Quantifying Radiation Transport Properties of Fuel Vapors for Fire Models

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Gas-phase infrared radiation absorption and emission impacts radiation heat transfer through fuel rich cores to fuel surfaces in large-scale fires. Models for the radiation transport through the fuel rich core is often compromised by the lack of temperature-dependent, spectrally-resolved measurements of absorptivity of fuel vapor species. While temperature-dependent absorptivity data in the mid-IR and near-IR has been codified into appropriate models for methane, similar absorptivity data over a range of temperatures for fuel species including ethane, ethylene, propane, propylene, n-heptane, toluene, methanol, and MMA has not previously been translated into appropriate statistical narrow band models to allow for radiation transport calculations in fire models. This paper presents the methodology and results of using previous FTIR experimental data for spectrally-resolved absorptivity measurements of fuel vapor species for temperatures up to 1000 K to develop narrow band models for the listed fuel vapor species. The Goody narrow-band model offers the best fits for the numerous IR bands over the range of fuel vapors and temperatures considered. The resulting narrow band parameters are implemented into the infrared radiation transport calculations to provide more accurate estimations of radiation feedback to fuel sources in non-premixed fires and combustion events.

1 Introduction

To facilitate improved modeling of pool and solid-phase fires where radiation feedback through the fuel rich core is the dominant mean of heat transfer to the fuel surface [1, 2], temperature-dependent and spectrally resolved transmissivity measurements of fuel vapor species in the near-IR and mid-IR are needed. Such detailed radiation IR absorption measurements have been accumulated for methane and codified for radiation transport calculations in the software RADCAL [3]. Researchers have also measured spectrally-resolved IR absorption coefficients for several other fuel vapor species up to high temperatures [4–7], but the spectral and temperature resolution of these past studies is limited and varied. As such, they do not provide the consistency for developing appropriate databases or calculations for radiation transport in fuel-rich vapor cores of fires. Thus, over the past several years, researchers at NIST and the University of Maryland have measured the spectral transmissivity of several fuels for a specified range of temperature with consistent spectral resolution (0.5 cm\(^{-1}\)) using Fourier transform infrared spectroscopy (FTIR) as reported in previous references [8–11].
Spectrally resolved measurements in the near-IR and mid-IR for ethane, ethylene, propane, propylene, n-heptane, toluene, methanol, and methyl methacrylate (MMA) vapors are presented in Figs. 1 and 2. The variations in the vibrational-rotational bands illustrated in these figures indicate that the differences in molecular structure of the fuel molecules lead to differences in the absorption bands, and as such specificity of the fuel vapor composition is critical for capturing the radiation transport through the fuel rich core of non-premixed flames. Details of the fuel spectra presented in the figures are enumerated here:

- **ethane** has three main spectral ranges: 730 - 1095 cm\(^{-1}\) which corresponds to rocking motion of CH\(_3\), 1250 - 1700 cm\(^{-1}\) corresponding to the bending motion of the C–H bounds, and 2550 - 3375 cm\(^{-1}\) corresponding to the stretching motion of the C–H bounds.

- **ethylene** has four main spectral ranges: 780 - 1250 cm\(^{-1}\) corresponding to the out-of-plane bending motion of CH\(_2\), 1300 - 1600 cm\(^{-1}\) corresponding to the in-plane bending of CH\(_2\), 1750 - 2075 cm\(^{-1}\) corresponding to the stretching of the C=–C bound, and 2800 - 3400 cm\(^{-1}\) corresponding to the stretching of the C–H bounds.

- **propane** has two main spectral ranges: 1175 - 1675 cm\(^{-1}\) corresponding to the bending motion of CH\(_3\), and 2550 - 3375 corresponding to the stretching of the C–H bounds.

- **propylene** spectrum can be divided into three main spectral ranges: 775 - 1150 cm\(^{-1}\) corresponding to the stretching motion of C–C and the rocking motion of CH\(_3\), 1225 - 1975 cm\(^{-1}\) corresponding to the stretching motion of C=–C and the bending motion of CH, and 2650 - 3275 cm\(^{-1}\) corresponding to the stretching motion of the C–H bounds.

- **n-heptane** spectrum is rather simple and can be divided into two separate bands: 1100 - 1800 cm\(^{-1}\) corresponding to one bending motion of CH\(_2\) and CH\(_3\), 2250 - 3275 cm\(^{-1}\) corresponding to the stretching motion of CH\(_2\) and CH\(_3\) groups. Note that n-heptane has 63 vibrational modes and therefore the fine structure of its spectrum is rather complex.

- **toluene** spectrum can be divided into five distinct bands: 700 - 805 cm\(^{-1}\) corresponding to one bending motion of the CH groups, 975 - 1175 cm\(^{-1}\) corresponding to another bending motion of the CH groups, 1275 - 1650 cm\(^{-1}\) corresponding to the bending motion of the CH\(_3\) groups, 1650 - 2075 cm\(^{-1}\) corresponding to the stretching motion of C=–C bounds, 2675 - 3225 cm\(^{-1}\) corresponding to the stretching motion of the C–H bounds.

- **methanol** spectrum can be divided into four main bands: 825 to 1125 cm\(^{-1}\) that corresponds to the stretching motion of C–O, 1125 - 1700 cm\(^{-1}\) that corresponds to the bending motion of the CH\(_3\) and OH groups, 2600 - 3225 cm\(^{-1}\) that corresponds to the stretching motion of C–H, and 3525 - 3850 cm\(^{-1}\) corresponding to the stretching motion of the O–H bound.

- **MMA** has the most complex spectrum of all of the fuels considered in this work. It can be divided into 6 distinct bands: 750 - 875 cm\(^{-1}\) that corresponds to the bending motion of CH\(_3\), 875 - 1050 cm\(^{-1}\) that corresponds to the bending motion of the CH\(_2\) groups, 1050 - 1250 cm\(^{-1}\) corresponding to the stretching motion of the C-O bounds, 1250 - 1550 cm\(^{-1}\) corresponding to the bending motion of the CH\(_3\) groups, 1550 - 1975 cm\(^{-1}\) corresponding to the stretching motion of the C=–C and C=O bounds, 2650 - 3275 cm\(^{-1}\) corresponding to the stretching motion of the C–H bounds.
This work presents our efforts to quantify the IR transmission spectra of these fuels into narrowband IR radiation absorption coefficients as a function of temperature such that radiation transport in fuel-rich regions of combustion events can be modeled. This work provides a methodology for processing these measurements and conveying them into tabulated narrow-band model parameters that can then be readily used with temperature-based interpolation in detailed radiation transport calculations in combustion modeling tools. The methodology and results of its implementation on the data presented in Figs. 1 and 2 provide the basis for expanding this work to other fuel species as appropriately detailed measurements are obtained. Results like these will aid in the development of more accurate numerical models of infrared radiation heat transfer inside the fuel rich core of large hydrocarbon fires, such as pool fires, where the infrared heat transfer is a controlling parameter of the fire dynamic [12].

2 Narrow Band Model

In order to facilitate relatively efficient spectrally-resolved radiation calculations, the detailed measurements shown above are best converted into narrow-band-model parameters that can be used in lieu of line-by-line models to represent the IR spectra of radiatively active species in radiation calculations for engineering applications. Narrow band models provide for relatively-fast computations of representing the spectra of individual species which can then be integrated over the entire band to get total heat transfer calculations or averaged without significant accuracy loss.

In the narrow band approach, the whole spectrum is divided into small spectral bands (in this case ranging from 5 to 25 cm\(^{-1}\) wide) over which the Planck function is assumed constant. Different statistical approaches are used to compute the average radiative properties of these narrow bands. The exact location and line strength of each individual line over a spectral range are not needed. Moreover, this information is only available or calculated from statistical thermodynamics for a handful of species with relatively simple molecular structure [13, 14]. For more complex fuel vapor species, each spectral narrow band is modeled based on a statistical representation of the location, shape, and line strength of the lines. The line shapes are all the more difficult to resolve because of broadening. In most engineering application at atmospheric pressure or higher, collisions within the gas-phase is the main line broadening mechanism [15, 16].

Three main narrow band models are considered in this work to model the IR absorption bands of the fuel vapor species considered: namely the Elsasser model, the Goody model, and the Malkmus model. Each model uses two parameters to characterize a narrow band [15, 17, 18]: the spectral mean absorption coefficient, \(\bar{\kappa}_\omega\), and the spectral collision broadening fine structure parameter, denoted \(a_{c,\omega}\), which relates with the narrow band mean collision broadening half-width, \(\gamma_c\), the effective broadening pressure, \(P_e\), and the narrow band mean spacing between the lines, \(d\), through the expression [15, 17, 18]:

\[
a_{c,\omega} = \frac{\gamma_c P_e}{d}.
\]

In this work, we assume spectral dependency of \(a_{c,\omega}\) and \(\bar{\kappa}_\omega\). This approach is an extension of the fitting process of the previous work of Kunitomo et al. [18] and Brosmer et al. [5].

The three models are comparable in performance. The Elsasser model assumes the spectral lines to
have the same shape, the same line strength $S$ defined as $S = \int \kappa_\omega d\omega$, and regular line spacing [16].

The Goody model assumes the line strength follows an exponential distribution [15] and the location of the lines is randomly distributed.

Finally, the Malkmus model was built based on similar considerations but assuming an exponential-tailed $S^{-1}$ distribution for the line strength.

The experimental data have been fitted with the three models using a least square fitting to determine $a_{c,\omega}$ and $\tilde{\kappa}_\omega$. The residual from the fitting procedure was very low for all of the three models considered, which indicates they compare very well with the experimental results. Comparisons between the experimental transmissivities and synthetic ones are presented in Ref. [19].

The selection of the best narrow band model was based by comparing the value of the integrated band intensity provided by the three models with the value obtained from experiment. The integrated band intensity is given by the expression:

$$\alpha = \int_{\text{band}} \tilde{\kappa}_\omega d\omega. \tag{2}$$

The authors are not aware of any other systematic survey of fuel vapors infrared properties at different properties and due to this limitation, the experimental values were taken from the experiments presented above using the extrapolation technique first proposed by Wilson and Wells [16, 20, 21]. A curve of growth was used to perform the extrapolation. Its expression relates the apparent integrated band intensity $A$, with the integrated band intensity:

$$A = \int_{\text{band}} -\ln \tau_\omega d\omega = \theta f \left( \frac{\alpha P_i L}{\theta} \right), \tag{3}$$

where $\theta$ represents a total band half width and $f$ is represented by:

$$f(x) = \frac{x}{\left(1 + (0.5\pi x)^\frac{5}{2}\right)^{\frac{1}{2}}} \tag{4}.$$

Fitting $A$ with the experimental transmissivities returns values of $\theta$ and $\alpha$. It was found that the integrated band intensities computed from the Goody model are in closest agreement with the experimental data for the experimental range of temperatures considered.

Table 1 tabulates the maximum relative errors associated with the Goody model for all the fuels. The relative error associated with the difference between the experimental transmissivities $\tau$ and the synthetic ones is denoted $\epsilon_{\tau,\text{frac}}$, while the relative error associated with the integrated band intensities is denoted $\epsilon_{\alpha,\text{frac}}$. The maximum relative error associated with $\tau$ is 5.0% and is associated with toluene. A careful examination shows that this error arises in the first band of toluene, defined between 700-800 cm$^{-1}$.

While for most of the fuels the maximum error associated with the integrated band intensity is less than 20%, toluene presents a greater relative error of 80%. This error is associated with the 4th band
of toluene, defined between 1650-2075 cm\(^{-1}\). Detailed examinations show that the experimental transmissivities are very close to 100 % and therefore are more likely to be subject to measurement errors and to systematic errors during the baseline correction of the experimental data. In particular, the apparent integrated band intensity of this band is ill-behaved at some temperatures and does not vary monotonously with the increase of the optical path-length \(P_iL\).

<table>
<thead>
<tr>
<th>Fuel</th>
<th>(\max(\epsilon_{r,\text{band}})) %</th>
<th>(\max(\epsilon_{\alpha,\text{band}})) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane</td>
<td>1.8</td>
<td>17.9</td>
</tr>
<tr>
<td>ethylene</td>
<td>1.3</td>
<td>3.6</td>
</tr>
<tr>
<td>propane</td>
<td>2.8</td>
<td>17.7</td>
</tr>
<tr>
<td>propylene</td>
<td>1.9</td>
<td>5.9</td>
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<td>3.8</td>
<td>4.6</td>
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<td>toluene</td>
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<td>81.0</td>
</tr>
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<td>methanol</td>
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<td>1.2</td>
</tr>
<tr>
<td>MMA</td>
<td>2.3</td>
<td>18.6</td>
</tr>
</tbody>
</table>

Table 1: Fuel maximum relative error between the Goody narrow band model and experimental measurements for transmissivity, \(\epsilon_{r,\text{band}}\), and for the integrated band intensity, \(\epsilon_{\alpha,\text{band}}\).

Figures 3, 4, and 5 plot the narrow band spectral mean absorption coefficient and collision fine structure parameter for heptane, methanol, and MMA, respectively. The resolution of the narrow band is 25 cm\(^{-1}\). These quantities are plotted for the spectral range corresponding to the stretching of the C–H bond, typically for wavenumbers between 2600 - 3300 cm\(^{-1}\). Virtually all the hydrocarbon fuels present this absorption band. Figures 1 and 2 show that this band is the most important band for all of the fuels considered, aside from ethylene, methanol, and MMA. This band is of great importance in high temperature environments because this wavenumbers range corresponds to the range of maximum Blackbody spectral radiance for temperatures between 1325 K to 1700 K, which are typically observed in fires.

The shape of the mean absorption coefficient follows the shape of the profile of the experimental transmissivity. Decrease of peak values of \(\kappa_{\omega}\) with temperature is observed for increasing temperature. Along with the decrease in peak values, a smearing out of the profiles is observed. This is expected at high temperatures. When the temperature of the medium is increased, rotational lines of higher energy, which are further away on either side from the vibration frequency, are privileged over those of lower energy.

Spectral evolutions of the collision broadening fine structure parameter are also plotted on Figs. 3, 4, and 5 at different temperatures. Values for heptane are lower than unity, and peak near the maximum of absorption. From the definition of \(a_{c,\omega}\) given by Eq. (1), it can be seen that values less than unity indicate a weak overlapping of the spectral lines. For methanol, Fig. 4 and MMA, Fig. 5, values of \(a_{c,\omega}\) are greater than unity, which suggests a strong overlapping of the lines. While this is a plausible and consistent interpretation, at least for MMA when considering the previous findings of Park et al. [22], examination of the curve of growth indicates that the experimental
conditions for these two fuels are very close to the weak line regime, for which the values of \( \alpha_{c,\omega} \) have no influence on the transmissivity [23].

The computed integrated band intensities from the SNB fitting of the C–H stretch band of all the fuels considered are given in Table 2, at their lowest experimental temperature. Heptane has the greatest integrated band intensity, followed in decreasing order by propane, ethane, methanol, toluene, propylene, MMA, and ethylene. This order reflects the decreasing importance of the absorption characteristics of these fuels at equal concentration. Heptane has the greatest propensity to absorb high energy incident radiation compared to other fuels in this spectral range.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>T (K)</th>
<th>( \alpha(T) ) ( \text{atm}^{-1}.\text{cm}^{-2} )</th>
<th>Fuel</th>
<th>T (K)</th>
<th>( \alpha(T) ) ( \text{atm}^{-1}.\text{cm}^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>heptane</td>
<td>293</td>
<td>3055.1</td>
<td>toluene</td>
<td>300</td>
<td>509.5</td>
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<td>296</td>
<td>508.7</td>
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<td>760.6</td>
<td>MMA</td>
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<td>methanol</td>
<td>296</td>
<td>683.6</td>
<td>ethylene</td>
<td>296</td>
<td>183.5</td>
</tr>
</tbody>
</table>

Table 2: Fuel integrated band intensity corresponding to the C–H stretch band. Values were obtained using the Goody model.

3 Application in RadCal

The narrow band model parameters derived above were integrated into RadCal, enhancing its capabilities. RadCal is a FORTRAN narrow band model developed by Grosshandler [3]. It features detailed infrared spectra of \( \text{CO}_2 \), \( \text{CO} \), \( \text{H}_2\text{O} \), \( \text{CH}_4 \), and soot, for temperatures between 295 K to 2500 K and for distances up to 50 meters. RadCal is based on the single-line group model, which treats all the lines in a spectral narrow band interval as though there are no large difference in their individual line strength. It models the spectral transmissivity of a narrow spectral interval as the combination between collision broadened lines and Doppler broadened lines, and treats non-homogeneous configurations using the Curtis-Godson approximation. See Ref. [15] for a more detailed description of the models used.

Verification tests were performed to assess the errors associated with the formulation in RadCal. They consisted in simulating the spectral transmissivity for conditions similar to experimental ones. The relative errors between experimental and simulated profiles were quantified. Very good agreement was obtained, with relative errors similar to those tabulated in Table 1.

To illustrate the differences in fuel spectra, calculations were performed for a simple flame configuration. The incident spectral radiance received in the direction perpendicular to a 1D planar flame was computed using RadCal. The profile of mixture fraction \( Z \) as function of elevation \( x \) (in meters) was defined here as:

\[
Z(x) = erfc(x^2).
\]

Temperature and species profiles were populated using a the Burke-Schumann flamelet with a reduce adiabatic flame temperature (by 30 %) from its value computed from thermodynamics
considerations in order to mimic the flame cooling due to radiative heat losses that happens in pool fire scenarios. Soot was incorporated in the flamelet considering an arbitrary top hat profile, where \( f v = 3 \text{ ppm} \) for \( Z \in [0.1; 0.3] \) and zero elsewhere. This soot profile is only used here for illustration purposes. The path-length was defined from infinity (considered 2 m above the surface) to the surface. It was divided into 100 homogeneous segments of 2 cm. Figure 6 plots the incident spectral radiance at the surface beneath the flame. Two fuels IR properties are considered: \( n \)-heptane and toluene. Some qualitative differences exist in the spectral radiance between the two, especially in the ranges 1000 - 3300 cm\(^{-1}\). This affects the total predicted incident radiance: 32.9 kW m\(^{-2}\) str for toluene and 32.5 kW m\(^{-2}\) str for \( n \)-heptane. Note that since soot behaves as a blackbody, its has the greatest impact in the resulting total radiance. The results shown in this simple test are dependent on the soot profile chosen. Caution must be observed in the selection of the soot flamelet profile.

4 Conclusion

Spectra of several fuel vapors (\( C_2H_4 \), \( C_2H_6 \), \( C_3H_6 \), \( C_3H_8 \), \( C_7H_8 \), \( C_7H_{16} \), \( CH_3OH \), \( C_5H_8O_2 \)) that have previously been measured at temperatures ranging from near ambient to near 1000 K for various path-lengths using FTIR spectroscopy have been quantified into narrow band parameters for applications in engineering based radiation transfer calculations. Of existing narrow band modeling approaches, the Goody statistical narrow band model was found to provide a good quality fit with the closest integrated band intensities when compared with the experimental values extrapolated from the measurements using a curve of growth. Spectra reconstructed from the narrow band model parameters are in close agreement with the experiments, the relative error is less than 5%. These parameters have been implemented into RadCal.

Acknowledgments

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References


Figure 1: From top left, clockwise: experimental transmissivity of ethane at $T = 296, 500, 800$ K, with an optical path-length of 0.34 atm.cm; experimental transmissivity of ethylene at $T = 296, 500, 801$ K, with an optical path-length of 0.31 atm.cm; experimental transmissivity of propylene at $T = 296, 491, 793$ K, with an optical path-length of 0.48 atm.cm; experimental transmissivity of propane at $T = 295, 513, 790$ K, with an optical path-length of 0.13 atm.cm. For all the experiments, the total pressure was set to 101 kPa and nitrogen was used as a broadening gas.
Figure 2: From top left, clockwise: experimental transmissivity of \textit{n}-heptane at $T = 293, 490, 794 \text{ K}$, with an optical path-length of 0.045 atm.cm; experimental transmissivity of toluene at $T = 300, 477, 795 \text{ K}$, with an optical path-length of 0.13 atm.cm; experimental transmissivity of MMA at $T = 396, 483, 803 \text{ K}$, with an optical path-length of 0.11 atm.cm; experimental transmissivity of methanol at $T = 293, 483, 804 \text{ K}$, with an optical path-length of 0.10 atm.cm. For all the experiments, the total pressure was set to 101 kPa and nitrogen was used as a broadening gas.
Figure 3: Spectral variation of narrow band spectral absorption coefficient (left) and collision fine structure parameter (right) of the C–H stretching band (2550-3250 cm$^{-1}$) of $n$-heptane for temperatures of 293, 450, and 794 K. The resolution is 25 cm$^{-1}$; the Goody narrow band model was used.

Figure 4: Spectral variation of narrow band spectral absorption coefficient (left) and collision fine structure parameter (right) of the C–H stretching band (2600-3200 cm$^{-1}$) of methanol for temperatures of 293, 443, and 804 K. The resolution is 25 cm$^{-1}$; the Goody narrow band model was used.
Figure 5: Spectral variation of narrow band spectral absorption coefficient (left) and collision fine structure parameter (right) of the C–H stretching band (2650-3250 cm\(^{-1}\)) of MMA for temperatures of 396, 483, and 803 K. The resolution is 25 cm\(^{-1}\); the Goody narrow band model was used.

Figure 6: Incident spectral radiance using IR properties of \(n\)-heptane (in dash-dot lines) and toluene (in solid lines). The total radiance is 32.5 kW.m\(^{-2}\).str when using \(n\)-heptane IR properties and 32.9 kW.m\(^{-2}\).str when using toluene IR properties.