

High spectral resolution solar absorption measurements of ethylene (C₂H₄) in a forest fire smoke plume using HITRAN parameters: Tropospheric vertical profile retrieval

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Abstract

The tropospheric mixing ratio profile of ethylene (C₂H₄) has been retrieved from a high spectral resolution ground-based infrared solar absorption spectrum. The spectrum was recorded during intense fires in New South Wales, Australia on January 1, 2002, and was analyzed with the C₂H₄ spectral parameters added to the 2000 HITRAN compilation. Absorption by C₂H₄ in the smoke-affected spectrum extends over a broad spectral range in a region with observable rotational fine structure. The fine structure occurs in addition to the 949.5 cm⁻¹ ν₇ band Q branch that is traditionally used to quantify C₂H₄ amounts from infrared atmospheric measurements assuming room temperature laboratory absorption coefficients. The measured spectrum is fitted to near the noise level with a retrieved vertical column of $(3.8 \pm 0.2) \times 10^{17}$

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molecules per square centimeter. The retrieved vertical C₂H₄ profile increases with altitude near the surface reaching a maximum of 37 parts per billion (10⁻⁹) near 1 km, decreasing above.

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1. Introduction

Ethylene (ethene, C₂H₄) is a well-known short-lived product of biomass fires [1] that has been measured in the atmosphere by a variety of techniques. Infrared atmospheric measurements of fires have been obtained from open-path absorption spectra [1–4], airborne in situ air sampling [5,6] and nadir-viewing thermal emission spectra [7]. Many of these previous infrared remote sensing measurements relied on the room temperature absorption cross sections of Hanst and Hanst [8]. The purpose of this investigation is to report the first analysis of atmospheric C₂H₄ from a high spectral resolution infrared solar spectrum recorded with a Fourier transform spectrometer (FTS) and spectral parameters from the HITRAN (High resolution TRANsmis-sion) 2000 database [9]. The HITRAN 2004 database [10] contains the same set of C₂H₄ parameters. The measurements were recorded during a period of intense bush fires in New South Wales (NSW), Australia, with an observation of dense ground-level smoke in addition to a visible smoke plume at higher altitude that passed directly through the solar ray path. The C₂H₄ tropospheric volume mixing ratio profile has been retrieved from the smoke-affected spectrum. A pre-fire spectrum is used as a reference.

Spectral line parameters for ethylene are a new addition to the HITRAN compilation [9,10], though the molecule appeared in both the GEISA (Gestion et Etude des Informations Spectroscopiques Atmosphérique) 1992 and 1997 databanks [11]. This HITRAN 2000 linelist for C₂H₄ contains eight bands for the main isotope, ¹²C₂H₄ and two bands for the rarer isotopic species ¹²C¹³CH₄. For the main isotopes the bands included are ν_{10} , $\nu_9 + \nu_{10}$, ν_7 , ν_4 , ν_9 , ν_{11} , $2\nu_{10} + \nu_{12}$, $\nu_9 + \nu_{10} - \nu_{10}$. For the second isotope, only the ν_9 and ν_{11} bands are included. The C₂H₄ data cover 700–1170 and 2918–3243 cm⁻¹. The C₂H₄ GEISA 1997 archive [11] is similar to the HITRAN 2000 one [9]. The lower wavenumber region contains parameters only for the main isotope and is dominated by absorption from the ν_7 band. We restrict the current investigation to this region, where the absorption is strong. Shorter wavelengths absorption is dominated by the strong CH fundamentals ν_9 and ν_{11} around 3106 cm⁻¹ [9]. The longer-wavelength region is accessible to instruments using nadir viewing thermal emission techniques [7], and hence could be used for space-borne thermal-emission remote sensing measurements of fire scenes. HITRAN 2000 C₂H₄ parameters assume an air-broadening coefficient of 0.087 cm⁻¹ atm⁻¹ at 296 K, 0.09 cm⁻¹ atm⁻¹ at 296 K for the self-broadening coefficient, 0.82 for n , the coefficient of the temperature-dependence of the air-broadening coefficient, and zero for the air-broadened pressure shift coefficient for all lines (see Table 1 of [9] for a definition of HITRAN 2000 parameters).

Ethylene is also of significant importance for studies of the atmospheres of the outer planets. Based on the need for accurate line-by-line spectral parameters for planetary atmospheres work for a range of temperatures, an atlas contains calculated positions, intensities at 296 K, lower state

energies, and quantum assignments for over 11,000 transitions from 700 to 1184 cm⁻¹ has been generated [12,13] and is available at <http://aurora.phys.utk.edu/~blass/ethyatlas/>

2. Solar measurements

The solar absorption spectra were recorded by one of us (A. Meier) with a Bomem model DA-8 FTS located at the University of Wollongong, Australia (latitude 34.45°S, longitude 150.88°E, 30 m above sea level). The station is located 56 km south of the main Sydney airport. The instrument was described previously [14,15], but was refurbished in August 2001, replacing the complete scanning mechanism and moving the dynamic alignment onto the scanning mirror. The measurements analyzed here consist of a pre-fire spectrum recorded on December 11, 2001, (with a maximum optical path difference of 250 cm) and a smoke-affected spectrum recorded on January 1, 2002, (with a maximum optical path difference of 100 cm). Both spectra were recorded with an optical band-pass filter that limited the spectral coverage to 710–1060 cm⁻¹. These spectra are part of a dataset of over seventeen hundred smoke-affected spectra recorded from the University of Wollongong during forest-fires between December 2001 and January 2003. Further description of these measurements and a comparison of column amounts of NH₃, CO, HCN, and H₂CO derived from the spectra with visible aerosol optical depth measurements have been reported by Paton-Walsh et al. [16].

3. Analysis

Fig. 1 illustrates the 945–952 cm⁻¹ region from the pre-fire (upper plot) and smoke-affected spectra, offset vertically for clarity. The pre-fire spectrum was recorded at an astronomical zenith angle of 56.79°, and the smoke-affected spectrum was obtained at an astronomical zenith angle of 12.84°. Both spectra show strong absorption by a nearly evenly-spaced sequence of four strong lines, which are marked by asterisks and identified as P-branch transitions of the

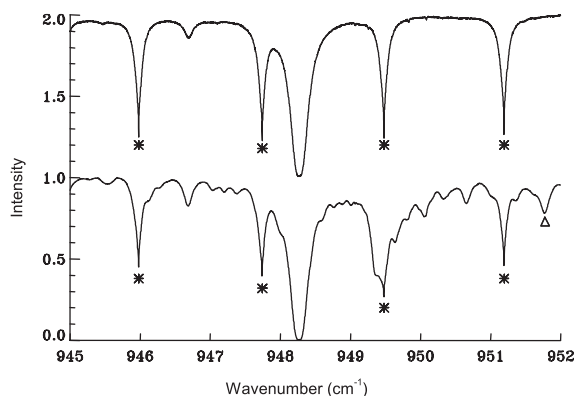


Fig. 1. The 945–952 cm⁻¹ region from the prefire (upper plot) and fire spectra, offset vertically for clarity. Lines of the ¹²C¹⁶O₂ 00°1 – (01°0, 020)_J band are marked with asterisks in both the prefire and fire spectra. An open triangle marks the location of a strong NH₃ line observed at 951.776 cm⁻¹. The spectra are normalized and offset vertically for clarity.

$^{12}\text{C}^{16}\text{O}_2$ $00^{\circ}1 - (01^{\circ}0, 020)_J$ band. Weak $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ lines are observable in the pre-fire spectrum, but not readily noticed in the lower resolution smoke-affected spectrum. The interval contains two observable H_2O lines, a weak transition at 944.859 cm^{-1} and an order of magnitude stronger line at 948.263 cm^{-1} . Both lines have similar absorption depths in the pre-fire and smoke-affected spectra. In the smoke-affected spectrum, many additional absorption features occur most of which can be attributed to lines of C_2H_4 with two transitions of NH_3 in the interval.

Fig. 2 displays the smoke-affected spectrum (top) and molecule-by-molecule simulations of the absorption by C_2H_4 , CO_2 , NH_3 , and H_2O , offset vertically for clarity. These molecules are the major contributors to the absorption in this region (additional molecules such as SF_6 absorb weakly in the spectra). Pure rotation lines of solar OH have also been identified in high spectral resolution solar absorption spectra [17] and produce weak features in the Wollongong solar spectra. The C_2H_4 ν_7 band Q branch has its strongest absorption at 949.45 cm^{-1} , at $\sim 0.02\text{ cm}^{-1}$ below the overlapping P(14) line of the $^{12}\text{C}^{16}\text{O}_2$ $00^{\circ}1 - (01^{\circ}0, 020)_J$ band. As shown in the smoke-affected spectrum and the corresponding simulation (second from the top), C_2H_4 absorbs significantly throughout the region with detectable fine structure. Room temperature laboratory spectra at 0.5 cm^{-1} resolution [8] show the structure extends from ~ 900 to 1000 cm^{-1} . The linelist includes the air-broadened pressure-shift coefficients measured for $^{12}\text{C}^{16}\text{O}_2$ lines at 0.0027 cm^{-1} resolution from room temperature laboratory spectra recorded with the McMath FTS [18]. The pressure shift is sufficient to be detectable in high spectral resolution ground-based solar spectra (see Fig. 6 of [18]). The measured positions and air-broadened shifts are included in HITRAN 2000 [9]. Lines of NH_3 are predicted at 948.232 and 951.776 cm^{-1} with the revised set of parameters [19] incorporated in HITRAN 2000 [9], though the lower wavenumber line is masked by stronger H_2O absorption.

In order to increase the signal-to-noise ratio the smoke-affected interferogram was retransformed to obtain a lower resolution spectrum calculated for a maximum optical path difference (OPD) of 50 cm. Retrievals were performed with the SFIT2 algorithm [20–22], which is based on a semi-empirical implementation of the Rodgers optimal estimation method [23]. Fig. 3 illustrates the C_2H_4 volume mixing ratio (VMR) averaging kernels computed for the

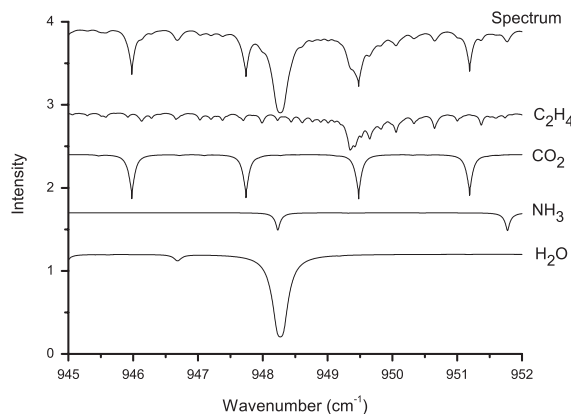


Fig. 2. Fire spectrum (top) and molecule-by-molecule simulations of the absorption by C_2H_4 , CO_2 , NH_3 , and H_2O , offset vertically for clarity for the $945\text{--}952\text{ cm}^{-1}$ region.

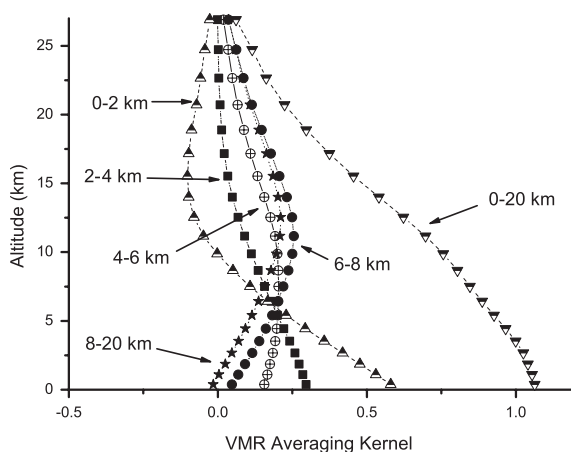


Fig. 3. Volume mixing ratio (VMR) averaging kernels calculated for the C_2H_4 fire measurement, the $945.0\text{--}952.0\text{ cm}^{-1}$ interval, the a priori profile, and covariance matrix, and assumed signal-to-noise described in the text.

$945.0\text{--}952.0\text{ cm}^{-1}$ region assuming an a priori mixing ratio of less than 0.2 parts per billion (10^{-9}) by volume at the surface decreasing with altitude. This a priori mixing ratio profile is typical of clean air and the optimal estimation is weighted heavily towards the measured spectrum, relative to the a priori, especially in the troposphere to achieve a good fit. The kernels are shown for layers interpolated to 2 km thick vertical shells between 0 and 8 km, as well as 8–20 and 0–20 km. A signal-to-noise ratio of 300 was assumed, consistent with the observation. The kernels are broad, peaking at approximately the midpoint in each layer near the surface, and gradually broadening, reflecting loss of sensitivity with altitude. There is good sensitivity to the true state of the atmosphere below 10 km. Above 12 km the retrieval is dominated by the contribution from the a priori profile. A similar clean air a priori profile was assumed for NH_3 to fit the unblended 951.776 cm^{-1} line in the smoke-affected spectrum. The covariance matrix was assumed diagonal with relative uncertainties of 3.0 in the bottom 10 (of 39) atmospheric layers from ground-level to ~ 9 km altitude and 1.0 in the upper 29 (of 39) atmospheric layers from ~ 9 to 100 km altitude. A correlation length of 4 km between layers was used. Vertical profiles of C_2H_4 and NH_3 were retrieved in this manner while H_2O and CO_2 were fitted by scaling the a priori profile for each by a single multiplicative factor.

Refractive ray-tracing and airmass weighted pressures and temperatures were computed with a model containing 39 atmospheric layers extending from the surface to 100 km [24]. The atmosphere assumes Sydney airport soundings for the day of observation. The vertical thickness of the layers increases smoothly with altitude from less than 1 km at the surface to 2 km at 30 km with wider layers above.

Fig. 4 illustrates the fit to the smoke-affected spectrum obtained from the $945.0\text{--}952.0\text{ cm}^{-1}$ window with the spectral parameters and settings described above. As can be seen from the plot of residuals (simulated spectrum–measured spectrum), the fit is not perfect, with poorer fits to the H_2O line at 946.678 cm^{-1} , the C_2H_4 Q branch at 949.362 cm^{-1} and the C_2H_4 manifold around $950\text{--}951\text{ cm}^{-1}$. These problems suggest inaccuracies in the spectral line-widths and line-intensities for C_2H_4 in HITRAN and will cause additional uncertainties in the profile retrieval.

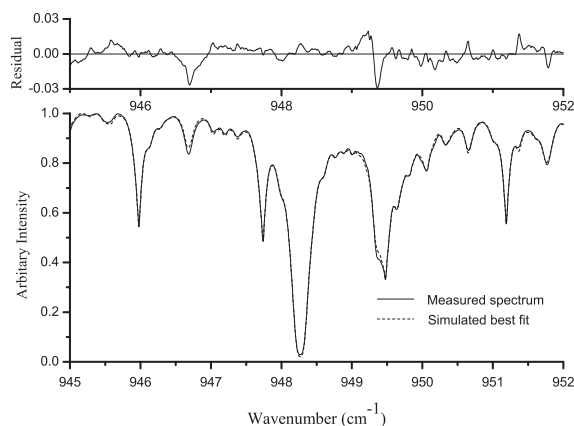


Fig. 4. Fit to the 945.0–952.0-cm⁻¹ region of the Wollongong fire spectrum. Residuals (measured minus calculated) are shown in the upper panel on an expanded vertical scale.

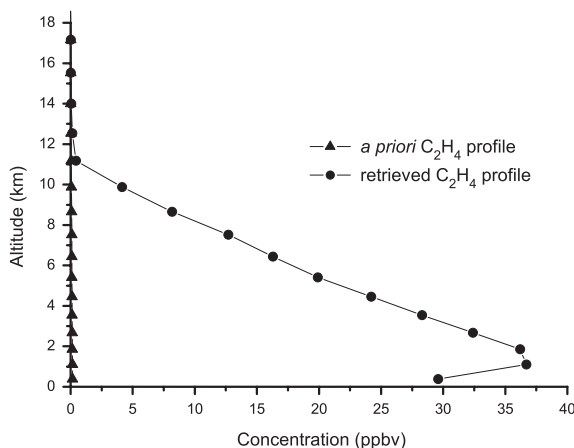


Fig. 5. Comparison between the retrieved and a priori C₂H₄ volume mixing ratio profiles plotted vs. mean altitude of the layers.

Fig. 5 illustrates the retrieved C₂H₄ vertical profile. The clean air a priori profile is also shown for comparison, but is dwarfed by the large concentrations retrieved from the smoke-affected spectrum. The retrieved profile has C₂H₄ mixing ratios in the order of tens of parts per billion by volume (ppbv, or nmol mol⁻¹) throughout the lower troposphere, reaching a maximum of 37 ppbv at a layer-average altitude of 1.1 km. The retrieved total column amount is $(3.8 \pm 0.2) \times 10^{17}$ molecules cm⁻². The vertical distribution for NH₃ is similar, but is not presented as only a single unblended feature occurred in the fitted spectral region and the result is less robust. The retrieved mixing ratio profiles of C₂H₄ and NH₃ are sensitive to the adopted a priori profiles, though there is little change in the fitting residuals with different a priori profile selections. Retrievals with other a priori profiles all require vertical distributions with maximum mixing ratios in the lower troposphere and the derived total column amounts are consistent to

within a few percent. Based on these tests, we estimate errors in the retrieved lower tropospheric mixing ratios due to uncertainties in the a priori profile may be as high as a factor of two below 5 km altitude, above which the retrieval is gradually dominated by the contribution of the a priori profile. The uncertainties are in addition to those associated with errors in the spectral parameters, the retrieval algorithm, and the assumed temperature profile. The sum of these additional systematic error sources is estimated to be $\sim 10\%$.

4. Discussion

The present investigation demonstrates the potential for quantifying C_2H_4 vertical tropospheric profiles from near $10\ \mu m$ smoke-affected solar absorption spectra analyzed with HITRAN 2000 [9] line-by-line spectral parameters. The combination of high spectral resolution observations and elevated C_2H_4 tropospheric abundances provide a useful test of the C_2H_4 spectroscopic parameters in the analyzed spectral region. The HITRAN 2000 parameters [9] appear to be adequate for retrieving C_2H_4 vertical profiles with significant C_2H_4 fine structure observed and fitted approximately in addition to the strong ν_7 band Q branch. However the ν_7 band Q branch may be about 5% stronger in the spectrum than predicted by the HITRAN 2000 parameters and revisions also may be needed to the assumed constant values for the air-broadening coefficient and its temperature dependence [9].

5. Summary and conclusions

A ground-based high spectral resolution solar absorption spectrum recorded from the University of Wollongong in eastern Australia during intense fires on January 1, 2002, has been analyzed to retrieve the vertical profile of tropospheric C_2H_4 assuming a set of line parameters based on the HITRAN 2000 compilation [9]. The C_2H_4 absorption in the fire spectrum shows fine structure in addition to the ν_7 band Q branch, which has its strongest absorption at $949.45\ cm^{-1}$. A vertical profile retrieval of C_2H_4 based on this set of spectral parameters and the SFIT2 algorithm [20–22] shows that most of this spectral interval can be fitted quite well in the smoke-affected spectrum, with a number of minor features visible in the plot of residuals. The derived vertical column amount is $(3.8 \pm 0.2) \times 10^{17}$ molecules cm^{-2} with a vertical profile distribution with a maximum volume mixing ratio of 37 ppbv near an altitude of 1 km above the station.

As already noted, past quantitative infrared measurements of C_2H_4 in fires have used room temperature absorption cross sections [8] in combination with lower resolution measurements with Fourier transform spectrometers either of laboratory smoke samples [2–4], by in situ sampling of plumes [5,6], or nadir thermal emission [7]. The C_2H_4 in situ aircraft measurements of emission ratios have been derived by plotting smoke plume concentrations relative to concentrations of a reference molecule such as CO [4,5]. Analysis with the updated set of spectral parameters in combination with the SFIT2 retrieval algorithm demonstrate the potential for direct C_2H_4 vertical profile retrievals from ground-based high spectral resolution solar spectra recorded at elevated abundances. Although not the primary focus of the present work, the

appearance of numerous strong spectral features in the same band-pass filter offers the potential for improving the NH₃ vertical profile information relative to the interval we have investigated.

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