

GROUND-BASED MEASUREMENTS OF THE ATMOSPHERIC COLUMN DENSITY OF ETHANE (C₂H₆) AND ACETYLENE (C₂H₂) BASED ON HIGH-RESOLUTION SOLAR IR SPECTRA

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We present the results of experimental measurements of C₂H₆ and column density carried out from solar spectra recorded in the 3 μm region at resolution 0.07 cm⁻¹. The measurements were carried out using the spectrometer facility at the Zvenigorod scientific station (Institute of Atmospheric Physics, Academy of Sciences of the USSR). The resulting column densities of 2 · 10¹⁶ molecules/cm² for C₂H₆ and (2 · 10¹⁵, 4 · 10¹⁵) molecules/cm² for C₂H₂ are in reasonable agreement with the available data on the atmospheric concentrations of these gases. These are the first measurements of this type in continental Europe.

Many research problems involving atmospheric trace gases require data on the entire atmosphere as a whole; such data are most conveniently obtained spectroscopically, using a method based on analysis of the solar IR spectrum at the bottom of the atmosphere. This method has been used to obtain various important geophysical results concerning the spatial distribution and time variations in many atmospheric trace gases.¹⁻³ The spectroscopic method has become especially important in recent years as it has become possible to carry out measurements from space.⁶ However, this in no way detracts from the role played by ground-based spectroscopy, since satellite-based observations can only provide information on the concentrations of atmospheric trace gases in the stratosphere and upper troposphere, while ground-based observations enable one to determine the column density of trace atmospheric gases in the atmosphere as a whole. In other words, satellite-based and ground-based observations are complementary from the point of view of studying atmospheric trace gases.

The Institute of Atmospheric Physics (USSR Academy of Sciences) has developed a high-resolution solar IR spectroscopic facility for carrying out a wide variety of research programs in atmospheric spectroscopy. This facility has enabled us to observe atmospheric trace gases having relative atmospheric concentrations of order 10⁻⁹–10⁻¹⁰ among the gases in this concentration range are the light hydrocarbons, which play an important role in atmospheric chemistry. However, there is too little experimental data on their spatial distribution, time variations, sources and sinks to determine their atmospheric cycles.

In this paper, we describe the technical characteristics of the facility and the results of our first experimental determinations of the column density of C₂H₆ and C₂H₂ above Zvenigorod.

At this point, we should note that spectroscopic measurements of ethane and acetylene have already been carried out from balloons, airplanes, spacecraft, and from the surface of the Earth.⁵⁻⁹ The novelty in the results presented here is that such measurements have never been carried out in continental Europe or in a lowland region.

Spectroscopic facility. The facility is based on a high-resolution echelle diffraction spectrometer. The optical portion of the spectrometer is based on a Girard slit spectrometer. The high optical quality means that the main resolution-limited factor is diffraction by the grating aperture (200 mm). Experience with solar spectra has shown that the theoretical resolution of the spectrometer can be reached in the 3–5 μm region: 0.07 cm⁻¹ at 3 μm and 0.04 cm⁻¹ at 5 μm (a cooled (–80°C) PbSe photodetector was used, the detector electronics had a time constant of 3 s, and the signal-to-noise ratio was 100). The spectrum was scanned by rotating the diffraction grating. The position of the grating was monitored to within 3 arcsec using a laser interferometer goniometer. A DVK-2 microcomputer was used to control the spectrometer, as well as to record and reduce the spectra.

Light from the Sun was fed into the spectrometer using a heliostat whose movable mirrors were located 20 m above the surface, which enables us to obtain nearly constant illumination at all daylight hours.

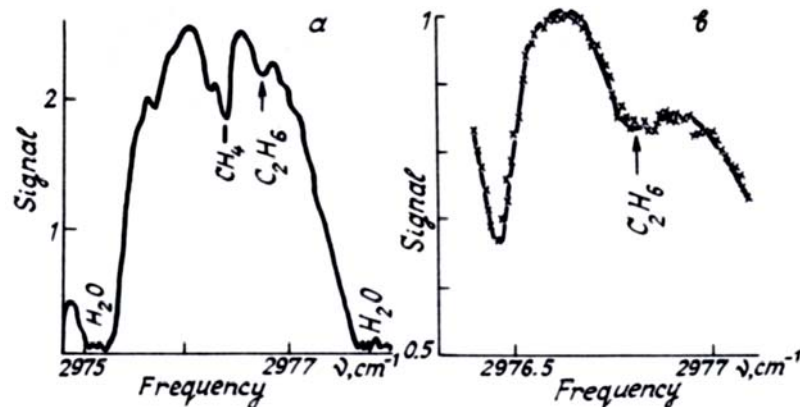


FIG. 1. (a) Atmospheric transmission spectrum. May 19, 1989, Zvenigorod, PQ_3 line of C_2H_6 (indicated by arrow). Mean geometric air mass 3.70. Resolution 0.07 cm^{-1} . (b) Results of spectral synthesis (solid curve) compared with the experimental results (crosses). Conditions same as in (a).

Results. For our measurement of the column densities of C_2H_2 and C_2H_6 , we selected the PQ_3 branch of the ν_7 band in ethane (2976.1 cm^{-1}) and the R9 line in the $\nu_2 + \nu_4 + \nu_5$ band of acetylene (3304.9686 cm^{-1}). Analysis of the experimental data and theoretical calculations by Rinsland, et al.^{6,8,9} indicated that these lines were sufficiently well-isolated from lines due to other gases and were readily visible in solar spectra.

The column densities of the gases were determined from the recorded spectra by carrying a least-squares fit of a synthesized spectrum to the measured spectrum. A detailed description of the estimation procedure for the column density has been given by Pugachev.⁴

1. C_2H_6 column density measurements. The recorded spectrum in the vicinity of the PQ_3 branch of the ν_7 band in acetylene is shown in Fig. 1a. The total water content at the time the measurements were taken was 0.75 g/cm^2 precipitated water. Although the C_2H_6 line is in the wing of a strong H_2O line, we see that it quite visible. Three gases were included in the synthesis: C_2H_6 , H_2O , and CH_4 . The weak O_3 lines which partially overlap the C_2H_6 lines were not taken into account in the present synthesis. We estimate the resulting error in C_2H_6 column density to be no greater than 1%. The spectroscopic constants of C_2H_6 were obtained from Rinsland, et al.,⁶ while the parameters of the H_2O and CH_4 lines were obtained from the CEISA data bank.¹⁰ Specific temperature and water profiles for the epoch of measurement were used in synthesizing the spectrum. The relative C_2H_6 concentration was assumed to be constant with altitude; CH_4 was assumed to have a constant mixing ratio of 1.6 ppm at all altitudes. Reduction of the spectra obtained on May 19, 1989 led to a vertical C_2H_6 column density of $2.0 \cdot 10^{16}$ molecules/ cm^2 , which corresponds to a mean tropospheric concentration of 1.1 ppb. The random error in this determination is 3%. The error due to the

lack of accuracy in the spectroscopic data is no greater than 10%.^{6e}

For comparison, we point out that the results of Tille, et al.¹¹ and Blake and Rowland¹² imply that we can expect a tropospheric concentration of 1.4–1.5 ppb for C_2H_6 in May at latitudes of 30–68° N. Taking the significant irregular variations in the concentrations of C_2H_6 with time into account, we conclude that our results are in reasonable agreement with existing results from the literature.

2. C_2H_2 column density measurements. Absorption lines from C_2H_2 have been observed in spectra obtained during fall and winter at Kitt Peak Observatory (USA).⁹ The high resolution (0.01 cm^{-1}) and high mountain altitude (2095 m above sea level, and thus only slightly affected by H_2O lines) enabled Rinsland, et al.⁹ to reliably detect and reduce 12 lines of C_2H_2 . However, we did not know whether it would also be possible to successfully carry out similar measurements under lowland conditions. Figure 2a shows a section of the spectrum near the R9 line of the $\nu_2 + \nu_4 + \nu_5$ band in C_2H_2 . We see that the shape of the spectrum is largely determined by the H_2O lines. At the time of measurement, the total water content was 0.68 g/cm precipitated water.

The characteristic structure of the R9 line is visible at the appropriate wavelength (3304.9686 cm^{-1}). Spectra of this section with visible C_2H_2 lines were obtained on March 21, 1989 and April 7, 1989. Figure 2b shows a typical example of the spectral synthesis. The spectroscopic constants were obtained from the CEISA data bank.¹⁰ The C_2H_2 profile with altitude was assumed to have a constant mixing ratio. A total of five gases was taken into account in the synthesis: C_2H_2 , H_2O , CO_2 , N_2O , and HCN . The resulting values for the column density of C_2H_2 were $4 \cdot 10^{15}$ molecules/ cm^2 from the March 21, 1989 spectrum and $2 \cdot 10^{15}$ molecules/ cm^2 from the April 7, 1989 spectrum; mean tropospheric concentrations of 0.2 ppb and 0.1 ppb were obtained.

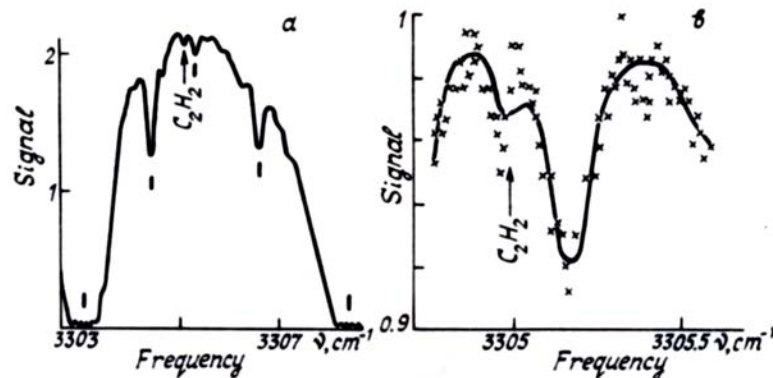


FIG. 2. Atmospheric transmission spectrum near the R9 Line of C_2H_2 (indicated by the arrow)(a). Vertical lines indicate the positions of H_2O lines. Mean geometric air mass 2.68. Result of spectral synthesis (solid curve) compared with the experimental results (crosses) (b).

Rinsland, et al.,⁹ present the results of C_2H_2 column density measurements using the same line (R9) for analysis in spectra recorded on February 23, 1981 and October 1, 1982 at Kltt Peak. The resulting values for the column density and mean tropospheric concentration are $2.34 \cdot 10^{15}$ molecules/cm² and 0.21 ppb for August 23, 1981 and $1.86 \cdot 10^{15}$ molecules/cm² and 0.13 ppb for October 1, 1982. Thus, we see that our results are in agreement with earlier results obtained by a similar method.

Conclusions. The above research indicates that the methods and instrumentation developed above enable us to measure the column densities of atmospheric trace gases having concentrations of order 10^{-9} – 10^{10} .

The test results obtained for the concentrations of C_2H_6 and C_2H_2 are in qualitative agreement with published results, and spectroscopic methods are appropriate for use in studying the atmospheric cycles of these and other atmospheric trace gases.

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