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Retrieval of methanol absorption parameters at terahertz frequencies using multispectral fitting

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ABSTRACT

A high-resolution broadband study of the methanol absorption spectrum was performed at 1.480–1.495 THz. The transmittance was recorded under both self- and air-broadening conditions for multiple pressures at a resolution of 500 kHz. A multispectral fitting analysis was then performed. The transition frequency, absolute intensity, self- and air-broadening coefficients, and self- and air-induced pressure shifts were retrieved for 221 absorption lines using the multispectral fitting routine. Observed in the data were two different series of transitions, both a b-type Q-branch with $K = -7 \leftarrow -6$ and an a-type R-branch with $J = 31 \leftarrow 30$. The retrieved frequency position values were compared with values from spectral databases and trends within the different series were identified. An analysis of the precision of the fitting routine was also performed.

1. Introduction

Methanol is one of the most abundant species observed in the interstellar medium (ISM) and astronomical data. Methanol has been observed in many astronomical regions including dark clouds [1], outflows [2], comets [3], and star formation regions [4]. In addition, many methanol maser lines have also been observed in astronomical spectra. More methanol maser lines have been identified than any other species [5] and it has been suggested that they may provide a way to identify early star formation regions [6–9]. In addition to its astronomical importance, methanol is an atmospheric trace gas. It is one of the most abundant oxygenated volatile organic compounds in the atmosphere [10–12]. It has also been suggested as a significant source of formaldehyde [13,14] and ozone [15] within the atmosphere.

Due to its often ubiquitous presence and importance in astronomical data, an accurate understanding of the methanol spectrum is important. Methanol has received much attention in the literature with the results being compiled into catalogs such as the Jet Propulsion Laboratory (JPL) [16], Cologne Database for Molecular Spectroscopy (CDMS) [17], and high-resolution transmission molecular absorption (HITRAN) [18] databases. The JPL database, which lists the largest number of transitions for methanol, is based on a quantum mechanical fitting of measured data in order to interpolate and extrapolate to unobserved transitions [19]. While this generally leads to accurate predictions, there are known issues. The interpolations provide good accuracy but the extrapolations can have larger uncertainties, especially for higher quantum numbers. In addition, there are known interactions and perturbations of the various quantum states in methanol [20]. These perturbations are often not accounted for in the model. Due to these difficulties, the JPL database is limited to $J \leqslant 40$ and $|K| \leqslant 20$ for the first three torsional states. More high-accuracy measured data is necessary in order to increase the accuracy of the predictive model, especially at higher quantum numbers and important but rarely studied frequencies.

Much of the methanol work in the literature has focused on the transition frequencies and not absolute intensities [21], resulting in larger uncertainties and discrepancies for the intensity predictions. Some studies have investigated the intensities [22,23], however more work is needed. Mekhtiev et al. [24] have observed that the inclusion of torsional effects into line strength calculations can lead to changes in the calculated intensity. Changes of up to 16% were noticed for transitions in the same torsional state, however the significance of the torsional terms increase as the change in the torsional number between the upper and lower states of the transition increases. Increases of up to three orders of magnitude were observed for some low intensity transitions. In addition to

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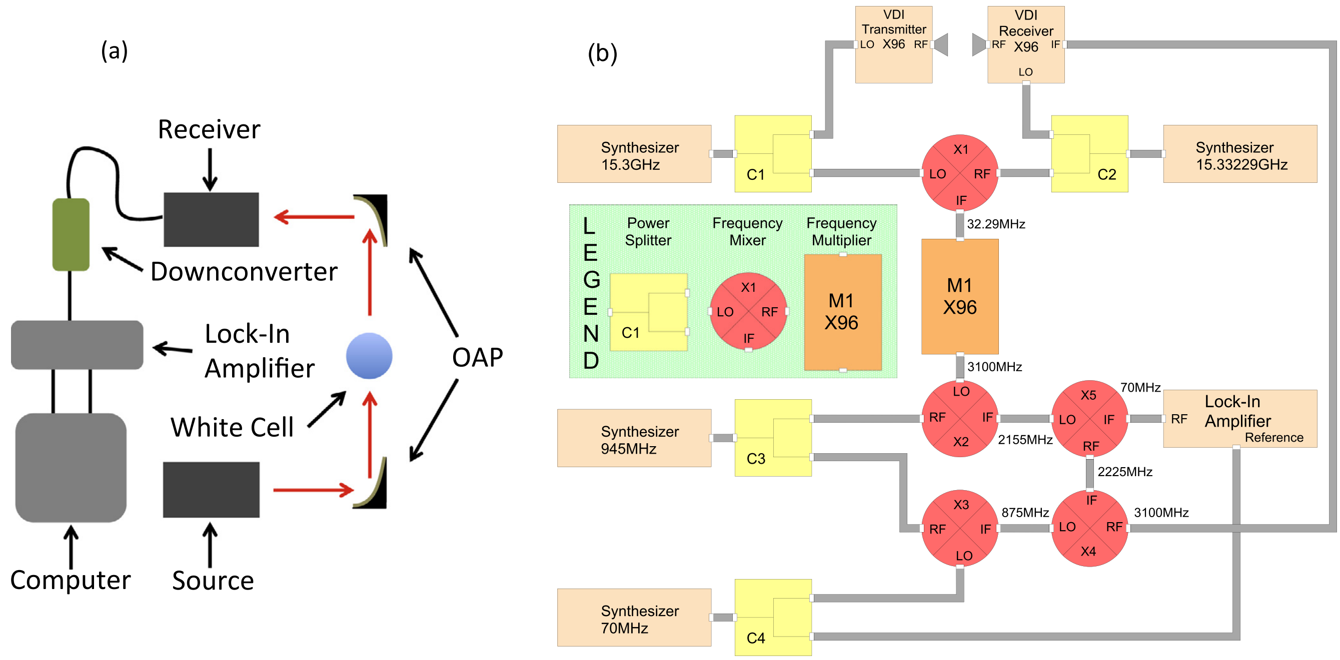

Fig. 1. (a) A schematic of the experimental setup and (b) a simplified diagram of the RF downconverter circuit, see Ref. [34] for a more detailed diagram.

Table 1
Partial pressures and temperatures observed in the present study.

Methanol (mTorr)	Dry air (mTorr)	Temperature (K)
74	0	297.9
134	0	297.3
285	0	297.8
353	0	297.9
639	0	297.3
723	0	297.8
214	237	297.6
639	237	297.6
99	488	297.8
378	488	297.8

affecting the line strength through correction terms, the value of the dipole moment of methanol has been observed to depend on the torsional state for pure rotation transitions [25].

Recently, new higher frequency instruments have been developed and deployed, such as the instruments in the Herschel Space Observatory (Herschel) [26], Stratospheric Observatory for Infrared Astronomy (SOFIA) [27], and Atacama Large Millimeter/submillimeter Array (ALMA) [28], that access the Terahertz region of the spectrum. Proper interpretation of returned data from these missions requires accurate knowledge of the spectrum at the observed Terahertz frequencies. Some studies have been performed at Terahertz frequencies [29,30], however more work is needed. The present work focuses on the atmospheric window at 1.5 THz, the widest and least absorbing window between 1 and 3 THz [31]. Atmospheric windows are important regions of the spectrum for ground-based observations that have to contend with water vapor absorption. In addition to being an atmospheric window, there is also an isolated Q-branch series of transitions within this window. Isolated Q-branch series have been suggested as a way to monitor the physical conditions of molecular clouds [32].

The present study utilizes a multispectral fitting approach applied to broadband high-resolution data in order to retrieve the transition frequency, absolute intensity, broadening parameters, and shifting parameters for 221 transitions of methanol. The multispectral fitting approach has been described and applied to data taken in the infrared by other authors [33]. The current implementation of the multispectral fitting technique for use on broadband high-resolution Terahertz data was first applied to atmospheric water vapor absorption [34–36]. The technique is able to determine the absorption parameters by recording the transmitted electric field using a coherent transceiver instead of using a second derivative line shape with an incoherent detector, where

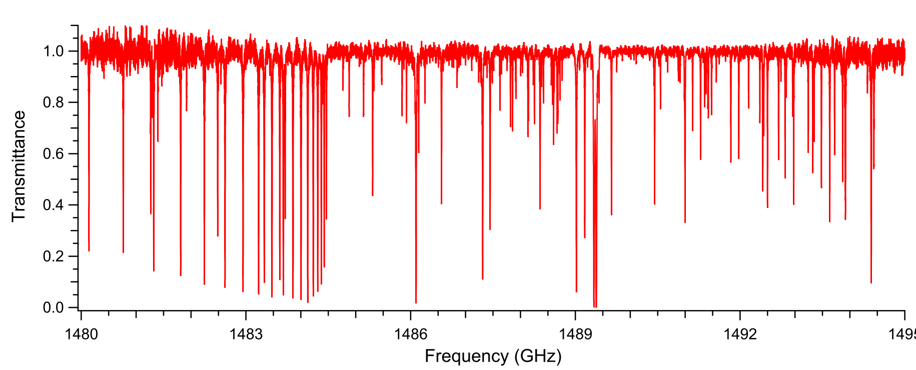

Fig. 2. Measured transmittance through 2 m of methanol at 134 mTorr of pressure.