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# Quantitative infrared absorption cross-sections of isoprene for atmospheric measurements

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Abstract

Isoprene (C<sub>5</sub>H<sub>8</sub>, 2-methyl-1,3-butadiene) is a volatile organic compound (VOC) that is one of the primary contributors to annual global VOC emissions. Produced by vegetation as well as anthropogenic sources, the OH- and O<sub>3</sub>-initiated oxidations of isoprene are a major source of atmospheric oxygenated organics. Few quantitative infrared studies have been reported for isoprene, however, limiting the ability to quantify isoprene emissions via stand-off infrared or in situ detection. We thus report absorption coefficients and integrated band intensities for isoprene in the 600–6500 cm<sup>-1</sup> region. The pressure-broadened (1 atmosphere N<sub>2</sub>) spectra were recorded at 278, 298 and 323 K in a 19.94 cm path length cell at 0.112 cm<sup>-1</sup> resolution, using a Bruker 66v FTIR. Composite spectra are derived from a minimum of seven isoprene sample pressures at each temperature and the number densities are normalized to 296 K and 1 atmosphere.

## 1 Introduction

Isoprene (C<sub>5</sub>H<sub>8</sub>, 2-methyl-1,3-butadiene) is a volatile organic compound (VOC) that is produced commercially as a reagent in the production of synthetic rubber and aviation fuel and is also emitted from the combustion of fossil fuel and biomass burning (Akagi et al., 2013; Hess et al., 2013). The amount of isoprene produced by non-biogenic processes, however, is only 0.1 % of the 600 Tg annual production estimated from living organisms including plants, animals and microbes (Hess et al., 2013; Guenther et al., 2012). The annual global isoprene emissions account for approximately one third of total VOC emissions, with methane contributing an additional third of the total and hundreds of other VOCs comprising the remainder (Guenther et al., 2012). Isoprene and other VOCs are of interest because of their role in controlling atmospheric oxidants and aerosol production. The limited knowledge of isoprene emissions, distributions and transformations (primarily due to a lack of measurements) is a major contributor to

# AMTD

7, 4163–4189, 2014

## Isoprene cross-sections

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



uncertainties in model simulations of regional air quality and global climate (Guenther et al., 2012).

Isoprene measurements are also of interest for their potential to characterize important biological processes. Isoprene concentrations in human breath, for example, vary from tens to hundreds of ppbv and have been used as an indicator of high blood cholesterol levels (Karl et al., 2001). In addition, isoprene may be a harbinger of stress in plants. For example, the foliage of some plants emit isoprene at extremely high rates and appear to have a role in protection from heat stress (Sharkey and Singaas, 1995) and possibly as a general protective mechanism for abiotic stress (Vickers et al., 2009).

Given that isoprene plays such an important role in the Earth system, it is not surprising that considerable effort has been made to develop analytical approaches for detecting and quantifying isoprene emissions. The techniques that have commonly been used include gas chromatography (GC) with detectors that include reduction gas, flame ionization, photoionization and mass spectrometers (Kim et al., 2013). More recently, continuous fast response detectors based on chemiluminescence and proton transfer reaction mass spectroscopy have increasingly been used for concentration and eddy covariance emission measurements on towers and aircraft (Potosnak et al., 2014; Karl et al., 2013). A number of studies have utilized infrared spectroscopy for standoff detection of isoprene (Akagi et al., 2014), however accurate quantification of these measurements is often hindered by a dearth of high-quality quantitative reference measurements. As a result, indirect methods are often employed in order to infer isoprene emissions. For example, satellite data on the isoprene oxidation product formaldehyde (HCHO) have been used in numerous studies (see Stavrakou et al., 2009, and references therein). This approach, however, is limited by the large uncertainties in accounting for the chemical and dynamical processes relating isoprene to formaldehyde (Barkley et al., 2012). The ability to sense isoprene using satellite sensors has the potential to transform the research community seeking to quantify emissions of this important trace gas, and preliminary observations have indicated that isoprene may be detected from space by the Earth Observing Tropospheric Emission Spectrometer

Isoprene  
cross-sections

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(TES) satellite (D. Fu, personal communication, 2013). Another advantage of potential spectroscopy approaches is that they tend to be more suitable for long-term measurements and networks than chemiluminescence and mass spectroscopy techniques, which require considerably more power, maintenance and operator expertise.

Despite the obvious need for quantitative infrared data and the potential for infrared observation of isoprene, as well as the relative abundance of UV cross-sections (e.g., Campuzano-Jost et al., 2004, 2000), the only quantitative infrared intensity studies of isoprene found in the literature report absorption cross-sections in the near-infrared (Denzer et al., 2011; Cias et al., 2007). While it is not unusual to record quantitative measurements of isoprene in conjunction with other experiments or for calibration purposes, these results are seldom reported in the literature. For example, Jobson et al. (1994) used infrared spectroscopy in conjunction with gas chromatography to quantify isoprene along with C<sub>2</sub>–C<sub>5</sub> alkane mixing ratios at a remote boreal site, but did not directly report their infrared band strengths or cross-sections. Quantitative FTIR spectra of isoprene and isoprene-*d*<sub>2</sub> also were measured by Kühnemann et al. (2002) in order to determine the detection limits of isoprene using infrared photoacoustic spectroscopy.

Nonetheless, there is an abundance of studies on the vibrational spectrum of isoprene, but most have focused on elucidating the structure and identifying its conformational equilibria (Compton et al., 1976; Traetteberg et al., 1984; Bock et al., 1987; Bock and Panchenko, 1989; Panchenko et al., 2008); fundamental modes typically were assigned during the structural analyses. Based on these previous vibrational assignment studies and structural determinations, and the need for quantitative absorption cross-section data, this paper makes the first comprehensive report of infrared band strengths of isoprene.

The results reported here are included in the quantitative Northwest Infrared (<http://nwir.pnl.gov>) database (Sharpe et al., 2004; Johnson et al., 2010), which contains spectra of common atmospheric gases, toxic industrial chemicals, as well as species known or suspected as biomass burning effluents, degradation products or precursors. Recent studies have included quantitative band strengths of HNCO (Roberts et al.,

**Isoprene  
cross-sections**

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Isoprene  
cross-sections**

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2010), H<sub>2</sub>O<sub>2</sub> (Johnson et al., 2009), and glycolaldehyde (Johnson et al., 2013), as well as the dicarbonyls glyoxal, methylglyoxal and diacetyl (Profeta et al., 2011). The availability of the quantitative band strengths allows evaluation programs such as MALT (Multiple Atmospheric Layer Transmission) (Griffith, 1996) to extract the mixing ratios, and ultimately the emission factors (EF, g of effluent per kg of fuel) of biomass burning effluents. Using the quantitative absorption cross-section information in the database and field measurements from either airborne or land-based systems, the EFs of dozens of species have been extracted in laboratory burns (Burling et al., 2010), as well as from prescribed fires in the US Southwest (Akagi et al., 2011) and the US Southeast (Burling et al., 2011; Akagi et al., 2013), including using open-path FTIR systems (Akagi et al., 2014). Some of these seminal EF measurements from the prescribed burns used the quantitative NWIR laboratory measurements of the related terpene species such as limonene, as well as both  $\alpha$ - and  $\beta$ -pinene for first observation of such species in biomass burning plumes (Burling et al., 2011; Akagi et al., 2013). In addition, results included in the database have been utilized by Adler et al. (2010) in the analysis of isoprene in human breath using a broadband frequency comb.

## 2 Experimental

Broadband infrared spectra were recorded with a Bruker-66v Fourier transform spectrometer, located at the Pacific Northwest National Laboratory (Sharpe et al., 2004), which had been modified to include a second aperture to reduce ghosting and warm aperture effects (Johnson et al., 2002). The instrumental parameters are summarized in Table 1, and consisted of typical mid-IR (600 to 6500 cm<sup>-1</sup>) components including a glow bar light source, a Ge on KBr beamsplitter, and a photoconductive HgCdTe detector (77 K). The scanner velocity was 60 kHz (HeNe fringe crossings s<sup>-1</sup>) and the instrument resolution was set to 0.112 cm<sup>-1</sup> (instrument resolution is defined as 0.9/maximum optical path difference). Interferograms were recorded and co-added and transformed using a Cooley–Tukey fast Fourier transform (FFT) algorithm with boxcar

**Isoprene  
cross-sections**

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



apodization. Phase correction was performed using the Mertz method (Mertz, 1967), with a phase resolution of  $4 \text{ cm}^{-1}$ ; and the high/low folding limits were set to  $15798$  and  $0 \text{ cm}^{-1}$ , respectively. Spectral intervals after the FFT were  $0.06 \text{ cm}^{-1}$  with  $2\times$  zero-filling. A software correction was applied by the FFT to account for the nonlinear response of the MCT detector (Keens and Simon, 1990). Bruker's OPUS software was used to operate the spectrometer, collect and perform the FFT, and perform the initial data reduction.

The optics bench of the spectrometer was evacuated in order to minimize water vapor and carbon dioxide gas absorptions. Air was removed from the isoprene samples (Aldrich, 99 %) by multiple freeze/pump/thaw cycles on a vacuum manifold connected directly to the gas cell in the spectrometer. A 2 inch diffusion pump, which is attached to the manifold and the gas cell (19.94 cm long, wedged KBr windows), was used to evacuate the gas cell before subsequently filling with the isoprene vapor. The gas cell is jacketed in such a manner that fluid from a circulation bath (Julabo F25) could temperature stabilize the cell. The pressure for each sample, which is listed in Table 2, was measured with a high-precision capacitance manometer (MKS 690A series Baratrons). The cell was then backfilled to a pressure of  $760 \pm 5$  Torr with high purity dry nitrogen. A background spectrum with the cell filled only with  $\text{N}_2$  was recorded at each temperature, typically averaging 512 interferograms. Two-hundred fifty-six interferograms were averaged for each sample spectrum. Spectra were recorded for seven sample pressures with the cell stabilized at  $278.20 \pm 0.02$  K, ten samples at  $298.18 \pm 0.02$  K and seven samples at  $323.12 \pm 0.02$  K. In order to exploit the full dynamic range of the instrument, a broad range of sample pressures was used. A data-weighting scheme is described below.

Each absorbance spectrum was calculated as  $-\log_{10}(I_{\text{sample}}/I_{\text{background}})$ . Individual spectra, recorded at each cell temperature, were combined into a composite spectrum by plotting the absorbance vs. the isoprene concentrations for each wavenumber bin in the measured spectra. The absorption coefficient,  $\epsilon(\nu)$ , is given by the fitted slope of the linear plot for each sample pressure,  $C_i$ , pathlength,  $\ell$ , at each wavenumber bin,  $\nu$

(Sharpe et al., 2004; Chu et al., 1999), viz.

$$A_i(\nu) = \varepsilon(\nu)\ell C_i \quad (1)$$

However, in order to minimize various nonlinearities associated with all absorption measurements, each absorbance value was weighted by  $T^2(\nu)$ , where  $T$  is the transmittance. Absorbances,  $A_i > 1.6$ , were simply given a weight of zero (Sharpe et al., 2002; Chu et al., 1999). The resulting composite spectrum for each temperature is effectively a plot of  $\varepsilon(\nu)$  for a molecule number density that has been normalized to 296 K. The composite spectra available on the website (<http://nwir.pnl.gov>) have wavenumber ( $\text{cm}^{-1}$ ) units on the abscissa and the ordinate is in units of  $(\text{ppmm})^{-1}$  for  $\log_{10}$  absorbance. Conversion factors between PNNL decadic units of  $(\text{ppm m})^{-1}$  ( $\log_{10}$ ) and common Napierian absorbances are:

$$9.28698 \times 10^{-16} \times \varepsilon(\nu) \text{ (ppm}^{-1} \text{ m}^{-1}, \log_{10}) = \varepsilon(\nu) \text{ (cm}^2 \text{ molecule}^{-1}, \log_e) \quad (2)$$

$$2.30259 \times 10^4 \times \varepsilon(\nu) \text{ (ppm}^{-1} \text{ m}^{-1}, \log_{10}) = \varepsilon(\nu) \text{ (cm}^{-1} \text{ atm}^{-1}, \log_e) \quad (3)$$

Integrated band intensities reported in the present work have been converted to units of  $\text{cm molecule}^{-1}$  with  $\log_e$  absorbances. The fitting process for producing the composite spectrum also calculates an uncertainty from the fit for each wavenumber bin. This resulting uncertainty vector describes the random (NIST type-A) uncertainties of the measurements. The average type-A uncertainties are 0.76 %, 0.26 %, and 0.93 % for the spectra taken at 278 K, 298 K and 323 K, respectively.

Systematic (NIST type-B) errors contribute the greatest uncertainty in the absorption coefficients. Following the methodology of Chu et al. (1999) and Sharpe et al. (2002), an upper limit for the systematic error is calculated based on the maximum uncertainty of experimental parameters, viz:

$$\mu_B = k[(\mu_L)^2 + (\mu_T)^2 + (\mu_P)^2 + (\mu_I)^2 + (\mu_{NL})^2]^{1/2} \quad (4)$$

where  $\mu_L$ ,  $\mu_T$ ,  $\mu_P$ ,  $\mu_I$ , and  $\mu_{NL}$  represent the pathlength, temperature, pressure, baseline drift of the spectrometer and nonlinear response of the detector. The value  $k = 2$  is

Isoprene  
cross-sections

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



chosen at the 95 % confidence limit ( $2\sigma$ ). Using the experimental uncertainties listed in Table 3, a type-B (systematic) error,  $\mu_B$ , is calculated to be 3 % for these static system measurements. It is assumed that the experimental uncertainties are uncorrelated and the uncertainty is assumed to be 3 % in the evaluation of the errors when discussing results for the various bands.

## 3 Results and discussion

### 3.1 Vibrational assignments

The ground state configuration of isoprene, shown in Fig. 1a, has been established to be planar *s-trans* (Lide and Jen, 1964). While the consensus in the literature supports this conclusion, there has been some dispute regarding the *s-cis* conformer (Fig. 1b), its fractional abundance at room temperature and whether the conformer is planar or gauche (Traetteberg et al., 1984; Bock et al., 1987; Cias et al., 2007; Panchenko et al., 2008; Panchenko and De Mare, 2008; Squillacote and Liang, 2005; Allodi et al., 2008). Compton et al. (1976) studied the temperature dependence of the infrared and Raman spectra of isoprene and assigned the fundamental modes of the planar *s-trans* and planar *s-cis* conformers. The authors concluded that the planar *s-cis* conformation (b) accounted for as much as 11 % and that the gauche form (Fig. 1c) was not observed.

The conformation analysis was reexamined by Traetteberg and coworkers (1984) who, using gas electron diffraction and theoretical techniques, determined that the gauche form did indeed exist, that it accounted for  $\sim 5\%$  at room temperature and that the planar *s-cis* was unlikely to be present at all. Subsequent ab initio analyses (Bock et al., 1987; Bock and Panchenko, 1989) confirmed this, although the angle of the gauche conformer was uncertain. More recent work, including a detailed study of a series of ten methyl-substituted 1,3-butadienes (Squillacote and Liang, 2005), established the gauche *s-cis* conformer of isoprene to be  $2.46 \text{ kcal mol}^{-1}$  ( $860 \text{ cm}^{-1}$ ) less stable than the planar *s-trans* form, while the planar *s-cis* conformer was theoretically

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





determined to be  $3.16 \text{ kcal mol}^{-1}$  less stable than the planar *s-trans* form. Thus, at the temperatures used in this work, roughly 98 % of the population was in the predominant, planar *s-trans* form and our results are therefore based on that conformer.

The ground state configuration (planar *s-trans*) of isoprene has  $C_s$  point group symmetry. There are 33 fundamental vibrational modes in which 22 have  $A'$  and 11 have  $A''$  symmetry. All modes are IR active. The  $A''$  fundamental modes will have C-type contours, whereas the  $A'$  modes will have A/B hybrids because the axis with the largest moment of inertia is perpendicular to the reflection plane. For isoprene, while most bands have A/B profiles, eleven have distinct C-type contours and are readily assigned as  $A''$  modes.

Figures 2 through 5 show portions of our composite isoprene vapor phase spectrum measured at 298 K with a quantitative  $y$  axis. Frequencies and vibrational assignments are listed in Table 4. Vibrational assignments follow primarily from Panchenko et al. (2008) and Compton et al. (1976), and ab initio frequencies from Panchenko et al. (2008) also are listed for reference. Although the two sources generally agree with respect to the fundamental modes of the *s-trans* conformer, there are minor differences in a few of the assignments and mode descriptions. For example, Compton et al. (1976) originally assigned the peak found at  $2956 \text{ cm}^{-1}$ , shown in Fig. 2, to an out-of-plane asymmetric  $\text{CH}_3$  stretch,  $\nu_{23}$ , and the peak at  $2985 \text{ cm}^{-1}$  to  $\nu_4$ , a symmetric  $\text{CH}_2$  stretch. Subsequent work (Traetteberg et al., 1984; Bock et al., 1987) was in agreement with these assignments. Panchenko et al. (2008) however, concluded that  $2956 \text{ cm}^{-1}$  was not a fundamental mode. Instead,  $\nu_{23}$  was assigned to  $2985 \text{ cm}^{-1}$  and  $\nu_4$  was assigned to  $3020 \text{ cm}^{-1}$  based on the vapor-phase Raman spectrum. For vapor-phase spectra, as shown in Fig. 2, however, band contours can be of great utility in assigning modes and are particularly useful in this instance. In agreement with Compton et al. (1976), the band at  $2956 \text{ cm}^{-1}$  is clearly a fundamental as it is the strongest C-H band in the spectrum. Moreover, its C-type profile indicates that it is an  $A''$  mode, namely the highest frequency  $A''$  mode,  $\nu_{23}$ , and is assigned as such.

**Isoprene  
cross-sections**

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Isoprene  
cross-sections**

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



In the C=C stretch region shown in Fig. 3,  $\nu_9$  is easily assigned to the A-type band at  $1605\text{ cm}^{-1}$ ; however,  $\nu_8$  is more problematic. Both Compton et al. (1976) and Panchenko et al. (2008) assign a peak at  $1638\text{ cm}^{-1}$  to  $\nu_8$ , which is not readily observed in this work (see Fig. 3). Instead, a very weak A/B-type band is observed at  $1651\text{ cm}^{-1}$  that we assign to the  $\nu_8$  fundamental.

Finally, the  $\nu_{16}$  band shown in Fig. 4 was assigned by Compton et al. (1976) to a very weak band at  $1145\text{ cm}^{-1}$ . This mode was subsequently reassigned by Traetteberg et al. (1984) to  $1069\text{ cm}^{-1}$  and later assigned by Panchenko et al. (2008) to  $1071\text{ cm}^{-1}$ . Our assignment of  $\nu_{16}$  follows Panchenko et al. (2008) and the peak at  $1069\text{ cm}^{-1}$  is assigned to  $\nu_{25}$ .

### 3.2 Integrated intensities

Integrated intensities for isoprene, shown in Table 5, were determined using the OPUS software suite (ver. 5.5) provided by Bruker Optics. The integration method (method A) uses zero as the baseline and performs a numerical integration between the wavenumber limits and the peak envelope. The measurements were recorded at three temperatures, 278, 298 and 323 K; however it is important to note that the resulting composite spectra are all scaled to a number density for 1 atm and 296 K. For the most part, the integrated band strengths agree among the different temperatures, adding further evidence that the spectra are composed primarily of the planar *s-trans* conformer, but there are two notable exceptions. For the band integration range  $1340\text{--}1220\text{ cm}^{-1}$ , with  $\nu_{14}$  and  $\nu_{15}$ , the integrated band intensity is 13 % higher in 323 K spectrum than it is in the 298 K spectrum. Similarly, in the  $820\text{--}720\text{ cm}^{-1}$  range, where  $\nu_{19}$  and  $\nu_{29}$  are located, the 323 K intensity is 19 % higher than in the 298 K spectrum. In both cases, however, there is virtually no difference between the 278 and 298 K spectra. While this may indicate a temperature dependence, it is unlikely due to the presence of an additional conformer. Qualitatively, the three spectra compare very well and there is no

evidence of extra modes or shifted peaks. Instead, because the modes in both of these areas are very weak, it is more likely due to the limitations in correcting the baseline.

Very few quantitative mid-infrared band strengths of isoprene are available in the literature, but a few papers report near-infrared absorption cross-sections ( $\sigma$ ). For example, Cias et al. (2007) determined  $\sigma$  of the C-H overtone at 1651.52 nm ( $6055\text{ cm}^{-1}$ ) to be  $3.24(\pm 0.16) \times 10^{-22}\text{ cm}^2\text{ molecule}^{-1}$ . Unfortunately, that mode is not observed in our spectra, thus no comparison can be made. A weak mode, however, is observed at  $6155\text{ cm}^{-1}$  with  $\sigma = 4.8 \times 10^{-21}\text{ cm}^2\text{ molecule}^{-1}$ . This value is  $\sim 25\%$  higher than the result reported by Denzer et al. (2011), who found  $\sigma = 3.6(\pm 0.2) \times 10^{-21}\text{ cm}^2\text{ molecule}^{-1}$  at 1624.7 nm ( $6155\text{ cm}^{-1}$ ). Given that this region is approaching the limits of our spectral range, the marginal agreement is not unexpected. In the mid-infrared, Kühnemann et al. (2002) measured the quantitative spectra of isoprene and its deuterated isotope, isoprene- $d_2$ , in order to determine the detection limits of isoprene using photoacoustic spectroscopy. Their results, however, give the absorption cross-sections for isoprene in the infrared to be almost exactly an order of magnitude larger than our measured values.

### 3.3 Remote sensing considerations

The data reported here represent the first comprehensive quantitative infrared cross-sections of vapor-phase isoprene. These data allow us to conjecture as to optimal bands and theoretical detection limits for this species. The most obvious choice is in the 7 to  $13\text{ }\mu\text{m}$  longwave window. In particular, the pair of Q-branches at  $906.3$  and  $893.8\text{ cm}^{-1}$  ( $\nu_{27}$  and  $\nu_{28}$ ) are ideal candidates for atmospheric monitoring. Both fall within the atmospheric window ( $11\text{ }\mu\text{m}$ ) and the presence of two adjacent bands of comparable intensity can provide further confirmation for isoprene detection. This reinforces not only the spectral assignment, but allows for higher levels of specificity of detection in atmospheric spectra, which are typically very cluttered with multiple analytes and interferents such as found in biomass burning spectra (Yokelson et al., 2013). Not only are both  $\nu_{27}$  and  $\nu_{28}$  of comparable strong intensity, both are in the heart

## Isoprene cross-sections

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Isoprene  
cross-sections**

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



of the longwave infrared spectral window. Furthermore, their close spectral proximity ( $13\text{ cm}^{-1}$  apart) may enable simultaneous observation of both and put them in range for observation using sensitive techniques such as quantum cascade lasers (QCLs), which can have broad tuning ranges (Hugi et al., 2009), greatly bolstering confidence and specificity for isoprene detection with infrared spectroscopy.

The differential cross-section for these two modes is roughly  $1.0 \times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ , which is  $\sim 1.2 \times 10^{-3}\text{ (ppmm)}^{-1}$  in  $\log_{10}$  units. Thus, in a 1 m path, an optical system with a sensitivity of greater than  $1.2 \times 10^{-3}$  would be able to detect 1 ppm of isoprene. With a 100 m pathlength, detection of 1 ppbv of isoprene would require  $1.2 \times 10^{-4}$  OD and, extrapolating further, 1 pptv could be detected in a 100 m path with  $1.2 \times 10^{-7}$  OD. In practice, however, broadband infrared methods are not this sensitive, but such sensitivities can be achieved using infrared laser techniques.

**4 Summary**

Using moderate-resolution infrared spectroscopy combined with a multiple burden approach, we have made seminal quantitative measurements on the atmospherically important isoprene molecule. We have modified some vibrational assignments assuming the planar *s-trans* configuration, partially in agreement with prior works. The isoprene spectrum is well suited for atmospheric monitoring as it has two very strong C-type bands ( $\nu_{27}$  and  $\nu_{28}$ ) both with strong cross sections,  $1.0 \times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ , and fortuitously separated by only  $13\text{ cm}^{-1}$ . The close proximity of the two strong bands adds much greater certainty and specificity for quantifying this species using congested mid-IR spectra.

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## Isoprene cross-sections

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Isoprene  
cross-sections**

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Isoprene  
cross-sections**

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Isoprene  
cross-sections**

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Isoprene  
cross-sections**

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## Isoprene cross-sections

C. S. Brauer et al.

**Table 1.** Instrumental parameters for the isoprene measurements.

	Instrument and absorption cell
Spectral range	6500 to 600 cm <sup>-1</sup> (1.534 to 16.667 μm)
Instrument resolution	0.112 cm <sup>-1</sup>
Apodization	Boxcar
Zerofill factor	2×
Phase correction	Mertz
Beamsplitter	KBr
IR source	Silicon carbide glow bar (22V)
Scanner velocity	60 kHz (HeNe crossing frequency)
Cell windows	2 in. dia. wedged KBr
Cell ballast pressure (N <sub>2</sub> )	760 ± 5 Torr (UHP N <sub>2</sub> )
Detector	Mid-band HgCdTe, photoconductive, 77 K operation
Folding limits	15 798 to 0 cm <sup>-1</sup>

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


**Isoprene  
cross-sections**

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Table 2.** Sample conditions for the isoprene measurements.

Temperature (K)	Sample Pressures (Torr <sup>*</sup> )	Path (cm)
278.20	1.11967, 2.2927, 3.3006, 5.2524, 10.6412, 21.25, 45.24	19.94
298.18	0.89149, 1.06447, 2.7667, 4.0640, 4.9813, 6.2751, 14.21, 21.45, 39.52, 70.97	19.94
323.12	1.02313, 2.2577, 3.1556, 5.3804, 10.3506, 21.09, 42.38	19.94

<sup>\*</sup> 760 torr = 1013 hPa.

## Isoprene cross-sections

C. S. Brauer et al.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


**Table 3.** Sources of systematic uncertainties and estimated contribution to the total uncertainty.

Symbol	Parameter	Fractional Contribution to Parameter Uncertainty
$\mu_L$	Optical pathlength	0.001 <sup>a</sup>
$\mu_T$	Temperature	0.001 <sup>b</sup>
$\mu_P$	Pressure	0.001 <sup>a</sup>
$\mu_I$	FTIR baseline drift	0.002 <sup>c</sup>
$\mu_{NL}$	Detector nonlinearity	0.015 <sup>c</sup>

<sup>a</sup> Estimated.

<sup>b</sup> Manufacturer specification as a fraction of the temperature in °C.

<sup>c</sup> Measured.

**Table 4.** Vapor-phase frequencies, vibrational assignments<sup>a</sup> and band integrals for observed mid-infrared bands of the planar *s-trans* form of isoprene.

Observed Frequency (cm <sup>-1</sup> )		Calculated Frequency (cm <sup>-1</sup> )	Sym (C <sub>2</sub> )	Mode	Approximate Mode Description
b	c	d			
3101.3	3101	3104	A'	v <sub>1</sub>	v <sup>asy</sup> (=C5H <sub>2</sub> )
3091.2	3091	3093	A'	v <sub>2</sub>	v <sup>asy</sup> (=C4H <sub>2</sub> )
3019.4	3017	3001	A'	v <sub>3</sub>	v(C1-H6)
2985.4	—	3018	A'	v <sub>4</sub>	v <sup>asy</sup> (CH <sub>3</sub> )
—	—	3012	A'	v <sub>5</sub>	v <sup>sy</sup> (=C5H <sub>2</sub> )
—	—	2996	A'	v <sub>6</sub>	v <sup>sy</sup> (=C4H <sub>2</sub> )
—	—	2913	A'	v <sub>7</sub>	v <sup>sy</sup> (CH <sub>3</sub> )
1650.9	—	1646	A'	v <sub>8</sub>	v(C2=C4)
1604.9	1604	1600	A'	v <sub>9</sub>	v <sup>asy</sup> (C1=C5)
1466.9	1467	1478	A'	v <sub>10</sub>	δ <sup>asy</sup> (CH <sub>3</sub> ) def.
1427.5	1428	1435	A'	v <sub>11</sub>	δ(=C5H <sub>2</sub> ) sci.
1418.8	1417	1407	A'	v <sub>12</sub>	δ(=C4H <sub>2</sub> ) sci.
1384.3	1384	1371	A'	v <sub>13</sub>	δ <sup>sy</sup> (CH <sub>3</sub> ) def.
1304.6	1303	1312	A'	v <sub>14</sub>	v(C1-C2)
1288.1	—	1288	A'	v <sub>15</sub>	δ(C1-H6) def.
1070.8	1071	1075	A'	v <sub>16</sub>	ρ <sup>sy</sup> (CH <sub>3</sub> ) rock
993.9	1003	1003	A'	v <sub>17</sub>	ρ(=C4H <sub>2</sub> ) rock
—	—	954	A'	v <sub>18</sub>	ρ(=C5H <sub>2</sub> ) rock
776.2	—	777	A'	v <sub>19</sub>	v(C2-CH <sub>3</sub> )
—	—	519	A'	v <sub>20</sub>	δ(C5C1C2) def.
—	—	412	A'	v <sub>21</sub>	δ(C4C2CH <sub>3</sub> ) def.
—	—	276	A'	v <sub>22</sub>	δ(C4C2C1) def.
2956.7	2985	2988	A''	v <sub>23</sub>	v <sup>asy</sup> (CH <sub>3</sub> )
1444.1	1444	1454	A''	v <sub>24</sub>	δ <sup>asy</sup> (CH <sub>3</sub> ) def.
1069.0	1069	1066	A''	v <sub>25</sub>	ρ <sup>asy</sup> (CH <sub>3</sub> ) rock
991.6	992	984	A''	v <sub>26</sub>	ω(C1-H6) wag
906.3	906	902	A''	v <sub>27</sub>	ω(C5H <sub>2</sub> ) wag
893.8	894	898	A''	v <sub>28</sub>	ω(C4H <sub>2</sub> ) wag
758.4	—	764	A''	v <sub>29</sub>	τ(=C4H <sub>2</sub> ) twist
—	—	625	A''	v <sub>30</sub>	τ(=C5H <sub>2</sub> ) twist
—	—	395	A''	v <sub>31</sub>	ω(C2-CH <sub>3</sub> ) wag
—	—	200	A''	v <sub>32</sub>	τ(C2-CH <sub>3</sub> ) tors.
—	—	157	A''	v <sub>33</sub>	τ(C2-C1) tors.

<sup>a</sup> Assignments generally follow Compton et al. (1976) and Panchenko et al. (2008). See text for discussion.

<sup>b</sup> This work.

<sup>c</sup> Gas phase values from Kühnemann et al. (2002) as reported by Panchenko et al. (2008).

<sup>d</sup> Calculated values from Panchenko et al. (2008).

Vibrational modes: ν, stretch; δ, bend; ρ, rock; τ, torsion and twist; ω, wag; asy, asymmetric; sy, symmetric.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Isoprene cross-sections

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

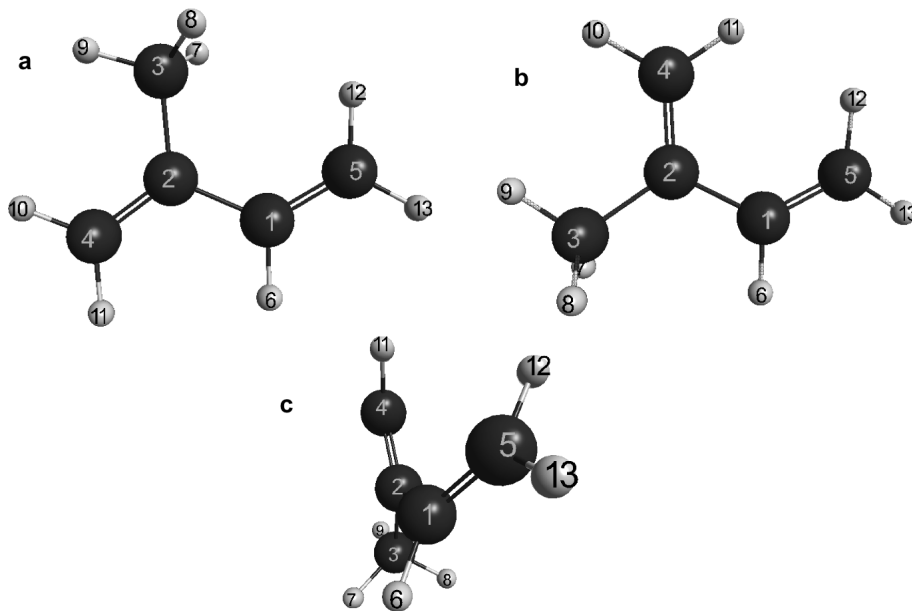
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Interactive Discussion

**Table 5.** Integrated intensities of isoprene.

Integrated Band Intensity <sup>a</sup> (cm molecule <sup>-1</sup> ) × 10 <sup>19</sup>			Band Integration Range (cm <sup>-1</sup> )
278 K <sup>b</sup>	278 K <sup>b</sup>	278 K <sup>b</sup>	
170(5)	170(5)	171(5)	3200–2800
48(2)	48(1)	48(2)	1680–1550
45(1)	44(1)	45(1)	1550–1340
4.2(1)	4.1(1)	4.7(1)	1340–1220
6.7(2)	6.6(2)	6.9(2)	1100–1040
27.1(8)	27.2(8)	27.7(8)	1040–950
115(3)	115(4)	116(4)	950–850
1.8(1)	1.7(1)	2.1(1)	720–820

<sup>a</sup> Values in parentheses represent the experimental (Type-B) errors.<sup>b</sup> Gas densities are normalized to 296 K.



**Fig. 1.** Isoprene in the planar *s-trans* (a) and *s-cis* (b) conformations. The gauche *s-cis* conformation is shown in (c) with the dihedral angle,  $C_4-C_2-C_1-C_5 = 35^\circ$ , corresponding to the structure calculated by Squillacote and Liang (2005) using the G3B3 method. Molecular structures were generated using the MacMolPlt graphical user interface (Bode and Gordon, 1999).

**Isoprene  
cross-sections**

C. S. Brauer et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

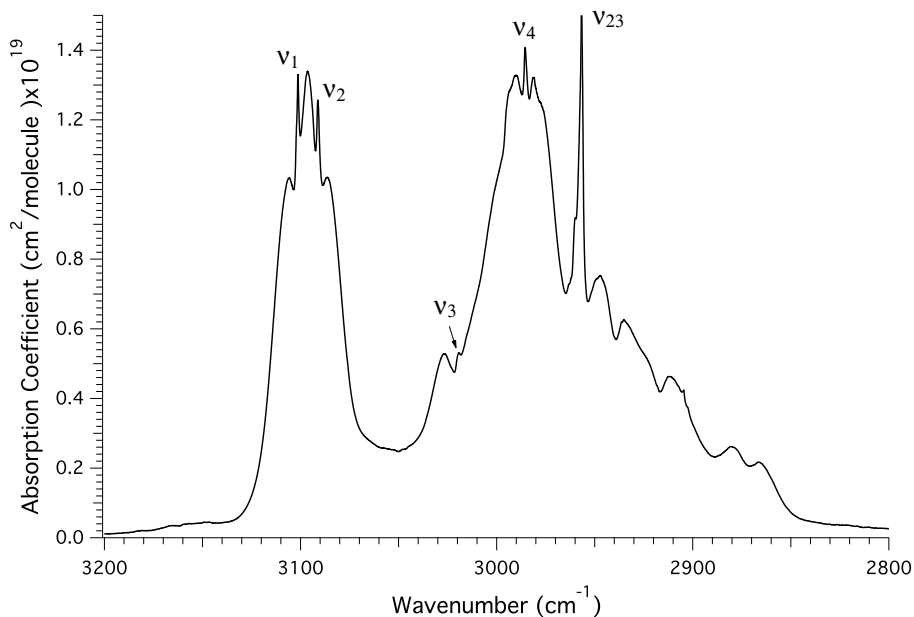
Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



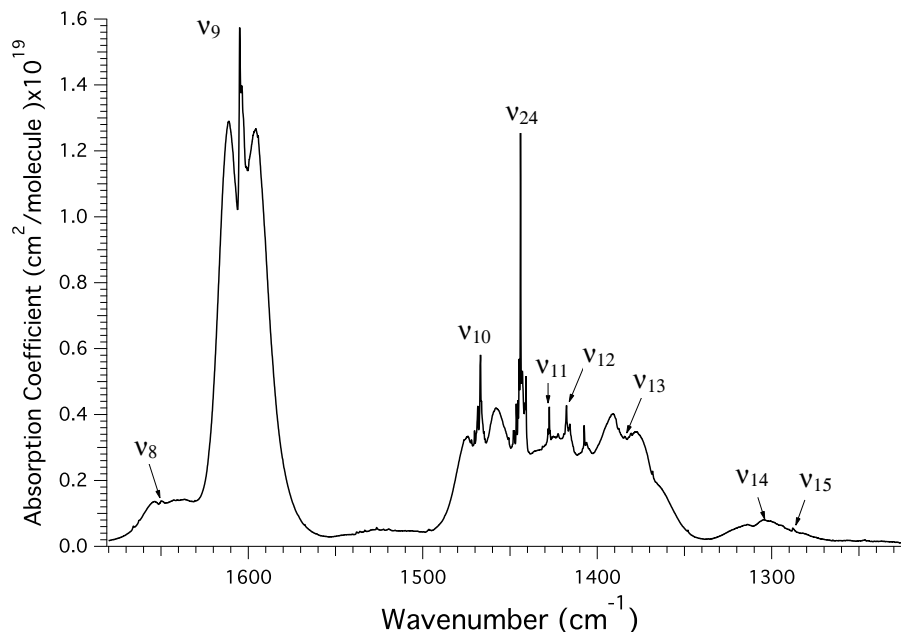


**Fig. 2.** Quantitative infrared spectrum showing the CH stretch region of isoprene. Absorption coefficients are given in Napierian units ( $\text{cm}^2 \text{molecule}^{-1}$ )  $\times 10^{19}$  for the composite spectrum recorded at 298 K.



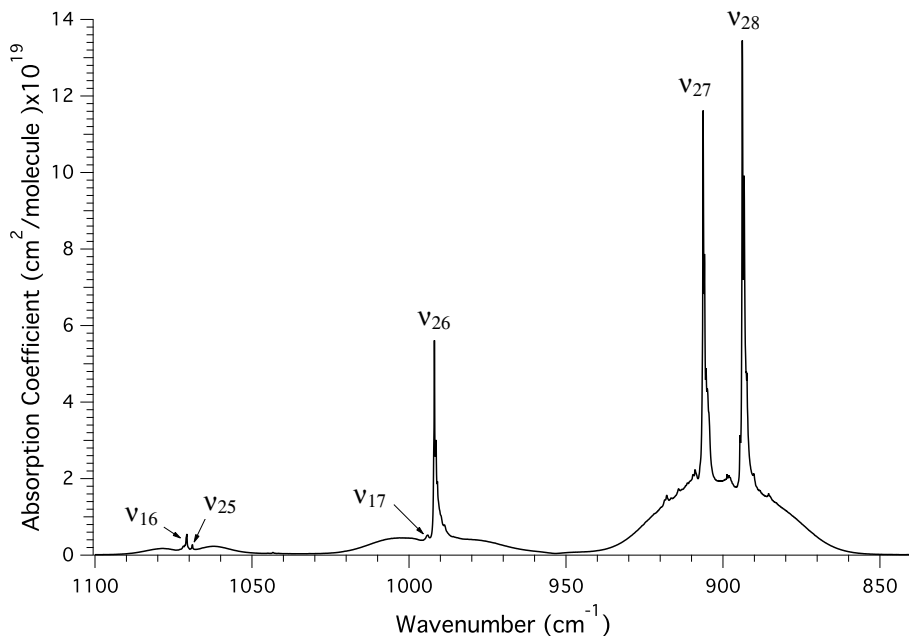
**Isoprene  
cross-sections**

C. S. Brauer et al.



**Fig. 3.** Quantitative infrared spectrum showing C=C stretching and CH bending modes of isoprene. Absorption coefficients are given in Naperian units (cm<sup>2</sup> molecule<sup>-1</sup>) × 10<sup>19</sup> for the composite spectrum recorded at 298 K.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



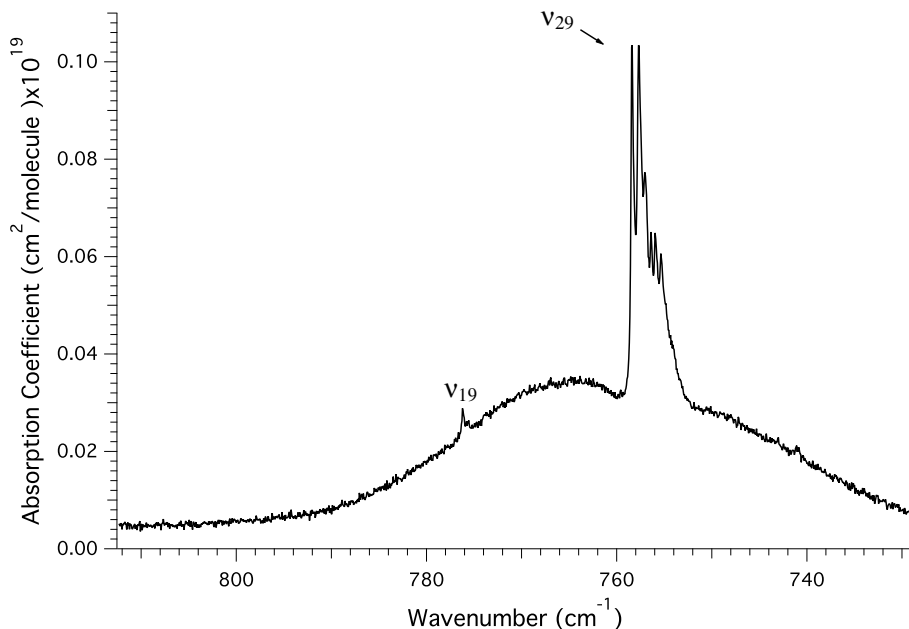
**Fig. 4.** Quantitative infrared spectrum of isoprene from 840 to 1100  $\text{cm}^{-1}$  recorded at 298 K. Absorption coefficients are given in Naperian units  $(\text{cm}^2 \text{molecule}^{-1}) \times 10^{19}$  for the composite spectrum recorded at 298 K.

**Isoprene cross-sections**

C. S. Brauer et al.

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	





**Fig. 5.** Quantitative infrared spectrum of  $\nu_{19}$  and  $\nu_{29}$  recorded at 298 K. Absorption coefficients are given in Naperian units ( $\text{cm}^2 \text{molecule}^{-1}$ )  $\times 10^{19}$  for the composite spectrum recorded at 298 K.

**Isoprene  
cross-sections**

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

