# ATLAS OF VERY HIGH RESOLUTION STRATOSPHERIC IR ABSORPTION SPECTRA

Volume I. Line Positions and Identifications

July, 2007 Edition

A. Goldman, R.D. Blatherwick, J.J. Kosters
F.J. Murcray and D.G. Murcray

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DIVISION OF ATMOSPHERIC SCIENCES
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(continued)

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PREFACE TO THE JULY, 2007 EDITION

This preface describes the current additions to the previous edition (May, 2005) of the Atlas of Very High Resolution Stratospheric IR Absorption Spectra.[109]

In the present edition, we have added 30 new frames covering the 1870-1930 $cm^{-1}$ region, thus bringing the total number of spectral features identified as genuine to over 14,400. Data for this region were recorded during sunset flight from Palestine, TX on June 4, 1990.

This spectral region is dominated by $CO_2$, $O_3$, $N_2O$, NO and $COF_2$, along with the $H_2O$ lines. The high resolution shows numerous features that are better resolved than in any previous atmospheric spectra, especially for $O_3$, $N_2O$, NO and $COF_2$ lines.

Most of the observed line parameters agree within a fraction of the resolution element with the latest line parameters.[100] Only few features remain unidentified. Table I, which lists the stronger of the unidentified lines, has been extended to include the new spectral region, which are in the 1890-1930 $cm^{-1}$ region.

Recent updates of the line parameters for the $HNO_3$ $v_5/2v_9$ bands[110] prompted us to work on the 860-880 $cm^{-1}$ region. This region was not included in previous atlas editions due to deficiencies in the theoretical modeling of the lines. The new line parameters have been incorporated into the study of both our atmospheric and laboratory spectra.

The study of the 1870-1960 $cm^1$ region is in continuation of our previous atlas studies of the 5 μm region, which continues to present spectroscopic surprises, regarding OCS,[71] $O_3$,[93] and their isotopic and hotbands lines. This region also includes numerous $COF_2$ lines from the $v_1$ band, which exhibit disagreements in relative intensities compared to the spectroscopic database.[100] The atmospheric $CO_2$, $N_2O$, and NO lines in this region are in very good agreement with the theoretical predictions.

For the analysis of solar lines for the atlas we continue to use the new solar atlas being developed by Hase et al.,[96,111] which models well all the known solar lines in the IR. Indeed, all the solar lines observed in the 1870-1960 $cm^{-1}$ region – solar CO, SiI, FeI, CaI, MgI, AlI, as well as the HI(6-10) line at 1949.825 $cm^{-1}$, are represented well in this model.

Related to the atlas work we continued the analysis and intercomparisons of high resolution solar absorption spectra obtained from the Network for the Detection of Atmospheric Composition Change (NDACC) sites [formerly the Network for the Detection of Stratospheric Change (NDSC)]. Representative recent publications are given in Refs. 112-114. Our NDSC involvement includes the continuing development and users support of the codes used by most NDSC science groups for the quantitative analysis of the observed ground-based solar spectra. The codes and the related spectroscopic database reside at DU and updated release are provided periodically.

As described in the previous edition,[109] work is in progress in collaboration with A. Perrin previously at LPMA, now at LISA, France on the spectroscopic analysis of the DU laboratory spectra of the $\nu_3$ region of HCOOH (centered at 1776.83 $cm^{-1}$).

The analysis of our stratospheric and laboratory spectra also continue to serve as a useful guide in the interpretation of recent aircraft and satellite borne IR atmospheric spectra, such as TES and ACE. Representative recent publications are given in Ref. 115-118.

In a recent study we have improved significantly parameters of the $N_2$ quadrupolar lines in the 4.2 μm region.[119] These lines have been long expected to provide a quantitative standard in the analysis of atmospheric IR spectra from all altitude regimes, but significant inconsistencies persisted. Our study of the improved line intensities continues, and will be also extended to the linewidths.[120]

Work is continuing in the 780-790 $cm^{-1}$, 860-880 $cm^{-1}$, 1930-1960 $cm^{-1}$, 2034-2040 $cm^{-1}$, 2060-2080 $cm^{-1}$ and 2100-2108 $cm^{-1}$ regions.

## PREFACE TO THE MAY, 2005 EDITION

This preface describes the current additions to the previous edition (September, 2002) of the Atlas of Very High Resolution Stratospheric IR Absorption Spectra.[94]

In the present edition, we have added 41 new frames covering the 790-800 $cm^{-1}$, 1470-1520 $cm^{-1}$, and 2118-2140 $cm^{-1}$ regions, thus bringing the total number of spectral features identified as genuine to over 13,300. Data for the 790-800 and 2128-2140 $cm^{-1}$ regions were recorded during sunset flights from Palestine, TX on June 6, 1988 and June 4, 1990 respectively. Data for the 1470-1520 $cm^{-1}$ region were recorded during a sunset flight from Ft. Sumner, NM on April 19, 1989 and a sunrise flight from Palestine, TX on June 17, 1991.

Table I, which lists the stronger of the unidentified lines, has been extended to include the new spectral regions. The few newly listed lines are in the 790-800 and 2120-2140 $cm^{-1}$ regions which are dominated by ozone lines.

The 790-800 $cm^{-1}$ region is dominated by $^{16}O_3$ lines from the $\nu_2$ and $2\nu_2$-$\nu_1$ bands, along with $CO_2$ lines, a few weak $NO_2$ $\nu_2$ band lines, weak $COF_2$ $\nu_6$ band lines, and a number of possible $HNO_3$ lines. The $CO_2$ Q-branch of the (11101) - (10002) band [in the notation v' - v" with v = ($v_1$ $v_2^{\ell}$ $v_3$ r)], around 791.45 $cm^{-1}$ is quite prominent in the atlas spectra, and is fully resolved in the high sun spectra, showing more details than any previous atmospheric spectra. A number of solar OH lines[55] also appear in this region.

The region from 1470 to1520 $cm^{-1}$ mainly contains features of $H_2O$, HDO, $CH_4$, several $O_2$ eq (electric quadrupole) and md (magnetic dipole) lines,[51] and solar lines due to CO, MgI, and SiI. The atlas spectra indicate that some of the theoretical $O_2$ line positions are shifted from the observed by more than 0.02 $cm^{-1}$, such as in the case of md lines at 1504.6133, 1508.5584, and 1516.5927 $cm^{-1}$. Further study of the line parameters is in progress.

The 2118-2140 $cm^{-1}$ interval is heavily dominated by $^{16}O_3$ from a number of bands, the strongest being the $\nu_1 + \nu_3$, but with no observable features of isotopic ozone lines. Additional features are due to $H_2O$, $CO_2$, atmospheric CO, $N_2O$, and solar CO lines.
In earlier editions of the Atlas, the study of the 5μm region revealed previously unidentified features of isotopic ozone lines[58,86] and isotopic and hot band OCS lines.[71] The ongoing work in this region recently showed unusually strong $^{16}O_3$ lines which have not been accounted for in any previous study and are interpreted by accidental resonance effects.[95] Particularly strong lines of this type are seen at 2066.1857, 2124.3634, 2131.1098 and 2134.0723 $cm^{-1}$. The 2118-2140 $cm^{-1}$ region added to the current edition includes these $^{16}O_3$ lines. The study of these resonance transitions is being extended to other spectral regions of ozone.

The analysis of solar lines for this atlas edition has been extended by the use of the new solar atlas being developed by Hase et al.,[96] which models well all the known solar lines in the IR.

The atlas and laboratory spectra studies continue to be essential in improving the spectroscopic database for atmospheric trace gases.

We recently obtained high resolution (0.002 $cm^{-1}$) laboratory spectra of HCOOH (formic acid) in the $\nu_3$ region (centered at 1776.83 $cm^{-1}$). This band is of sufficient intensity to be significant in atmospheric spectra, and line parameters for this band will extend our recent studies on laboratory and atmospheric HCOOH in the $\nu_6$ region (centered at 1104.85 $cm^{-1}$).[72,97,98] Work is in progress in collaboration with A. Perrin of LPMA France on the spectroscopic analysis of the laboratory spectra.

The updated HITRAN database[99-102] includes a number of contributions based on our atlas work. The newly discovered strong $^{16}O_3$ lines mentioned above[95] will be included in future editions. Other aspects of the database include the update of cross sections of heavy molecules that appear in the atmospheric spectra,[103] and updated partition functions,[104] and Einstein A-coefficients corresponding to HITRAN line intensity parameters.[105]

Other continuing studies related to findings from the Atlas work include the analysis and intercomparisons of high resolution solar absorption spectra obtained from the Network for the Detection of Stratospheric Change (NDSC) sites. Representative recent publications are given in Refs. 106-108.

Work is continuing in the 780-790 $cm^{-1}$, 2034-2040 $cm^{-1}$, 2060-2080 $cm^{-1}$ and 2100-2108 $cm^{-1}$ regions.

# PREFACE TO THE SEPTEMBER, 2002 EDITION

This preface describes the current additions to the previous edition (October, 2000) of the Atlas of Very High Resolution Stratospheric IR Absorption Spectra.[83]

In the present edition, we have added 30 new frames covering the 810-840 $cm^{-1}$, 900-920 $cm^{-1}$ and 2108-2118 $cm^{-1}$ regions, thus bringing the total number of spectral features identified as genuine to over 11,800. Data for this new edition were recorded during the balloon flight made from Palestine, Texas, on June 6, 1988 and June 4, 1990. Both flights were sunset flights.

Table I, which lists the stronger of the unidentified lines, has been extended to include the new spectral regions. Most of the newly listed lines are weak.

In the region 810-840 $cm^{-1}$ we identified previously unresolved $O_3$ lines and a large number of weak features that are due to $NO_2$ $\nu_2$ lines. Many of the $NO_2$ features are uncertain and are listed with a "?". The $CO_2$ Q-branch (v'-v") = (12201-11102) lines near 828.25 $cm^{-1}$ are well resolved in the spectra, with some overlapping $O_3$ lines. No ClO features, except possibly one, at 831.9545 $cm^{-1}$, are identified in these midlatitude spectra, but the interfering lines at the expected ClO positions are cataloged in the atlas. The $2\nu_6$ Q-branch of $CHF_2{}^{35}C\ell$ (HCFC-22) at 829.054 $cm^{-1}$ is isolated from its neighboring $CO_2$ lines, and is consistent with the $\nu_4$ Q-branch at 809.1 $cm^{-1}$ discussed in section B of the Description of the Atlas (we are using the more recent assignments of $2\nu_6$ and $\nu_4$ instead of the previous $2\nu_2$ and $\nu_7$ respectively). A small contribution of the $HNO_3$ $3\nu_9$-$\nu_9$ Q-branch near 830.3 $cm^{-1}$ is also observed. This region includes several solar emission lines and solar OH lines, originally discovered during our earlier atlas work at DU.

The region 900-920 $cm^{-1}$ is dominated by numerous $HNO_3$ lines from the $\nu_5/2\nu_9$ bands. The atlas high resolution (0.003 $cm^{-1}$), enabled the identification of many resolved $HNO_3$ features which are not accounted for by theoretical line positions.[63] The frames in this region are expanded in amplitude, for a clearer display of the $HNO_3$ lines. Further laboratory spectra and theoretical analysis are required for these bands. A few $CO_2$ lines, mostly overlapping with $HNO_3$ lines, are listed. A number of solar OH lines are evident in these spectra. In the 918-920 $cm^{-1}$ region, the larger zenith angle scans show that the $HNO_3$ lines are superimposed on $CC\ell_2F_2$ lines in the lower stratosphere. Q-branch lines of $CC\ell_2F_2$ $\nu_8$ region are evident in the spectra near 919.8 $cm^{-1}$.

The atlas work in the above two regions aided in the study of the spectral species considered in the recent study[84] of $SF_6$ and $SF_5CF_3$.

In the region 2108-2118 $cm^{-1}$ we identified, for the first time, a large number of isotopic ozone lines due to the $^{16}O^{16}O^{17}O$ and $^{16}O^{16}O^{18}O$ species in the $\nu_1$+$\nu_3$ bands. Many of these isotopic lines are completely resolved from the main isotope $^{16}O_3$. This study was aided by our laboratory study of isotopic ozone , and the results are described in recent publications.[85,86] These findings are consistent with our previous identification of $^{16}O^{16}O^{17}O$, $^{16}O^{17}O^{16}O$ $\nu_3$ lines in the 996-998 $cm^{-1}$ and 1000-1002 $cm^{-1}$ intervals (see preface to the 1998 edition). The 2108-2118 $cm^{-1}$ region is also rich in solar CO lines, and also shows known atmospheric $CO_2$ lines.

The atlas and laboratory spectra studies continue to be essential in improving the spectroscopic database for atmospheric trace gases. Recent summary of the atlas work and the laboratory studies was presented.[87]

We recently obtained high resolution laboratory spectra of the main bands of $COC\ell_2$, the strongest being $\nu_5$ around 851.01 $cm^{-1}$ and $\nu_1$ around 1828.2 $cm^{-1}$ (A. Goldman and T.M. Stephen, 2001 and 2002, unpublished). These spectra were used to confirm the tentative identification of the $\nu_5$ band in atmospheric spectra, and are being used further for line parameters analysis.[88]

Our theoretical line intensity calculations for the $a^1\Delta_g$ - $X^3\Sigma_g^-$ (0,0) 1.27μm band of $O_2$, based on an earlier work,[50] provided significant improvement in the modeling of the atmospheric absorption in this region (G.C. Toon and A. Goldman, 2001, unpublished; study in progress). The interest in this band has increased recently due to its role in accurate measurements of atmospheric $CO_2$.

Continuing contributions to the HITRAN database relying on findings from the atlas work include the weak isotopic ozone lines mentioned above.[86] Other aspects of the database include an update of cross-sections of heavy molecules that appear in the atmospheric spectra.[89]

Other continuing studies related to findings from the Atlas work include the analysis and intercomparisons of high resolution solar absorption spectra obtained from the Network for the Detection of Stratospheric Change (NDSC) sites. Representative recent publications are given in Refs. 90-92.

Atlas related studies are essential in establishing global spectral consistency of modeling various atmospheric bands of different molecules. A typical study still in progress was presented by Goldman et al.,[82] and continues on the basis of new laboratory results.[93]

Work is continuing in the 790-800 $cm^{-1}$, 2034-2040 $cm^{-1}$ and 2070-2080 $cm^{-1}$ regions.

## PREFACE TO THE OCTOBER, 2000 EDITION

This preface describes the current additions to the previous edition (June, 1998) of the Atlas of Very High Resolution Stratospheric IR Absorption Spectra.[70]

In the present edition, we have added 25 new frames covering the 1180-1220 $cm^{-1}$ and 1230-1240 $cm^{-1}$ regions, thus bringing the total number of spectral features identified as genuine to over 9500. Data for this new edition were recorded during the June 6, 1988 sunset balloon flight made from Palestine, Texas.

In these frames, one can recognize a number of $O_3$ and $COF_2$ features consisting of overlapping transitions, for which the theoretical line positions need improvements (of the order of 0.003 $cm^{-1}$, exceeding the resolution magnitude of the spectra). Also, some of the theoretical line parameters for weak absorptions by $CH_4$ and $HNO_3$ do not fit the data within this magnitude.

Table I, which lists the stronger of the unidentified lines, has been extended to include the new spectral regions. The unidentified lines in the 2020-2060 $cm^{-1}$ regions (introduced in the June 1998 edition) are still considered as due to isotopomers of the ozone molecule. In the newly introduced regions, a number of relatively strong features near 1234 and 1238 $cm^{-1}$ could be of yet unidentified lower and upper stratospheric source, respectively.

In the 2040-2070 $cm^{-1}$ region we identified and quantified several $\nu_3$ $^{16}O^{12}C^{34}S$ and $\nu_3+\nu_2-\nu_2$ $^{16}O^{12}C^{32}S$ lines among the $\nu_3$ $^{16}O^{12}C^{32}S$ lines.[71] These weak, but important, lines were previously observed and marked as "unidentified" in our atlas.[70]

The atlas and laboratory spectra studies continue to be essential in improving the spectroscopic database for atmospheric trace gases.

For better quantification of HCOOH from the 1105 $cm^{-1}$ Q-branch, we have generated new spectral line parameters for the $\nu_6$ band of HCOOH using our high resolution laboratory spectra. This study[72] also showed that the previously neglected HDO strong line in this region needs to be included in the analysis.

In the 2μ region, we have used new DU 0.002 $cm^{-1}$ resolution laboratory spectra of $NO_2$, and completed new analysis of the $2\nu_1-\nu_3$ and $3\nu_3$ bands for spectroscopic constants and spectral line parameters.[73]

Our continuing investigation of the $O_2$ line parameters lead to the resolution of a widespread misinterpretation in the application of the $a^1\Delta_g$ $X^3\Sigma_g^-$ 1.27μ emission to upper atmosphere measurements.[74]

In order to improve the quantitative analysis of the atmospheric spectra, the calculations of the partition functions and weighted transition moments squared listed in the spectroscopic databases[75] have been reviewed in detail.[76] Corrections found needed for a number of molecules, including NO, OH, ClO, HCN, $NO_2$ and $ClONO_2$, are presented in that study.[76]

Additional line parameters work has been completed for the OH $A^2\Sigma^+-X^2\Pi$ bands,[77] extending our previous work to higher v transitions, applicable to atmospheric and astrophysical spectra.

Studies closely relying on findings from the Atlas work include analysis and intercomparisons of high resolution solar absorption spectra obtained from Network for the Detection of Stratospheric Change (NDSC) sites. Representative publications are given in Refs. 78-80.

Atlas related studies are essential in establishing global spectral consistency of modeling various atmospheric bands of different molecules. A typical study in progress is presented by Goldman et al.[81]

Work is continuing in the 2034-2040 $cm^{-1}$ and 2070-2080 $cm^{-1}$ regions.

Work has started on extension of the atlas to the 810-840 $cm^{-1}$ region, where important features, including those of ClO, have not been fully classified yet.

## PREFACE TO THE JUNE, 1998 EDITION

This preface describes the current additions to the previous edition (March, 1997) of the Atlas of Very High Resolution Stratospheric IR Absorption Spectra.[60]

In the present edition, we have added 9 new frames covering the regions 996-998 $cm^{-1}$, 1000-1002 $cm^{-1}$ and 2024-2034 $cm^{-1}$, thus bringing the total number of spectral features identified as genuine to over 7500. Data for this new edition were recorded during balloon flights from Palestine, Texas, on June 6, 1988 and June 4, 1990. Both flights were sunset flights.

In the region 2024-2034 $cm^{-1}$, the work from the previous atlas edition[60] was continued, with special attention to the isotopic ozone lines[58], due to $^{16}O^{18}O^{16}O$ and $^{16}O^{16}O^{18}O$ $\nu_1$+$\nu_3$, 2$\nu_1$ and 2$\nu_3$ transitions. The solar lines in this region were identified as described previously[60].

Table I, which lists the stronger of the unidentified lines, has been extended to include the new spectral regions. Many of the yet unidentified lines in the 2020-2060 $cm^{-1}$ regions are probably due to isotopomers of the ozone molecule.

Work is continuing in the 2034-2040 $cm^{-1}$ and 2070-2080 $cm^{-1}$ regions.

In the regions 996-998 $cm^{-1}$ and 1000-1002 $cm^{-1}$, the $\nu_3$ lines of $^{16}O^{17}O^{16}O$ and $^{16}O^{16}O^{17}O$ were identified for the first time in the balloon spectra[61]. The very high resolution of these spectra allows numerous line features to be analyzed. For clarity, these intervals are presented in 1 $cm^{-1}$ frames (with the corresponding 1 $cm^{-1}$ tables), instead of the usual 2 $cm^{-1}$ frames. It should be noted that at the time of the initial atlas work in this region[4] the incomplete knowledge of the isotopic ozone spectroscopy allowed only the identification of $^{16}O^{18}O^{16}O$ and $^{16}O^{16}O^{18}O$ lines. All the previous results for these intervals were replaced in the new edition.

Extension work of these intervals is in progress.

The investigation of the $O_2$ continuum in the $X^3\Sigma_g^-(v'')$ - $X^3\Sigma_g^-(v')$, $a^1\Delta_g(v')$, $b^1\Sigma_g^+(v')$ bands, showing the importance of pressure-induced absorption bands near 1$\mu$ reported earlier[51,53,54] has been extended to provide semi-empirical modeling of these bands in atmospheric spectra[62].

The atlas and laboratory spectra studies have been essential in improving the spectroscopic database for atmospheric trace gases. Thus, recent spectroscopic reviews have been prepared for several molecules, including $O_2$,[51] $HNO_3$,[63] $ClONO_2$,[64] NO[65] and $NO_2$.[66] A number of line parameters sets have been significantly improved for modeling high resolution atmospheric spectra, including $O_2$,[51] HBr,[67] HI[68] and $HNO_3$.[69] The HBr and HI parameters now include hyperfine structure splitting, which is evident in high resolution spectra.

Recognizing the significant atmospheric spectral features of several weaker $HNO_3$ bands,[63] the new spectroscopic analysis of the $\nu_8$+$\nu_9$ band,[69] centered at 1205 $cm^{-1}$, is important for a more consistent understanding of $HNO_3$. It is also important for quantifying other atmospheric molecules in this region.

Atlas frames in the 1200-1210 $cm^{-1}$ are in progress.

## PREFACE TO THE MARCH, 1997 EDITION

This preface describes the current additions to the recent previous edition (October, 1994) of the Atlas of Very High Resolution Stratospheric IR Absorption Spectra.

For the present edition, we have added 27 new frames covering the regions 1520-1540 $cm^{-1}$, 1610-1620 $cm^{-1}$, 2020-2024 $cm^{-1}$, and 2040-2060 $cm^{-1}$, thus bringing the total number of spectral features identified as being genuine to over 6500. Data for this new edition were recorded during balloon flights from Palestine, Texas, on June 4, 1990, June 17, 1991, and from Ft. Sumner, New Mexico, on April 19, 1989. The 1991 flight was a sunrise flight, while all the other flights represented in this atlas were sunset flights.

The regions 1520-1540 $cm^{-1}$, 1610-1620 $cm^{-1}$ are dominated by $H_2O$, $CH_4$ and $NO_2$, and also include electric quadrupole and magnetic dipole transitions of $O_2$. The initial intervals analyzed in the 2000-2100 $cm^{-1}$ region are dominated, in the lower stratosphere, by $O_3$, $CO_2$ and $H_2O$, and contain important features of OCS and isotopic ozone (see below).

A significant number of absorption features due to solar species are observed in the above regions, mostly solar CO ($\Delta v=1$ lines, especially strong in the 2000-2100 $cm^{-1}$ region), but there also are lines from neutral Mg, Si, Al, and Fe. The solar lines identification has been aided by the ATMOS atlas[32,47] and the updated CO line parameters[48].

A number of studies that developed on the basis of the recent atlas work are described in references 43-45, 47,49. Two review papers about the atlases work were recently given[46,52].

Additional line parameters have been generated during the atlas work, which also apply to a wider range of studies of stratospheric spectra. Subsequent to the work on the intensity problem of the magnetic dipole $O_2$ transitions[50], a comprehensive update of the $O_2$ line parameters has been conducted[51]. The $O_2$ work has been extended to include the investigation of the $O_2$ continuum in the $X^3\Sigma_g^-(v'')$ - $X^3\Sigma_g^-(v')$, $a^1\Delta_g(v')$, $b^1\Sigma_g^+(v')$ bands, showing the importance of pressure-induced absorption bands near 1µ that have been previously neglected in atmospheric studies[51,53,54].

An extensive update of the OH and NO $X^2\Pi(v'',v')$ transitions is in progress[55,56]. New spectral line parameters have been generated for the OH $X^2\Pi$-$X^2\Pi$ transitions for $\Delta v=0,...,6$, with $v'=0,...,10$, and $J_{max}=49.5$. The initial $^{14}N^{16}O$ set includes transitions for $\Delta v=0,...,5$, with $v'=0,...,14$, and $J_{max}=125.5$. HITRAN type line parameter sets with low intensity cutoffs are provided at 296 K and high temperatures (6000 K and 3000 K for OH and NO respectively). Recent theoretical and experimental improvements in line intensities and line positions have been incorporated into the calculations.

The atlas work on selected intervals in the 2000-2100 $cm^{-1}$ region furthered the previous isotopic $O_3$ work (conducted mostly in the 10µ and far infrared[57]) with both balloon-borne and ground-based FTIR solar absorption spectra in the 5µ region. The results identify numerous new spectral features of $^{16}O^{18}O^{16}O$ and $^{16}O^{16}O^{18}O$ ($\nu_1+\nu_3$, $2\nu_1$ and $2\nu_3$ lines) suitable for their atmospheric quantification as well as for identifying interfering species[58] in the analysis of other molecules.

The study of stratospheric and tropospheric OCS is best done from spectral microwindows in the $\nu_3$ band, especially in the 2040-2060 $cm^{-1}$ region[59]. The atlas work identifies in detail all the interfering species in this region.

Table I, which lists the stronger of the unidentified lines, has been extended to include the new spectral regions. Many of the yet unidentified lines in the 2020-2060 $cm^{-1}$ regions are probably due to isotopomers of the ozone molecule.

Work is continuing in the 2020-2030 $cm^{-1}$ and 2070-2080 $cm^{-1}$ regions.

## PREFACE TO THE OCTOBER, 1994 EDITION

This preface describes the current additions to the recent previous edition (April, 1993) of the Atlas of Very High Resolution Stratospheric IR Absorption Spectra.

In the present edition, we have added 25 new frames covering the region 1560-1610 $cm^{-1}$, thus bringing the total number of spectral features identified as being genuine to over 4000. Data for this new edition were recorded during balloon flights from Palestine, Texas, on June 17, 1991 and from Ft. Sumner, New Mexico, on April 19, 1989. The 1991 flight was a sunrise flight, while all the other flights represented in this atlas were sunset flights.

The region added in this new edition is dominated by $H_2O$, $CH_4$, and $NO_2$, and also includes electric quadrupole transitions of $O_2$. Work is in progress on the intensity problem of the magnetic dipole $O_2$ transitions, by considering both the parallel and perpendicular magnetic moments.

A significant number of absorption features due to solar species are observed, mostly solar CO, but also Mg, Si, Al, and Fe. As in the previous edition some of these solar lines were identified with the aid of the ATMOS atlas[32].

Additional line parameters have been introduced to the ongoing atlas work (see below) and to the wider range of stratospheric spectra, such as the update of the HCl line parameters[39].

The recently updated $HNO_3$ $\nu_5/2\nu_9$ and $ClONO_2$ $\nu_4$ line parameters were also used for quantitative analysis of several of the University of Denver balloon flights[40]. Subsequent studies of $HNO_3$ laboratory and stratospheric spectra, and molecular line parameters analysis, resulted in several new findings. This includes the extension of the previous $HNO_3$ $\nu_9$ analysis to cover the hot bands $3\nu_9$-$2\nu_9$, $3\nu_9$-$\nu_5$ in the 400 $cm^{-1}$ region[41], and the identification of the $3\nu_9$-$\nu_9$ band Q branch at 830.4 $cm^{-1}$ in the stratospheric spectrum[42]. The $\nu_9$+$\nu_5$-$\nu_9$ Q branch at 885.4 was also identified, in both laboratory and atmospheric spectra, and line parameters work is in progress.

For the ongoing search for the ClO (0-1) lines in the stratospheric spectrum, an accurate update of the line parameters has been undertaken[38,43].

Additional studies that developed on the basis of the recent atlas work are described in references 43-45. A review paper about the atlases work was recently given[46].

Work is currently underway in the 1520-1540 and 1610-1620 $cm^{-1}$ regions.

# PREFACE TO THE APRIL, 1993 EDITION

This preface describes the additions to the recent previous edition (April, 1992) of the Atlas of Very High Resolution Stratospheric IR Absorption Spectra.

In this edition, we have added ten new frames covering the region 1540-1560 $cm^{-1}$, thus bringing the total number of spectral features identified as being genuine to over 3300. Data for this new addition were recorded during a balloon flight from Palestine, Texas on June 17, 1991, with the exception of the top displayed scan (high sun scan), which is from a flight conducted from Ft. Sumner, New Mexico on April 19, 1989. The 1991 flight was noteworthy in that it was a sunrise flight, whereas the other flights represented in this atlas were all sunset flights.

The region added in this new edition is dominated by absorptions due to $H_2O$ and $CH_4$. However, there are also absorptions lines due to electric quadrupole and magnetic dipole transitions of $O_2$. The previous magnetic dipole $O_2$ line parameters[23] have been updated[30]. The new line positions agree well with the atlas spectra, but the intensity problem has not been fully resolved yet.
In addition, there is a significant number of absorptions due to solar species, most notably solar CO, but also Mg, Si and Fe. Some of these solar lines were identified with the aid of the ATMOS Atlas[32]. A few of the features identified as solar are not plainly visible on the displayed spectra, but were marked on the basis of additional high sun spectra obtained during this and previous flights.

Additional line parameters have been introduced to the ongoing atlas work. This includes the $HNO_3$ $\nu_5$, $2\nu_9$ region based on the work of Maki and Wells[33]; $ClONO_2$ in the $\nu_4$ region, calculated at D.U. from the constants of Bell et al[34], and normalized against D.U. laboratory data; $NO_2$ in the $\nu_2$ region based on the work of Perrin et al[35], and an update of the pure rotation OH lines[36].

Continuing work on the $O_3$ isotopes, in collaboration with other groups, lead to the identification of many $^{16}O^{16}O^{17}O$ and $^{16}O^{17}O^{16}O$ lines[37] in the spectra used for the atlas. The search for measurable infrared ClO lines is still ongoing[38].

Work is currently under way in the 1560-1580 $cm^{-1}$ region.

## I. INTRODUCTION

This atlas is an extension of our recent stratospheric[1] and ground-based atlases[2,3] to higher spectral resolution (~0.002 $cm^{-1}$), initiated with the December 1990 atlas[4]. The spectra presented here were recorded during various balloon flights conducted by our group in connection with ongoing research projects.

In this edition, the spectra and the tables of line positions and identifications are included in separate volumes, as in the past[1,2,4].

## II. DESCRIPTION OF THE ATLAS

### A. General

The spectra presented here were obtained with the University of Denver Michelson-type interferometer spectrometer system which has a total path difference of 250 cm and an unapodized FWHM resolution of ~0.002 $cm^{-1}$. Wavenumber calibration was performed using accurately known positions of $CO_2$ and $N_2O$ absorption lines. The spectra are displayed in figures hereafter referred to as frames. Each frame shows signal amplitude as a function of wavenumber over a 2 $cm^{-1}$ interval for three or four different sun angles. The scaling for all scans on a given frame is the same, but the scans have been displaced vertically for clarity, and the zero of amplitude is shown explicitly only for the bottom scan. The date that the spectra on each frame were recorded is shown at the top of that frame. Also listed at the top of each frame are altitude-angle pairs for the scans shown in that frame, from top to bottom. Each frame has a 0.1 $cm^{-1}$ overlap at both the high and low wavenumber ends to assist the user in aligning adjacent spectral regions. The positions of the observed spectral lines are indicated by vertical marks which are numbered consecutively in each frame. In frames with three scans, these vertical ticks are marked on the middle scan (as well as at the top of the frame), while on frames showing four scans they appear on the second scan from the top. Each frame is numbered independently. In some cases the absorption feature marked cannot be clearly seen in the spectra, but its existence has been established from several additional spectra taken at different zenith angles. Occasionally, such a feature can be seen more clearly in one of the other displayed scans, and therefore is also marked on that scan.

For each frame there is a corresponding table of line positions and molecular identifications. In those cases in which there are multiple identifications, the sequence in which the molecular species are listed represents the relative importance of these species in producing that line as it appears in the scan associated with the tick marks. The criterion for the inclusion of a given species in such cases of multiple identification for a single (blended) observed line is somewhat subjective. All species having absorption lines within a resolution element of the observed line are included if their contribution to the observed total absorption is estimated to be visibly discernable. Species identifications which are considered dubious are marked with question marks, while lines which are believed to be too strong or too broad to be attributable solely to the indicated species are denoted by "+?" or "?+". Absorption features with which we have been unable to associate a molecular species are denoted by a question mark in the identification column. None of the unidentified features has peak absorption greater than ~6%. Table I lists the sequence number and position of all unidentified lines having peak absorptions approximately equal to or greater than 5%.

The tabulated line positions were determined using the same line-marking computer program employed in our previous atlases[1-4]. For well resolved lines, line positions given here have an estimated accuracy of ±0.0002 $cm^{-1}$ with reference to standard calibration lines of $CO_2$ and $N_2O$. Updated laboratory spectra[5,6] and spectral line parameters[7] have been important to the atlas results.

### B. The Spectra

This preliminary edition of the Atlas of Very High Resolution Stratospheric Absorption

Spectra contains forty three frames, covering the intervals 800-810 $cm^{-1}$, 934-960 $cm^{-1}$, 992-1002 $cm^{-1}$, 1220-1230 $cm^{-1}$, 1240-1260 $cm^{-1}$ and 1680-1690 $cm^{-1}$. More than 3000 spectral features in these data have been identified as being genuine telluric or solar absorption features.

The data in the 800-810 $cm^{-1}$ 934-960 $cm^{-1}$, 1220-1230 $cm^{-1}$ and 1240-1260 $cm^{-1}$ regions were recorded during a balloon flight conducted by our group from Palestine, Texas on the afternoon and early evening of June 6, 1988. During this flight, full resolution data were recorded until the solar zenith angle was 94.81°. Lower sun data were then recorded at reduced resolution (~0.02 $cm^{-1}$) for zenith angles down to 95.41°.

In the 800-810 $cm^{-1}$ region, we have plotted four scans per frame. The top of these is actually the sum of 24 scans, recorded while the solar zenith angle increased from 63° to 73°, so that the value given on the frames (68°) represents an average.

Although the Q branch of the $\nu_4$ band of $ClONO_2$ (at 780.2 $cm^{-1}$) is clearly visible in data from the June flight at solar zenith angles below 92°, the weaker $\nu_3$ band Q branch at 809.4 $cm^{-1}$ falls directly on top of a strong $CO_2$ line at 809.3717 $cm^{-1}$, so that the $ClONO_2$ fine structure cannot be seen. Away from the $CO_2$ line, the weaker fine structure is not visible, but one can see clear evidence of the continuum absorption from this band on the 94.1° and 94.8° scans between 809.0 and 809.7 $cm^{-1}$. (This becomes apparent if one overlays the low sun data with the coadded high sun scan.) In addition, at the very lowest zenith angles recorded during the flight (95.2°, 95.3° and 95.4°, not shown here), one sees the $\nu_7$ Q branch of $CHF_2Cl$ (CFC-22) at 809.1 $cm^{-1}$ beginning to appear on the low wavenumber side of the $ClONO_2$ continuum.

Laboratory spectra[5] of $HO_2NO_2$ show two prominent features of the 802.5 $cm^{-1}$ Q branch of this molecule at 802.57 $cm^{-1}$ and 802.79 $cm^{-1}$. More recent laboratory spectra of $HO_2NO_2$ recorded at the University of Denver with the flight instrument show that both of these features split under high resolution into two nearly equal components. The feature at 802.57 resolves into lines at 802.5697 and 802.5754 $cm^{-1}$. In the lower stratosphere, these lines would undoubtedly be pressure broadened into a single feature at 802.573 $cm^{-1}$. Similarly, the 802.79 $cm^{-1}$ feature resolves into two components at 802.7859 and 802.7903 $cm^{-1}$, which would blend at 802.788 $cm^{-1}$. A very weak feature at 802.5728 $cm^{-1}$ in the flight data for 94.8° and lower angles appears to coincide very well with the first of these $HO_2NO_2$ features. A nearby weak $CO_2$ line predicted[6] to be at 802.5848 $cm^{-1}$ but not visible in the data, is too far away to be blended with the $HO_2NO_2$ line. The $HO_2NO_2$ feature at 802.7881 $cm^{-1}$ lies less than a resolution element from a much stronger $O_3$ line at 802.7900 $cm^{-1}$ and is not visible. The data do not appear to show evidence of any continuum absorption from the $HO_2NO_2$ Q branch.

Spectra in the 934-960 $cm^{-1}$ region are dominated by $CO_2$ at the lower wave numbers and by $CO_2$ and $O_3$ at the high frequency end of this interval. Below 934 $cm^{-1}$, contributions from CFC-12 are evident. In addition there are a number of pure rotational lines belonging to the $^2\Pi(0\text{-}0)$ and $^2\Pi(1\text{-}1)$ bands of solar OH visible in the high sun data displayed here, which is the average of 24 scans with sun angles between 63° and 73°.

Two lines belonging to the $\nu_3$ band of $SF_6$, visible on the 94.8° scan at 947.8 $cm^{-1}$, have been marked. The presence of $SF_6$ in the spectrum is verified by additional lower resolution scans taken at lower zenith angles.

The spectra in the 992-1002 $cm^{-1}$ region were obtained during a balloon flight from Fort Sumner, New Mexico, on the afternoon of November 18, 1987. During this flight, data were obtained only for solar zenith angles less than 85°. In this region, dominated almost exclusively by ozone absorption, we have identified the lines according to isotopic species.

Spectra in the 1220-1230 $cm^{-1}$ region, as indicated above, were recorded on June 6, 1988. This region is characterized by absorption due to $CH_4$, $N_2O$, $O_3$, $CO_2$, $COF_2$, and $HNO_3$. A single solar absorption line, due to Si I, occurs at 1222.7990 $cm^{-1}$.

Efforts to unambiguously identify absorption features in this region attributable to HOCl have so far proven fruitless. Although this region contains a few unidentified lines just above the noise level of the data, only two of these (1221.3234 and 1229.5618) are within a resolution element of an isolated HOCl line. Several other isolated HOCl lines in the region (such as those at 1222.0586, 1223.1506, 1224.1907, 1224.4318, 1226.4922, 1227.2185, 1227.2911, and 1227.5184 $cm^{-1}$) cannot be seen in the data. Many of the other strong HOCl lines in the region are overlapped by absorptions due to other molecules. Examples are the HOCl lines at 1222.3608, 1223.3976, 1225.4633, 1226.1905, 1226.2610, 1228.0810, and 1228.5419 $cm^{-1}$ and the doublets at 1227.4645, 1227.4661 and 1228.4966, 1228.4980 $cm^{-1}$.

The predominant molecular absorbers in the 1240-1260 $cm^{-1}$ region are $N_2O$, $CH_4$, and $CO_2$. In addition, there are a few weak $O_3$ lines, some $H_2O$ lines, and numerous small absorption lines of $COF_2$. Finally, there are a few very weak lines, at or near the noise level, which coincide with strong $H_2O_2$ lines (as seen in laboratory spectra recorded at DU), which have been identified as "$H_2O_2$?" in the table of molecular identifications.

A number of studies that developed on the basis of the recent atlas work are described in References 7-31. These include studies of long term trends of several species[22], and $O_2$ electric quadrupole and magnetic dipole lines[23]. The more recent studies include line parameters analysis of $H_2O_2$ and $NO_2$ from laboratory spectra[26,31], and $N_2$ from atmospheric spectra[27], as well as the identification and analysis of $SO_2$ spectra from Mt. Pinatubo's eruption[28].

A balloon flight made from Palestine, Texas on June 4, 1990, provided high resolution long path solar spectra in the 1650-2150 $cm^{-1}$ region. Studies of selected regions are in progress, including the $HNO_3$ $\nu_2$ region[24] and the OCS $\nu_3$ region. The spectra in the 1680-1690 $cm^{-1}$ are included in this edition of the atlas. They are dominated by absorptions due to stratospheric $O_3$ and $HNO_3$ and by numerous absorption lines of solar CO.

Data from our recent balloon flight of June 17, 1991, is currently under analysis in the 1540-1560 $cm^{-1}$ region. These data will be added to the next edition of the atlas.

## C. Line Identification

Line identification for all atmospheric and solar species except $O_3$ were based on the most recent version of the AFGL atmospheric line parameters compilation[7] and our high resolution laboratory spectra[6] and theoretical calculations. The solar OH lines are verified mostly by the high sun coadded spectra. The $O_3$ lines identifications are based on a recent line parameters update[17,20]. The $SF_6$ line parameters are based on a combination of several studies[22]. Many contributions to the new line parameters compilations[24-31] are based on the atlas work reported here.

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Table I. Unidentified Lines with Peak Absorption Greater than 5%

| Seq. No. | $\nu$(observed) ($cm^{-1}$) | Seq. No. | $\nu$(observed) ($cm^{-1}$) |
|---|---|---|---|
| 44 | 791.1958 | 21 | 831.4308 |
| 13 | 798.4283 | 25 | 831.7520 |
| 10 | 800.3221 | 9 | 832.3310 |
| 7 | 802.4638 | 11 | 832.6499 |
| 8 | 802.4675 | 20 | 833.3379 |
| 12 | 802.7242 | 24 | 833.5465 |
| 3 | 806.0949 | 28 | 833.9873 |
| 30 | 813.0585 | 7 | 836.5335 |
| 34 | 813.1773 | 3 | 838.1403 |
| 47 | 813.6863 | 103 | 903.3911 |
| 56 | 813.9502 | 74 | 905.2200 |
| 23 | 814.7586 | 5 | 906.0664 |
| 13 | 816.9200 | 17 | 906.2287 |
| 15 | 817.0578 | 35 | 908.7210 |
| 6 | 820.1800 | 3 | 910.0242 |
| 22 | 820.7695 | 101 | 911.5325 |
| 46 | 821.6650 | 109 | 913.5575 |
| 3 | 822.1731 | 140 | 915.8184 |
| 26 | 823.4697 | 68 | 916.7916 |
| 31 | 823.7950 | 125 | 917.5187 |
| 8 | 824.4728 | 116 | 919.3350 |
| 9 | 824.6533 | 127 | 919.5154 |
| 10 | 824.6781 | | |
| 16 | 827.0595 | | |
| 21 | 827.3075 | | |
| 48 | 829.5996 | | |
| 5 | 830.2905 | | |
| 11 | 830.6863 | | |

Table I. Continued

| Seq. No. | ν(observed) ($cm^{-1}$) | Seq. No. | ν(observed) ($cm^{-1}$) |
|---|---|---|---|
| 2 | 992.0293 | 62 | 1211.7385 |
| 4 | 992.0400 | 50 | 1219.2343 |
| 51 | 992.8723 | 47 | 1227.2384 |
| 87 | 999.1649 | 20 | 1230.3933 |
| 43 | 996.3303 | 56 | 1231.0437 |
| 73 | 996.5713 | 21 | 1232.4278 |
| 81 | 996.6328 | 51 | 1233.0341 |
| 110 | 996.8265 | 53 | 1233.0600 |
| 20 | 997.2126 | 56 | 1233.1275 |
| 91 | 997.7890 | 71 | 1233.4021 |
| 11 | 1000.0706 | 90 | 1233.8229 |
| 51 | 1000.3550 | 19 | 1234.2420 |
| 7 | 1182.1438 | 20 | 1234.2615 |
| 35 | 1182.8006 | 81 | 1235.5340 |
| 63 | 1183.3855 | 33 | 1236.7234 |
| 11 | 1184.3642 | 37 | 1236.8104 |
| 48 | 1189.1182 | 40 | 1236.8425 |
| 16 | 1198.5804 | 55 | 1237.1363 |
| 61 | 1204.5496 | 61 | 1237.3055 |
| 5 | 1208.0684 | 97 | 1237.9709 |
| 6 | 1208.0761 | 2 | 1238.0577 |
| | | 70 | 1239.6238 |
| | | 79 | 1239.7742 |

61: broad feature, scan 92.61°, 1237.3050

97: broad feature, scan 92.61°, 1237.9694

2: broad feature, scan 92.61°, 1238.0571

Table I. Continued

| Seq. No. | $\nu$(observed) ($cm^{-1}$) |
|---|---|
| 65 | 1253.2515 |
| 13 | 1523.4260 |
| 2 | 1524.1883 |
| 14 | 1538.4634 |
| 17 | 1538.4998 |
| 20 | 1538.5655 |
| 2 | 1564.4396 |
| 3 | 1568.4656 |
| 15 | 1586.6392 |
| 42 | 1589.8413 |
| 39 | 1591.5528 |
| 42 | 1591.6237 |
| 29 | 1605.3823 |
| 40 | 1608.9715 |
| 1 | 1614.0050 |
| 103 | 1615.9862 |
| 57 | 1681.1161 |
| 98 | 1683.6433 |
| 60 | 1685.2130 |
| 11 | 1686.2750 |
| 75 | 1687.1696 |
| 8 | 1688.0974 |
| 70 | 1689.1194 |
| 17 | 1890.7270 |
| 34 | 1921.7046 |
| 35 | 1921.7110 |

Table I. Continued

| Seq. No. | ν(observed) ($cm^{-1}$) | Seq. No. | ν(observed) ($cm^{-1}$) |
| --- | --- | --- | --- |
| 1 | 2020.0185 | 70 | 2028.9667 |
| 6 | 2020.0856 | 54 | 2030.9667 |
| 21 | 2020.3135 | 63 | 2030.8596 |
| 51 | 2020.7001 | 65 | 2030.8752 |
| 57 | 2020.7624 | 70 | 2030.9363 |
| 87 | 2021.1455 | 92 | 2031.2593 |
| 94 | 2021.2572 | 93 | 2031.2643 |
| 120 | 2021.6530 | 140 | 2031.8899 |
| 129 | 2021.7706 | 27 | 2032.4525 |
| 136 | 2021.9029 | 52 | 2032.7462 |
| 15 | 2022.1609 | 129 | 2033.7708 |
| 59 | 2022.8347 | | |
| 90 | 2023.3888 | | |
| 91 | 2023.4173 | | |
| 106 | 2023.6708 | | |
| 121 | 2023.8958 | | |
| 126 | 2023.9749 | | |
| 127 | 2023.9820 | | |
| 10 | 2024.0980 | | |
| 26 | 2024.4440 | | |
| 10 | 2024.0980 | | |
| 26 | 2024.3289 | | |
| 34 | 2024.4440 | | |
| 136 | 2025.9780 | | |
| 85 | 2027.2734 | | |
| 132 | 2027.9901 | | |
| 4 | 2028.0513 | | |
| 56 | 2028.7941 | | |

Table I. Continued

| Seq. No. | ν(observed) ($cm^{-1}$) |
|---|---|
| 6 | 2040.0714 |
| 30 | 2040.3801 |
| 59 | 2040.6954 |
| 127 | 2041.4739 |
| 157 | 2041.8732 |
| 9 | 2042.1080 |
| 11 | 2042.1541 |
| 35 | 2042.4486 |
| 56 | 2042.7259 |
| 81 | 2043.0989 |
| 85 | 2043.1664 |
| 98 | 2043.2690 |
| 99 | 2043.2862 |
| 101 | 2043.3213 |
| 110 | 2043.4236 |
| 117 | 2043.5320 |
| 118 | 2043.5379 |
| 135 | 2043.8359 |
| 140 | 2034.8909 |
| 61 | 2044.8185 |
| 75 | 2044.9987 |
| 87 | 2045.1744 |
| 102 | 2045.3471 |
| 28 | 2046.3622 |
| 53 | 2046.6589 |
| 23 | 2048.2527 |
| 32 | 2048.3638 |
| 130 | 2049.5054 |
| 132 | 2049.5249 |

| Seq. No. | ν(observed) ($cm^{-1}$) |
|---|---|
| 26 | 2050.3210 |
| 114 | 2051.4916 |
| 155 | 2051.9049 |
| 53 | 2052.6160 |
| 56 | 2052.6383 |
| 106 | 2053.2664 |
| 107 | 2053.2705 |
| 151 | 2053.8685 |
| 155 | 2053.9148 |
| 54 | 2054.5833 |
| 59 | 2054.6644 |
| 124 | 2055.4663 |
| 129 | 2055.5265 |
| 135 | 2055.5931 |
| 11 | 2056.0880 |
| 25 | 2056.2610 |
| 34 | 2056.3758 |
| 38 | 2056.4412 |
| 89 | 2056.9990 |
| 105 | 2057.2026 |
| 72 | 2109.6124 |
| 93 | 2111.9907 |
| 75 | 2113.4554 |
| 25 | 2116.5159 |
| 52 | 2117.0858 |
| 24 | 2126.6162 |
| 25 | 2126.6359 |
| 88 | 2129.8109 |
| 89 | 2129.8256 |
| 43 | 2137.5754 |