JOURNAL OF THERMOPHYSICS AND HEAT TRANSFER
Vol. 20, No. 4, October–December 2006

Technical Notes

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Enhanced Long-Wavelength Infrared Extinction from Soot Agglomerates

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I. Introduction

THE optical properties of small agglomerated soot particles are an active area of research. However, most measurements have been performed at visible wavelengths, where the effects of agglomeration upon emission and absorption are weak. Consequently, it is difficult to perform definitive tests of the theory at visible wavelengths. A brief note by Roessler and Faxvog[1] is the only observation the authors are aware of that points out the remarkable sensitivity of soot to agglomeration in the long-wavelength infrared (LWIR). They observed an anomalously large LWIR/visible extinction coefficient ratio based on a two-color 515 nm vs 10.6-μm extinction measurement of room-temperature agglomerated acetylene smoke (0.13 vs approximately 0.05 based on Mie theory for Rayleigh-sized particles). Mackowski et al.[2,3] observed a minor enhancement of the midwavelength infrared (MWIR)/visible extinction coefficient ratio for agglomerated soot produced by several different fuels. However, because, the longest wavelength used in their measurement was only 3.8 μm, the effect of agglomeration was too small to be conclusive. With the advent of new theoretical models and computer codes to predict the optical properties of agglomerates, these old observations take on a new significance as researchers attempt to refine and validate theoretical models. A modern confirmation of this effect in the LWIR, where the refractive index is more favorable to producing strong shape effects, is desirable to motivate new research. The authors therefore undertook to substantiate this earlier measurement by using a flame rather than cooled smoke and by using an additional laser to provide a more definitive result.

II. Experimental

A rich, premixed sooting acetylene/air flame was supported on a sintered bronze, water-cooled, premixed, porous-plug burner with an active area of 9.5 by 17.1 cm. A no. 6 mesh screen was placed 5 cm above the burner face to stabilize the flame. The fuel and airflows were measured with thermal mass flow meters having a full-scale range of 100 standard liters per minute (SLPM) (1667 cm^3/s). The fuel flow was set at a constant 11.2 SLPM (187 cm^3/s), and the air was varied to provide overall fuel equivalence ratios from 2.4 to 2.6. Scanning electron microscope (SEM) photographs of collected samples showed agglomerates composed of spherical monomers of $\approx$50 nm radius, but a more careful characterization of the agglomeration state was beyond the scope of our effort.

Three lasers were used to measure soot extinction. The visible laser was a 20-mW, 633-nm HeNe laser (Spectra Physics Corp., model 106-1). The MWIR laser was a 40-mW 3.39-μm HeNe laser (Jodon Corp., model HN20G-IR 3.39). The LWIR laser was a 3.5-W 11.2-μm carbon dioxide isotope (^{13}C) laser (Line Lite model 941S) attenuated to 150 mW to avoid detector overload. The transmitted laser powers were measured using Laser Precision Co. model RPK 545 pyroelectric detectors with a broadband coating, each with an appropriate narrow bandpass laser line filter. The detector acceptance angles were approximately 21, 11, and 5 mrad, for the visible, MWIR, and LWIR, respectively. The detector output voltages were recorded at a rate of 10 Hz in blocks of 30 to 60 s on a personal computer using a Data Translation Corp. A/D converter board under the control of a Global Lab software package. The laser beams were centered 1.4 cm above the burner face. This location was high enough to avoid the soot inception zone near the burner surface and yet low enough to be in the steady laminar flow zone. The ^{13}C isotope was used in the CO_2 laser to minimize the possibility of absorption by hot $^{12}CO_2$ in the flame. The HITRAN 1996 database indicated less than 1% flame absorption in the region near the laser wavelength. We saw no evidence of absorption of the 3.39-μm laser line by the P7 v_3 CH_4 line or any other gaseous absorber. The principal experimental consideration was to obtain a sufficiently long optical path in the LWIR to acquire a good soot extinction signal. The laser beams were therefore transmitted through the flame using a single pass for the visible, a double pass for the MWIR, and a quadruple pass for the LWIR.

A representative laser transmission measurement is shown in Fig. 1. Similar signals were obtained at the other laser wavelengths. At the start of each run, the laser beams were blocked to determine the dc offset. The soot concentration varied as the fuel equivalence ratio was adjusted. At the end of each run, the flame was extinguished and the 100% laser transmission levels were measured. As can be seen from the stability of the signals, the collection aperture was large enough so that beam-steering from refractive index gradients in the flame was not a problem. Table 1 displays the optical depths, -ln(transmission), per single pass through the flame vs the

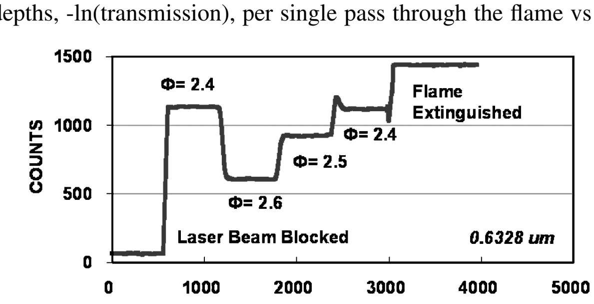

Fig. 1 Typical laser transmission data.

Received 9 October 2004; revision received 18 December 2004; accepted for publication 20 December 2004.

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Table 1 Measured optical depth per single pass through the flame

Φ	Visible	MWIR	LWIR
2.6	0.93	0.25	0.17
2.5	0.47	0.14	0.07
2.4	0.27	0.07	0.03

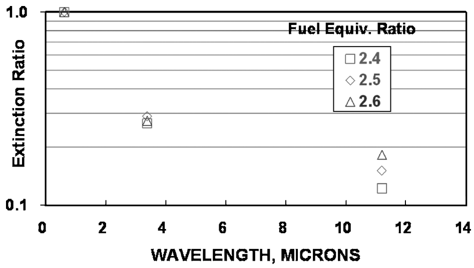

Fig. 2 Normalized extinction ratios.

fuel equivalence ratio Φ. The important parameter in our experiment is not the absolute optical depth but the ratios thereof. At all wavelengths, the variation in these ratios was dominated by the reproducibility of the flame. The standard deviations of the extinction ratios were ±11.5, 13.2, and 14.8% at equivalence ratios of 2.4, 2.5, and 2.6, respectively.

III. Analysis

Figure 2 displays these same data normalized to the optical depth in the visible channel. As long as multiple scattering can be neglected, these ratios equal the ratios of the MWIR and LWIR extinction coefficients to the visible coefficient at 0.6328 μm. Whereas the MWIR/visible ratio is independent of fuel equivalence ratio, the LWIR/visible ratio is not. Figure 3 shows Mie predictions of the MWIR/visible and LWIR/visible extinction coefficient ratios (specifically the ratios of the Mie extinction efficiency parameter Q_{ext}) vs soot particle radius for five different sets of soot optical properties.[4–8] The shaded horizontal bars represent the mean values of the measured extinction coefficient ratios, and the width of each bar represents a one-standard-deviation uncertainty estimate. It includes both the calibration uncertainty of the detectors and the variation from run to run. Although there is considerable scatter in the predicted extinction ratios due to differences in optical properties, the observed MWIR/visible ratio can be satisfactorily explained by Mie theory using reasonable soot particle sizes ($r \leq 50$ nm). Had this not been the case, the validity of our experiment would be in serious question. However, the only particle size that explains the LWIR/visible extinction ratio is unreasonably large. In addition, there is no particle size that simultaneously explains both the MWIR/visible and LWIR/visible extinction ratios within the context of Mie theory. This figure also makes it apparent that uncertainty in the optical properties, especially in the LWIR, complicates the interpretation of these measurements.

The open circles and triangles in Fig. 3 are predictions of the T-Matrix agglomerate model of Mackowski et al.[9,10,§] for Rayleigh-sized monomers. This model is an exact solution of Maxwell's equations for agglomerates composed of spherical monomers. It is applicable to monomers of any size, but we have used Rayleigh-sized monomers in Fig. 3 as the reasonable choice for flame soot. This choice is supported by our SEM photomicrographs. Provided that the agglomerate itself is Rayleigh size (which at a wavelength of 11.2 μm is almost certainly the case), the scattering is negligible compared to absorption. In addition, the absorption is proportional to the total mass of the agglomerate and is independent of the monomer size. This is the same behavior exhibited by single spheres in the Rayleigh size limit. The only difference is that the LWIR mass absorption coefficient is significantly larger for agglomerated spheres than for single spheres. In general, the extinction predicted by the T-Matrix code depends on the individual monomer size, the total number of monomers, N, and the geometric structure of the agglomerate. This is far too detailed for practical application to sooty flames. Therefore, Mackowski performed the tedious job of averaging code results over a statistical ensemble of thousands of fractal agglomerates to derive a simplified curve fit,[11] that expresses the absorption of Rayleigh-sized agglomerates vs the number of monomers, N. The absorption coefficient attains an asymptotic value for $N > 10$, and this is the value shown in Fig. 3. The symbols for the agglomerates are plotted vs a specific particle size only to avoid excessive clutter in the figure. They apply equally to any size below the Rayleigh limit (approximately $r < 150$ nm in the LWIR). Depending on the choice of optical properties, the agglomerate model predicts about a factor of 2 increase in the LWIR absorption. The measured factor is closer to ≈3. Whereas the T-Matrix agglomerate code assumes ideal touching spherical monomers, observations of agglomerates sampled from flames with high fuel equivalence ratios[12] indicate that actual geometry is more complicated and exhibits tendencies toward a filamentary structure. This is potentially significant because the LWIR mass extinction coefficient of a long Rayleigh-sized cylinder is approximately one order of magnitude greater than for a sphere.[2,13] Thus even a small tendency toward filamentary structure may have a large effect on the net extinction coefficient.

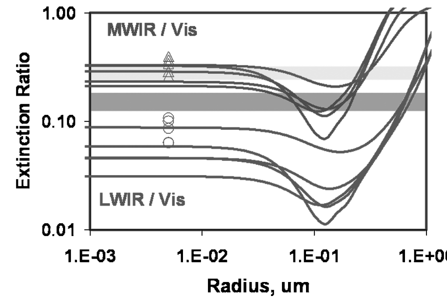

Fig. 3 Mie theory (—) vs T-Matrix agglomerate code (△, ○) for five different sets of soot optical properties (data and associated uncertainties denoted by horizontal bands).

IV. Summary

In conclusion, the observed LWIR/visible extinction ratio in our acetylene flame, 0.15 ± 0.03, agrees with the value previously observed by Roessler and Faxvog for cooled acetylene smoke (0.13). This is approximately three times greater than expected on the basis of Mie theory for Rayleigh-sized spherical particles. The close agreement between these two measurements suggests that the elevated LWIR extinction is a general property of agglomerated flame soot and not an anomaly of either experiment. Furthermore, there is no particle size and no reasonable choice of optical properties that simultaneously explains our visible, MWIR, and LWIR data within the framework of Mie theory. The T-Matrix agglomerate code of Mackowski shows improved agreement with the data, but it still underpredicts the LWIR extinction. The authors hope that this short note will motivate others to pursue more definitive investigations.

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