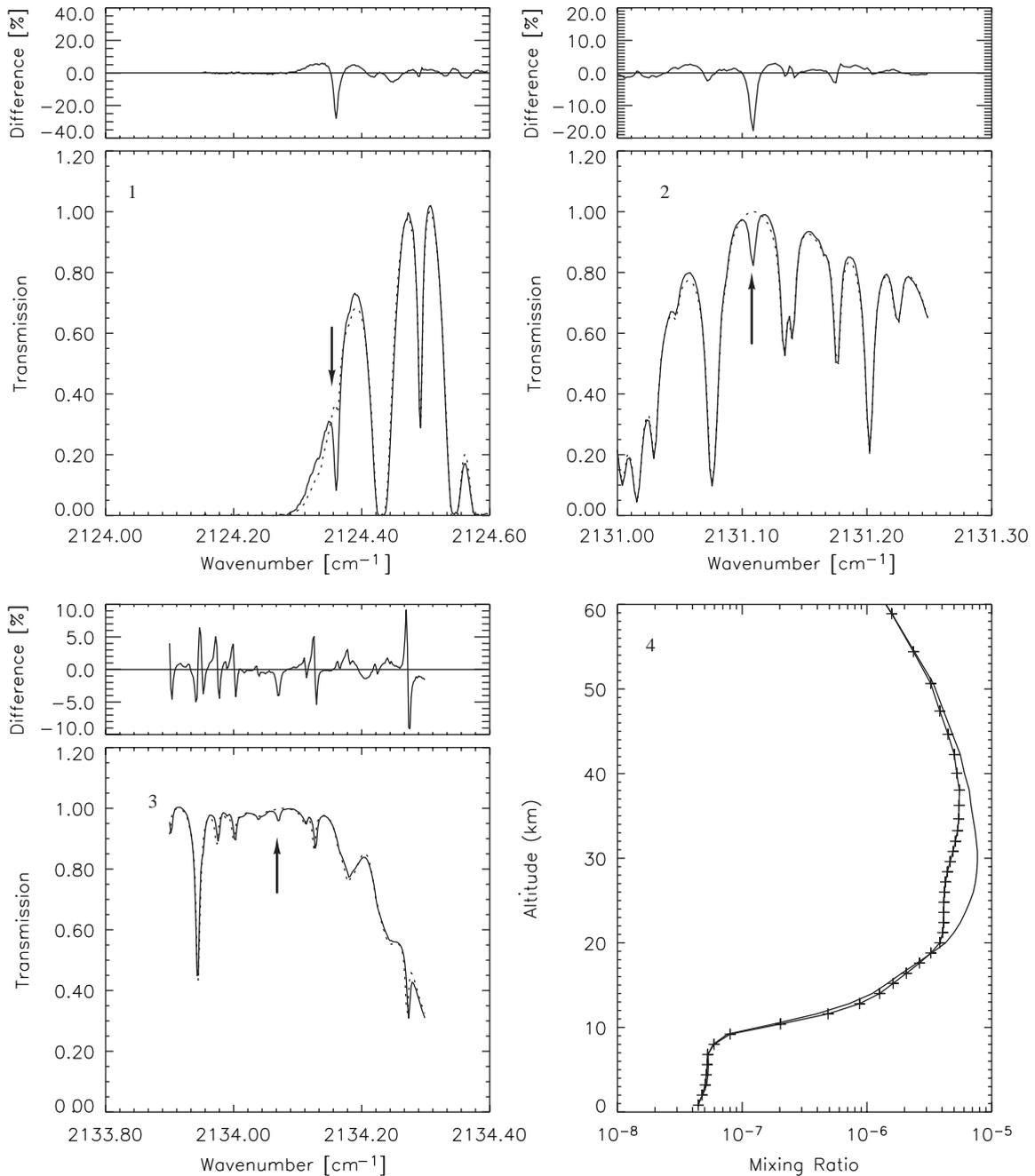


Fig. 4. Spectral least-squares fitting in the 2124.3, 2131.1 and 2134.1 cm^{-1} microwindows around three of the enhanced $^{16}\text{O}_3$ lines. Panel-pairs 1–3 show the observed (solid line), calculated (dotted line), and the difference (upper plot) spectra. Panel 4 shows the a priori (unmarked line) and retrieved O_3 vertical profiles. The 0.003 cm^{-1} resolution spectra were obtained on 7 March, 2003 at Thule, Greenland, at a solar zenith angle of 85.5° . Line parameters are from the HITRAN 2004 database [7].

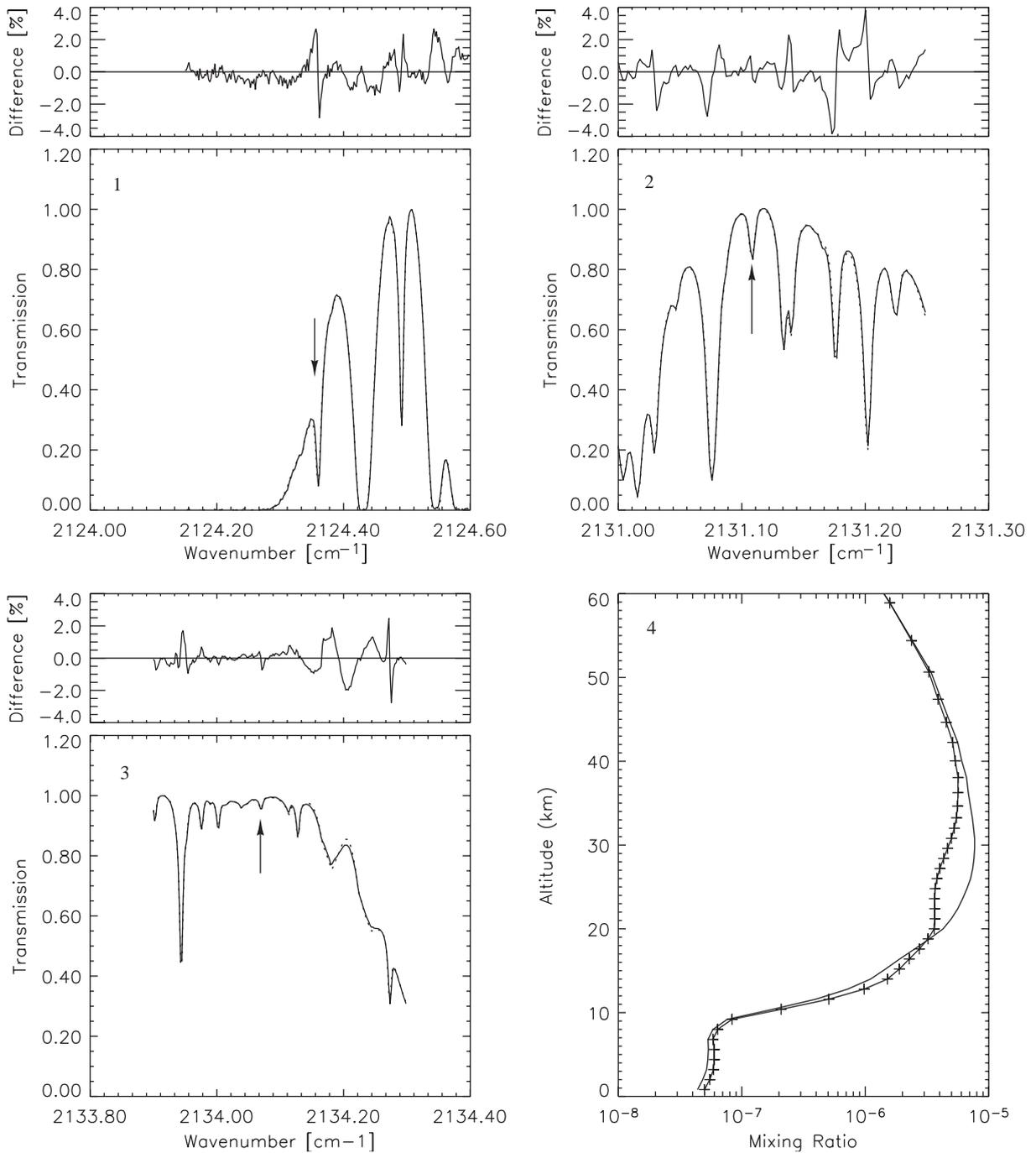


Fig. 5. Similar to Fig. 4, but with the ozone-revised database (this work).

Fig. 4 shows a simultaneous fit to the three features at 2124.36, 2131.11 and 2134.07 cm^{-1} (panels 1–3) and the retrieved O_3 profile using an iterative optimal estimator technique and the HITRAN 2004 line parameters. The spectrum was recorded on 7 March, 2003 from the Network for the Detection of Stratospheric Change (NDSC) site in Thule, Greenland at a solar zenith angle of 85.5° . The calculated spectrum also includes an updated semi-empirical solar spectrum (F. Hase, private communication 2004). The fits reveal not only the obvious absence of the resonance lines but a poor fit to many of the other O_3 lines. Note the poor fit to the background in panels 1 and 2 and the wavenumber shifts of most of the features in panel 3. Using identical fitting parameters and constraints but replacing the HITRAN 2004 O_3 lines with the Reims lines, Fig. 5 shows an overall improvement in all three microwindows. This is evident in the different plots, where the rms values are reduced from 10% to 2.3%. Some discrepancies still exist but the new line parameters would improve the precision of the total column retrieved from these individual intervals by a factor of 2–4.

3. Conclusions

A number of unexpectedly strong absorption features of $^{16}\text{O}_3$ have been identified in high-resolution balloon-borne atmospheric solar spectra and in spectra from ground-based observations in the $5\ \mu\text{m}$ region. High-resolution laboratory spectra and theoretical calculations of the enhanced intensities on the basis of accidental resonances provide quantitative interpretation of these lines. Together with the previously identified $^{16}\text{O}^{16}\text{O}^{18}\text{O}$, $^{16}\text{O}^{18}\text{O}^{16}\text{O}$, $^{16}\text{O}^{16}\text{O}^{17}\text{O}$, and $^{16}\text{O}^{17}\text{O}^{16}\text{O}$ lines, the spectroscopic identification of previously unexplained ozone features is closer to completion.

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