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Prepared by:

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The objective of this delivery order was to make modifications in infrared radiative transfer modeling programs and inversion techniques for remote sensing of the Earth's atmosphere and planetary atmospheres. The work on this delivery was based on the involvement of several UAH students, working primarily under the supervision of Dr. M. Abbas of MSFC. The periods worked by the students were:

<table>
<thead>
<tr>
<th>Student Name</th>
<th>Period Worked</th>
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<tr>
<td>C.-H. Lin</td>
<td>10/90-12/90</td>
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<tr>
<td>C. Keffer</td>
<td>6/91(2 weeks)</td>
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<td>R. Cleary</td>
<td>12/91-5/92</td>
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<tr>
<td>C. Noun</td>
<td>12/91 and 6/92</td>
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<tr>
<td>A. Joshi</td>
<td>2/92-5/92</td>
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<td>K.-H. Kim</td>
<td>2/92-9/92</td>
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<td>I. Sawaneh</td>
<td>6/92-9/92</td>
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The purpose of this work was to assist with the development of analytical techniques for the interpretation of infrared observations. We have (1) helped to develop models for continuum absorption calculations for water vapor in the far infrared spectral region; (2) worked on models for pressure-induced absorption for $O_2$ and $N_2$ and their comparison with available observations; and (3) developed preliminary studies of non-local thermal equilibrium effects in the upper stratosphere and mesosphere for infrared gases.

These new techniques were employed for analysis of balloon-borne far infrared data by Traub's group at the Harvard-Smithsonian Center for Astrophysics. The empirical continuum absorption model for water vapor in the far infrared spectral region, and the pressure-induced $N_2$ absorption model were found to give satisfactory results in the retrieval of the mixing ratios of a number of stratospheric trace constituents from balloon-borne far infrared observations. A presentation on this work was presented at the Spring meeting of the American Geophysical Union, and a full paper
has been accepted for publication in the Journal of Geophysical Research. Copies of the presentation abstract and the accepted paper are attached.
Stratospheric Minor Constituent Distributions from Far-Infrared Thermal Emission Spectra

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Abstract

We retrieve mixing ratio profiles of O₃, H₂¹⁸O, H₂¹⁷O, H₂¹⁸O, HF, and HCl from far-infrared thermal emission observations of the limb in the 80-220 cm⁻¹ spectral region. The observations were made with a balloon-borne Fourier-transform spectrometer as a part of the 1983 Balloon Intercomparison Campaign (BIC-2). A subset of the data was analyzed previously using the method in Traub et al. [1982, 1991]; in the present paper, we use an alternative method of calibration and analysis, given in Abbas et al. [1985]. The retrieved constituent profiles are compared with the measurements made with other instruments on the BIC-2 flights. The results for the concentrations of H₂¹⁷O and H₂¹⁸O obtained in this study indicate no isotopic enhancement or depletion with a standard deviation of about 20%.

1. Introduction

Far-infrared thermal emission spectroscopy provides a powerful tool for studies of stratospheric thermal structure and constituent distributions, via the numerous rotational transitions in this spectral region. Stratospheric limb observations of thermal emission spectra having high spectral resolution and high sensitivity can be analyzed to retrieve vertical profiles of temperature and constituent species abundances. Some recent results from far-infrared spectra obtained with high altitude balloon-borne instruments include: H₂O, H₂¹⁷O, H₂¹⁸O, HDO,¹⁶O¹⁸O¹⁸O,¹⁶O¹⁸O¹⁸O [Abbas et al., 1984b, 1985; Carli and Park, 1988; Dinelli et al., 1991; Guo et al., 1989; Rinsland et al., 1991]; CO [Abbas et al., 1988]; HCN [Abbas et al., 1987b, Carli and Park, 1988]; HF, HCl [Carli and Park, 1988; Park and Carli, 1991]; O(³P) [Lin et al., 1987]; HOCl [Chance et al., 1989]; HO₂, OH,
H₂O₂ [Traub et al., 1990; Chance et al., 1991a; Park and Carli, 1991]; HBr [Park et al., 1989; Traub et al., 1992].

After the surprising measurements indicating an enhancement in stratospheric heavy ozone concentrations [e.g., Maursberger, 1981, 1987; Abbas et al., 1987c; Goldman et al., 1989], there has been a considerable amount of interest in observing the isotopic distribution of other constituents, in particular of water vapor. Theoretical considerations [Kaye, 1987, 1990] indicate a small depletion in the stratospheric H₂¹⁸O distribution relative to normal water vapor. Measurements by Carli et al. [1990] from far-infrared thermal emission observations and Rinsland et al. [1991] from middle infrared solar absorption observations showed no enhancements or small depletions indicating agreement with the theoretical predictions. Inconsistent with with the two latter investigations, the results obtained by Guo et al. [1989] showed substantial relative enhancements in the H₂¹⁸O concentration.

We report here the results of an analysis which was carried out with two objectives in mind. The first objective is to analyze the existing set of 1983 far-infrared spectra for O₃, H₂O, HF, and HCl using a method of calibration, angle determination, and analysis which was developed independently from that originally used on a subset of this data. The second objective is to analyze the spectra for H₂¹⁷O and H₂¹⁸O, which has not been done previously, and to compare these results with those of other investigations.

2. Observations

Far-infrared stratospheric limb thermal emission spectra were obtained with a double-beam Fourier-transform spectrometer [Traub et al., 1982, 1991] launched on a balloon flight from Palestine, Texas, on June 23, 1983, as part of the Balloon Intercomparison Campaign (BIC-2). The spectra analyzed in this paper were obtained between about 10 am and 10 pm local time at a float altitude of about 37 km. The field of view is a circular beam with 0.3deg full width at half maximum, which corresponds to a vertical resolution of about 2 km at the limb. The telescope pointing direction is controlled in azimuth to about 1deg by the gondola, and in elevation by a single-axis stabilization system which employs a gyroscope for short term reference (gondola sway) and an inclinometer for long term reference (gondola tilt).

The usable spectral range is about 80 to 220 cm⁻¹, and the unapodized spectral resolution is 0.032 cm⁻¹. A complete limb-scan sequence comprises spectral observations at seven angles: a black-body reference, a high-elevation background scan, and five scans near the limb with tangent heights from 21 to 37 km. Three segments of the observed, calibrated, summed spectra from a complete limb sequence are shown in Figs. 1-3. Selected
spectral features due to the rotational lines of O₃, H₂¹⁶O, H₂¹⁷O, H₂¹⁸O, HF, HCl, and O₂ are identified.

3. Calibration and Angle Determination

One purpose of the present paper is to give an alternative analysis of the observations discussed above. In this section we discuss common and different features in both the calibration and the angle determination.

That part of the calibration, which is common to both methods, is as follows. Raw spectra are intensity-calibrated by subtracting a "cold" background spectrum and dividing by the difference of a "hot" reference blackbody spectrum and the cold spectrum. The cold spectrum is derived from an upward-looking atmospheric spectrum; the narrow emission lines are clipped off numerically, and the result smoothed so as to preserves all instrumental features, such as the filter bandpass and window interference fringes. The hot spectrum is derived from a spectrum of the on-board blackbody, similarly smoothed. Raw spectra of the stratosphere are converted to an absolute flux scale by subtracting a cold spectrum, dividing by the difference of the hot and cold spectra, and multiplying by the Planck function corresponding to the measured temperature of the reference blackbody. These temperatures were measured with 3 thermistors which were calibrated by the manufacturer and checked before installation by a water-ice triple point measurement; the measurement precision was smaller than 1 K. Nadir-referenced limb-viewing angles were measured by an on-board single-axis platform which was referenced to a low-drift gyro and inclinometer [Coyle et al., 1986; Traub et al., 1986]; the precision of pointing was about 0.02 deg.

The first method (hereafter “Method 1”) is as follows. (a) The onion-peel, non-linear least-squares retrieval method is the same as used to obtain all previously published profiles from the FIRS-1 and -2 instruments, as discussed in previous publications [e.g., Traub et al., 1982, 1991]; (b) The intensity calibration of the data relies on the in-flight determination of the reference black-body temperature. (c) The pointing angles are controlled by the on-board pointing system [Coyle et al., 1986; Traub et al., 1986]. Method 1 was employed to retrieve constituent profiles from data obtained by FIRS-1 flown on BIC-2, and by FIRS-2 on subsequent balloon flights. In particular, profiles from BIC-1 have been published for H₂O [Mureray et al., 1990], O₃ [Robbins et al., 1990], HF [Mankin et al., 1990], and HCl [Farmer et al., 1990]. These 4 papers show that the FIRS-1 profiles are in very good agreement with those of the other investigators in the BIC campaign, with the exception of H₂O, for which the FIRS-1 profile is higher than average. Thus, except for the reasons cited in the following paragraph, we have, a priori, no reason to doubt the accuracy of Method 1.
The second method (hereafter "Method 2"), constituting the alternative analysis discussed in this paper, is as follows. (a) The onion-peel, non-linear least-squares inversion technique is the same as that discussed in previous publications [Abbas et al., 1984a,b; 1985; 1987a,b,c, 1988]. (b) The flux intensity scale is calibrated using the observed fluxes at the peaks of saturated emission lines. (c) The pointing angles are obtained from an analysis of three observed O$_2$ lines at 83.469, 85.349, and 106.421 cm$^{-1}$.

The reasoning behind our Method-2 adjustment of the intensity scale is the following. In principle, the intensity of any optically thick spectral line should depend only on the atmospheric temperature profile. However, we found that the observed peak intensities of fully saturated H$_2$O lines, which should reflect atmospheric temperatures in the vicinity of the balloon float height, were slightly smaller than the values calculated with the radiative transfer model. In order to match the peak intensities of the observed and calculated lines, the observed spectra were multiplied by a factor of 1.02 to 1.03, depending on the wavenumber. This implies that the reference blackbody is actually about 3 to 4 K warmer than the thermisters indicated.

The reasons for employing the pointing angles retrieved from the observed spectra are two-fold. (i) The mixing ratio profile of H$_2$O (and to a much lesser extent O$_3$, HF, and HCl) retrieved by employing the nadir angles from Method 1 appeared to be systematically higher than the average of other experiments on the same gondola. (ii) More striking however, we found that the three observed O$_2$ lines were poorly matched by the calculated lines when we used the standard O$_2$ mixing ratio and the nadir angles from Method 1. This discrepancy could arise partly from errors in the AFGL O$_2$ line-broadening coefficients, since these parameters are subject to considerable uncertainties [Chance et al., 1991b]. The broadening coefficient of the 83.469 cm$^{-1}$ line of O$_2$ at 245 K (priv. comm. by Nolt et al., cited in Chance et al. [1991b]) is larger than the AFGL value by about 16%. Experimental data on the other two lines employed in the present analysis are not available. However, errors of the order of the above magnitude in the broadening coefficients are not sufficient to explain the mismatch between the observed and calculated O$_2$ lines.

Another possibility is that the assumed altitude of the balloon is in error. We believe that this is unlikely to be a significant effect in the present case because, according to our published error analyses [cf. Murcray et al., 1990; Robbins et al., 1990; Mankin et al., 1990; Farmer et al., 1990] the uncertainty in mixing ratio at any point in the profile is only about 3-4% for H$_2$O, O$_3$, HF, or HCl; of the seven other error sources identified in these BIC-2 studies, the estimated contribution is either about the same amount (from, for example, pointing uncertainty) or substantially larger (from pressure broadening uncertainty).

Recognizing the above uncertainties, we proceed nevertheless, in the spirit of a
numerical experiment. The results for the retrieved pointing angles are as follows. From the lowest to highest viewing angle, initially corresponding to nadir angles of 86.0, 86.5, 87.2, 88.1, and 91.0\deg, we find the best-fit angles to all be revised in the sense of viewing lower, by amounts $0.14(0.02)$, $0.18(0.01)$, $0.26(0.02)$, $0.45(0.05)$, and $0.95(0.20)\deg$, respectively. Values in parentheses are the rms scatter of the three oxygen lines used in the calculation. The average shift is $0.40\deg$ downward. (For completeness, we note that neither the magnitude nor the systematic variation of these angular offsets can be explained by any known properties of the pointing platform.)

In Chance et al. [1991b] it was pointed out that the oxygen line broadening coefficients in the AFGL catalog might be represented better by values which were about 20\% larger, although it was not recommended that this correction be adopted until more extensive laboratory measurements be undertaken. To see what effect such a change in the broadening parameter might have, we repeated the above calculation with broadening parameters which were 20\% larger, and found the best-fit angles to again be shifted in the sense of viewing lower in altitude, but now by amounts $0.04(0.12)$, $0.10(0.03)$, $0.17(0.06)$, $0.21(0.12)$, $0.56(0.60)\deg$, respectively. Here again the values in parentheses are the rms scatter of the three lines. The average shift is $0.22\deg$ downward. Clearly the larger broadening parameters give shifts which are about half the nominally required values, which suggests that perhaps the broadening parameters are indeed too small. However, the increased broadening parameter still requires that the viewing angles be shifted by substantial (albeit smaller) amounts; also, the rms scatter is larger, indicating poorer overall agreement between the three oxygen lines. In conclusion, this exercise shows us that (i) the magnitude of the angle correction increases with tangent altitude, and (ii) part of the correction (but not all of it) might be ascribable to broadening parameter error. In the remainder of this paper, we adopt the oxygen-derived angles as determined by the nominal broadening coefficients, to give nadir angles of $86.00 - 0.14 = 86.86$, etc., and use these alternative viewing angles to derive mixing ratio profiles for the SAO BIC-2 species, plus two water vapor isotopes.

4. Abundance Analyses

The radiative transfer model and the analytical techniques employed in obtaining the results presented in this paper have been discussed in several previous publications [e.g., Abbas et al., 1984b, 1985, 1987a]. The model is based on full layer-by-layer and line-by-line calculations including the Earth's curvature and atmospheric refraction effects. The calculated spectra are convolved with a Hamming function having a full width at half maximum of $0.064\ cm^{-1}$. The molecular spectral data are from the Air Force Geophysical Laboratory 1986 edition of the trace gas compilation HITRAN [Rothman et al., 1987],
which was updated to accommodate recent data for HF and HCl [K. Chance, priv. comm. 1991]. The temperature-pressure profile used in the analysis was obtained from radiosonde measurements near the balloon path. The spectral lines employed are listed in Table 1.

In addition to the spectral line contribution of atmospheric constituents, the radiance calculations include pressure-induced $N_2$ absorptions with maximum at about 90 cm$^{-1}$, and water vapor continuum absorptions throughout the analyzed spectral region. The pressure-induced $N_2$-$N_2$ and $N_2$-$O_2$ absorptions were calculated using a model developed at Goddard Space Flight Center [G. L. Bjoraker, priv. comm. 1990]. An empirical model for continuum water vapor absorption in the 80-220 cm$^{-1}$ spectral region was constructed from the currently available observations and employed in the calculations.

The iterative inversion method employed is a nonlinear least-squares fitting technique which proceeds by successively retrieving mixing ratios from the top to the lower levels at tangent heights corresponding to the observation angles. A set of frequencies around suitable spectral lines is chosen for each observation angle such that the weighting functions are narrow and sharply peaked at the tangent heights. The spectral lines employed in the analysis are isolated, and have small values of the lower state energy in order to minimize the temperature dependence of the line strength. The effect of a finite field of view on radiative transfer and inversion calculations is negligibly small and is ignored.

5. Constituent Distributions

Using the inversion technique discussed above, vertical profiles of $O_3$, H$_2^{16}$O, H$_2^{18}$O, H$_2^{17}$O, HF, and HCl have been derived. These profiles are compared with (i) those obtained earlier using Method-1 calibration on a subset of the present data, (ii) those obtained from other data sets but using a Method-2 analysis for water isotopes, and (iii) those obtained independently by other groups. We expect that there could be real differences between the results of the current analysis and the previously-published (Method 1) results, owing to the fact that the current data base covers the full flight (11.0 hours of observation, looking both west and north from the balloon), whereas the previous results covered only the designated intercomparison part of the flight (1.5 hours, looking west).

5.1. Ozone

The ozone profile obtained from the 17 lines in Table 1 is shown in Fig. 4, and a comparison of the observed and calculated spectra for the ozone line at 114.16 cm$^{-1}$ is shown in Fig. 5. The average uncertainty (1 standard deviation) of points in the retrieved profile is about 16%; this is the quadrature sum of the fitting errors (4 to 10%), pointing errors (6 to 11% of column), and line parameter errors (6% of column).
For comparison we also show the results obtained from other BIC experiments carried out on the same flight [Robbins et al., 1990]: Atmospheric Environment Service (AES) in situ electrochemical cell sondes experiment; National Physical Laboratory (NPL) mid-infrared atmospheric emission grating spectrometer; and Office National d'Etudes et de Recherches Aerospatiales (ONERA) infrared grille absorption spectrometer. The present profile is in general agreement with these other profiles.

Comparing the profiles from this work and the original analysis (Smithsonian Astrophysical Observatory, SAO) we see that the present profile yields smaller mixing ratios at high altitudes and larger mixing ratios at low altitudes. This may be a reflection of the corresponding O\textsubscript{2} curves, which have qualitatively similar shifts. Quantitatively, as noted in Robbins et al. [1990] the original analysis of SAO data gave a curve which differed from the BIC-2 weighted mean value (derived from 7 experiments on 2 days) by about +4% offset, with an rms scatter of 12%. By coincidence, the results of the present analysis deviate by essentially identical amounts. Thus, on balance, although the present analysis clearly yields an ozone profile which is weaker at high altitude and stronger at low altitude than the original analysis, there still is no significant difference in shift or rms with respect between either of these profiles and the BIC-2 "standard" ozone profile.

5.2. Water Vapor (H\textsubscript{2}O\textsuperscript{18})

The vertical profile for H\textsubscript{2}O\textsuperscript{18} retrieved from the 11 lines in Table 1 is shown in Fig. 6. The average standard deviation is about 15%, calculated in the same way as for ozone, above. Also shown for comparison in Fig. 6 are the measurements made by other groups in the BIC 2 campaign [Murcray et al., 1990]: AES, atmospheric emission measurements in ascent in the 6.3 \textmu m region; Denver University (DU), infrared emission measurements in the 25-26 \textmu m region; NPL, mid-infrared emission measurements in the 1339-1350 cm\textsuperscript{-1} region; and SAO. The measurements by AES, NPL, and SAO were made on the balloon flight on June 20, 1983, while the DU measurements were made three days earlier on June 17.

The present profile for H\textsubscript{2}O\textsuperscript{18} is lower than that of the original SAO analysis, dropping from an average of roughly 5 ppmv to 3.5 ppmv. Part of this drop is attributable to the different methods of analysis, and part is likely due to the fact that the lines used in the original analysis were highly saturated, so the results were quite sensitive to both the intensity scale factor and the broadening coefficients. The present profile clearly falls well within the range of water profiles measured by the other BIC 2 experiments in Fig. 6, instead of being well above the range as was the case from the original analysis. (But of course this does not insure that the result is correct, because the other measurements shown have considerable scatter themselves. Indeed, on a climatological basis, one might
expect to see a monotonic increase with height, from about 3.5 ppmv near 20 km to about 4.8 ppmv near 40 km, which does not match any of the curves shown in Fig. 6.)

A comparison of the observed (solid line) and synthetic (dashed line) spectra for a typical line of H$_2^{16}$O is shown in Fig. 7, indicating a good fit of the peak intensities, the continuum, and the line shapes.

5.3. H$_2^{18}$O

The present retrieval of H$_2^{18}$O is based on 10 spectral lines identified in Table 1. The derived profile, with the mixing ratios normalized to their natural abundances in accordance with the HITRAN data base, is shown in Fig. 8. The error bars represent the total standard deviation of the measurement, calculated as the quadrature sum of the random and systematic errors. Also shown on the same figure is the simultaneously measured H$_2^{16}$O mixing ratio profile (circles) discussed just above. The next figure shows a comparison of the observed (solid line) and the synthetic spectra (dashed line) indicating a good fit of some lines employed in the analysis.

In Fig. 8 we see that the H$_2^{18}$O and H$_2^{16}$O profiles are almost identical. No enhancement or depletion of the heavier isotope is seen. The ratio of the two profiles is essentially unity, with an average standard deviation of the ratio of about 20%. This result is in good agreement with two previous findings: Rinsland et al. [1991], from an analysis of the ATMOS Spacelab 3 infrared solar absorption spectra in the 1414 to 1690 cm$^{-1}$ region; and Carli et al. [1991], from balloon-borne far-infrared observations in the 46 to 72 cm$^{-1}$ made on a flight on October 5, 1982, during BIC 1. Both of the above referenced studies reported small depletions or no enhancements in the stratospheric H$_2^{18}$O profile relative to the simultaneously measured H$_2^{16}$O profile. The result of no enhancement or a small depletion in stratospheric heavy isotopic water vapor is consistent with theoretical considerations [Kaye, 1990].

The enigmatic results presented by Guo, Abbas, and Nolt [1989] indicating significant enhancements in the H$_2^{18}$O concentrations are therefore inconsistent with three studies: Carli et al. [1991] from the same data set; Rinsland et al. [1991] from a different data set; and the present study.

The reason for the discrepancy in the result obtained by Guo et al. [1989] is not clear. It may be noted that the water vapor mixing ratios obtained by Rinsland et al. [1991] are generally higher by about 35-40% than those obtained by Carli et al. [1991] from a different data set. The H$_2^{16}$O profile obtained by Guo et al. [1989] is almost identical to the profile obtained independently by Carli et al. [1991] from the same data set with a different retrieval method (see Fig. 3 of Carli et al.). Also, the H$_2^{18}$O absolute mixing
ratio profiles of Guo et al. [1989] and of Rinsland et al. [1991] generally overlap within the error bars. The $\text{H}_2^{16}\text{O}$ profile of the latter reference, however, is 35-40% higher over most of the altitude range.

5.4. $\text{H}_2^{17}\text{O}$

The isotope $\text{H}_2^{17}\text{O}$ was retrieved using the 7 lines listed in Table 1. The vertical profile is shown in Fig. 10, along with that of the normal isotope. The error bars represent the total standard deviation from random and estimated systematic error. The next figure shows a comparison of observed (solid line) and synthetic spectra (dashed line) calculated with the retrieved mixing ratio profile, indicating a good fit between the two spectra.

A comparison of the mixing ratio profiles of $\text{H}_2^{16}\text{O}$ and $\text{H}_2^{17}\text{O}$ indicates that the concentrations of these two isotopes are essentially the same, within the uncertainties. As in the previous case, the ratio of the two profiles is close to unity, with an average standard deviation of the ratio of about 20%.

This result is consistent with those of Rinsland et al. [1991] obtained from ATMOS observations, and of Carlî et al. [1991] obtained from BIC-2 observations, both of which reported small depletions or no significant deviation from the normal distribution within the error bars.

5.5. Hydrogen Fluoride and Hydrogen Chloride

The HF profile in Fig. 12 is derived from the two isolated lines given in Table 1. The average standard deviation is about 16%. A comparison of the observed and synthetic HF spectral line at 204.54 cm$^{-1}$ is shown in the next figure.

In Fig. 13 the other HF profiles are as follows: SAO, as previously published, from BIC-2; Instituto di Ricerca sulla Onde Electromagnetiche (IROE), from thermal emission measurements with a balloon-borne far infrared spectrometer on October 5, 1982, during BIC 1; University of Liege (UL), from middle infrared absorption measurements with a grating spectrometer in the 4040 cm$^{-1}$ region, from observations made on June 17, 1983; and the model prediction of Ko and Sze [WMO, 1985]. In contrast with case for ozone, the HF results here are not systematically shifted with respect to the SAO values, but instead there appears to be more scatter on both the high and low sides. The reason for this is not clear, but may be in part due to the steepness of the HF profile, which makes the lower layers relatively minor contributors compared to those above, making the retrieval more sensitive to noise.

The HCl profile retrieved from four spectral lines in Table 1 is shown in Fig. 14. Plots
of the observed and calculated spectra for one line are shown in the next figure. Also shown on Fig. 14 are: the average of the 5 profiles obtained by the BIC-2 experiments carried out by University of Liege, ONERA, AES, SAO, and IROE; and the model profile calculated by Ko and Sze [WMO, 1985, Vol. II]. As originally analysed with Method 1, the SAO mixing ratios for HCl tended to fall about 15% above the mean curve drawn through the HCl profiles measured by 5 independent instruments in BIC-2 [Farmer et al., 1990]. However in the present analysis, using Method 2, the 3 upper data points fall clearly below the average curve, echoing the general pattern observed for the other species discussed in this paper.

6. Conclusions

In this paper we presented the results of an analysis which was carried out with two objectives in mind. The first objective was to analyze an existing set of 1983 far-infrared spectra for O$_3$, H$_2$O, HF, and HCl using a method of calibration, angle determination, and analysis which was developed independently from that originally used on a subset of this data. The second objective was to analyze the spectra for H$_2^{17}$O and H$_2^{18}$O, which had not been done previously, and to compare these results with those of other investigations.

We find the following results. The current analysis (Method 2) gives mixing ratio profiles of O$_3$, H$_2$O, HF, and HCl which are often shifted significantly with respect to the original analysis (Method 1). The shifts are usually in the direction of a mean value, as determined from the other experiments which flew simultaneously, but in a few cases the shifts either overcompensate or seem to add noise. Overall, the Method-2 calibration seems to generally improve the derived profiles, but the improvement is not universal, and there is no explanation for why the on-board temperature and angle parameters should be in error by the implied amounts.

On the other hand, the determination of isotope ratios of water should be relatively independent of the above caveats, since some of the systematic effects of scaling drop out when ratios of abundances are taken. We find that there is no evidence for either enhancement or depletion of stratospheric water isotopes H$_2^{18}$O and H$_2^{17}$O with respect to the main isotope, with a standard deviation of about 20%.

Acknowledgements.

We thank K. V. Chance, D. G. Johnson, and K. W. Jucks for helpful comments. This work was supported in part by NASA grant NSG 5175.
References


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Fig. 13. Comparison of the observed and synthetic (dashed curve) HF line at 204.54 cm$^{-1}$ for a limb sequence of five angles with tangent heights at 21, 24, 28, 32, and 37 km with increasing radiance for lower altitudes.

Fig. 14. The HCl profile retrieved from the BIC-2 far infrared data analyzed in this work. Also shown for comparison is the average profile compiled from the results obtained by other BIC-2 experiments UL, ONERA, AES, SAO, and IROE.

Fig. 15. Comparison of the observed and synthetic (dashed curve) HCl line at 186.390 cm$^{-1}$ for a limb sequence of five angles with tangent heights at 21, 24, 28, 32, and 37 km with increasing radiance for lower altitudes.
Table 1. Center Frequencies (cm$^{-1}$) of the Analyzed Spectral Lines

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<th>O$_3$</th>
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<th>H$_2^{18}$O</th>
<th>H$_2^{17}$O</th>
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Figure 8

H$_2$O

MIXING RATIO (ppmv)

H$_2^{18}$O (BIC 2)
H$_2^{18}$O (BIC 2)

ALTITUDE (km)
Fig. 8
Fig. 11

H$_2^{17}$O

RADIANCE (W cm$^{-2}$ sr$^{-1}$/cm$^{-1}$) * 10$^{-7}$

WAVE NUMBER (cm$^{-1}$)
with a three-dimensional mechanistic atmospheric model. The mechanistic model is run with either casus or westerly winds in the lower equatorial strata, thus simulating the casus and westerly phases of the dynamical QBO. Ozone chemistry is parameterized through the relaxation of the model to a zonal mean distribution. The resulting climatological mean is specified from a two-dimensional mechanistic model run with both fully complete chemical schemes. In accord with fairly complete chemical models, the model appears to be sensitive to the casus and westerly phases of the dynamical QBO. The polar vortex is more disturbed during the westerly phase of the QBO. As well as examining the relation between the polar ozone concentrations and the dynamical QBO, we examine the effects of the parameterized ozone chemistry on the atmospheric QBO. The results between the mechanistic and the QBO are in good agreement.

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