A Database of Narrow-Band Parameters for Fuels Commonly Encountered in Fire Applications

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Abstract

The objective of this paper is to derive narrow band (NB) parameters for the Malkmus statistical narrow band model from the medium resolution transmission measurements carried out at NIST (Wakatsuki et al., Proc. Combust. Inst. 31 (2007) 2573-2580) up to about 1000 K for nine fuels commonly encountered in fire applications, namely methane, methanol, ethane, ethylene, propane, propylene, heptane, methyl methacrylate and toluene. These NB parameters can be used to generate a database of NB k-distributions of these fuels in order to apply the k-distribution methods to model their contributions to radiative heat transfer. The accuracy of this NB database, the EM2C NB database for methane (Perrin and Soufiani, JQSRT 103 (2007) 3-13), and HITRAN 2012 for methane, methanol, ethane, and ethylene is assessed by comparison with the measured medium resolution transmissivities and spectrally-integrated radiative properties. Results show that the EM2C database is the most accurate for methane over the entire range of the temperature and the fuel partial pressure path length considered. The line parameters in HITRAN 2012 are not available for some important bands

of methanol, ethane and ethylene and this spectroscopic database cannot be used with confidence above 600 K. The Malkmus narrow band database derived in the present study is found to reproduce spectrally-integrated radiative properties with error less than 20%, which suggests that it can be used for engineering applications. Finally, applications to radiation calculations along lines of sight with methane concentrations and temperatures representative of pool fires show that both the present Malkmus narrow band and the NIST databases can predict accurately the radiative intensity for small scale pool fires whereas discrepancies of the order of 30% are expected in the case of methane pool fires with a heat release rate of 176 kW.

Key words: Fuels, Medium Resolution Transmission Measurements, Malkmus Model, Narrow Band Database, Narrow Band k-Distributions, Spectroscopic Database.

Nomenclature

F	fraction of $\Delta\eta_e$ which belongs to $\Delta\eta$ [-]
f	k-distribution function [cm]
g	cumulative k-distribution function [-]
I_b	blackbody intensity (Planck function) [W/cm ² /sr]
k	absorption coefficient variable [cm ⁻¹]
l	path length [cm]
p	pressure [atm]
R	ratio of the maximum to minimum value of the line intensity [-]

S	line intensity [$\text{cm}^{-1}/\text{mol.cm}^{-2}$]
S_m	maximum value of the line intensity [$\text{cm}^{-1}/\text{mol.cm}^{-2}$]
T	temperature [K]
x_i	mole fraction of i^{th} species [-]

Greek

α	absorptance [cm^{-1}]
β_M	Average line width to line spacing ratio [-]
β_{MS}	self broadening parameter in the Malkmus model [-]
β_{MA}	air broadening parameter in the Malkmus model [-]
$\Delta\eta$	resolution of the NB database [cm^{-1}]
$\Delta\eta_e$	experimental resolution [cm^{-1}]
ε	emissivity [-]
κ_η	spectral absorption coefficient [cm^{-1}]
$\bar{\kappa}_M$	Pressure based absorption coefficient [$\text{atm}^{-1}.\text{cm}^{-1}$]
$\bar{\kappa}_e$	pressure-based absorption coefficient deduced from $\bar{\tau}_e$ [$\text{atm}^{-1}.\text{cm}^{-1}$]
η	wavenumber [cm^{-1}]
$\bar{\tau}_e$	measured transmissivity at medium resolution of 1cm^{-1} [-]

$\bar{\tau}_{ext}$ extrapolated transmissivity at medium resolution of 1cm^{-1} [-]

$\bar{\tau}_{\Delta\eta}$ reduced transmissivity with the NB spectral resolution of 25cm^{-1} [-]

σ_e relative error on the measured transmissivity [-]

$\sigma_{\Delta\eta}$ relative error on the reduced transmissivity [-]

Subscript

e experimental data

ext extrapolated

η wavenumber

Abbreviations

FS Full spectrum

MMA Methyl methacrylate

NB Narrow band

NBCK Narrow band correlated-k

1. Introduction

In the last decade k-distribution methods, such as the narrow band correlated-k (NBCK) model, the full-spectrum k-distribution (FSK) model and their extensions, have emerged as the most promising methods for engineering radiative heat transfer calculations due to their good accuracy and efficiency [1-4]. Their capability to model radiative heat transfer within

the fuel rich core of pool fires was assessed by comparison with the exact line-by-line solutions, showing that they provide much better predictions than the methods currently used in fire simulators [5, 6]. In addition, in agreement with previous studies [7, 8], the radiative contribution of the gaseous fuel was found to play an important role in the radiative feedback toward the pool surface [5, 6].

A key prerequisite for the use of k-distribution methods in radiative heat transfer calculations in engineering applications is that a database of k-distributions must be available. Modest and co-workers [9, 10] demonstrated that the NB level is the best format to build such a database. This implies that, for each gas considered in the database, NB k-distributions must be stored for given sets of NBs, mole fractions, temperatures and pressures [10]. Storing k-distributions at the NB level provides several advantages, with the most important one being that accurate k-distributions at both NB and FS levels can be efficiently assembled for an arbitrary mixture of radiating gases and non-gray particles [9]. The NB k-distribution database can be built either directly from spectroscopic databases [10] or from NB transmissivity models, taking the advantage that the latter is the Laplace transform of the NB k-distribution function [11].

A NB database of k-distributions for carbon monoxide, carbon dioxide and water vapour can be generated [5-7, 9, 10] from HITEMP [12] and CDSD-1000 [13] spectroscopic databases, which were found to provide a good description of the line data over the range of temperatures encountered in combustion applications [14-16]. In order to apply this database to pool fire simulations it should be extended by adding k-distributions of fuels. HITRAN 2004 [17] was used to generate k-distributions for methane and ethylene [18, 19]. However, HITRAN was mainly developed for atmospheric applications and is expected to become inaccurate at temperatures higher than 600 K [10-22]. In addition, only a limited number of

hydrocarbon fuels, such as methane, methanol, ethane, ethylene, and acetylene, is available in HITRAN. In the case of methane, Perrin and Soufiani [22] developed an extended spectroscopic database which was found able to provide band absorptances and total emissivities in good agreement with available experimental data up to 1500 K. This database was used to derive NB parameters for the Lorentzian Malkmus statistical NB model [22 23]. Other well-known databases, such as the NIST [24] and the PNNL [24] databases, provide the absorption cross-sections of many species, but at low temperatures (50°C) and are not appropriate for combustion and fire applications.

NB k-distribution functions can also be computed by considering the inverse Laplace transform of NB transmissivity [1, 11]. An analytical expression for the k-distribution function can be obtained when the Lorentzian Malkmus statistical NB model is considered [26]. The problem is then reduced to the determination of NB parameters. NB parameters were derived either from spectroscopic databases as done by the EM2C team [22, 23, 27] for carbon dioxide, water vapor, carbon monoxide, and methane or from NB transmissivity measurements (see [28, 29, 16]). In this paper, the second procedure was employed, since, as discussed previously, line-by-line data (HITRAN) are available only for a limited number of hydrocarbon fuels and can be inaccurate at temperatures relevant to fire and combustion applications. The medium resolution (1 cm^{-1}) transmission measurements carried out at NIST up to 1000 K for nine fuels (methane, methanol, ethane, ethylene, propane, propylene, heptane, methyl methacrylate and toluene) [7, 30, 31] are used to accomplish this task. These experimental results are used to extend the database of NB k-distributions developed in Refs [5, 6] for CO₂, H₂O and CO from CDSD-1000 [13] and HITEMP 2010 [32] spectroscopic databases to include these nine fuels by using the Wang and Modest procedure [10]. The paper is organized as follows: the experimental procedure and the experimental uncertainties are presented in section 2. Section 3 describes the theoretical framework used to obtain the

NB parameters from measurements and to generate the k-distribution database. The results are presented and discussed in Section 4 with the accuracy of the NB database, the EM2C NB database [22, 23], and HITRAN 2012 [33] evaluated. Finally, Section 5 summarizes the conclusions drawn from this study.

2. Experiments

The medium resolution transmission measurements performed at NIST for nine fuels, namely methane, methanol, ethane, ethylene, propane, propylene, heptane, toluene and methyl methacrylate (MMA) [7, 30, 31], constitutes the starting point of this study. The experimental setup is briefly described in Section 2.1 whereas experimental uncertainties are estimated in Section 2.2. More details about the experimental setup and the experimental procedure can be found in Ref. [30].

2.1. Experimental set up and procedures

A Matteson Galaxy 7020 FTIR was used to measure transmissivities over a spectral interval ranging from 700 cm^{-1} to 4000 cm^{-1} at a resolution of 1 cm^{-1} . The signal was averaged over 128 scans. The IR beam passed through a 31.75 cm cell and into an external Mercury Cadmium Telluride (MCT) detector (M10465 Graseby Infrared). The total pressure, p , was 1 atm. A mixture of fuel and nitrogen flowed through the cell, the flow rates of N_2 being adjusted to provide the desired fuel mole fraction within $\pm 2\%$ $\Delta x/x = \pm 2\%$. Typically, three or four pressure path lengths ranging from about 1.6×10^{-3} to 1.6 atm·cm were considered. The cell was located inside a furnace. The set point was adjusted to maintain the inlet and outlet gas line temperature within 5 K ($\Delta T = 5\text{ K}$). For each fuel, seven temperatures in the range from 295 K to 1000 K were considered, with 1000 K being close to the temperature ($\sim 1100\text{ K}$) at which the fast pyrolysis of most hydrocarbons occurs.

The temperature of the windows was kept below 700 K to prevent oxidation of ZnSe by directing a jet of N₂ on the outside of the windows. The uncertainty in variations of the absorption coefficient due to temperature variations near the cooled windows, $\Delta\kappa_e/\kappa_e$ was estimated to be $\pm 4\%$, $\pm 5\%$, and $\pm 6\%$ for 600K, 800K, and 1000K, respectively [30]. Table 1 summarizes the conditions of measurements for each fuel.

2.2. Experimental uncertainties

The experimental errors on the measured transmissivities are analyzed following the procedure described in Refs. [14-16]. The measured NB absorption coefficient $\bar{\kappa}_e$ is defined as:

$$\bar{\tau}_e = \exp(-\bar{\kappa}_e x p l) \quad (1)$$

where $\bar{\tau}_e$ is the experimental NB transmissivity, x is the fuel mole fraction, p is the total pressure and l is the path length. The uncertainty in transmissivity results from uncertainties on mole fraction, $\Delta x/x$, uncertainties on temperature, $\Delta T/T$, and uncertainties on the absorption coefficient due to temperature variation near the cooled windows, $\Delta\kappa_e/\kappa_e$. The relative error on the path length is estimated to be negligible. **The uncertainties on line intensity and line shape profile caused by temperature uncertainty were found to have an imperceptible influence on the NB absorption coefficient. As a consequence, the temperature uncertainty are assumed to affect NB absorption coefficient only through gas density and the root mean square relative error on transmissivity can be expressed as [14-16]:**

$$\sigma_e = \frac{\Delta \bar{\tau}_e}{\bar{\tau}_e} = -\log \bar{\tau}_e \sqrt{\left(\frac{\Delta \bar{\kappa}_e}{\bar{\kappa}_e}\right)^2 + \left(\frac{\Delta T}{T}\right)^2 + \left(\frac{\Delta x}{x}\right)^2} \quad (2)$$

3. Narrow-band k-distribution from Malkmus Model

3.1. Theory

NB models are based on the discretization of the spectrum into relatively small spectral intervals (typically between 5 to 50 cm^{-1}), $\Delta\eta$, over which the Planck function and the radiative properties of particles and walls are essentially constant. The Malkmus model is recognized as the most suitable statistical NB model for radiating gases. In this model, the line probability distribution is assumed to have the following expression [1]:

$$P(S) = \frac{1}{S \ln R} [\exp(-S/S_m) - \exp(-RS/S_m)] \quad (3)$$

where S_m is the maximum value of the line intensity and R is the ratio of the maximum to minimum value of the line intensity. $P(S)$ is the probability density function and thus satisfies $\int_0^\infty P(S) dS = 1$. The NB averaged transmissivity is then expressed as [1]:

$$\bar{\tau}_{\Delta\eta} = \exp \left[-\frac{\beta_M}{\pi} \left(\sqrt{1 + \frac{2\pi p l \bar{\kappa}_M}{\beta_M}} \right) \right] \quad (4)$$

where the parameters of the NB model, $\bar{\kappa}_M$ and β_M , represent the pressure based absorption coefficient and mean line width to the line spacing ratio, respectively. $\bar{\kappa}_M$ **depends in the first order approximation only on temperature [27] and according to Ref. [16] β_M is expected to depend only on the fuel mole fraction, x , as:**

$$\beta_M = x\beta_{MS} + (1-x)\beta_{MA} \quad (5)$$

where β_{MS} and β_{MA} are the self and the air broadening parameters, respectively. For a given temperature, the NB averaged transmissivity can be computed from Eq. 4 provided that the three model parameters are known.

The averaged NB transmissivity can also be computed from the NB k-distribution function or from the cumulative NB k-distribution function as [1]:

$$\bar{\tau}_{\Delta\eta} = \int_0^{\infty} f(k) \exp(-kl) dk = \int_0^1 \exp[-k(g)l] dg \quad (6)$$

where $f(k)$ is the NB k-distribution function and $g(k) = \int_0^k f(k') dk'$ is the NB cumulative k-distribution function. Eq. 6 shows that the NB transmissivity is the Laplace transform of the absorption coefficient probability density function $f(k)$. $f(k)$ can be then deduced from the transmissivity given by the Malkums model by considering an inverse Laplace transform of Eq. 4. The following analytical expression was obtained by Domoto [26]:

$$f(k) = \frac{1}{2\pi k} \left(\frac{2\beta_M xp \bar{\kappa}_M}{k} \right)^{1/2} \exp \left[\frac{\beta_M}{2\pi} \left(2 - \frac{xp \bar{\kappa}_M}{k} - \frac{k}{xp \bar{\kappa}_M} \right) \right] \quad (7)$$

Eq. 7 can be integrated to give the cumulative density function [11]:

$$g(k) = \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{a}{\sqrt{k}} - b\sqrt{k} \right) \right] + \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{a}{\sqrt{k}} + b\sqrt{k} \right) \right] \quad (8)$$

with $a = \sqrt{\frac{\beta_M xp \bar{\kappa}_M}{2\pi}}$ and $b = \sqrt{\frac{\beta_M}{2\pi xp \bar{\kappa}_M}}$. Although an analytical expression for $k(g)$ does not exist, it can be found numerically by using a Newton-Raphson iteration method. In general only few iterations are required when k_{max} (where $f(k)$ peaks) is used as the initial value of k [11].

The NB parameters for each NB and for a set of temperatures allow generating a database of NB $k(g)$ distributions. $k(g)$ distributions can be stored efficiently by considering sets of mole fractions and temperatures and by using the fixed g-concept introduced by Wang and

Modest [10]. Typically, mole fraction and temperature intervals of 0.25 and 100 K are used [10]. The fixed-g concept consists in considering a fixed set of g-values (typically 128) corresponding to abscissas of a Gaussian quadrature scheme [10]. This allows the determination of accurate mixed k-distributions for a gas mixture from the k-distributions of constituents contained in the database by using the mixing and assembly procedures given by Modest and Riazzi [9]. In addition, for arbitrary species mole fractions and temperatures, the NB absorption coefficient for each band can be computed from the database by carrying out linear interpolations on x and spline interpolations on T [10]. In the present study, the NB parameters for the Malkmus model for each fuel are determined from the measured transmissivity for a set of temperatures in the range 295 K-1000 K (see Table 1). The resolution proposed by Wang and Modest [10] and adopted in Ref. [5, 6] is considered (see Table 2).

3.2. Determination of the narrow band parameters

The resolution of experimental transmissivities is reduced to that of the NB database. The transmissivity for the required band is then computed as a weighted sum of the experimental transmissivities as [16]:

$$\bar{\tau}_{\Delta\eta} = \sum \frac{F\Delta\eta_e}{\Delta\eta} \bar{\tau}_e \quad (9)$$

where F is the fraction of the experimental NB which falls to the required NB of the NB database, $\Delta\eta_e$ is the resolution of the experimental data (1 cm^{-1}) and $\Delta\eta$ is the resolution of the NB database, *i.e.*, 25 cm^{-1} on the spectral interval of interest ranging from 700 cm^{-1} to 4000 cm^{-1} (see Table 2). The experimental standard deviations may also be weighted to estimate an error for $\bar{\tau}_{\Delta\eta}$ [16]:

$$\sigma_{\Delta\eta} = \frac{\Delta \bar{\tau}_{\Delta\eta}}{\bar{\tau}_{\Delta\eta}} = \sum \frac{F \Delta \eta_e}{\Delta \eta} \sigma_e \quad (10)$$

$\bar{\tau}_{\Delta\eta}$ were used to obtain NB Malkmus parameters.

Two methods can be used to optimize the parameters. In the first, the parameter values are optimized by matching the curve of growth for each optical thickness. In the second, the absorption coefficient, $\overline{\kappa_M}$, is adjusted in the optically thin limit, whereas β_{MS} and β_{MA} are obtained by using a nonlinear least square fitting of the curve of growth for each optical thickness [27]. The second method is used in the present study.

Table 1 shows that the measurements were carried out for three or four rather weak fuel partial pressure path lengths. In order to improve the generality of the NB parameters, the number of reduced transmissivities to perform the fitting procedure was extended by extrapolating measured transmissivities to a wider range of pressure path lengths. Typically, one hundred pressure path lengths ranging from 10^{-3} to 100 atm·cm were considered to determine the NB parameters. The extrapolation procedure was based on the assumption that the pressure-based absorption coefficient, $\bar{\kappa}_e$, is weakly dependent on the fuel mole fraction. As a consequence, $\bar{\kappa}_e$ can be determined from the measured NB transmissivities and used to extrapolate the measurements to other pressure path lengths:

$$\bar{\kappa}_e = -\log \bar{\tau}_e / xpl \quad (11)$$

and

$$\bar{\tau}_{ext} = \exp(-\bar{\kappa}_e x_{ext} pl_{ext}) \quad (12)$$

where $\bar{\tau}_{ext}$ represent the extrapolated transmissivity with a resolution of 1 cm^{-1} corresponding to the extrapolated fuel partial pressure path length. The accuracy of this procedure is

examined in Fig. 1, which represents $\bar{\tau}_{\Delta\eta}$ for methane at temperatures of 297 K and 1000 K. For each NB, $\bar{\kappa}_e$ was determined from a transmissivity with a resolution of 1 cm^{-1} computed from HITRAN 2012 [33] for $x = 0.0028$. Figure 1 shows that the extrapolated transmissivities determined from $\bar{\kappa}_e$ are in overall good agreement with those determined directly from HITRAN 2012 [33], demonstrating the validity of the extrapolation procedure. Nevertheless, larger discrepancies are observed for $x = 0.9$ than for $x = 0.05$, which shows that the extrapolation procedure becomes increasingly inaccurate for large pressure path length extension beyond the measurement conditions.

4. Results and discussions

4.1. Comparison of calculated transmissivities with reduced experimental data

Figures 2-10 show a comparison between the NB transmissivities calculated from the Malkmus NB parameters developed in this study and the reduced experimental data for methane, methanol, ethane, ethylene, propane, propylene, heptane, MMA and toluene, respectively. Methane, methanol, ethane and ethylene are included in the HITRAN spectroscopic database [33]. **For these molecules, the reduced NB transmissivities were also computed from the line data of HITRAN 2012 [33] at the same resolution as the NB database (25 cm^{-1}). In these calculations, the line shape profile was assumed to follow a Lorentz profile when the ratio between the collision broadening line half-width and the Doppler line half-width is greater than 5. When this condition is not satisfied a Voigt profile is considered [34].**

These transmissivities are plotted in Figs. 2-5. For methane, NB transmissivities calculated with the EM2C database [22, 23] are also included for comparison (see Fig. 2). Although the spectral resolution for these transmissivities is also 25 cm^{-1} , it is important to notice that the centers of the NBs are shifted by 12.5 cm^{-1} as compared to those in the present NB database.

Figures 2 to 10 show that the calculated transmissivities reproduce very well the experimental data on the whole, demonstrating the quality of the fit. For methane, transmissivities computed with HITRAN 2012 are in reasonable agreement with the experimental data for temperatures up to 600 K (see Fig. 2). Figure 2c shows that HITRAN 2012 significantly **overestimates** the transmissivities compared to the experimental data at 1000 K, which is consistent with the conclusions reported in [22]. HITRAN 2012 does not include all the hot lines necessary to predict accurately high temperature spectra, explaining the observed discrepancies. Figure 2c shows also clearly the improvements provided by the EM2C database at 1000 K.

In order to evaluate the EM2C database in a proper manner, the transmissivities displayed in Fig. 11 are computed by using its spectral discretization [22, 23]. At 297 K, the excellent accordance between the transmissivities determined from HITRAN 2012 and the experimental data suggests the good accuracy of HITRAN 2012 at this temperature. The EM2C database also provides predictions in very good agreement with the experimental data, despite somewhat **overpredictions** of 2.7 % and 6.8% at 1300 cm^{-1} and 3025 cm^{-1} , respectively. At 600 K, the agreement between the experimental data and the two databases is found to be excellent for all the NBs. Nevertheless, some small discrepancies of the order of 2% between, on the one hand, both experimental data and HITRAN 2012 and, on the other hand, the EM2C database are still observed. As expected from the previous studies [22, 23], the EM2C database predictions display a much better agreement with the experiments at 1000 K than those obtained with HITRAN 2012. A very good agreement between the experiments and the EM2C is obtained for the ν_3 band (**$2700\text{--}3300\text{ cm}^{-1}$**), despite the localized discrepancies of the order of 26% at 3000 cm^{-1} . In the ν_4 band, the transmissivities computed with the EM2C database are also found to **overestimate** the experimental data. At these temperatures, measurements of transmissivities are challenging and it is reasonable to believe

that their accuracy is reduced. In particular, the cooling of the windows to prevent oxidation induces a non-uniform profile of temperatures in the cell, with temperatures near the windows significantly lower than those imposed in the cell [30]. In the ν_4 band transmissivities were found to be sensitive to temperature and to increase as the temperature decreases. This can, then, explain that the EM2C calculations underestimate the data since the non-uniformity of the temperature is not taken into account in the simulations.

For methanol the line data of HITRAN 2012 are only available for the C-O stretching band (around 1033 cm^{-1}). Figure 3 shows that the predicted transmissivities for this band are in reasonable agreement with the experimental data at 293 K, but become less and less accurate as the temperature increases. Figure 4 displays the computed and experimental transmissivities for ethane. HITRAN 2012 predicts accurately the transmissivity in the range from 600 to 1800 cm^{-1} at a temperature of 296 K, but large discrepancies are observed at 600 and 1000 K. In addition, Fig. 4a₂ shows that HITRAN 2012 provides poor predictions of the transmissivity for the CH₃ stretching band even at room temperature (around 3000 cm^{-1}). Comparisons between the transmissivities computed with HITRAN 2012 and the experimental data for ethylene depict a similar overall behavior as that for the other fuels (see Fig. 5). A reasonable agreement is observed at room temperature (see Figs. 5a₁-a₃). However, large discrepancies are encountered at higher temperatures.

4.2. Accuracy of the NB database

Figures 2 to 10 show that the calculated transmissivities reproduce accurately the experimental data from which the present Malkmus NB parameters are derived. However, as shown in Fig.1, the extrapolation procedure can lead to larger discrepancies for values of the fuel partial pressure path length outside the range of measurements.

The objective of this section is to assess the accuracy of the NB database. Methane is considered to accomplish this task due to the availability of, on the one hand, a significant amount of experimental data and, on the other hand, the EM2C NB database that can be used as a reference in view of the results reported in Ref. [22]. This assessment is performed by comparing the integrated radiative properties computed with the present NB database to those computed with the EM2C database and experimental data. These integrated properties were also computed from HITRAN 2012 and from the pressure-based absorption coefficient, $\bar{\kappa}_p$, deduced from the NIST experimental data (see Eq. 11). The data obtained with the latter model will be referred to as NIST database hereafter. It is important to keep in mind that this denomination concerns the medium resolution transmission measurements performed by Wakatsuki and co-workers [7, 30, 31] and not the database of absorption cross-section [24].

Figure 12 shows the total emissivities, defined as $\varepsilon = \frac{1}{I_b(T)} \int_0^\infty (1 - \exp(-\kappa_\eta l)) I_{b\eta}(T) d\eta$, as a function of the temperature for different pressure path lengths. The computed emissivities are compared with the data of Brosmer and Tien [35]. As expected, the total emissivities computed with the EM2C database are in good accordance with the experimental data whereas those computed with HITRAN 2012 underestimate significantly the total emissivity above 600 K. It is also expected that the current NB database provides emissivities in close agreement with those obtained using the absorption coefficients derived from the NIST measurements. This demonstrates that the NB database has the same accuracy as the NIST database from which the Malkmus NB parameters were derived. Comparison with the EM2C database shows that the NB database and the NIST emissivities exhibit the largest discrepancies for a fuel partial pressure path length of 2 cm·atm and temperatures lower than 600 K. Relative errors of 22% and 30% are observed at 297 K and 500 K, respectively. Regardless of the path lengths considered, both

the NB and the NIST databases are found to be more accurate than HITRAN 2012 for temperatures greater than 600 K.

Figure 13 shows the band absorbance for the ν_4 (800-2000 cm^{-1}) and the ν_3 (2000–3500 cm^{-1}) bands defined as $\alpha = \int_{band,i} (1 - \exp(-\kappa_\eta l)) d\eta$. The experimental data correspond to the measurements of Lee and Happel [36]. The observations for the band absorbance shown in Fig. 13 are overall similar to those for the total emissivities shown in Fig. 12. The EM2C database provides accurate absorbances for all the temperatures considered, whereas HITRAN 2012 becomes significantly inaccurate above 600 K. The absorbances predicted from the present NB and NIST databases are in close agreement and present a substantial improvement over the HITRAN 2012 results above 600 K. Comparisons with the EM2C absorbances show that the largest relative errors are about 14% for the ν_3 region and 30% for the ν_4 region and occur at temperature of 297 K and 400 K, respectively.

Figure 14 shows the pressure-based Planck-mean absorption coefficient of methane. Results from the EM2C database and HITRAN 2012 are in good agreement up to 600 K. Above this temperature HITRAN 2012 starts to underestimate significantly the Planck-mean absorption coefficient due to the absence of hot lines. The Tien's data were obtained by integrating the exponential wide band data across the spectrum, based on correlations of low-resolution experiments [37]. The data of Tien are higher than the EM2C results by about 30%. Results of the present NB and NIST databases are in relatively good agreement. Both databases provide predictions in better agreement with the EM2C data than the Tien correlation and are more accurate than HITRAN 2012 above 600 K. Results of the present NB and NIST databases are within 20% of the EM2C Planck-mean absorption coefficients.

Radiative heat transfer calculations are conducted along two non-isothermal non-homogeneous paths involving methane concentration and temperature representative of those encountered along the axis of a pool fire (see Figs. 15 a₁ and b₁). The temperatures and methane concentrations were taken from the simulations reported in [5, 38], where two methane turbulent buoyant diffusion flames, generated on a burner 0.38 m in diameter with heat release rates of 33.4 and 175.8 kW were considered. The optical thicknesses, based on the Planck mean absorption coefficient, are 0.25 and 1.87 for the 34 and 176 kW pool fires, respectively. Figs. 15 a₂ and b₂ show the axial evolution of the integrated radiative intensity. In both cases, very large discrepancies were observed between EMC2 and HITRAN 2012 predictions, confirming that HITRAN 2012 is not suitable for such kind of applications. The predicted radiative intensities calculated with NIST and the present NB databases are very similar and the comparisons with the EM2C calculations show that they are significantly more accurate than the HITRAN 2012 predictions. For the 34 kW pool fire, a very good agreement is observed with the EM2C computations (see Fig. 15 a₂). For the 176 kW pool fire, the absorption of methane between $z = 0.5$ m and the burner exit is overpredicted, which result in a maximum relative error of the order of 35% at the burner exit.

It should be pointed out that the spectral resolution of the NIST database is too low to be used directly in CFD calculations. In fire simulators, these data are generally used to generate the Planck mean-absorption coefficients which are used as radiative properties for the radiatively participating gases in the radiative transfer equation [39, 40]. Calculations with the Planck mean absorption coefficients computed from the NIST database are referred to as ‘NIST Planck’ in Fig. 15 a₂ and b₂. It can be observed that the discrepancies obtained by using the Planck mean absorption coefficients are significantly greater than those observed for the present NB and NIST databases. As expected, these discrepancies are found to increase as the optical thickness increases.

5. Conclusions

A database of Malkmus NB parameters for nine fuels, namely methane, methanol, ethane, ethylene, propane, propylene, heptane, MMA, and toluene was generated from the NIST transmissivity measurements for temperatures ranging between 295 K and 1000 K. The accuracy of this database was evaluated by comparisons with experimental data and with the EM2C NB database for methane and the spectroscopic database HITRAN 2012 for methane, methanol, ethane and ethylene. The following conclusions can be drawn:

- 1) The EM2C NB database is recommended for radiative transfer calculations involving methane.
- 2) HITRAN 2012 gives rise to large error at temperatures above 600 K. In addition, this database does not include some important bands for methanol and ethylene.
- 3) The Malkmus NB database developed in this study has the same accuracy as the NIST database from which the Malkmus NB parameters were derived. These databases predict spectrally-integrated radiative properties within about 20% of measurements, showing that they can be used for engineering applications.
- 4) Applications to radiation calculations along lines of sight with methane concentrations and temperatures representative of pool fires suggest that both the Malkmus narrow band and NIST databases are accurate for small scale pool fires. For larger scale pool fires, however, relative errors of about 30% are observed.
- 5) The use of Planck-mean absorption coefficient should be avoided if accurate predictions are required.

As a final remark, it is important to point out that the accuracy of the Malkmus NB database can be substantially improved if the measured transmissivity were available for a wider range of fuel partial pressure-pathlength product than the current NIST database. The NB

parameters derived in this study can be readily used to generate a NB k-distribution database based on the Malkmus NB model.

The database of Malkmus NB parameters described in this study is available upon request.

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Table 1. Experimental conditions [30]. For each fuel measurements were conducted for seven temperatures referred to as T_i with $i=1$ to 7. For each temperature, the first line indicates the value of the temperature whereas the following lines indicate the fuel concentrations in ppm.

Fuel/Temperature	T_1	T_2	T_3	T_4	T_5	T_6	T_7
Methane	297K	400K	450K	499K	600K	800K	1000K
	491	491	491	491	491	24140	24140
	1032	1032	1032	1032	1032	31838	31838
	1933	1933	1933	1933	1933	39415	39415
	2832	2832	2832	2832	2832	51937	51937
Methanol	293K	396K	443K	483K	570K	804K	1000K
	1570	1590	1445	1540	1574	1692	1543
	2256	2323	2235	2213	2286	2472	2302
	2912	2935	2960	2857	2904	3193	3055
Ethane	296K	400K	400K	500K	600K	800K	1000K
	2559	2559	2559	2559	2559	2559	2559
	6632	6632	6632	6632	6632	6632	6632
	10672	10672	10672	10672	10672	10672	10672
Ethylene	296K	400K	450K	500K	601K	801K	1000K
	2470	2470	2470	2470	2470	2470	5660
	5660	5660	5660	5660	5660	5660	9619
	9619	9619	9619	9619	9619	9619	14328
Propane	295K	396K	435K	513K	578K	790K	1009K
	1000	1000	1000	1000	1000	1000	1000
	2500	2500	2500	2500	2500	2500	2500
	4000	4000	4000	4000	4000	4000	4000
Propylene	296K	390K	444K	491K	594K	793K	1003K
	5000	5000	5000	5000	5000	5000	5000
	10000	10000	10000	10000	10000	10000	10000
	15000	15000	15000	15000	15000	15000	15000
Heptane	293K	400K	450K	490K	593K	794K	1000K
	474	458	480	474	479	468	548
	985	951	982	964	992	952	971
	1554	1500	1564	1561	1588	1389	1149
MMA	297K	396K	441K	483K	597K	803K	1014K
	1716	1670	1600	1613	1716	1716	1716
	2474	2413	2330	2474	2474	2474	2474
	3162	3217	2978	3162	3162	3162	3162
Toluene	300K	396K	440K	477K	587K	795K	999K
	2548	2548	2340	2617	2557	2627	2821
	3183	3021	2666	3032	3026	3043	3260
	4278	3929	3446	3964	3729	4021	4345

Table 2. Nominal NB ranges for the NB database [10].

Spectral Intervals (cm ⁻¹)	Resolution (cm ⁻¹)	Number of NBs
200-300	10	10
300-4000	25	148
4000-5000	50	20
5000-10000	100	50
10000-15000	250	20
Total		248

List of Figure Captions

Figure 1. Validity of the extrapolation procedure for methane for two temperatures of a) 297K and b) 1000K. The indexes denote 1) the ν_4 band and 2) the ν_3 band.

Figure 2. Comparison between calculated transmissivities and reduced experimental transmissivities for methane for: a) 297K, b) 600K, and c) 1000K. The indexes denote 1) the ν_4 band and 2) the ν_3 band.

Figure 3. Comparison between calculated transmissivities and reduced experimental transmissivities for methanol for: a) 293K, b) 570K, and c) 1000K. The indexes denote 1) the C-O stretching and the CH_3 bending bands and 2) the CH_3 stretching and O-H stretching bands.

Figure 4. Comparison between calculated transmissivities and reduced experimental transmissivities for ethane for: a) 296K, b) 600K, and c) 1000K. The indexes denote 1) the CH_3 rock, the C-C stretching and CH_3 deform bands and 2) the CH_3 stretching band.

Figure 5. Comparison between calculated transmissivities and reduced experimental transmissivities for ethylene for: a) 296K, b) 600K, and c) 1000K. The indexes denote 1) the $=\text{CH}_2$ out of the plane bending band, 2) the C-H in plane and out the plane bending bands and 3) the CH_3 and $=\text{CH}_2$ stretching bands.

Figure 6. Comparison between calculated transmissivities and reduced experimental transmissivities for propane for: a) 295K, b) 578K, and c) 1009K. The indexes denote 1) the C-H bending band and 2) the C-H stretching band.

Figure 7. Comparison between calculated transmissivities and reduced experimental transmissivities for propylene for: a) 296K, b) 594K, and c) 1003K. The indexes denote 1) the $=\text{CH}_2$ out of the plane bending band, 2) the C-H in plane and out the plane bending bands and the C=C stretching band and 3) the CH_3 and the $=\text{CH}_2$ stretching bands.

Figure 8. Comparison between calculated transmissivities and reduced experimental transmissivities for heptane for: a) 295K, b) 593K, and c) 1000K. The indexes denote 1) the C-H bending band and 2) the C-H stretching band.

Figure 9. Comparison between calculated transmissivities and reduced experimental transmissivities for MMA for: a) 297K, b) 597K, and c) 1014K. The indexes denote 1) the $=CH_2$ out of the plane bending band, 2) the C-O stretching, the CH_3 bending, the C=C and C=O stretching bands, and 3) the CH_3 and the $=CH_2$ stretching bands.

Figure 10. Comparison between calculated transmissivities and reduced experimental transmissivities for toluene for: a) 300K, b) 587K, and c) 999K. The indexes denote 1) the phenyl=CH out of the plane bending and the phenyl=CH in the plane bands, 2) the phenyl C=C stretching band and 3) the CH_3 and =CH stretching band.

Figure 11. Comparison between calculated transmissivities and reduced experimental transmissivities for methane for: a) 297K, b) 600K, and c) 1000K. The indexes denote 1) the v_4 band and 2) the v_3 band. The spectral discretization is that of the EM2C database.

Figure 12. Comparisons between total emissivities of methane calculated from the NB database, the NIST database, the EM2C database, HITRAN 2012 and the data from Brosmer and Tien [35] deduced from absorption measurements. Methane is assumed to be diluted in nitrogen with a total pressure of 1 atm.

Figure 13. Comparisons between band absorptances of pure methane with $l=7.62$ cm and $p=1.013$ atm calculated from the NB database, the NIST database, the EM2C database, HITRAN 2012 and the data of Lee and Happel [36].

Figure 14. Comparison between Planck-mean absorption coefficients for methane calculated from the NB database, the NIST database, the EM2C database, HITRAN 2012 and the correlation of Tien [37].

Figure 15. a₁) and b₁) axial profiles of temperature and methane molar concentration for the 34 kW and the 176 kW pool fires, respectively. a₂) et b₂) axial profiles of radiative intensity for the 34 kW and the 176 kW pool fires, respectively.

Figure 1.

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