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Absorption Cross Section at 3.39 μm of Alkanes, Aromatics and Substituted Hydrocarbons

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Abstract

The present study reports gas phase absorption cross sections at 3.39 μm of 21 liquid hydrocarbons. Measurements were performed in the temperature range 303-413 K using an infrared He-Ne laser. In addition to n-alkanes, a number of cyclo-alkane, aromatic, and substituted hydrocarbons were investigated. The results demonstrate that (i) the absorption cross sections are temperature independent in the studied range, and that (ii) the aromatic and substituted hydrocarbons exhibit much smaller cross sections than n-alkanes for an identical number of C-H bonds. A tentative empirical correlation has been developed and shown to accurately predicts the cross section.

Key words: Absorption cross section, hydrocarbon, He-Ne laser

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1. Introduction

The absorption of an infrared He-Ne laser light at 3.39 μm by C-H bonds is an inexpensive and powerful diagnostic tool for studying the dynamics of hydrocarbon fuels in reactive systems. This technique has been applied in many combustion related studies using a variety of experimental setups. Davidson et al. [1, 2] and Haylett et al. [3] used He-Ne laser light absorption to perform time-resolved measurements of heptane, dodecane and hexadecane concentration behind reflected shock waves. Sato and Hidaka [4] and Hidaka et al. [5, 6] respectively studied acetone pyrolysis and oxidation as well as ethanol and dimethyl ether pyrolysis in shock-tube. Tomita et al. [7, 8, 9] performed fuel concentration measurements in the vinicity of the spark plug in a spark ignition engine. Hinckley and Dean [10] used He-Ne laser sensing to characterize the filling process in a multi-cycle pulsed detonation engine. Boettcher at al. [11] studied the effect of heating rates on low temperature hexane-air combustion.

A number of studies report absorption cross sections for various hydrocarbons. Edwards and Burch [12] measured the absorption coefficient of methane at different pressures and discussed the applicability of this technique to atmospheric methane concentration measurement. Jaynes and Beam [13] measured the absorption coefficient at room temperature for methane, ethane, propane, pentane, hexane, heptane, decane, ether, ethanol, toluene, acetone, gasoline, kerosene, JP-4 and JP-5. Olson et al. [14] used the shock-tube technique to measure the absorptivity of methane, acetylene, ethylene, ethane, propane, n-butane and n-pentane in the temperature range 300-2000 K. Tsuboi et al. [15] report measurements for methane, ethane, propane, n-pentane, n-hexane, n-heptane, n-octane, n-nonane, iso-octane, methanol, ethanol, butanol, acetone and benzene. The studied temperature range was 292-1100 K. Perrin and Hartmann [16] measured the absorptivity of methane in the 290-800 K temperature range. Yoshiyama et al. [17] report absorption cross section for methane and propane in the temperature and pressure ranges of 285-420 K and 100-800 kPa, respectively. Drallmeier [18] measured the absorption coefficient of 2-methylbutane, n-hexane, n-heptane, iso-octane, n-nonane, n-decane, 1-hexene, toluene and o-xylene. The temperature was 295 K and the pressure ranged between

27 and 87 kPa. Klingbeil et al. [19] report the temperature and pressure dependency of the absorption cross section of methane, ethylene, propane, n-heptane, iso-octane, n-decane, n-dodecane, gasoline, Jet-A and JP-10. Measurements were performed at temperatures and pressures between 298-673 K and 67-267 kPa, respectively. Grosh et al. [20] used Fourier transform infrared spectrometry to measure the absorption coefficients of propane, n-butane, ethanol and iso-octane. Their measurements were performed at temperatures between 298 and 473 K and at pressures between about 50 and 1800 kPa.

Although some absorption cross section data are available for some aromatic and substituted hydrocarbons, most previous studies have focused on n-alkanes. Real fuels such as kerosene type fuels contain a wide range of hydrocarbons [21], so that their surrogates can notably include aromatic and cyclo-alkane compounds [21, 22]. Also, because C-H bonds in almost any hydrocarbon absorb IR He-Ne laser light, this diagnostic can be potentially extended to the study of a wide range of fuels including (i) propellant model fuels (nitro-alkanes) [23], (ii) auto-ignition enhancers (nitrates) [24, 25, 26], (iii) fuel tracers (ketones) [27, 28] and (iv) additives and alternative fuels (alcohols and ethers) [29, 30, 31].

The purposes of the present study are (i) to provide absorption cross sections at 3.39 μm for a wide variety of hydrocarbons, including ketone, ether, alcohol, aromatic, n-alkane, cyclo-alkane and nitro and nitrate compounds; and (ii) to examine the relationship between the cross section value and the chemical structure. First, the materials and methods used are described. Second, the results obtained are presented and discussed.

2. Materials and methods

2.1. Materials

A schematic of the experimental setup used in the present study is shown in Figure 1. A 2mW He-Ne laser, Thorlabs H339P2, emitting at 3.39 μm was used as the light source. The light beam was chopped at 300 Hz at avoid detector saturation. A beam splitter was used to send a part of the light to a reference detector, Thorlabs PDA20H PbSe, while the rest of the beam travels through the 10.16 cm long test cell. A signal detector, Thorlabs PDA20H PbSe, measures the intensity of the latter beam. The reference detector was used to account for the laser intensty variation and high frequency noise. Before each of the two detectors, a narrow pass band filter (CW=3400 nm; FWHM=68 nm) was used to select the wavelength at which the He-Ne laser line interacts with the C-H bond absorption line. The test cell was equipped with two 2 mm thick sapphire windows and was connected to a pressure transducer and a septum. Both the test cell and the line were equipped with heating tapes and insulated with glass wool. Two temperature controllers were used to ensure an homogeneous temperature within the experimental setup. Measurements were performed in the range 303-413 K. The temperature in the test cell was monitored using a K-type thermocouple. Prior to each fuel measurement, the test cell was evacuated to less than 15 Pa and the intensity ratio was recorded. Then, the liquid fuel was introduced through the septum and the intensity ratio was recorded again. In the present study, 21 liquid fuels of high grade purity were investigated. Table 1 presents the list of the fuels tested.

2.2. Data analysis and uncertainty

After the fuel injection through the septum, the pressure transducer was used to control the pressure in the test cell. The fuel concentration was calculated using the pressure and temperature measurements assuming a perfect gas. Once it was stabilized, the reference and signal detector intensities were recorded over 1 s at a sampling rate of 10 kHz. Some examples of experimental signals are given as a supplemental material. The ratio of the incident, I^0, to transmitted, I, intensities at a given frequency, ν, can be related to the fuel concentration, C_{Fuel}, using the Lambert-Beer's law,

$$I = I^0 \cdot exp\left(-L \cdot C_{Fuel} \cdot \sigma_\nu\right), \tag{1}$$

where L is the path length and σ_ν is the absorption cross section at frequency ν. Since a reference detector was used, the absorption cross section is expressed as follows

$$\sigma_\nu = -\frac{1}{L \cdot C_{Fuel}} \cdot ln\left(\frac{I_{sig} \cdot I^0_{det}}{I_{det} \cdot I^0_{sig}}\right), \tag{2}$$

where sig and det subcripts refer to signal and reference, respectively.

The absorption cross section corresponds to the slope of $-\frac{A}{L} = f\left(C_{Fuel}\right)$, with A corresponding to

$$A = ln\left(\frac{I_{sig} \cdot I^0_{det}}{I_{det} \cdot I^0_{sig}}\right). \tag{3}$$

The absolute uncertainty on the absorption cross section is given by the following relationship

$$\Delta\sigma_\nu = \frac{\partial\sigma_\nu}{\partial L}\Delta L + \frac{\partial\sigma_\nu}{\partial C_{Fuel}}\Delta C_{Fuel} + \frac{\partial\sigma_\nu}{\partial A}\Delta A. \tag{4}$$

Considering a perfect gas, the relative uncertainty is expressed as

$$\frac{\Delta\sigma_\nu}{\sigma_\nu} = \frac{\Delta L}{L} + \frac{\Delta T}{T} + \frac{\Delta P}{P} + \frac{\Delta A}{A}. \tag{5}$$

In the present experiment, $\frac{\Delta\sigma_\nu}{\sigma_\nu}$ was found to be less than 5 %.

3. Results and discussion

This section is devoted to the presentation and discussion of the results obtained in the present study. First, the absorption cross sections measured for n-alkanes are presented. Second, results for aromatic and cyclo-alkane compounds are described. Third, the cross sections for various substituted hydrocarbons are shown. Finally, a comparison is made between the measured absorption coefficients and the prediction of a tentative empirical correlation.

3.1. n-alkanes

Since numerous data are available for n-alkanes, a series of measurements have been performed for n-pentane up to n-decane in order to validate the present experimental setup. Figure 2 a) shows the evolution of -(1/L).ln(I/I0) as a function of the fuel concentration for all the investigated n-alkanes. The temperature was held constant at 373 K. It is clear that the absorption cross section increases as the number of C-H bonds in the fuel molecule increases. The effect of temperature on the cross section has been investigated in the range 303-413 K and is illustrated in Figure 2 b). Considering the uncertainty associated with the measurements, it can be concluded that the absorption cross section of large n-alkanes is independent of temperature in the studied range. This result is consistent with the observations of Klingbeil et al. [19] who reported a small temperature dependency for such compounds, but over a much wider range of temperature, from 298 to 673 K. This feature is not observed for small alkanes, methane and ethane, which exhibit strong temperature and pressure dependencies [19]. The variation of the absorption cross section with temperature is related to the temperature dependency of the partition function, the lower level energy, the energy of the transition and the Doppler shift. The variation of the cross section with pressure is related to pressure-induced broadening and shifting of the absorption line. No measurements for these small alkanes have been performed in the present study since numerous data are already available as summarized by Klingbeil et al. [19]. Table 1 presents the absorption cross section values for all compounds as a function of temperature. The values obtained for all the studied n-alkanes are consistent with previous measurements by Jaynes and Beam [13], Tsuboi et al. [15], Horning et al. [32], Sharpe et al. [33] and Klingbeil et al. [19]. Also, good agreement was observed between the present measurements for n-hexane, n-octane and n-nonane and previous ones made in our lab [11, 34] using slightly different experimental configurations. However, the present values for n-heptane and n-decane are significantly higher than those reported by Drallmeier [18].

3.2. Aromatics and cyclo-alkanes

Because real fuels contain significant amounts of aromatic and cyclo-alkane hydrocarbons, measurements were performed for benzene, toluene, n-propyl benzene and n-propyl cyclohexane. Figure 3 shows the evolution of the absorption cross section of toluene, n-propyl benzene and n-propyl cyclo-hexane as a function of temperature. To allow a clear comparison with n-alkanes, the cross section of pentane and octane are also plotted in Figure 3. As can be seen, no temperature dependence can be observed. Toluene exhibits a cross section around 5 m^2/mol. Considering the number of C-H bonds, 8, a value close to that of propane, on the order of 20 m^2/mol, would be expected. Jaynes and Beam [13] reported a value of 13.93 m^2/mol for toluene in clear disagrement with the present results since such a large difference cannot be explained even by large uncertainties. On the contrary, good agreement was found with the measurements by Drallmeier [18] who reported a value around 4.8 m^2/mol. A cross section of 18 m^2/mol was measured for n-propyl benzene. The corresponding n-alkane with the same number of C-H bonds is pentane which possesses a much higher cross section around 33 m^2/mol. No other data for n-propyl benzene were found for comparison with the present measurements. Concerning n-propyl cyclohexane, it can be noted that (i) a value around 52 m^2/mol was measured and that (ii) it agrees well with that of the corresponding n-alkane with the same number of C-H bonds, octane. Once again, no other data for n-propyl cyclohexane were found for comparison. Measurements performed for benzene are reported in Table 1. The cross sections were very low, between 4.10^{-3} and 5.10^{-2} m^2/mol, and are not believed to be reliable because of the detection limit of the present experimental setup. However, these measurements indicate that the C-H bonds in aromatic cycles do not contribute to the absorption at 3.39 μm. Indeed, the presence of double C-C bonds induces a shift of the adjacent C-H bonds stretching frequency toward a higher frequency [35]. On the contrary, C-H bonds in cyclo-alkane seem to contribute the same way than those in linear n-alkanes.

3.3. Substituted hydrocarbons

In order to investigate the effect of various functional group on the absorption at 3.39 μm, measurements were performed for ketone, ether, alcohol, nitro and nitrate compounds. A list of these chemicals along with the absorption cross section values can be found in Table 1. Figure 4 shows the evolution of the cross section for acetone, ethanol, ethyl acetate, isopropl nitrate, and 1- and 2-nitropropane as a function of temperature. The cross section for these compounds ranges between 2.5 m^2/mol for acetone and 6.9 m^2/mol for 1-nitropropane. No temperature dependence was observed. Tsuboi et al. [15] and Jaynes and Beam [13] respectively reported 2.50 and 2.70 m^2/mol for the cross section of acetone, in good agreement with the present measurements. For ethanol, the same authors reported cross sections of 8.7 and 6.8 m^2/mol, respectively. The present value, about 6.90 m^2/mol, is in close agreement with that of Jaynes and Beam but significantly lower than that of Tsuboi et al. Concerning the other compounds presently investigated, no data were found in the literature for comparison. All of the studied substituted hydrocarbons exhibit very low cross sections as compared to n-alkanes with the same number of C-H bonds. Also, it is interesting to note that the 2-nitropropane demonstrates a much lower absorption cross section, around 4.4 m^2/mol, than 1-nitropropane, around 6.9 m^2/mol. This clearly indicates that both the substitution chemical nature and the structure of the molecule affects the value of the absorption cross section at 3.39 μm. These features are discussed in the next section.

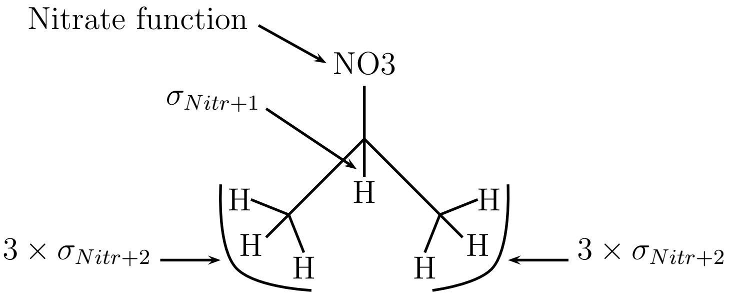
3.4. Empirical correlation

As previously underlined, if considering compounds of different chemical nature, there is no clear relationship between the absorption cross section value and the number of C-H bonds in a molecule. This feature can be emphasized by plotting the cross section as a function of the C-H bond number as in Figure 5 which includes both the present measurements and data from the literature [11, 13, 15, 18, 19, 32, 33, 34]. The position of a vibration absorption line depends on the mass of the atoms linked and on the strength of the bond. The intensity of the absorption line depends on the number of equivalent bonds and on the value and variation of the dipole moment of the chemical functional group. For most of the compounds in the present study, the chemical structure is characterized by functional group containing carbon-oxygen bonds. Conservely, a nitrogen atom can be linked to a carbon atom such as in nitro-alkanes. The presence of these various functional groups, with atoms of high electro-negativity, induce a modification both of the bond strength and of the dipole moment of the adjacent C-H bonds which modify the strength of the absorption line. Thus the absorption cross section at the He-Ne laser line frequency differs according to the functional groups in the molecule and its chemical structure. This feature has been used to develop a tentative empirical correlation which can be described as follows

$$\sigma_{total} = \sum_{i=1}^{n} N_i \cdot \sigma_i, \tag{6}$$

with: N_i: the number of C-H bonds of type i; σ_i: the absorption contribution of a C-H bond of type i.

The coefficients σ_i in Equation 6 represent the contribution of each type of CH bond to the total cross section. The values of σ_i shown in Table 2 were determined by carrying out a least-squares solution to the multiple linear regression problem for the temperature-averaged total cross section of 19 of the 21 species in Table 1. Benzene and ethyl acetate have not been considered because the measurement uncertainty for benzene was high and ethyl acetate was the only ether studied. As an example of how to apply the correlation, consider the isopropyl nitrate molecule shown below.



Relationships obtained for acetone, isopropyl alcohol (IPA) and 2-nitropropane are given respectively by:

$$\sigma_{Acetone} = 6 \times \sigma_{Ket+2} = 6 \times 0.405 = 2.43 m^2/mol \tag{7}$$

$$\sigma_{IPA} = \sigma_{Al+1} + 6 \times \sigma_{Al+2} = 1.55 + 6 \times 1.27 = 9.17 m^2/mol \tag{8}$$

$$\sigma_{2-nitropropane} = \sigma_{Nitr+1} + 6 \times \sigma_{Nitr+2} = 0.486 + 6 \times 0.705 = 4.72 m^2/mol \tag{9}$$

with: σ_{X+y} corresponding to the contribution of a C-H bond located y bonds away from the X functional group.

Figure 6 compares the predicted and measured the absorption cross section at 3.39 μm for 19 hydrocarbons. Aspreviously underlined, benzene was excluded because of its too low cross-section whereas ethyl acetate has not been considered because only one ether has been studied. It is seen that the proposed correlation enables prediction of the cross section of all these chemical compounds in the temperature range 303-413 K. Considering all the hydrocarbons presently investigated, the mean error of the prediction is 3.7 % and the maximum error is 12.4 %. The errors in predicting the absorption cross-section is comparable to the uncertainty of the experimental values. Considering the literature data, the mean error in predicting the absorption cross-section is 13.3 % when three non-consistent measurements are excluded. Although good agreement is obtained here, it is important to note that the set of data used to develop the correlation is too limited to draw definite conclusions with respect to its applicability to a wide range of hydrocarbons.

4. Conclusion

In the present study, gas phase absorption cross sections at 3.39 μm of various liquid hydrocarbons have been measured in the temperature range 303-413 K, using an infrared He-Ne laser. 21 hydrocarbons have been investigated including n-alkane, cyclo-alkane, aromatic, and substituted hydrocarbons. The results demonstrate that (i) the absorption cross sections are mostly temperature independent in the studied range, and that (ii) the aromatic and substituted hydrocarbons exhibit much smaller cross sections than n-alkanes, for an identical number of C-H bonds. Although general good agreement has been obtained between the present measurements and previous ones, some discrepencies have been found. Several techniques and procedures have been used in previous studies and the development of a standardized method would help resolve these discrepencies. A tentative empirical correlation has also been developed and shown to predict the cross section with an average error of 3.4 %. The generalization of this approach would be useful in designing and modeling experiments but a much larger set of experimental data is required to develop a reliable and widely applicable correlation.

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Figure captions

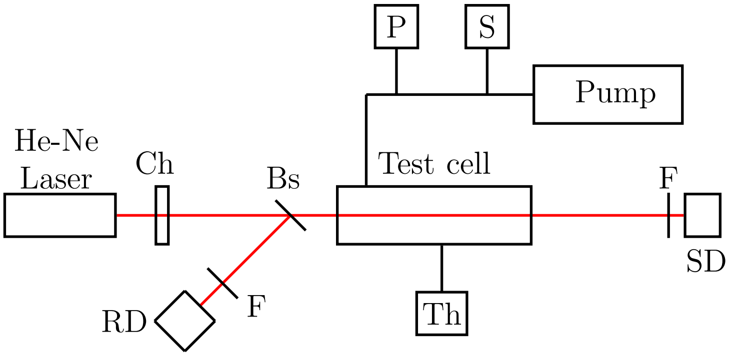
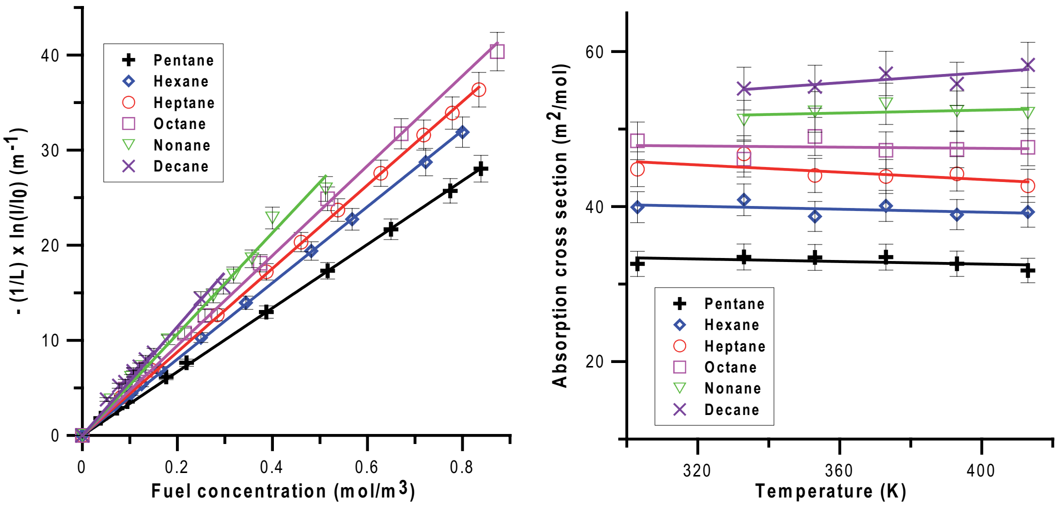
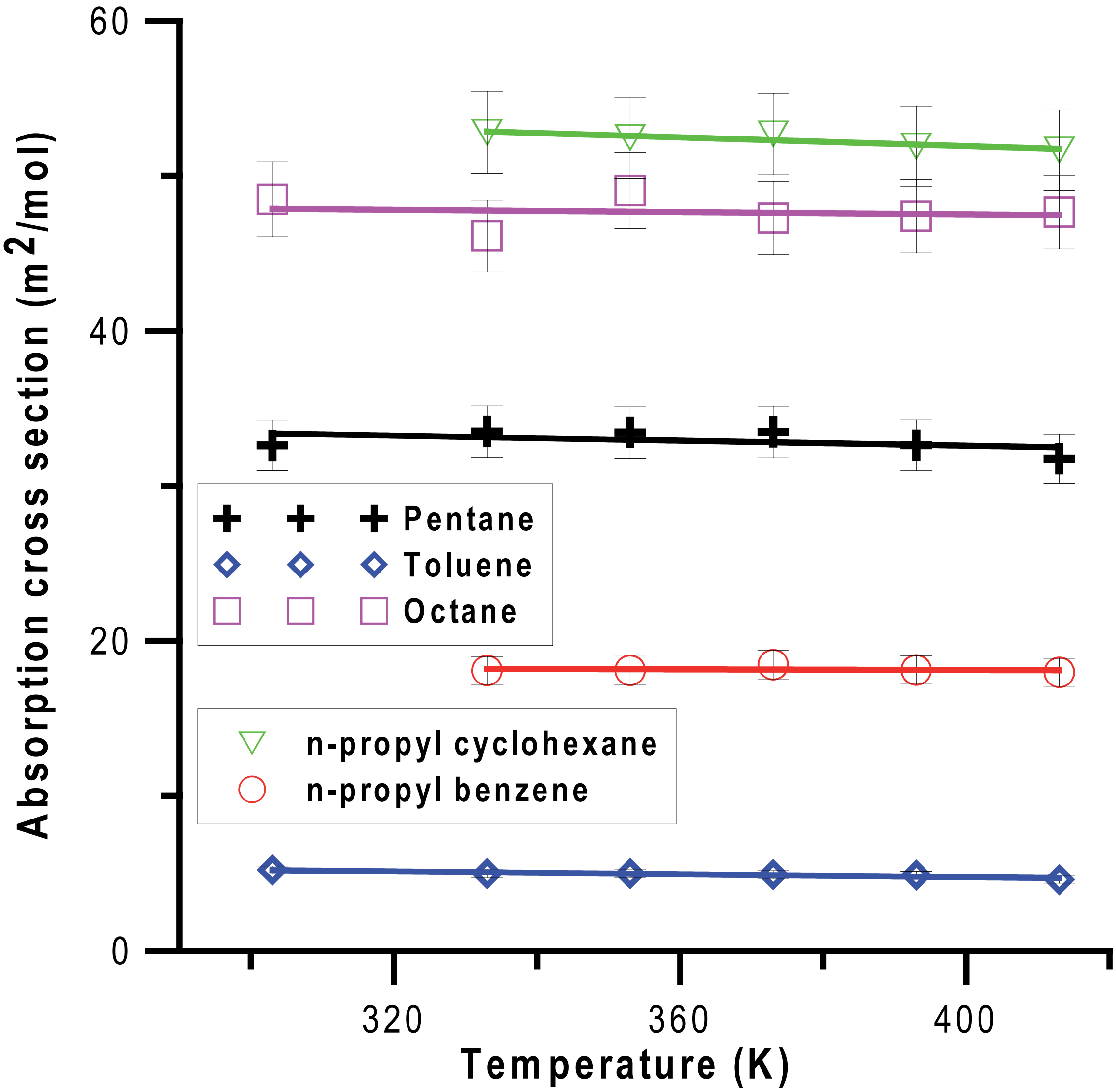


Figure 1


- (1/L) x ln(I/I0) (m-1)
0
10
20
30
40
0
0.2
0.4
0.6
0.8
Fuel concentration (mol/m3)
Pentane
Hexane
Heptane
Octane
Nonane
Decane
Absorption cross section (m2/mol)
20
40
60
320
360
400
Temperature (K)

a) b)

Figure 2



60
40
20
0
Absorption cross section (m^2/mol)
320
360
400
Temperature (K)
Pentane
Toluene
Octane
n-propyl cyclohexane
n-propyl benzene

Figure 3

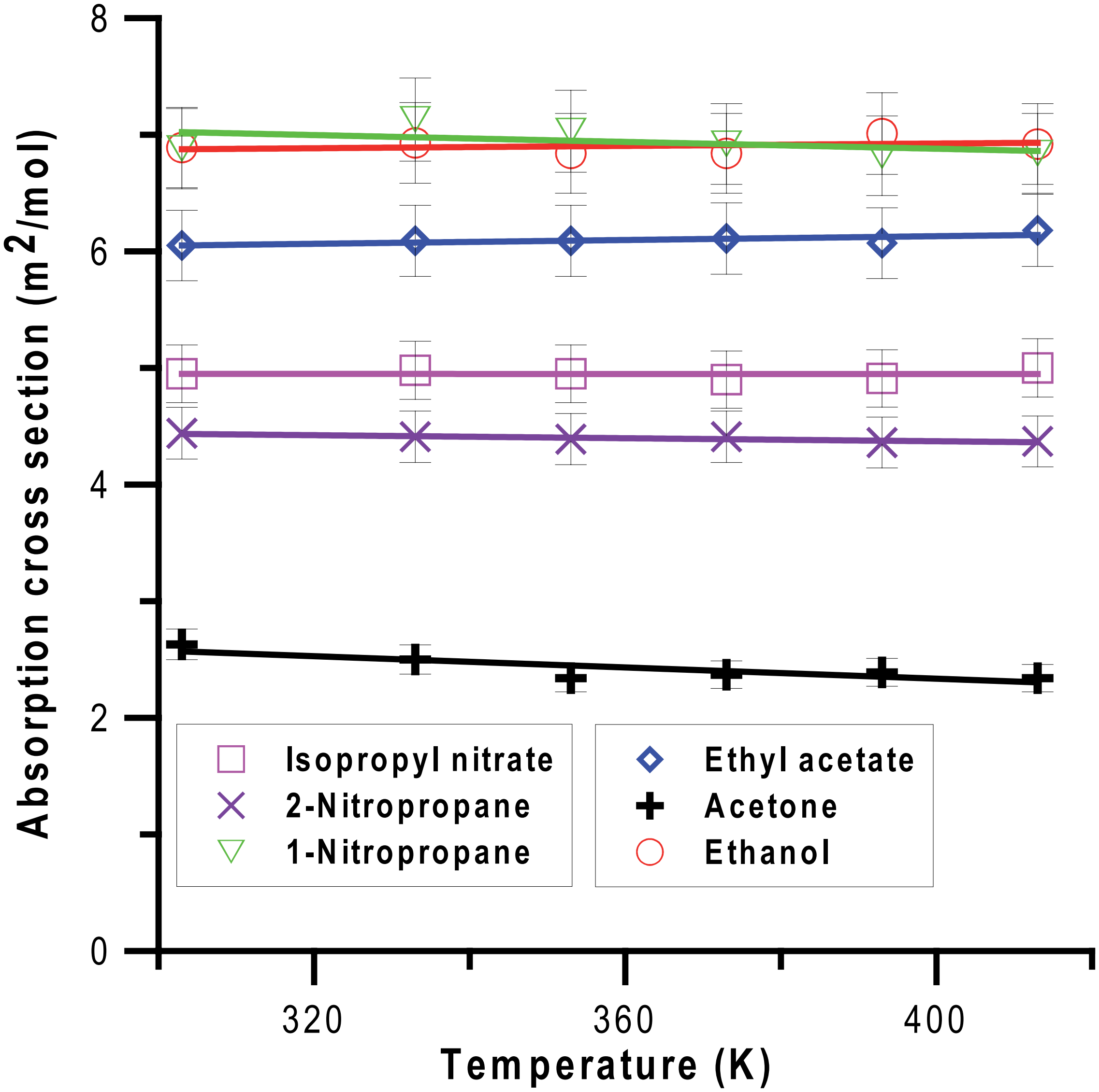

8
6
4
2
0
Absorption cross section (m2/mol)
320
360
400
Temperature (K)
Isopropyl nitrate
2-Nitropropane
1-Nitropropane
Ethyl acetate
Acetone
Ethanol

Figure 4

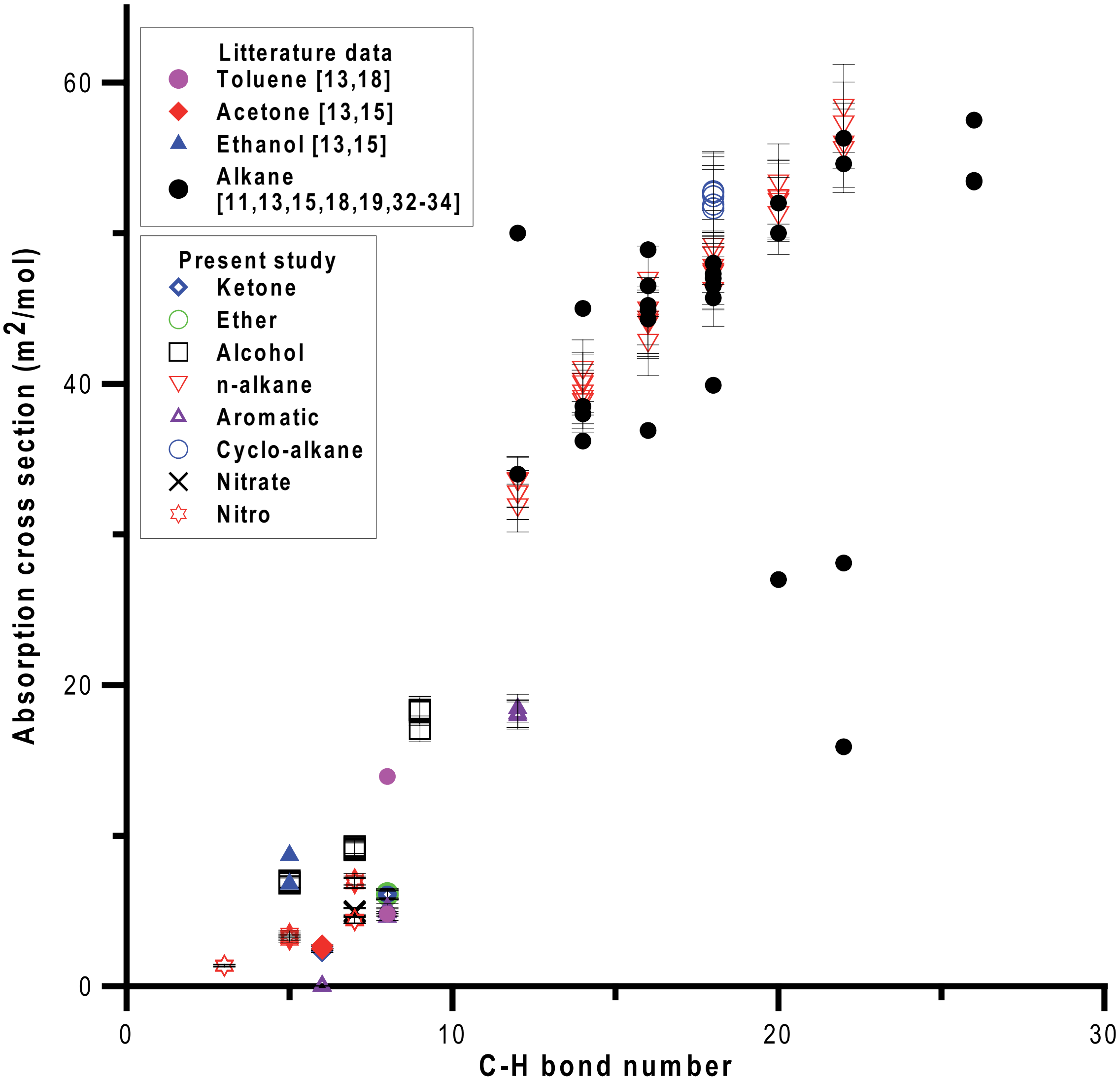
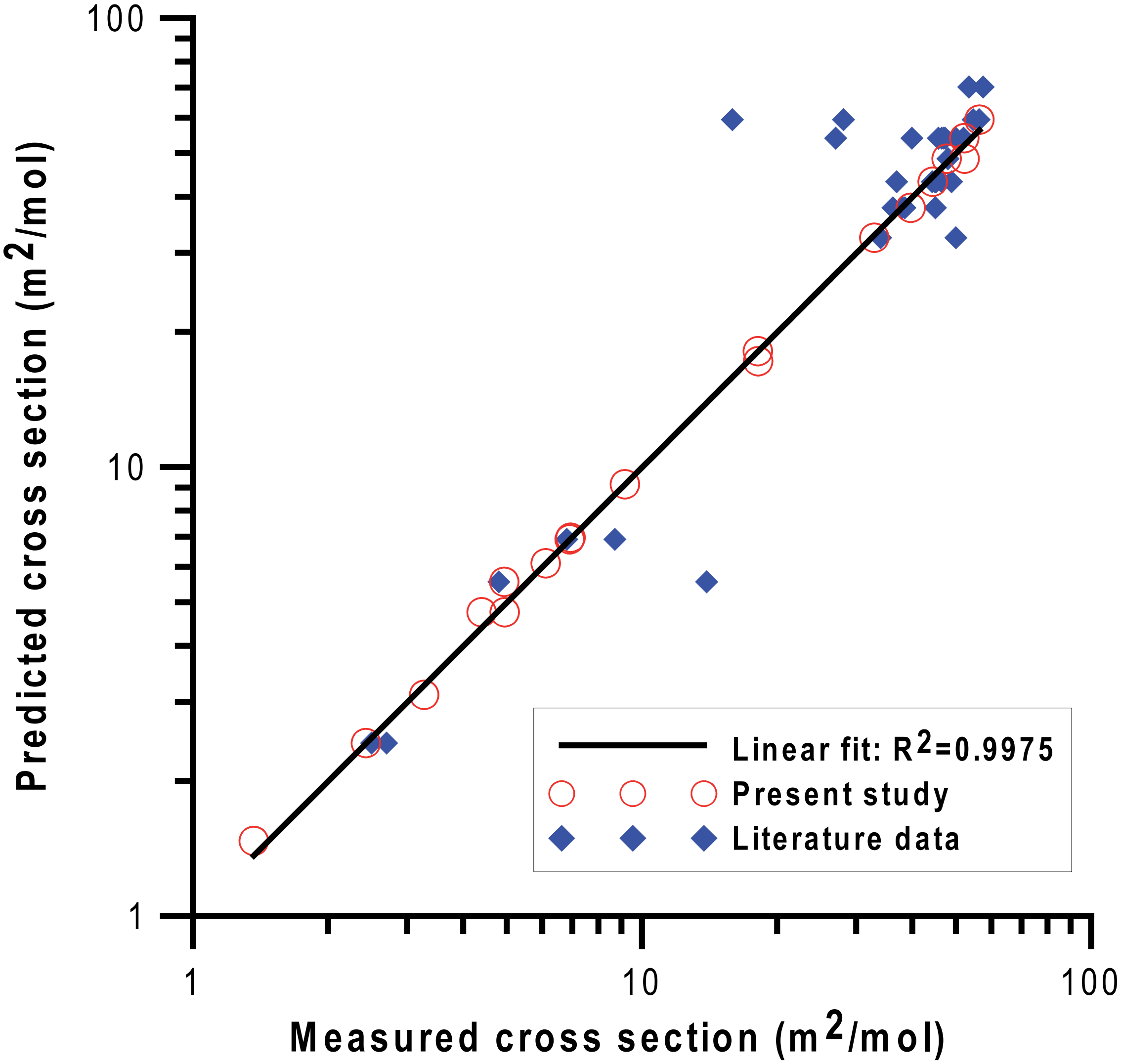

Litterature data
Toluene [13,18]
Acetone [13,15]
Ethanol [13,15]
Alkane [11,13,15,18,19,32-34]
Present study
Ketone
Ether
Alcohol
n-alkane
Aromatic
Cyclo-alkane
Nitrate
Nitro
Absorption cross section (m^2/mol)
0
20
40
60
0
10
20
30
C-H bond number

Figure 5



100
10
1
1
10
100
Predicted cross section (m2/mol)
Measured cross section (m2/mol)
Linear fit: R2=0.9975
Present study
Literature data

Figure 6

Table captions

Table 1

Name	Family	303 (K)	333 (K)	353 (K)	373 (K)	393 (K)	413 (K)
Acetone	K	2.63	2.50	2.34	2.37	2.39	2.34
Methyl ethyl ketone	K	6.08	6.00	6.06	6.14	6.20	6.15
Ethyl acetate	E	6.05	6.09	6.09	6.11	6.07	6.18
Ethanol	A	6.89	6.93	6.84	6.84	7.01	6.92
Isopropyl alcohol	A	9.27	9.12	9.05	9.08	9.16	9.28
Isobutyl alcohol	A	17.09	18.34	18.34	18.32	18.23	18.34
Pentane	n-A	32.61	33.50	33.44	33.48	32.62	31.75
Hexane	n-A	39.92	40.87	38.73	40.09	38.96	39.31
Heptane	n-A	44.82	46.80	44.02	43.88	44.22	42.68
Octane	n-A	48.49	46.12	49.05	47.27	47.39	47.65
Nonane	n-A	-	51.15	52.21	53.26	52.30	52.04
Decane	n-A	-	-	55.47	57.17	55.84	58.28
Benzene*	Ar	0.02	0.05	0.01	-	-	-
Toluene	Ar	5.22	4.99	4.99	4.93	4.89	4.60
n-Propyl benzene	Ar	-	18.09	18.10	18.46	18.12	17.97
n-Propyl cyclohexane	C-A	-	52.78	52.45	52.69	51.9	51.65
Isopropyl nitrate	NitA	4.95	4.98	4.95	4.90	4.91	5.00
Nitromethane	NitO	1.38	1.36	1.36	1.40	1.36	1.34
Nitroethane	NitO	3.08	3.50	3.37	3.29	3.20	3.20
1-Nitropropane	NitO	6.88	7.13	7.03	6.92	6.82	6.84
2-Nitropropane	NitO	4.44	4.41	4.39	4.41	4.36	4.37

Table 2

Bond specific cross-section	Contribution (m^2/mol)
σ_{Alkane}	2.70
σ_{Ket+2}	0.405
σ_{Ket+3}	1.36
σ_{Al+1}	1.55
σ_{Al+2}	1.27
σ_{Al+3}	2.29
σ_{Ar+1}	1.85
σ_{Nitr+1}	0.486
σ_{Nitr+2}	0.705
σ_{Nitr+3}	1.52