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FTIR measurements of mid-IR absorption spectra of gaseous fatty acid methyl esters at $T=25$–$500\ ^{\circ}C$

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ABSTRACT

Gas-phase mid-infrared (IR) absorption spectra (2500–3400 cm^{-1}) for eleven fatty acid methyl esters (FAMEs) have been quantitatively measured at temperatures between 25 and 500 °C using an FTIR spectrometer with a resolution of 1 cm^{-1}. Using these spectra, the absorption cross section at 3.39 μm, corresponding to the monochromatic output of a helium–neon laser, is reported for each of these fuels as a function of temperature. The data indicate that the 3.39 μm cross section values of saturated FAMEs vary linearly with the logarithm of the number of C–H bonds in the molecule.

1. Introduction

Optical, non-invasive diagnostics for quantitative fuel sensing in combustion applications such as scramjets and diesel engines have become important analysis tools in the testing and improvement of advanced propulsion systems [1]. As such, optically probing the mid-infrared (mid-IR) C–H stretch feature (2500–3400 cm^{-1}) has gained special attention as a method of detecting fuel molecules, since many fuels of practical importance are hydrocarbons. In order to make quantitative spectroscopic measurements of gas phase fuel concentration, the absorption cross section of each fuel (σ), which specifies how much light is absorbed by one mole of a particular molecule per meter of absorbing distance, must be well-characterized. Specifically, cross section values at 3.392235 μm (2947.909 cm^{-1}), corresponding to the monochromatic output of a helium–neon (HeNe) laser, are of special importance due to the prevalence and simplicity of this specific laser diagnostic technique [2–4].

One particular class of hydrocarbons that is being considered for its renewable aspects is fatty acid methyl esters (FAMEs), which are a primary component of biodiesel fuel [5–7]. These molecules consist of a long hydrocarbon chain ending in an ester group $O{=}C\text{–}O\text{–}CH_3$. FAMEs can be either saturated or unsaturated. While normal alkanes and 1-alkenes have been extensively studied (see Refs. [2–4,8,9] and references therein), to our knowledge no quantitative data exist for gas-phase mid-IR cross sections of FAMEs at temperatures above 50 °C. Cross section data at elevated temperatures are important for diagnostic use in heated shock tubes [10], aerosol shock tubes [11–13], internal combustion engines [14–17], pulse detonation engines [18], and other combustion reactors.

A disadvantage of studying FAMEs compared to most normal alkanes and alkenes is that FAMEs have very low vapor pressures and fast decomposition rates. This inhibits

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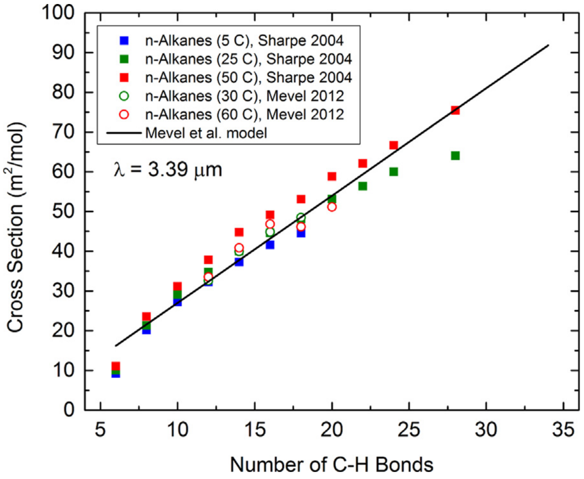

Fig. 1. Comparison of 3.39 μm cross section data from Sharpe et al. [8] and Mével et al. [4] with the Mével linear extrapolation model.

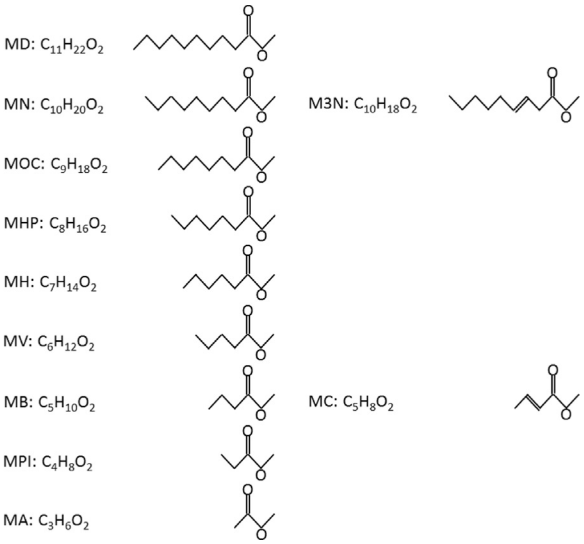

Fig. 2. Molecular diagrams of FAMEs examined in this study. Fully saturated FAMEs are shown on the left, and mono-unsaturated FAMEs are displayed on the right next to their saturated counterparts.

high-temperature study of the large FAMEs actually present in biodiesel fuel (such as methyl stearate, $C_{19}H_{38}O_2$) in the gas phase due to the long experimental times required for spectroscopic study over the full (2500–3400 cm^{-1}) C–H stretch IR spectrum. Instead, extrapolations of cross sections for large FAMEs must be made based on available data for smaller and medium-sized FAMEs. Models to predict cross section values of hydrocarbon molecules by extrapolation based on similar geometrical features and trends in temperature-dependence have been proposed previously [4,19,20]. In particular, the model of Mével et al. [4] employs a linear additive extrapolation method for predicting the 3.39 μm HeNe cross section (up to $T = 140\ ^\circ C$), which was shown to work well for small and mid-sized hydrocarbons (Eq. (1), with $\sigma_{alkane} = 2.70\ m^2/mol$ and N_{CH} being the number of C–H bonds in the molecule). Unfortunately, this model only approximately captures the trends seen in normal alkane 3.39 μm cross section data for molecules larger than those observed in the Mével et al. study (Fig. 1).

$$\sigma_{Mevel} = N_{CH}\sigma_{alkane} \qquad (1)$$

Based on the above discussion, there is a clear need to expand the current knowledge base of mid-IR hydrocarbon fuel spectra to include FAME data. Moreover, an updated prediction model is needed to enable extrapolation of 3.39 μm cross section data for small and medium-sized FAMEs to larger molecular sizes, including those of actual biodiesel components. Therefore, we have quantitatively measured the gas-phase mid-infrared absorption spectra of eleven FAMEs between 25 and 500 °C using a Fourier transform infrared (FTIR) spectrometer with a resolution of 1 cm^{-1}. These FAMEs, shown in Fig. 2 and detailed in Table 1, include nine fully saturated compounds: methyl acetate (MA, $C_3H_6O_2$), methyl propionate (MPI, $C_4H_8O_2$), methyl butanoate (MB, $C_5H_{10}O_2$), methyl valerate (MV, $C_6H_{12}O_2$), methyl hexanoate (MH, $C_7H_{14}O_2$), methyl heptanoate (MHP, $C_8H_{16}O_2$), methyl octanoate (MOC, $C_9H_{18}O_2$), methyl nonanoate (MN, $C_{10}H_{20}O_2$), and methyl decanoate (MD, $C_{11}H_{22}O_2$); and two mono-unsaturated compounds: methyl crotonate (MC, $C_5H_8O_2$) and methyl-3-nonenoate (M3N, $C_{10}H_{18}O_2$). Furthermore, using these spectra, we report the absorption cross section at 3.39 μm for these fuels as a function of temperature. Finally, we propose a new extrapolation method for

Table 1
Properties and purity of fuels studied. Vapor pressure information is taken from Ref. [21].

Fuel	Abbreviation	Formula	Molecular Weight [g/mol]	Vapor Pressure at 100 °C [Torr]	Purity [%]
Methyl acetate	MA	$C_3H_6O_2$	74.1	2814.8	99.87
Methyl propionate	MP	$C_4H_8O_2$	88.1	1425.1	99.99
Methyl butanoate	MB	$C_5H_{10}O_2$	102.1	698.0	99.7
Methyl valerate	MV	$C_6H_{12}O_2$	116.2	316.1	99.99
Methyl hexanoate	MH	$C_7H_{14}O_2$	130.2	148.1	99.9
Methyl heptanoate	MHP	$C_8H_{16}O_2$	144.2	56.9	99.8
Methyl octanoate	MOC	$C_9H_{18}O_2$	158.2	33.9	99.9
Methyl nonanoate	MN	$C_{10}H_{20}O_2$	172.3	17.4	98.8
Methyl decanoate	MD	$C_{11}H_{22}O_2$	186.3	6.5	99.7
Methyl crotonate	MC	$C_5H_8O_2$	100.1	–	99.4
Methyl 3-nonenoate	M3N	$C_{10}H_{18}O_2$	170.2	–	99.2