



Mid-infrared spectroscopy of Uranus from the Spitzer infrared spectrometer: 2. Determination of the mean composition of the upper troposphere and stratosphere



Glenn S. Orton^{a,*}, Julianne I. Moses^b, Leigh N. Fletcher^c, Amy K. Mainzer^d, Dean Hines^e, Heidi B. Hammel^f, Javier Martin-Torres^g, Martin Burgdorf^h, Cecile Merlet^c, Michael R. Lineⁱ

^a MS 183-501, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA

^b Space Science Institute, 4750 Walnut St., Suite 205, Boulder, CO 80301, USA

^c Atmospheric, Oceanic & Planetary Physics, Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, UK

^d MS 321-535, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA

^e Space Telescope Science Institute, 3700 San Martin Drive, Baltimore, MD 21218, USA

^f Association of Universities for Research in Astronomy, 1212 New York Avenue NW, Suite 450, Washington, DC 20005, USA

^g Instituto Andaluz de Ciencias de la Tierra (CSIC-INTA), Avda. De las Palmeras, 4, 18100 Armilla, Granada, Spain

^h HE Space Operations, Flughafenallee 24, D-28199 Bremen, Germany

ⁱ Department of Astronomy and Astrophysics, University of California – Santa Cruz, Santa Cruz, CA 95064, USA

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ABSTRACT

Mid-infrared spectral observations Uranus acquired with the Infrared Spectrometer (IRS) on the Spitzer Space Telescope are used to determine the abundances of C₂H₂, C₂H₆, CH₃C₂H, C₄H₂, CO₂, and tentatively CH₃ on Uranus at the time of the 2007 equinox. For vertically uniform eddy diffusion coefficients in the range 2200–2600 cm² s⁻¹, photochemical models that reproduce the observed methane emission also predict C₂H₆ profiles that compare well with emission in the 11.6–12.5 μm wavelength region, where the ν₉ band of C₂H₆ is prominent. Our nominal model with a uniform eddy diffusion coefficient $K_{zz} = 2430 \text{ cm}^2 \text{ s}^{-1}$ and a CH₄ tropopause mole fraction of 1.6×10^{-5} provides a good fit to other hydrocarbon emission features, such as those of C₂H₂ and C₄H₂, but the model profile for CH₃C₂H must be scaled by a factor of 0.43, suggesting that improvements are needed in the chemical reaction mechanism for C₃H_x species. The nominal model is consistent with a CH₃D/CH₄ ratio of $3.0 \pm 0.2 \times 10^{-4}$. From the best-fit scaling of these photochemical-model profiles, we derive column abundances above the 10-mbar level of $4.5 + 0.1 - 0.8 \times 10^{19}$ molecule-cm⁻² for CH₄, $6.2 \pm 1.0 \times 10^{16}$ molecule-cm⁻² for C₂H₂ (with a value 24% higher from a different longitudinal sampling), $3.1 \pm 0.3 \times 10^{16}$ molecule-cm⁻² for C₂H₆, $8.6 \pm 2.6 \times 10^{13}$ molecule-cm⁻² for CH₃C₂H, $1.8 \pm 0.3 \times 10^{13}$ molecule-cm⁻² for C₄H₂, and $1.7 \pm 0.4 \times 10^{13}$ molecule-cm⁻² for CO₂ on Uranus. A model with K_{zz} increasing with altitude fits the observed spectrum and requires CH₄ and C₂H₆ column abundances that are 54% and 45% higher than their respective values in the nominal model, but the other hydrocarbons and CO₂ are within 14% of their values in the nominal model. Systematic uncertainties arising from errors in the temperature profile are estimated very conservatively by assuming an unrealistic “alternative” temperature profile that is nonetheless consistent with the observations; for this profile the column abundance of CH₄ is over four times higher than in the nominal model, but the column abundances of the hydrocarbons and CO₂ differ from their value in the nominal model by less than 22%. The CH₃D/CH₄ ratio is the same in both the nominal model with its uniform K_{zz} as in the vertically variable K_{zz} model, and it is 10% lower with the “alternative” temperature profile than the nominal model. There is no compelling evidence for temporal variations in global-average hydrocarbon abundances over the decade between Infrared Space Observatory and Spitzer observations, but we cannot preclude a possible large increase in the C₂H₂ abundance since the Voyager era. Our results have implications with respect to the influx rate of exogenic oxygen species and the production rate of stratospheric hazes on Uranus, as well as the C₄H₂ vapor pressure over C₄H₂ ice at low temperatures.

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* Corresponding author.

E-mail address: glenn.orton@jpl.nasa.gov (G.S. Orton).

1. Introduction

Determinations of atmospheric composition on Uranus are difficult because the low temperatures and low hydrocarbon column abundances make the planet extremely faint at mid-infrared wavelengths – a situation that differs from that of the other Solar-System giant planets. Atmospheric dynamical mixing on Uranus is comparatively weak, perhaps as a result of the planet's small internal heat source, so that methane (CH_4) is not transported to very high stratospheric altitudes, and photochemical production of other disequilibrium hydrocarbons is correspondingly suppressed (e.g., [Atreya et al., 1991](#)). The cold atmospheric temperatures force methane to condense in the troposphere, and although some CH_4 vapor makes it up past the tropopause cold trap to help heat the stratosphere via absorption of sunlight in the near-infrared vibrational bands, the stratospheric methane abundance is very depleted in Uranus compared with the other outer planets.

The small amount of methane that does make it into the stratosphere is subject to photolysis by ultraviolet radiation, just as on the other giant planets, and the subsequent atmospheric photochemistry produces heavier hydrocarbons such as acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), methylacetylene (the C_3H_4 isomer hereafter designated $\text{CH}_3\text{C}_2\text{H}$), and diacetylene (C_4H_2), as well as methyl radicals (CH_3) and other reactive intermediates (see the photochemical models of [Atreya and Ponthieu, 1983](#); [Summers and Strobel, 1989](#); [Bishop et al., 1990](#); [Moses et al., 2005](#), and the *Spitzer Space Telescope* observations of [Burgdorf et al., 2006](#)). Oxygen-bearing constituents such as water (H_2O) and carbon dioxide (CO_2) can also be present in the stratosphere of Uranus from external sources such as cometary impacts, satellite debris, or Kuiper-belt grains ([Feuchtgruber et al., 1997, 1999](#); [Burgdorf et al., 2006](#)). Abundance determinations for these hydrocarbon and oxygen species can help illuminate the details of the complex chemistry taking place in giant-planet atmospheres, as well as provide constraints on impact rates and the source of exogenic material on the giant planets.

However, detection of these species is difficult and requires sensitive instrumentation. Acetylene has previously been detected on Uranus from *Voyager* Ultraviolet Spectrometer (UVS) observations ([Herbert et al., 1987](#); [Yelle et al., 1989](#); [Bishop et al., 1990](#)) and Earth-based mid-infrared observations ([Orton et al., 1987](#); [Encrenaz et al., 1998](#)). Ethane has been identified from the *Voyager* UVS occultations ([Bishop et al., 1990](#)) and tentatively from ground-based mid-infrared observations ([Hammel et al., 2006](#)). Stratospheric H_2O has been reported from *Infrared Space Observatory* (ISO) observations ([Feuchtgruber et al., 1997, 1999](#)). Carbon monoxide, which is outside the spectral range of *Spitzer* spectra, has been detected in the infrared by [Encrenaz et al. \(2004\)](#) and in the submillimeter range by [Cavalié et al. \(2014\)](#). The *Spitzer Space Telescope* Infrared Spectrometer (IRS) is two orders of magnitude more sensitive than previous space-based instruments ([Houck et al., 2004](#)), allowing the first unambiguous infrared detections of C_2H_6 , $\text{CH}_3\text{C}_2\text{H}$, C_4H_2 , and CO_2 on Uranus, as well as providing abundance determinations for previously detected species like CH_4 and C_2H_2 ([Burgdorf et al., 2006](#)). Observations of these additional species supply important new constraints for photochemical models.

C_2H_2 observations of Uranus have hinted at possible increases in the acetylene abundance with time, with the apparent peak C_2H_2 mixing ratio increasing from $\sim 10^{-7}$ in the *Voyager* era ([Bishop et al., 1990](#)) to $\sim 4 \times 10^{-7}$ in the ISO era ([Encrenaz et al., 1998](#)) to $\sim 2 \times 10^{-6}$ in the *Spitzer* era ([Burgdorf et al., 2006](#)). The rotational pole of Uranus is nearly in its orbital plane, and the planet experiences unprecedented seasonal forcing as a result of this $\sim 98^\circ$ obliquity. Hydrocarbon production rates depend on solar insolation and thus will be seasonally variable, as may the stratospheric temperatures and circulation (e.g., [Friedson and Ingersoll,](#)

[1987](#); [Conrath et al., 1990](#)). To investigate the possibility of time variability in the global-average thermal structure or hydrocarbon abundances on Uranus due to the northern hemisphere slowly rotating into view after its long ~ 21 -year winter, we have acquired new *Spitzer*/IRS disk-averaged spectra of Uranus in December 2007, just 10 days after the Uranus northern vernal equinox. In [Orton et al. \(2014\)](#), hereafter called Paper 1, we discuss (a) the acquisition, calibration, and reduction of these *Spitzer*/IRS spectra; (b) the derivation of the global-average thermal structure on Uranus from the analysis of the H_2 S(1), S(2), and S(3) quadrupole lines and the broad, continuum-like, collision-induced absorption features of H_2 ; and (c) the derivation of the tropospheric methane and helium abundance, again from the analysis of the broad continuum-induced absorption in the 9–20 μm region.

In the current paper, we focus on molecular features in the 7–17 μm region. The high signal-to-noise ratio of these recent *Spitzer*/IRS spectra allows us to derive much improved values for the abundances of various atmospheric gases over those described by [Burgdorf et al. \(2006\)](#). We use newly developed one-dimensional (1D) photochemical models to predict the vertical profiles of the molecular constituents in order to more accurately model the *Spitzer* spectra. The thermal structure and tropospheric methane profile used in the model are constrained from the observational analysis described in Paper 1. The resulting updated photochemical models provide notably improved fits to the *Spitzer* spectra compared with results from previous photochemical models developed to fit the *Voyager* and ISO data (e.g., [Summers and Strobel, 1989](#); [Bishop et al., 1990](#); [Moses et al., 2005](#)); however, the apparent changes required by the new modeling do not conclusively suggest time variability in hydrocarbon abundances. We discuss the implications of our model-data comparisons with respect to molecular abundances, stratospheric photochemistry, vertical transport, and influx rates of exogenic oxygen-bearing species.

2. Observations

We observed Uranus over the course of 9.2 h on 2007 December 16–17, obtaining spectra from four different modules of *Spitzer*/IRS: Short High (SH), Short Low (SL), Long High (LH) and Long Low (LL). Using all four modules, wavelengths in the 5–37 μm range were sampled with resolving powers $R = \lambda/\Delta\lambda = 90$ –600 (see [Fig. 1](#)). For the work described in this paper, we used three spectral modules: SL1 ($\lambda = 7.46$ –14.05 μm , with $\lambda/\Delta\lambda = 8.2667$), LL2 (13.98–21.43 μm with $\lambda/\Delta\lambda = 5.9048$) and selected orders of SH (9.95–19.30 μm with $\lambda/\Delta\lambda \sim 600$; see Paper 1 for a more detailed description of these modules). The beam size (3.6–10 arcsec, depending on wavelength, see Paper 1) was larger than the 3.35 arcsec diameter of Uranus, so the planetary disk was not spatially resolved—only globally averaged fluxes were obtained. However, some information on longitudinal spatial variations could be obtained because the observations acquired with different modules were not simultaneous, so that each module sampled a different range of planetary longitudes as Uranus rotated beneath the slit (see Paper 1 for further details). Apparent inconsistencies in the derived fluxes at wavelengths that overlap within the different modules suggest some longitudinal variability. These inconsistencies complicate our current analysis; the derivation of C_2H_2 is particularly affected due to a 10% difference in flux between the LL2 and SL1 modules near $\sim 14 \mu\text{m}$, where acetylene emission is prominent. The presence of similar discrepancies at wavelengths where other hydrocarbon emissions are present, combined with the lack of inconsistencies at wavelengths where the H_2 continuum dominates, suggests real longitudinal differences in stratospheric hydrocarbon emission rather than some kind of observational artifact such as a difference in the spillover of radiance from the disk of

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