

Vertical Column Abundances and Seasonal Cycle of Acetylene, C₂H₂, above the Jungfraujoch Station, Derived from IR Solar Observations

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Abstract. Monthly mean total vertical column abundances of acetylene have been determined from series of infrared solar spectra recorded at the Jungfraujoch station, Switzerland, between June 1986 and April 1991. The data have been obtained by nonlinear least-squares fittings of the ν_3 band R19 transition of C₂H₂ at 776.0818 cm⁻¹. The average of 22 monthly mean total vertical columns of C₂H₂ retrieved during that time interval of almost 5 years was found to be equal to $(1.81 \pm 0.12) \times 10^{15}$ molec/cm², which corresponds to an average mixing ratio of (0.22 ± 0.013) ppbv (parts per billion by volume) in a troposphere extending from the altitude of the station (3.58 km), up to 10.5 km. Despite the large variability found from year to year, a least-squares sine fit to the data reveals a seasonal variation with an amplitude of about $\pm 40\%$ of the mean; the maximum occurs during mid-winter and the minimum in the summer. The present results are compared critically with similar *in-situ* data found in the literature. A sinusoidal fit to all such free troposphere measurements made *in-situ* between 30° N and 60° N indicates good agreement in shape and phase with the seasonal variation derived above the Jungfraujoch, but their average column abundance, 2.3×10^{15} molec/cm², is about 30% higher; this difference is explained on the basis of non-upwelling meteorological conditions generally prevailing during ground-based remote solar observations.

Key words: Acetylene, atmospheric composition, solar observations.

1. Introduction

A large number of nonmethane hydrocarbons (NMHCs), whose major sources are located at the Earth's surface (Ehhalt *et al.*, 1986), have been observed in the planetary boundary layer, mainly by *in-situ* sampling and gas chromatographic detection (Rasmussen and Khalil, 1983; Greenberg and Zimmerman, 1984; Ehhalt *et al.*, 1985; Rudolph, 1988; Singh *et al.*, 1988; Rudolph *et al.*, 1989). Among these, only ethane, C₂H₆, and acetylene, C₂H₂, have been remotely observed in ground-based, aircraft- and space-borne infrared solar spectra. Their spectroscopic detection is possible because of their strong absorption features in infrared atmospheric windows and their relatively large production at the ground, combined with moderately long atmospheric lifetimes exceeding a few months.

The ground-based infrared (IR) spectroscopic detection of C₂H₆ was reported

by Zander *et al.* (1982). Reviews of remote slant column investigations and the specific spectroscopy involved have been published by Rinsland *et al.* (1987) and by Ehhalt *et al.* (1991). Absorption lines of the strongest IR band of C_2H_2 , the ν_5 fundamental at 729.155 cm^{-1} , were first identified in balloon-borne solar absorption spectra of the upper troposphere by Goldman *et al.* (1981), and soon after in ground-based observations by Zander *et al.* (1982). Despite successful applications by Rinsland *et al.* (1985, 1987) and by Pugachev *et al.* (1990) in which transitions of the $\nu_2 + \nu_4 + \nu_5$ band of C_2H_2 near $3\text{ }\mu\text{m}$ were used (according to Varanasi and Bangaru (1974), the sum of the strengths in that band and in the nearby Fermi resonant ν_3 band is a factor ~ 3 weaker than the ν_5 integrated strength), IR remote sensing of acetylene in the atmosphere can best be carried out using the strongest ν_5 band transitions. As part of the investigation of the telluric concentration of C_2H_2 based on solar spectra recorded in 1985 during the ATMOS/Spacelab 3 mission, Rinsland *et al.* (1987) provided spectroscopic details for three of the most prominent and isolated lines of that C_2H_2 band, i.e., the transitions R10 at 755.0056 cm^{-1} , R15 at 766.7249 cm^{-1} , and R19 at 776.0818 cm^{-1} , as well as the identification of interferences which need to be considered in the retrieval process.

In this paper, we report results derived from the spectroscopic analysis of the ν_5 band R19 transition of C_2H_2 observed in solar spectra recorded at the Jungfraujoch station, Switzerland. This transition appears to be the best isolated C_2H_2 feature for determining the total column abundance of that gas from the ground.

2. Data Base and Analysis

All solar spectra discussed in this study have been recorded by one of us (Ph. Demoulin) at the International Scientific Station of the Jungfraujoch (ISSJ) located in the Swiss Alps at 3580 m altitude (lat. 46.55° N ; long. 7.89° E) using a non-commercial Fourier transform spectrometer built at the Institute of Astrophysics of Liège. An unapodized spectral resolution of 0.006 cm^{-1} is typically adopted for observations over the 8 to $13\text{ }\mu\text{m}$ domain, and in combination with a HgCdTe detector cooled with liquid nitrogen, signal-to-RMS noise ratios (S/N) between 150 and 200 are achieved in individual spectra. As the central absorption of the target ν_5 R19 line of C_2H_2 is only on the order of 2 to 5% of the local continuum amplitude for observations made at zenith angles between about 75 and 85° , it was decided to average spectra recorded at zenith angles equal to within a few degrees and work with 'monthly mean' runs having corresponding S/N ratios usually in excess of 600 at the location of the R19 C_2H_2 line (in higher sun observations the C_2H_2 absorption becomes too weak while in near-horizontal runs, the interferences become excessive). Both sunrise and sunset data were included in the averages. In most cases, two monthly mean spectra corresponding to the averages of runs from 75 to 80° and from 80 to 85° zenith angles were produced. The resultant spectra were assigned mean zenith angles and dates of observation calculated on the basis of the individual scans involved. The ISSJ C_2H_2 data base consists of

some 200 individual solar spectra recorded on 117 different days over the 5 year of measurements between June 1986 and April 1991 has led to averaged spectra for 22 individual months. Typically, four spectra on three different days were coadded to produce a monthly mean spectrum with the minimum number of scans equal to 1 and the maximum equal to 10 on five different days. Both the R10 and the R15 lines of the same band are also clearly observed in the ISSJ spectra, but they were not considered here because of significant interference by other telluric constituents (primarily O_3 , CO_2 , and H_2O).

The retrieval of C_2H_2 total column amounts from the observed C_2H_2 ν_5 -R19 absorptions was based on their nonlinear least-squares spectral fitting. In many instances, two different retrieval algorithms were used, one developed at the NASA Langley Research Center, Hampton, Va., by one of us (C. P. Rinsland), and the other at the Jet Propulsion Laboratory, Pasadena, Ca. Both of these algorithms, as well as supporting programs, have been described by Norton and Rinsland (1991). The minimization of the residuals (sum of the squares of the differences between the observed and the calculated signals) was achieved by iteratively scaling an assumed relative 'reference' volume mixing ratio (VMR) profile by a single multiplicative factor. VMR values of the reference profile at typical altitudes of 3.5, 5, 10, 15, 20, and 25 km were equal to 53.0, 37.0, 23.0, 4.5, 0.4, and 0.04 pptv (parts per trillion by volume, or $\times 10^{-12}$ ppv), respectively. The 'Mid-Latitude Standard Atmosphere' (U.S. Standard Atmosphere, 1966; 1976) was used in all retrievals. Tests with other physical models indicated that the uncertainty introduced by adopting the above-mentioned standard model all year round introduced, at most, $\pm 3\%$ differences in the retrieved C_2H_2 columns, a consequence of the moderate temperature dependence of the strength of the R19 transition whose lower state energy, E'' , is equal to 446.8 cm^{-1} . All spectroscopic parameters necessary to compute the synthetic spectra in the vicinity of the C_2H_2 R19 feature were taken from the ATMOS line parameters compilation (Brown *et al.*, 1987) which, in this particular spectral region, is identical to the AFGL-1986 compilation (Rothman *et al.*, 1987), except for the O_3 lines which were updated on the ATMOS line list based on the work of Pickett *et al.* (1988). Recently, line parameters for the ν_8 band of HNO_3 (Maki and Olson, 1989) have also been added to the ATMOS compilation in this spectral region.

The central frame of Figure 1 reproduces the fit of the mean September 1989 spectrum between 775.9 to 776.3 cm^{-1} ; the zenith angle is 82.61° . The full trace corresponds to the observed spectrum, while the discrete crosses represent the calculated data. The target C_2H_2 absorption is marked by an arrow. All other spectral features are due to O_3 , HNO_3 , and CO_2 . Absorption by the wing of the strong pure rotational line of H_2O at 775.552 cm^{-1} contributes to the signal decrease over the lower wavenumber side of the interval. The ATMOS solar atlas (Farmer and Norton, 1989) shows that no significant solar lines occur in this spectral region. The upper frame reproduces the residuals without inclusion of C_2H_2 in the calculation; the root-square sum (RSS) of the residuals over the spectral interval depicted

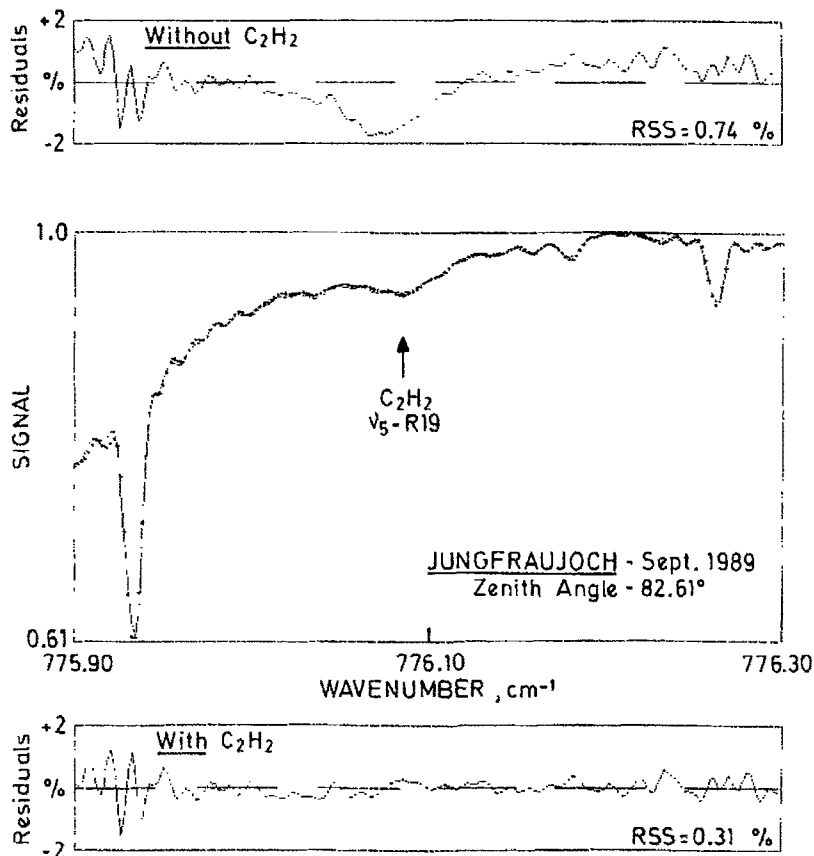


Fig. 1. Example of a line-by-line least-squares curve fitting (discrete crosses) in the vicinity of the C_2H_2 ν_5 band R19 line as appearing in a mean September 1989 spectrum (full trace) derived by co-adding five individual solar observations made at the Jungfraujoch. The upper and lower frames reproduce the residuals (observed minus calculated signals), respectively, without and with C_2H_2 present in the computed atmospheric spectra. The root square sum (RSS) of the residuals over the entire interval from 775.9 to 776.3 cm^{-1} decrease by a factor 2.5 when the C_2H_2 target absorption is included in the fit.

in the figure is equal to 0.75%. The bottom residuals are obtained after adding acetylene in the atmosphere according to the relative reference VMR profile characterized before, but scaled to minimize the sum of the squares of the residuals; five fitting iterations involving the molecules C_2H_2 , H_2O , O_3 , and HNO_3 , produced a RSS equal to 0.31%, almost a factor 2.5 lower than in the upper frame. In this September 1989 example, the corresponding vertical column abundance of C_2H_2 , obtained by integrating the product of the scaled C_2H_2 reference VMR profile and the atmospheric number density, was found to be equal to 2.15×10^{15} molec/ cm^2 . No special attempt was made to fit the ozone absorption lines. This is the main reason for finding the largest residuals in both upper and lower frames associated with the two strong O_3 lines at 775.9341 and 776.2631 cm^{-1} . In all of the spectra analyzed, the C_2H_2 R19 target feature remained weak enough that its central

absorption was proportional to the amount of acetylene along the atmospheric slant path to the sun.

3. Results and Discussion

3.1. IR - Remote Sensing Data

The total vertical column abundances of C_2H_2 above ISSJ retrieved from the monthly mean spectra are plotted versus time in Figure 2. To better demonstrate the seasonal variation, the same columns are also reproduced versus calendar month in Figure 3. When monthly mean spectra were available at two different mean zenith angles (see the pairs of points for the same abscissa in Figure 2), the mean of the two retrieved C_2H_2 vertical column amounts was adopted and reported in Figure 3. The error bars drawn in Figures 2 and 3 reflect the total one-sigma random uncertainty associated with each individual monthly mean column. They incorporate the effects from error sources such as the finite S/N ratio ($\pm 10\%$), the observational geometry ($\pm 2\%$), the adopted standard temperature profile ($\pm 3\%$), interferences due to weak overlapping lines mainly HNO_3 and CO_2 ($\pm 4\%$), and the assumed C_2H_2 relative VMR profile ($\pm 8\%$); their combination

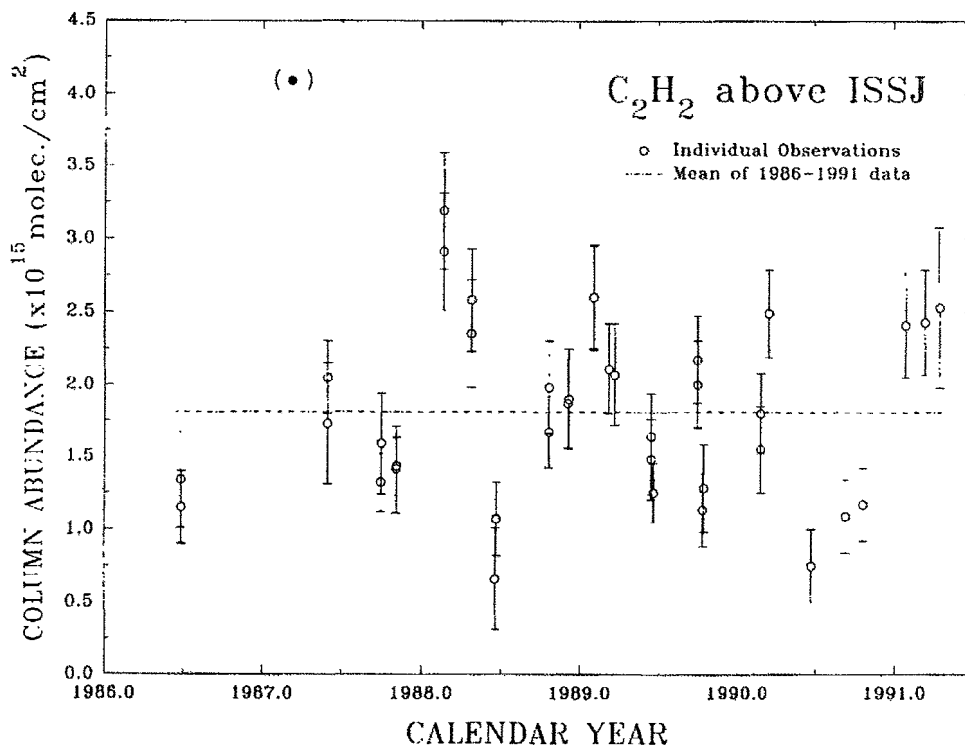


Fig. 2. Time series monthly mean vertical column abundances of C_2H_2 observed above the Jungfraujoch station between June 1986 and April 1991. The error bars reproduce the total random uncertainty for each individual retrieval. The dash-dotted line corresponds to the average total vertical column abundance of acetylene above ISSJ (1.81×10^{15} molec./ cm^2) during the five years of observations, excluding, however, the unusually high column of C_2H_2 observed in March 1987.

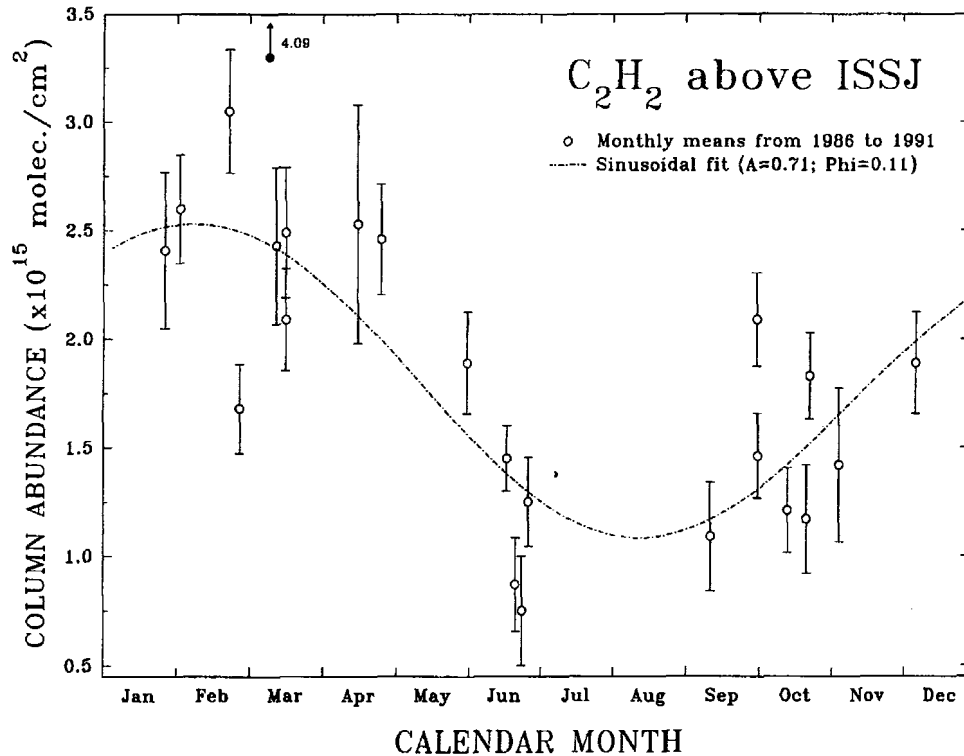


Fig. 3. Plot of the total vertical column abundances of C_2H_2 above the Jungfraujoch station, versus time of the year, derived from all monthly mean spectra obtained between June 1986 and April 1991. The dash-dotted curve reproduces the least-squares sine fit to the data derived over that same time interval (with the exclusion of the high value of March 1987). The error bars indicate the extent of the 1-sigma random uncertainty.

corresponds to a typical 1-sigma total precision of $\pm 14\%$. The uncertainty in the adopted VMR profile was treated as a random error because of significant variability observed among the C_2H_2 columns found here, thereby confirming findings on tropospheric variability reported by other groups (Rasmussen and Khalil, 1983; Ehhalt *et al.*, 1985; Singh *et al.*, 1988). This situation is quite different when dealing with a long lived species such as SF_6 for which the uncertainty produced by an assumed VMR profile is likely to introduce a systematic contribution to the total error budget (Zander *et al.*, 1991). Systematic errors here are mainly the result of possible uncertainties in the spectroscopic line parameters ($\sim \pm 7\%$) and in the retrieval algorithms ($< \pm 5\%$); this total systematic uncertainty of $\pm 9\%$ is not included in the error bars drawn in Figures 2 and 3; it affects the retrieved vertical column abundances in a linear fashion, but has no effect on the seasonal and long-term trend results.

The average of the 22 retrieved monthly columns of C_2H_2 encompassing the June 1986 to April 1991 time period (the high column of March 1987, i.e., 4.09×10^{15} molec./ cm^2 indicated as a full circle in Figure 2, has been discarded) is equal to $1.81 \pm 0.12 \times 10^{15}$ molec./ cm^2 ; it is drawn in Figure 2 as a dash-dotted line. That column corresponds to a mean constant VMR throughout the troposphere

equal to 0.22 ± 0.013 ppb (parts per billion) when assuming an average tropopause height of 10.5 km above ISSJ. Despite the limited number of data points available and their uneven distribution throughout the years (no observations in July–August and only a few in December–January), a definite seasonal cycle is present in the data set as visualized by the dash-dotted curve in Figure 3 which represents a least-squares sinusoidal fit to the observations; its amplitude is about $\pm 40\%$ of the mean column, with the maximum of $\sim 2.50 \times 10^{15}$ molec/cm² occurring near mid-winter and the minimum of $\sim 1.10 \times 10^{15}$ molec/cm² during the summer.

Because of a large interannual variability (see Figure 2), the superposition of a seasonal cycle with an exponential or a linear temporal change results in a positive but quite uncertain trend of 2.3 ± 4.6 %/yr (one sigma error) between June 1986 and April 1991, when also omitting here the abnormally high column of March 1987. At the outset of this work, we expected to be able to retrieve an accurate C₂H₂ column abundance from a few 1950–51 infrared solar spectra recorded at ISSJ with a Pfund-type grating spectrometer by Migeotte *et al.* (1956), but because of the limited spectral resolution (~ 0.25 cm⁻¹) coupled with a relatively low S/N ratio of these observations (~ 50), we could only derive an approximate total column abundance upper limit of 6×10^{15} molec/cm². This, together with the present results, only allows the setting of an upper limit for a possible C₂H₂ column decrease of 3.3%/yr. over the last 3–4 decades. The question of the secular trend in the vertical column abundance of C₂H₂ above ISSJ cannot be answered on the basis of the existing 1950–51 and 1986–91 data base treated here.

How does the mean 1986–1990 C₂H₂ vertical column abundance above ISSJ compare with total columns observed at other places? Surprisingly, only a few such measurements have been carried out over the last decade or so. From the analysis of the P13 and R9 lines of the $\nu_2 + \nu_4 + \nu_5$ band of C₂H₂ in solar spectra recorded at Kitt Peak National Solar Observatory (31.9° N, 111.6° W), Rinsland *et al.* (1985) derived total vertical column amounts of C₂H₂ equal to 2.28×10^{15} and 2×10^{15} molec/cm², respectively on 23 February 1981 and 1 September 1982. When scaling these columns to account for the difference in altitude between Kitt Peak (2095 m) and ISSJ (3580 m), one obtains comparative values of 1.83×10^{15} and 1.61×10^{15} molec/cm², respectively, for February 1981 and October 1982. This result is quite similar to the ISSJ mean column of 1.72×10^{15} molec/cm², but 30% lower in February and 30% larger in October than the values read off the ISSJ seasonal curve in Figure 3. The total vertical column abundance of C₂H₂ derived from a solar spectrum recorded at Kitt Peak on 26 April 1981 by Zander *et al.* (1982) was equal to $(0.46 \pm 0.11) \times 10^{15}$ molec/cm², significantly lower than those reported by Rinsland *et al.* (1985). That value was retrieved from the equivalent width measurement of the ν_5 band R19 line observed in that spectrum, and part of the apparent underestimation of the column may be due to 'experimental loss' (Smith *et al.*, 1985) which affects the measured equivalent widths of pressure-broadened absorptions such as the acetylene transition considered here.

A C_2H_2 column upper limit of 1.5×10^{15} molec/cm² derived by Rinsland *et al.* (1988) from a February 1987 solar spectrum recorded at Mauna Loa (19.5° N, 155.6° W) is slightly less than the Kitt Peak result of February 1981 scaled to the Mauna Loa altitude of 3.4 km, and also 50% lower than the corresponding scaled ISSJ column fit for February; this can be explained by the well-established latitudinal variation of C_2H_2 whose concentration decreases from mid- towards lower latitudes of the Northern Hemisphere, both at the surface and throughout the troposphere (Ehhalt *et al.*, 1986; Rudolph, 1988).

Infrared remote spectroscopic measurements of the total vertical column abundance of C_2H_2 above Zvenigorod (some 50 km west of Moscow; 56° N, 37° E; 200 m alt.) have also been obtained recently by Pugachev *et al.* (1990). Not much detail is provided on the accuracy of their results, but the mean of the two reported columns, i.e., 4×10^{15} and 2×10^{15} molec/cm², respectively, on 21 March 1989 and 7 April 1990, when scaled to the ISSJ altitude, reduces to about 1.7×10^{15} molec/cm², comparable to the mean column above ISSJ; the factor 2 difference between their pair of results obtained 16 days apart indicates a considerable variability in the C_2H_2 column above Zvenigorod.

3.2. Comparison with In Situ Data

There are several sets of acetylene measurements in the free troposphere by *in-situ* techniques, but only a few with a vertical extent throughout the troposphere and into the lower and middle stratosphere. In general, they were made by the collection of whole air samples and subsequent analysis in the laboratory by gas chromatography. Cronn and Robinson (1979) report acetylene mixing ratios of about 0.2 ppbv in the upper troposphere at 37° N and a sharp decrease in the lowest stratosphere. Aiken *et al.* (1987) reported C_2H_2 mixing ratios of 0.06 and 0.05 ppbv for 11.6 and 14 km, respectively. Rudolph *et al.* (1984) provide vertical profiles of C_2H_2 for altitudes up to nearly 35 km. At 32° N, they observed acetylene mixing ratios around 0.05 ppbv near the tropopause (16 km) decreasing to less than 0.01 ppbv above 30 km. For 44° N over southern France, they reported a complete profile from 3 to 30 km altitude obtained on 16 June 1979; at this latitude, they found only a weak gradient in the C_2H_2 volume mixing ratio in the lower stratosphere with values slightly less than 0.2 ppbv up to nearly 20 km and a decrease by a factor 10 between 20 and 30 km. From this complete VMR profile, we calculate a vertical column abundance above 3.6 km altitude equal to 3.39×10^{15} molec/cm², assuming the standard atmosphere-air density profile for 45° N. This is almost twice as high as the mean ISSJ column abundance of 1.81×10^{15} molec/cm² found here, and over 2.5 times larger than the corresponding June value from the seasonal curve of Figure 3. It should be noted, however, that the acetylene mixing ratios measured by Rudolph *et al.* (1984) over southern France, decreased between 3 and 8 km by a factor of roughly 3, whereas C_2H_2 showed no systematic vertical gradient in the remote troposphere (Rudolph, 1988; Ehhalt *et al.*, 1985). This

Table I. Acetylene mixing ratios in the troposphere from airborne *in-situ* measurements

Location	Altitude (km)	Date	Mixing ratio (ppbv)	Latitude (°N)	Ref.
Northern Californian Coast, Ocean	2.5-9.5	February/March 1985	0.22 ± 0.02	38	(1)
Northern Californian Coast, Land	2.5-9.5	February/March 1985	0.32 ± 0.03	38	(1)
Central Europe	2.5-4.5	March 1980	0.45 ± 0.13	51	(6)
Mediterranean Sea	2.0-5.0	March 1982	0.10 ± 0.03	38	(4)
Norway	2.5-11	March 1985	0.78 ± 0.03	66	(5)
English Channel	0.5-3.3	March 1986	0.42 ± 0.07	50	(3)
Northern Californian Coast	2.5-10.5	April 1977	0.23 ± 0.06	37	(7)
East Coast of North America	2.0-11	April 1984	0.48 ± 0.18	40-50	(11)
Southern Californian Coast	0.1-12	April 1985	0.29 ± 0.06	32	(8)
Northern Californian Coast	0.1-11	April 1985	0.36 ± 0.13	38	(8)
Canadian Northwest Coast	2.0-8.3	April 1985	0.41 ± 0.13	58	(8)
Canadian Southwest Coast	0.1-13	April 1985	0.26 ± 0.08	47	(8)
Alaska	0.4-10	April 1985	0.72 ± 0.17	66	(8)
Barrow, Alaska	1.6-10	April 1985	0.51 ± 0.12	70	(8)
Barrow, Alaska	0.4-3.5	May 1982	0.34 ± 0.03	70	(2)
North of Ireland	0.5-3.3	May 1985	0.34 ± 0.02	56	(3)
Southern France	4.5-11	June 1979	0.24 ± 0.03	45	(9)
East Coast of North America	2.0-11	June 1984	0.11 ± 0.05	40-50	(10)
Central Europe	1.2-6.6	July 1981	0.08 ± 0.02	52	(6)
Ireland	0.5-6	July 1981	0.21 ± 0.11	52	(4)
Panama	2.5-10	July 1981	0.08 ± 0.08	9	(7)
Mediterranean Sea & Biscay	2.0-6.0	July 1982	0.10 ± 0.02	38-45	(4)
English Channel	0.5-3.3	July 1985	0.11 ± 0.04	50	(3)
Northern Colorado	2.5-8.5	July/August 1984	0.105 ± 0.01	40	(1)
North Sea	0.5-3.3	August 1983	0.190	52	(3)
Northern Californian Coast	2.5-8.5	August 1984	0.055 ± 0.005	38	(1)
Norway	1.2-6.6	September 1981	0.08 ± 0.03	70	(6)
Norway	2.0-5.0	September 1981	0.30 ± 0.04	70	(4)
Mediterranean Sea	2.0-5.0	September 1982	0.10 ± 0.01	42	(4)
North of Ireland	0.5-3.3	September 1985	0.11 ± 0.01	56	(3)
Central Europe	2.0-10.5	October 1981	0.18 ± 0.07	51	(6)
North Sea	0.5-3.3	October 1985	0.31 ± 0.04	52	(3)
Central Europe	3.0-4.8	November 1981	0.36 ± 0.09	52	(6)
Eastern England	0.5-3.3	November 1984	0.65 ± 0.07	53	(3)
Bristol Channel	0.5-3.3	December 1982	1.39 ± 0.02	51	(3)
Mediterranean Sea	0.5-2.0	December 1982	0.20 ± 0.06	42	(4)

(1) Singh *et al.* (1988); (2) Rasmussen *et al.* (1983); (3) Lightman *et al.* (1990); (4) Tille *et al.* (1985); (5) Rudolph (1990); (6) Rudolph *et al.* (1982); (7) Cronn and Robinson (1979); (8) Greenberg *et al.* (1991); (9) Rudolph *et al.* (1984); (10) Rudolph (1988); (11) Ehhalt *et al.* (1985).

suggests that these measurements were influenced by local or regional acetylene sources and are not representative of the background troposphere.

From all the *in-situ* measurements in the troposphere and stratosphere we estimate that the stratosphere contributes less than 20% to the total acetylene column abundance above 3.6 km. Therefore, as a first approximation, we can use measure-

ments extending vertically over the remote troposphere to estimate the total column abundance. An overview of the airborne *in-situ* measurements of tropospheric C₂H₂ is given in Table I. Similar to the variations observed in the optical remote sensing column abundance measurements, there is substantial scatter between the different *in-situ* results, and large standard deviations are likely to include short-term variability, especially when dealing with samplings within or near the boundary layer. The average tropospheric C₂H₂ volume mixing ratio for all results between 30° N and 60° N latitude reported in Table I is 0.25 ppbv, with a standard deviation of 0.15 ppbv. Part of this variability seems to be due to a systematic seasonal cycle comparable to the seasonal variation observed in the ISSJ data set. A least-squares sine fit to the *in-situ* measurements between 30° N and 60° N gives a yearly mean of 0.26 ± 0.03 ppbv and an amplitude of 0.13 ± 0.04 ppbv; the maximum occurs during February–March and the minimum in August–September. This variation is caused by the seasonal change in the OH abundance. In shape and phase, this cycle is very similar to the seasonality found in the column abundance measurements above ISSJ. To compare the tropospheric VMR values derived *in situ* with the seasonal variation found in the column abundance, the seasonally varying height of the tropopause has to be taken into account. Assuming that the acetylene mixing ratio is constant within the troposphere and that the mean tropopause heights are 10 km in winter and 11.5 km in summer, we calculate an average column abundance of 2.3×10^{15} molec/cm² for the troposphere above 3.6 km. This value is almost 30% higher than the average measured total column abundance above ISSJ, a difference which exceeds the statistical errors and the experimental systematic uncertainties of the two measuring techniques (typically $\pm 15\%$ and $\pm 9\%$, respectively, for *in-situ* and remote investigations).

The *in-situ* measurements were made by several groups with independent absolute calibrations, and it is therefore very unlikely that calibration errors can explain a systematic difference of some 30%. Furthermore, we cannot completely exclude the possibility that our assumption of a constant acetylene mixing ratio profile in the free troposphere is incorrect, although the available data are not compatible with the existence of a significant and systematic vertical gradient. A possible explanation may relate to the fact that optical remote measurements in the absorption mode with the Sun as background source is only carried out when the sky is clear. It has been shown that convective cloud systems are an important mechanism for the exchange of trace gases between the boundary layer and the free troposphere (Gidel, 1983; Chatfield and Crutzen, 1984; Ehhalt *et al.*, 1985). Due to the specific weather conditions necessary for optical column abundance measurements from the ground, situations influenced by convective cloud systems will, to some extent, be excluded. The airplane-based *in-situ* measurements are not affected by such bias and therefore are more likely to include meteorological situations with fast vertical exchange processes due to convective cloud systems. This may well account for part of the observed discrepancy between the averages of the column abundance measurements above the Jungfraujoch station and those derived from

the tropospheric *in-situ* samplings (meteorological conditions have seldom been reported with sufficient details to warrant quantification of the convective exchange mechanism raised here).

In addition to the airborne measurements, there are several series of C_2H_2 measurements at remote or semi-remote locations at the Earth's surface. These show even larger variability. Some cover sufficiently long time periods with an adequate sampling frequency that seasonal cycles can clearly be derived. Kessel and Bächmann (1991) report measurements from a mountain station (Wank, 1.8 km altitude; 48° N; 11° E) in southern Germany between 1986 and 1988. They find a seasonal cycle for acetylene with lowest values around 0.3 to 0.4 ppbv in summer and maxima of 1.5 to 2.0 ppbv in February. With an average of 0.72 ppbv these values exceed the acetylene mixing ratios above ISSJ by a factor of 4 and the results of the airborne measurements listed in Table I by a factor of 3. This is most probably due to the impact of local sources of C_2H_2 since Wank is close to the city of Garmisch-Partenkirchen, the center of a very popular recreation area. Lower acetylene concentrations were measured from a mountain station on Tenerife (Izana, 2.4 km altitude; 28° N; 16° W) by Schmidt (1990). With a yearly average of 0.28 ppbv, a summer (June, July, August) average of 0.1 ppbv and a winter (December, January, February) maximum of 0.40 ppbv, they are comparable to the free tropospheric data for mid-northern latitudes, but with a winter/summer ratio of nearly 5, the seasonal variability seems to be slightly more pronounced. Extremely low acetylene mixing ratios were reported by Rudolph *et al.* (1989) for the Neumayer station (71° S; 8° W) in Antarctica. Between 1982 and 1985, they observed a minimum of about 0.005 ppbv during austral summer (January, February, March) and largest values of 0.015 ppbv in late austral winter (August through October). They explain this seasonality with the faster photochemical removal of acetylene by OH radicals in summer, and a contribution from southern hemisphere biomass burning which is in phase with the observed seasonality.

The existence of marked seasonal variations in the mixing ratio of C_2H_2 at high northern latitudes has also been established. Rasmussen *et al.* (1983) reported measurements from Barrow, Alaska (70° N) which show a decrease from an average of 0.75 ppbv at mid-March 1982 to about 0.1 ppbv in early June. Hov *et al.* (1984) derived an average of about 0.07 ppbv from samples taken in the boundary layer of the Norwegian Arctic (74.5–79° N) during the end of July 1982, while late March 1983 values averaged 0.95 ppbv. Comparable values of about 1 ppbv acetylene were also reported by Hov *et al.* (1989) for the Norwegian Arctic in spring 1985 (66° N and 79° N) and 1986 (79° N). Rudolph and Ehhalt (1981) found an average of 0.13 ppbv over the North Atlantic and the Barents Sea (70° N–81° N; 1° W–27° W) in August 1979. At high northern latitudes, the summer acetylene mixing ratios are comparable to those from remote areas at mid-latitudes, but in winter the Arctic acetylene mixing ratios seem to be substantially higher than those at lower latitudes. In winter at high latitudes, the photochemical removal of light hydrocarbons is negligible and the exchange with lower latitudes much slower than

in summer. This can result in an accumulation of light hydrocarbons during winter in the Arctic troposphere (Isaksen *et al.*, 1985) and, thus, a larger seasonality. Indeed, the observed change of roughly an order of magnitude between summer and winter is larger than measured at lower latitudes. Unfortunately, the published measurements of acetylene at high latitudes are rather sparse and cover only a few relatively short periods of observations so that more data are needed to derive a representative seasonal cycle.

The comparison of *in-situ* measurements of concentrations with remote total column amounts requires assumptions which have transpired all along the previous discussions: on future observational campaigns, both *in-situ* and remote, the systematic collection of ancillary data (i.e., regarding the tropopause height, the history of the air parcels studied, meteorological conditions, etc.) as well as coordination of measurements by the two techniques through the same airmasses, should allow a better quantification of the ultimate techniques' performances and help to establish and interpret the observed short-term variability of gases of intermediate lifetime, as is the case of C_2H_2 .

4. Conclusion

It appears that the vertical column abundances of acetylene measured above the Jungfraujoch station are suitable to derive representative acetylene mixing ratios in the free troposphere at mid-latitudes. In general, the observed seasonal variations are comparable to those derived from airborne *in-situ* measurements and those reported from ground-based stations. The phase of the seasonal cycle is compatible with the seasonal change of the removal rate by reaction with OH radicals, but meridional transport may also have some effect. Also, at all sites, significant short-term variability is observed. Thus, precise determination of the magnitude and phase of the seasonal cycle requires frequent measurements over a period encompassing several years. The presently available data are not sufficient to allow a reliable analysis of a secular trend. The optical infrared remote column abundance measurements average over a considerable altitude range, a substantial advantage for the investigation of representative seasonal cycles and long term trends of trace gases with life times of only a few months or less.

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