Determination of Planck Mean Absorption Coefficients for HBr, HCl, and HF

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The Planck mean absorption coefficient, a_p, has been calculated for HBr, HCl, and HF over a temperature range from 300 K–2300 K using data from the 1996 edition of the HITRAN molecular database. Plots of a_p versus temperature showed monotonically decreasing behavior over this temperature range, with peak values at 300 K of 45.9 (atm-m)$^{-1}$, 5.3 (atm-m)$^{-1}$, and 1.95 (atm-m)$^{-1}$ for HF, HCl, and HBr, respectively. The magnitude of these values suggests that HBr, HCl, and HF can significantly impact calculations of radiative transfer in flames containing these species. Two sets of additional calculations were performed for CO to validate the methodology used for calculation of a_p for HBr, HF, and HCl. In the first approach, which employed the narrow band model RADCAL, the calculation procedure was similar to that of the present calculations. The second approach utilized tabulated values of the integrated intensity for each CO band and an average value of the Planck function within each band. Results from the three methods showed general agreement. Polynomial expressions are provided as fits to a_p as a function of temperature for HBr, HCl, HF, and CO. [DOI: 10.1115/1.1416689]

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Introduction

In large-scale tires, radiation is the dominant mode of heat transfer [1]. In non-sooting and moderately sooting fires, the participation of heated gases and soot. through absorption and emission of infrared radiation. plays a significant role in radiative exchange. The Planck mean absorption coefficient, a_p, characterizes radiative emission in the source term of the generalized energy equation for an absorbing/emitting (non-scattering) medium [2]. Because it is a function only of the local temperature, a_p can be conveniently tabulated and efficiently used in complex radiative heat transfer calculations. The Planck mean absorption coefficient. a_p, is defined as

$$a_p = \frac{\int_{\Delta\omega} \kappa_\omega E_{\omega,b} d\omega}{\sigma T^4} \tag{1}$$

To calculate a_p from **Eq.** (1), the spectral absorption coefficient. κ_ω, for a gas or gas mixture, is needed as a function of temperature. In the more general case of a scattering medium, the absorption coefficient is replaced by the extinction coefficient. β_ω as follows:

$$\beta_\omega = \kappa_\omega + \sigma_\omega , \tag{2}$$

where σ_ω is the scattering coefficient. However, for a gas, scattering is typically neglected and the extinction coefficient is equivalent to the absorption coefficient. The radiative properties. including κ_{ω}. of molecular combustion species such as H_2O, CO_2, and CO have been relatively well characterized. A narrow hand model (RADCAL) was developed which evaluates Eq. (1) for relevant combustion species including CO, , H_2O, CO, CH_4, and soot [3]. Alternatively, Abu-Romia and Tien [4] presented a method for calculating a_p that is based on a simplified narrow band approach. This approach utilizes the integrated intensity of individual gas bands that can be determined independently and tabulated. This method **has** the advantage that it is easily **implemented** for cases in which the integrated intensity is a known

function of temperature. Tien [5] presented results based on this model for CO_2. H_2O, N_2O, NH_3, SO_2, CH,. CO, and NO. Grosshandler and Thurlow [6] extended this method to derive an expression for a_p based on the equivalence ratio for flames burning H_2, CO, CH_3OH, and CH, in air, and lean regions of other generic flames.

Radiative transfer involving species such as HBr, HCl, and HF has not been studied extensively. These species are found in flames inhibited by halogenated compounds and are also present in incinerators. They are difficult species to study experimentally due to their corrosive nature. Halogenated compounds are widely used as tire suppression agents. HCl is a stable combustion product that attains near equilibrium concentrations in inhibited hydrocarbon flames [7]. The same behavior can be expected for HF. Calculations have shown that HF and HBr can achieve local mass fraction levels on the order of 5 percent and 10 percent, respectively, in CF_3Br inhibited CH_4/air counterflow flames [8]. While the production of CF_3Br (Halon 1301) has been halted due to its adverse effects on stratospheric ozone, it is still widely used as a tire suppressant. Additionally, heptafluoropropane and other **halogenated** species are considered viable alternatives to CF_3Br in some applications. While these agents inhibit flames primarily through chemical effects, heat loss to the surroundings by radiative emission can also influence extinction. Radiation can be particularly significant in weakly strained fames [.]. Therefore, it is important to characterize the radiative properties of HF and HBr so that flame emission can be modeled more accurately.

The Planck mean absorption coefficient can be used to characterize radiative emission from gases of any optical thickness [2] and is thus a useful parameter, particularly since it can be determined a priori. The aim of this study was to calculate a_p for HBr, HCl, and HF for use in simplified flame models [10] using spectral data previously measured [11].

Methodology

The absorption coefficient for a single spectral line can be expressed as the product of line intensity (S), line shape (g), and the concentration of absorbing molecules (N) [12]

$$\kappa_\omega = S . g(\omega - \omega_0) . N, \tag{3}$$

where w is the wave number (cm^{-1}) and $w_{,}$ denotes the center of an absorbing line. Tlie concentration can be related to temperature through tlie ideal gas law

$$N = N_L \cdot \left(\frac{296}{T}\right), \tag{4}$$

where N_L is Loschmidts' number $(N_L = 2.479 \cdot 10^{19}$ molecules/cm^3/atm at 296 K)[1]. Tlie Lorentz line shape, which is generally used for applications at atmospheric pressure and moderate temperatures, was used. This profile has the form

$$g(\omega) \quad \frac{}{(\omega - \omega_0)^2 + \gamma_p^2}, \tag{5}$$

where γ_p is the pressure-broadened line half width at half maximum (HWHM)

$$\gamma_p = \Gamma \cdot \left(\frac{296}{T}\right)^n P_{,}. \tag{6}$$

$P_{,}$ is the total pressure and Γ' is the air broadened half width parameter $(\text{atm-cm})^{-1}$. In the case of broadened lines, the absorption coefficient is obtained by summing contributions from overlapping adjacent lines [5].

A program was written to calculate the absorption coefficient according to Eqs. (3)–(6) using data from the 1996 edition of tlie HITRAN molecular database [11]. Calculations were performed lor each gas over the spectral range from 0 cm^{-1}–8500 cm^{-1}, which included the fundamental and first overtone bands corresponding to vibration-rotation transitions, in addition to pure rotational bands that appear in the far-IR. The latter of these transitions are significant only at temperatures below approximately 600 K. Table I lists the spectral ranges that contain absorption bands for each molecule, along with the corresponding band centers. Calculations were performed from 300 K to 2300 K, a range of temperatures appropriate for combustion calculations.

In addition to HBr, HCI. and HF, calculations were performed lor CO to validate the methodology and accuracy of the program through comparison with results from two narrow band approaches. Reviews of radiation hand models are available in the literature [2,5]. One study utilized RADCAL [3], a narrow-band model that solves the equation of radiative transfer for a non-homogeneous, ahsorbing and emitting mixture of gases and soot. The CO model employed by RADCAL is from Malkmus and Thompson [13] who applied the anharmonic oscillator model to calculate emissivity for temperatures as high as 7000 K using band integrated intensity rneasureinents [14]. This model includes only the fundamental CO band, neglecting rotational and overtone bands. Neglecting the contribution of the rotational band between 0 cm^{-1}–200cm^{-1} was justified by considering its intensity. The contribution of this band can he significant at low temperatures. however for CO its intensity is a factor of 10^3 lower than the fundamental band and the contribution to a_p is less than 0.5 percent. However. the first overtone hand is more signilicant, particularly at higher temperatures where the contribution to a_p is on the order of 1–2 percent. This can be seen by comparing values of band integrated intensity in Table I [11].

The second approach was that of Abu-Romia and Tien [4], who utilized the Elsasser narrow band inodel to derive a general expression for the Planck mean absorption coefficient

$$a_p = \frac{\int_0^\infty \kappa_\omega E_{\omega,b} d\omega}{\sigma T^4} = \sum_j \frac{\overline{E_{b,j}} \alpha_j}{\sigma T^4}. \tag{7}$$

In this expression, the summation is over any bands that make a significant contribution to the absorption coefficient. The approxi-

Table 1 Spectral parameters for each molecule based on [11]. The top row in each molecular category represents data for a rotational transition. The middle and bottom rows represent the fundamental and first overtone vibration-rotation bands, respectively.

Molecule	Spectral Bands of Absorption Lines, cm^{-1}	Band Center, cm^{-1}	Integrated Intensity at T = 296 K $\alpha(\text{atm}^{-1}\text{cm}^{-2})$
HF	41 – 625		1394.45
	3269 – 4369	3960	189.61
	6999 – 7995	7749	12.30
HBr	16 – 383		11723
	2123 – 2791	2559	35.37
	4591 – 5164	5027	0.39
HCl	20 – 438		262.40
	2399 – 3161	2885	155.35
	5159 – 5830	5666	3.52
CO	3 – 190		0.46
	1795 – 2317	2143	250.36
	3836 – 4361	4260	1.97

mation is made that the blackbody emissive power varies linearly across each ahsorption hand so that the value evaluated at the band center, $(\overline{E_{b,j}})$, ciin be used. The only required parameter is the temperature dependent integrated intensity. α_j. which characterizes absorption for each band. Tien [5] compiled a list of values for combustion related species, however more recent measurements are available for CO [IS]. Alternatively, values can be obtained from HITRAN [11] at 296 K and scaled to higher temperatures [16].

Results

Validation of Methodology. Figure I compares the CO calculations performed in this study with results from the narrow band approaches discussed previously. The calculations that were performed in this study using Eqs. (1) and (3)–(6) are labeled "This Study". The values of a_p determined from RADCAL and fit to a 4th order polynomial [17] are labeled "RADCAL Fit". Data calculated from Eq. (7) based on [5,18] is expanded in Fig. I as "Integrated Intensity [5,18]". An estimate of α from HITRAN at $T = 296$ K is given in Table I. A plot of a_p based on Eq. (7), with α taken from Table I [11], is shown in Fig. I and labeled "Integrated Intensity [11]". Only the fundamental and first overtone bands were considered for the data labeled "Integrated Intensity [5,18]" and "Integrated Intensity [11]".

The temperature dependence of α lor the calculations using Eq. (7) was taken from Breeze ct al. [16]. It is worth emphasizing that a_p values from Eq. (7) are based on independent measurements of the CO integrated intensity. α [11,18] and a wide range of values can be found in the literature [18]. Recent measurements. how-

ever, show better agreement. Adjusting the value of α for the 2143 cm^{-1} CO band from Table 1 [11] to a temperature of 273 K yields α (273)=271.5 atm^{-1} cm^{-2}. This falls within the range given in [18] and is less than 3 percent below the value prescribed in [15].
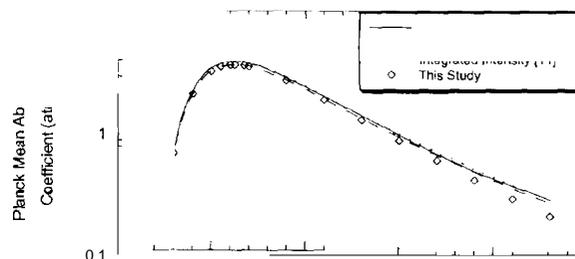
The agreement between calculations shown in Fig. 1 is quite good considering the range of data sources. The difference in values predicted by Eq. (7) stems from the use of α values from more than one source. The Planck mean absorption coefficient calculated using Eqs. (1), (3)–(6) is 28 percent lower than the value predicted by Eq. (7) using HITRAN data [11] at a temperature of 2300 K. However, flame temperatures between 1200 K–1500 K are found in many applications [1], and over this range the agreement between methods is within 6 percent. Calculations using HITRAN at 2300 K were not appreciably different from those using its high temperature analog, HITEMP [19].

Discussion of HBr, HCl, HF, and CO calculations. Figure 2 shows the Planck mean absorption coefficient for HBr, HCl, HF and CO, calculated over a temperature range from 300 K–2300 K using data from the 1996 edition of the HITRAN molecular database. HF has the highest a_p value throughout the range 300 K $\leqslant T \leqslant$ 2300 K. The relative magnitude of a_p can be predicted by examining the integrated intensity values for each absorption/ emission band in Table 1; HF has the highest α value in each range. The plots of a_p for HBr, HCl, and HF all have the same general feature, a monotonic decrease with increasing temperature, which is different than that of CO. This is due to the fact that HBr, HCl, and HF each have significant rotational bands located between 0 cm^{-1}–700 cm^{-1}, while the CO band in this range is a factor of 10^3 less intense than its fundamental band. At low temperatures, absorption bands at small wave number locations are significant. At progressively higher temperatures, bands centered at larger wave number positions become dominant due to the shift in emissive power in Eq. (7). This is shown in Fig. 3, which plots the transmittance of the absorption bands for each molecule at room temperature between 0 cm^{-1}–6000 cm^{-1}. Also shown in this figure are plots of the normalized blackbody emissive power, $E_{\lambda,b}/\sigma T^4$, for temperatures of 300 K, 700 K, and 1100 K.

Uncertainties in line intensity and line width are generally near 5 percent and 10 percent, respectively, in the HITRAN database [20]. Furthermore, tunable diode laser measurements of HF and HBr have shown deviations from HITRAN data that are outside of this range for these species [21,22]. However, it has been estimated that the accuracy of spectrally integrated irradiance is better than that for individual lines [20].

Sample Application. The Planck mean absorption coefficient for CO$_2$ is a factor of 4 to 5 times higher than that of H$_2$O and
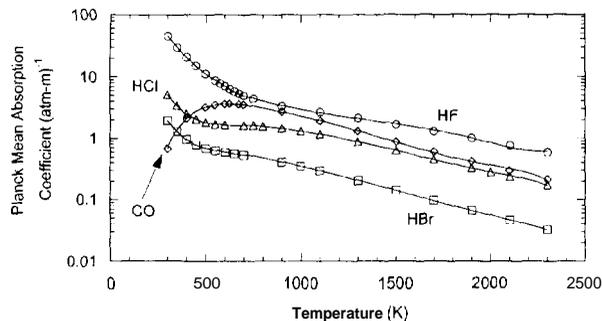
Fig. 2 Calculated values of Planck mean absorption coefficient for HBr, HCl, HF, and CO. Calculations are based on Eqns. (1) and (3)–(6) with data from the 1996 edition of the HITRAN molecular database [11]. The following symbols are used to identify individual species: HBr (□), HCl (△), HF (○), and CO (○) Polynomial expressions from Eq. (8) are represented by solid lines through the points.
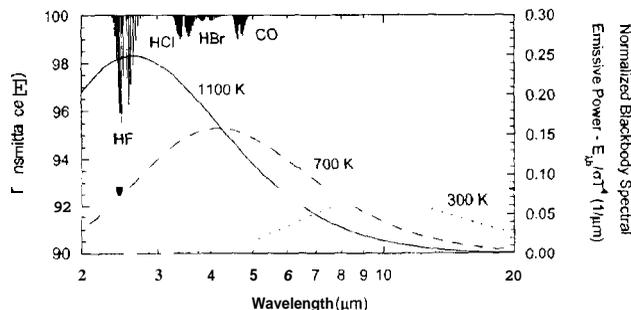
Fig. 3 Spectral transmittance, τ_λ, of the rotational and fundamental vibration-rotation HBr, HCL, HF, and CO bands for the condition $T=$ 300 K is plotted on the left vertical axis. The spectral blackbody emissive power, normalized by σT^4, is plotted on the right vertical axis for temperatures of 300 K, 700 K, and 1100 K.

10–15 times higher than that of CO over the temperature range 1100 K–2300 K. Throughout this range, however, a_p values for HF and HCl are comparable to those for CO. Additionally, Masri [8] reports that HF and HBr mass fractions are comparable to CO$_2$ and H$_2$O in CF$_3$Br inhibited flames. Therefore, the inclusion of HBr, HCl, and HF in radiative emission calculations of inhibited hydrocarbon flames may be significant.

To estimate the impact of HF and HBr on total flame emission, a homogeneous volume of heated products in a CF$_3$Br inhibited CH$_4$/air counterflow flame [8] was considered. The results showed that, for optically thin conditions, HF and HBr were found to account for approximately 7 percent and 1 percent, respectively, of the total flame emission. The a_p values for HCl lie between those of HF and HBr, so a similar contribution might be expected from HCl emission in incinerator or flame applications.

Polynomial Fit to Data. Polynomial expressions were fit to the HBr, HCl, HF, and CO data over two temperature regimes: 300 K $\leqslant T \leqslant$ 700 K and 700 K $\leqslant T \leqslant$ 2300 K. These are shown in Fig. 3 as solid lines through the points. The expressions were of the form:

$$a_p = \sum_{n=0}^{4} a_n T^n$$

Table 2 lists values of the coefficients a_n. The r^2 correlation coefficient for each polynomial was 0.999 or better. The maximum difference between the calculated a_p values and polynomial values was 7 percent, with an average difference of less than 1 percent.

The effect of spectral overlap between absorption bands was not included in these fits. Significant overlap does exist between the HF fundamental at 3960 cm^{-1} and the H$_2$O and CO$_2$ bands nearby. At 300 K there is negligible overlap between the fundamental HCl and HBr bands; however, at higher temperatures as these bands broaden the overlap will increase and possibly spread into the range of the CO$_2$ band at 2350 cm^{-1}. Water lines in the

Table 2 Values of the polynomial coefficients to be used with Eq. (8)

a_n in Eq. 8		HF	HBr	HCl	CO
a_0	300 K – 700 K	435.74	20.583	56.261	6.2773
	700 K – 2300 K	21.322	1.3211	0.3090	6.2016
a_1	300 K – 700 K	-2.7099	-1.3398x10^{-1}	-3.6651x10^{-1}	-8.0223x10^{-2}
	700 K – 2300 K	-4.3028x10^{-2}	-1.3603x10^{-3}	5.9271x10^{-3}	-1.8068x10^{-3}
a_2	300 K – 700 K	6.6504x10^{-3}	3.4124x10^{-4}	9.3093x10^{-4}	3.2405x10^{-4}
	700 K – 2300 K	3.7464x10^{-5}	3.8057x10^{-7}	-8.0002x10^{-6}	-4.9650x10^{-6}
a_3	300 K – 700 K	-7.4327x10^{-6}	-3.8865x10^{-7}	-1.0569x10^{-6}	-4.6257x10^{-7}
	700 K – 2300 K	-1.5053x10^{-8}	3.0545x10^{-11}	3.6388x10^{-9}	3.5195x10^{-9}
a_4	300 K – 700 K	3.1531x10^{-9}	1.6594x10^{-10}	4.5099x10^{-10}	2.2200x10^{-10}
	700 K – 2300 K	2.2591x10^{-12}	-1.9485x10^{-14}	-5.6193x10^{-13}	-6.5751x10^{-13}

$0-400$ cm^{-1} region overlap with HF, HBr, and HCl lines in this range. Additionally, at higher temperatures, the overlap of H_2O with overtone bands of HF, HBr, and HCl will increase. These effects are usually negligible in optically thin conditions [2,17] and no correction was derived to accommodate band overlap.

Conclusions

Values of the Planck mean absorption coefficient have been calculated for HBr, HCl, HF, and CO based on data from the 1996 edition of the HITRAN molecular database. For temperature conditions where a_p is significant ($a_p > 0.5$ atm^{-1} m^{-1}), the values of a_p for CO compare favorably with those from two narrow band models. Polynomial expressions were provided based on tits to a_p versus temperature data. The inclusion of HBr, HCl, and particularly HF can significantly contribute to emission calculations for tire suppression or incinerator scenarios where halogenated compounds are present.

Acknowledgments

Nomenclature

a_p = Planck mean absorption coefficient (atm-m)$^{-1}$
α = band integrated intensity (atm^{-1}-cm^{-2})
β_ω = extinction coefficient (atm-cm)$^{-1}$
σ_ω = scattering coefficient (atm-cm)$^{-1}$
S = line intensity (cm/molecule)
P = pressure (atm)
T = temperature (K)
E_{ob} = blackbody emissive power (W/m^2/μm)
g = line shape function (cm)
Γ = air broadened half width parameter (cm-atm)$^{-1}$
n = air-broadening temperature coefficient
N = concentration (molecules/cm^3/atm)
κ_ω = absorption coefficient (atm-cm)$^{-1}$
γ = pressure broadened line half width (cm^{-1})
ω = wave number (cm^{-1})
σ = Stefan-Boltzmann constant (W/m^2/K^4)

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