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Exhausts for Spark-Ignited and Diesel I.C. Engines**

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OPTICAL DETECTION AND SIZING OF "HYPER-FINE" ORGANIC PARTICLES
IN THE EXHAUSTS OF SPARK-IGNITED AND DIESEL I.C. ENGINES

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Introduction

Recently, there has been an increased attention within the scientific community to the presence of carbonaceous fine and ultrafine particles in the atmosphere, because of their impact on the environment and their adverse effects on human health. Particularly, recent studies have established a worrying correlation between the concentration of ultrafine organic particles in the atmosphere and the respiratory illness [1]. Donaldson *et al* [2] have shown that material which is relatively inert when inhaled as micrometer-sized particles can be highly inflammogenic for particles in nanometer size range, because they deposit in deep lung. Also, it has been suggested that, since particles in the accumulation mode ($0.1\mu\text{m} < d < 1\mu\text{m}$) can act as a sink for the nuclei mode ($d < 0.1\mu\text{m}$), the decrease of the number of fine particles could result in a many-fold increase of the number of ultrafine ones [3,4].

Yet, some recent studies on combustion systems [5,6] have shown that only a minor fraction of the organic matter sampled in the combustion by-products is chemically speciated, the remaining being unidentified. Finally, specific investigations on rich flames [7,8] have inferred the existence of nanoparticles ($d \approx 2\text{nm}$) in the reaction zone much smaller than soot nuclei ($d = 20\text{-}40\text{ nm}$) and in conditions below the threshold of soot formation.

In this framework, more detailed investigations on i.c. engines exhausts are of interest since they can lead to assess the role of diesel and spark-ignition engines as sources of ultrafine organic particles. In fact, the unidentified carbon fraction might be emitted mostly in the form of

extremely fine particles, undetectable by existing instruments, which escape any control and abatement process and are released continuously to the atmosphere.

Preliminarily, it is worth addressing a nomenclature problem. Figure 1 shows an overall scheme of the most used classification of particle sizes [9]. Atmospheric particles are ordinarily classified into three- distributions of sizes or "modes" [10], namely "coarse" ($d > 1.0 \mu\text{m}$), "accumulation" ($0.1 \mu\text{m} > d > 1.0 \mu\text{m}$), and "nucleation" ($d < 0.1 \mu\text{m}$) mode. On the other hand, the terms "fine" and "ultrafine" are also commonly used for particles with sizes smaller than $1.0 \mu\text{m}$ and $0.1 \mu\text{m}$, respectively. In addition, the term "nanometric" is increasingly used for ultrafine particles. Nevertheless, ambiguity still remains about the distinction between particles with sizes in the range $0.01 \mu\text{m} > d > 0.1 \mu\text{m}$, e.g. soot nuclei, and still smaller particles, e.g. molecular clusters, with sizes below $0.01 \mu\text{m}$. Accordingly, it seems appropriate to refer to such particles as "hyperfine" particles, which add to and complete the classification presently covered by the "fine" and "ultrafine" terms.

This paper focuses on the experimental problem of searching and detecting carbonaceous hyperfine particles, emitted in the exhausts of both compression-ignited and spark-ignited i.c. engines. New experimental methods will be described, which are capable of detecting nanometric particles and, on the other side, of providing further insights on the characterization of i.c. engines emissions. They are based on the well-assessed optical extinction and scattering techniques, but operated with spectrally resolved, broadband ultraviolet light.

Experimental data consist in a) extinction spectra on air-diluted exhausts and b) extinction *and* scattering spectra on water-trapped combustion species. Evaluation from experimental spectra of size, volume fractions and optical properties of detected nanoparticles is reported.

Experimental apparatus

In this work, we report on optical investigations on the exhausts of two in-use cars, roughly representative of the circulating sheep, with A) a compression-ignited (diesel) engine and B) a spark-ignited engine, equipped with and a three-way catalyst, fueled with unleaded gasoline, respectively. They have been operated at the chassis dynamometer on a fixed working point (3000rpm, 3rd gear, 50% load). The duration of each test run was 13 min and the fuel consumption monitored. For brevity, in the following they will be referred to as 'diesel' and 'gasoline' cases, respectively.

In a first set of tests, the exhaust emissions are firstly diluted with air in a dilution tunnel at an average dilution ratio $R_d=1:10$, as in standard test procedures, and then brought to a 1.0 m long optical path, where ‘in situ’ optical extinction measurements are carried out. In the following, the corresponding samples will be termed AD (‘air-diluted’) exhausts.

In other tests, the exhaust emissions, without any dilution, have been cooled in a heat exchanger; so that combustion water was forced to condense and thus to trap non-volatile combustion by-products for ‘ex situ’ optical analysis. Accordingly, such samples are referred to as WT (‘water-trapped’), indicating trapped species or condensed (combustion) water, as appropriate.

Optical techniques

Broad-band light extinction and scattering techniques, spectrally resolved in the ultraviolet band (190nm-400nm), have been used in the experiments reported here, the former on both ‘air-cooled’ and ‘water-trapped’ samples, the latter only for detection of ‘water-trapped’ particles.

The well-assessed spectral extinction technique involves the measurement of the attenuation (or extinction) of light through a homogeneous medium of length l , cm, according to the Lambert-Beer’s law:

$$I_t(\lambda) = I_o(\lambda) \cdot \exp[-\alpha_{ext}(\lambda) l], \quad (1)$$

where $I_o(\lambda)$ and $I_t(\lambda)$ are the incident and the transmitted light intensities at the wavelength λ , cm, respectively and $\alpha_{ext}(\lambda) = N_p \cdot \sigma_{ext}(\lambda)$, cm^{-1} , is the extinction coefficient. For absorbing scatterers much smaller than the wavelength, the latter can be expressed [11] as :

$$\alpha_{ext}(\lambda) = N_p \cdot (\pi d_p^2 / 4) \cdot 4 \cdot (\pi d_p / \lambda) \cdot \text{Im}\{(m_p^2 - 1) / (m_p^2 + 2)\} \quad (2)$$

where N_p , cm^{-3} , is the number concentration of molecules/particles,

$\sigma_{ext}(\lambda)$, cm^2 , is the extinction cross-section of the interacting molecule/particle,

$m_p(\lambda) = n_p(\lambda) + i \cdot k_p(\lambda)$ is the complex refractive index of the molecule/particle.

The ‘light scattering’ technique is well known as well, and widely applied in many fields, particularly for optical diagnostics of combustion processes and species. For unpolarized light and for particles much smaller than the wavelength λ , the light-matter interaction is termed ‘Rayleigh scattering’ and is described by the scattering efficiency $Q_{sca}(\lambda) = N_p \cdot \sigma_{sca}(\lambda)$, given by:

$$Q_{sca}(\lambda) = (8/3) \cdot N_p \cdot (\pi d_p^2/4) \cdot (\pi d_p/\lambda)^4 \cdot \text{Re}^2\{(m_p^2-1)/(m_p^2+2)\} \quad (3)$$

In the experiments reported here, a new kind of light source [12] has been used. It exploits the laser-induced optical breakdown of air, obtained by tightly focusing a pulsed beam of coherent light. The resulting plasma kernel is : A) extremely hot, reaching electron temperatures as high as 10^5K ; B) short-lived, with a lifetime of few tens of nanoseconds; C) spatially confined in a volume of 10^{-2}mm^3 . Its spectral emission spans from visible down to the deep ultraviolet band, thus providing enough radiation for applications involving weak light-matter interactions or detection of trace species.

Figures 2A-2C show the experimental setups for the extinction and scattering measurements. A Nd-YAG, Q-switched laser beam ($\lambda = 1.06\ \mu\text{m}$, 200 mJ/pulse, 7 ns pulse duration, 10 pulses/s) fires the plasma, which constitutes the light source, in the focus F of the ellipsoidal mirror M1 (for AD- and WT- extinction and scattering). In the extinction measurements, a small fraction of light travels through either the AD exhausts which flow in the optical path (Fig. 2A) or the WT samples in a fluorimetric quartz cell (Fig. 2B) and is then dispersed and recorded. In light scattering experiments, the quartz cell is placed in the near focus of the ellipsoidal mirror M2 (Fig. 2C). The ellipsoidal mirror M2 (Fig. 2C) condenses the emitted light in its far focus. The light scattered by the sample is collected by the mirror M2 and brought to its far focus on the input slit of the detector assembly.

Results

Extinction measurements

Spectral extinction measurements carried out on air-diluted (AD) exhausts have been reported in Fig. 3.A and show the extinction coefficient $\alpha_{\text{ext}}(\lambda)$, units of cm^{-1} , as a function of the wavelength λ of the incident radiation in the ultraviolet range 190nm-400nm, for 'diesel' and 'gasoline' exhausts, as indicated. The absorption lines grouped in the wavelength range 200 nm - 230 nm are distinctive of NO. Around 400nm, the wide NO₂ absorption band appears too. In AD 'diesel' extinction spectrum, the "soot" feature shows up, with the typical broadband, λ^{-1} spectral behavior.

The extinction coefficient of WT samples was nearly 10^4 times higher than AD exhausts'. So it has been necessary to dilute the collected samples progressively, until different best dilutions have been reached for extinction and scattering measurements, respectively.

Figure 3.B shows the extinction spectra $\alpha_{\text{ext}}(\lambda)$ of WT 'diesel' and 'gasoline' samples, rescaled and referred to undiluted samples. The WT extinction spectra appear quite different from the corresponding AD's in Fig. 3.A, involving a selective trapping of some species. In particular, most soot particles turn out to have escaped water trapping.

Scattering measurements

The extinction technique, in principle, cannot discriminate whether the absorbing species are molecules, e.g. polyaromatics, or a suspension of fine carbonaceous particles, since their absorption spectra might be similar. The light scattering technique can remove the ambiguity, since particles provide detectable scattering signals, whereas the expected concentrations of molecules, if any, scatter light at vanishing levels.

Experimental scattering raw data are affected by multiplicative factors: i) the spectral emission intensity of the incident light and ii) the overall spectral response of the optics-spectrometer-detector assembly; as well as by additive contributions, namely iii) stray light from the quartz cell, iv) fluorescence, if any, and v) the spectral scattering of the WT sample (water + trapped species). Retrieval of the 'pure' scattering data from raw scattered signals requires careful cleaning procedures. Firstly, fluorescence has been extracted from the signals, by means of a couple of further scattering measurements, carried out with and without a low-pass filter (cutoff wavelength $\lambda_c=280\text{nm}$). Next, signals have been corrected for multiplicative spectral factors, by making the ratio with the acquired spectrum of the incident light, and for stray light from cell walls. Detailed procedures and techniques are described elsewhere [13]. Finally, the resulting intensities have been calibrated to the absolute value of the scattering efficiency of pure water $Q_w = 5.2 \times 10^{-1} \text{ cm}^{-1} \text{ sr}^{-1}$ at $\lambda=366 \text{ nm}$ [14].

Figure 4 reports on the absolute scattering efficiencies $Q(\lambda)$, in units of $\text{cm}^{-1} \text{ sr}^{-1}$, as functions of wavelength over the band 200 nm - 400 nm, of WT 'diesel' and 'gasoline' samples. Also shown, for reference, is the theoretical scattering of water (dashed line at the bottom). The 'excess' scattering from WT matter over pure water is attributed to particles. In Fig. 4 the minimum of

scattering level around 250 nm can be interpreted as due to the matching of the real refractive index of the particles to that of pure water.

From the experimental data of Figg.3.B and 4 and from the relationships (2) and (3), it is possible to retrieve the average size d_p , the number concentrations N_p and the optical properties $m_p(\lambda) = n_p(\lambda) + i \cdot k_p(\lambda)$ of the scatterers on the whole UV spectrum, as detailed in [13].

The computed values of sizes and volume fractions of particles trapped in the condensed combustion water, for two kinds of engines are reported in Table I.

It turns out that: A) $d_p \approx 2$ nm for both 'gasoline' and 'diesel' WT samples, which then fall into the above defined range of "hyperfine" particles; B) the volume fractions $f_v = N_p \cdot (\pi d_p^3 / 6)$ of particles in undiluted condensed combustion water is $f_v \approx 30$ ppm and ≈ 85 ppm, respectively, which correspond, assuming spherical particles, to number concentrations N_p of the order of 10^{16} particles/cm³ in condensed water.

The third column in Table I reports the estimated ratios of the carbon content in WT samples $[C]_{WT}$ to that of fuel $[C]_{fuel}$, which is of the order of 10^{-4} .

Discussion and conclusions

Firstly, it is worth stressing some features of the data set reported in the work. The spectral measurements have been extended down to ultraviolet wavelengths as low as 190 nm and have been obtained with a quite high signal-to-noise ratio, even though in unoptimized conditions.

The key-tool is the particularly intense ultraviolet emission of the light source, since it allowed us to gather robust experimental results in a spectral region ($\lambda < 250$ nm) where literature data are scarcely available and yet physically relevant.

Retrieved values of particles' sizes and concentrations are quite surprising. Firstly, we have no notice so far of similar findings in the exhausts of both 'diesel' and spark-ignited engines. The extremely small size of the particles suggests to look at them as molecular clusters, rather than well-grown solid bodies, as even soot nuclei can be considered.

Further analysis of the extinction spectral data, detailed elsewhere [13], evidences the organic composition of such matter, which includes aromatic functionalities, related to the existence in the clusters of sub-units of two- and three-benzenic rings.

Also, the total number of particles emitted in the exhausts turns out to be equal or even higher than those actually trapped in the condensed water, according whether water-trapping efficiency is equal or less than unity, respectively.

Our preliminary data address the question about how and when such "hyperfine" particles are formed, whether during high-temperature combustion processes, or by nucleation within the exhaust tail-pipe, or even through condensation in water of organic vapors. To this end, it is worth noting that our findings at the exhausts of i.c. engines parallel and extend recent investigations in nearly-sooting flames [15], which reported the sequential formation in the reaction zone of two distinct classes of carbonaceous particles, namely "hyperfine" organic particles and "ultrafine" soot nuclei.

Our preliminary data on size and number of particles, detected in the exhausts of both diesel and s.i. engines, encourage further investigations, since they involve quite important implications on combustion processes, health effects, measurements requirements, exhausts aftertreatments.

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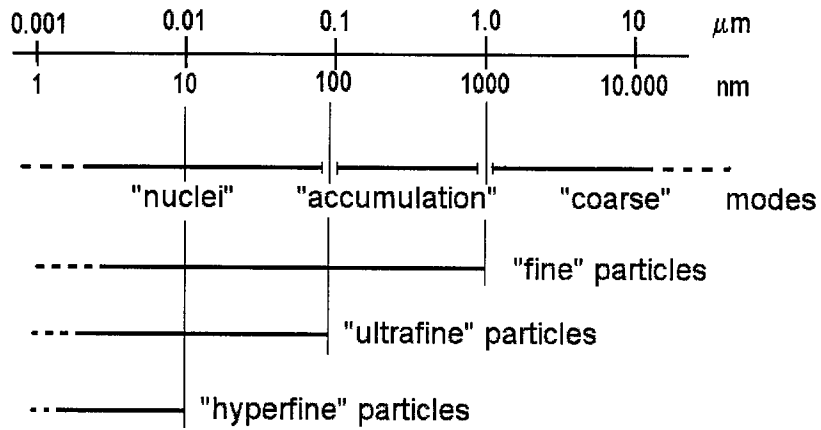


Figure 1: Classification of particles "modes" and sizes

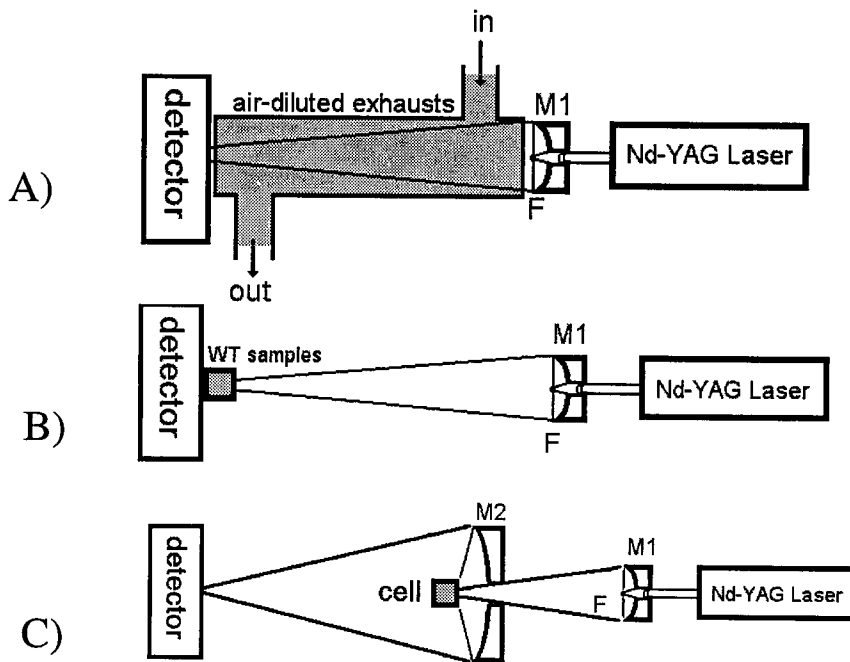


Figure 2: Optical setup for spectral extinction measurements

A) on air-diluted, AD, exhausts

B) on water-trapped, WT, samples

C) for scattering measurements on WT samples.

F, Ultraviolet light source, generated by optical breakdown of Nd-YAG laser pulses;

M1, ellipsoidal condensing mirror; M2, ellipsoidal collecting mirror;

SM+PAD, spectrometer+photodiode array detector assembly.

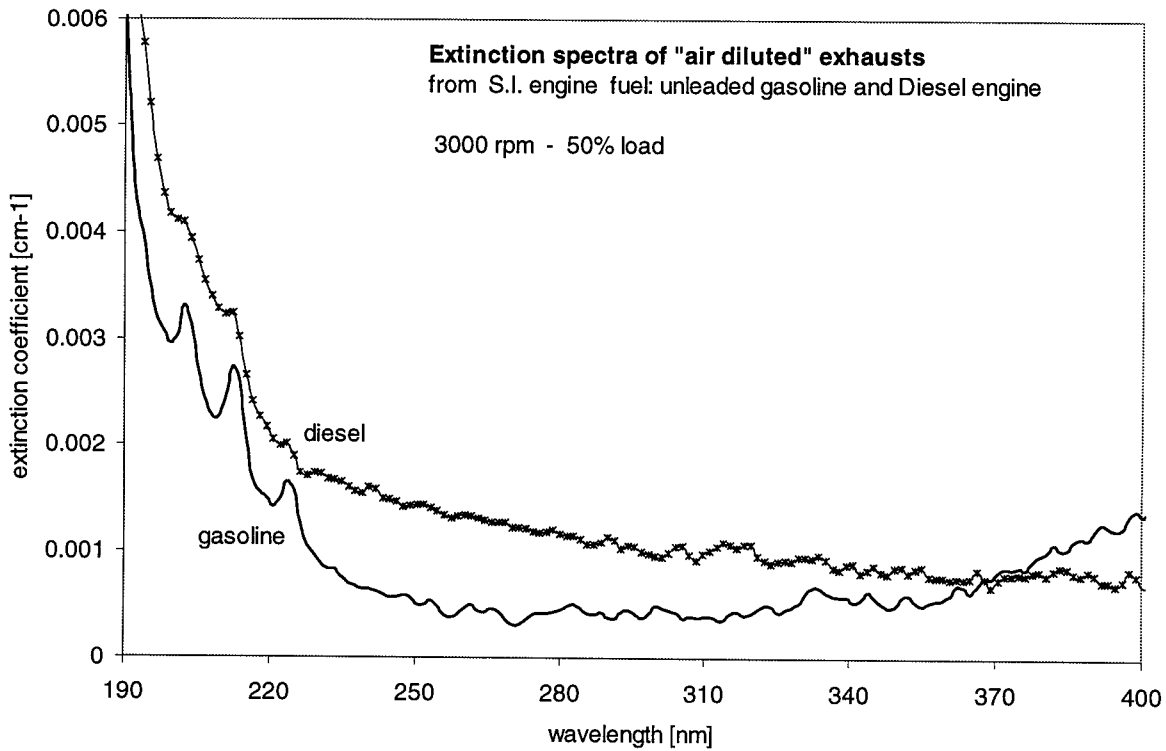


Figure 3A. :Extinction coefficient $\alpha_{\text{ext}}(\lambda)$, in cm^{-1} , as a function of the wavelength in the spectral range 190nm-400nm, for air-diluted (AD) exhausts from 'gasoline' (thin solid line) and 'diesel' (thick solid line) engines, respectively.

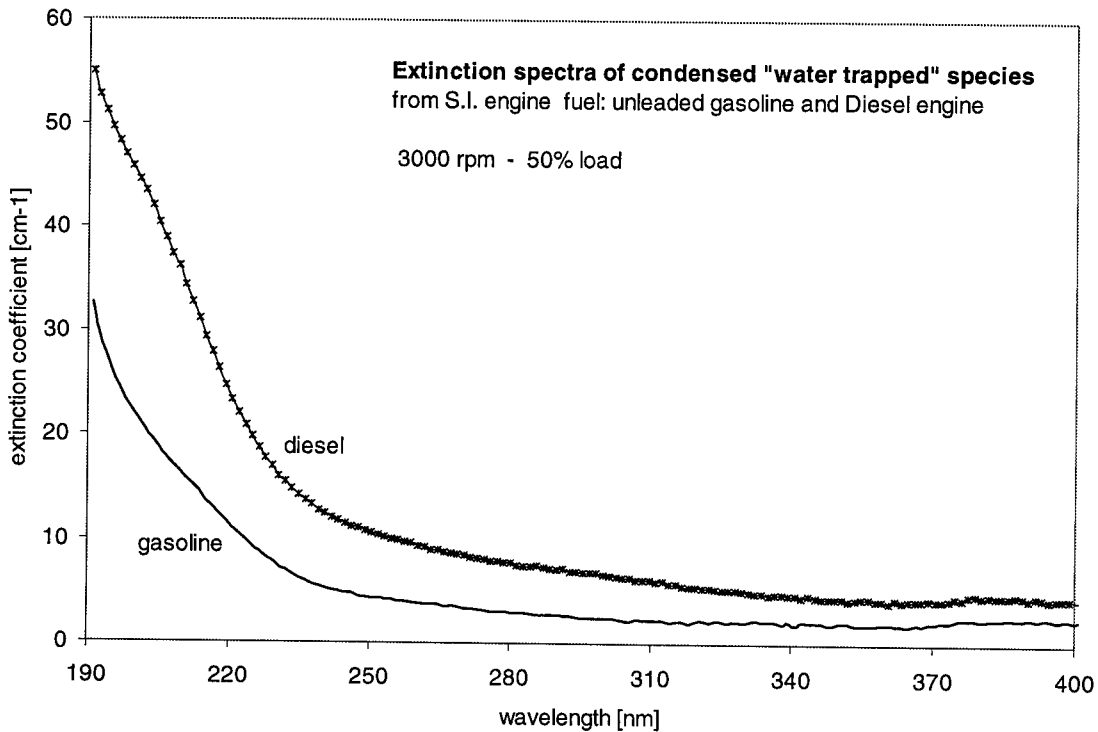


Figure 3B. :Extinction coefficient $\alpha_{\text{ext}}(\lambda)$, in cm^{-1} , as a function of the wavelength in the spectral range 190nm-400nm, for water-trapped (WT) exhausts from 'gasoline' (thin solid line) and 'diesel' (thick solid line) engines, respectively.

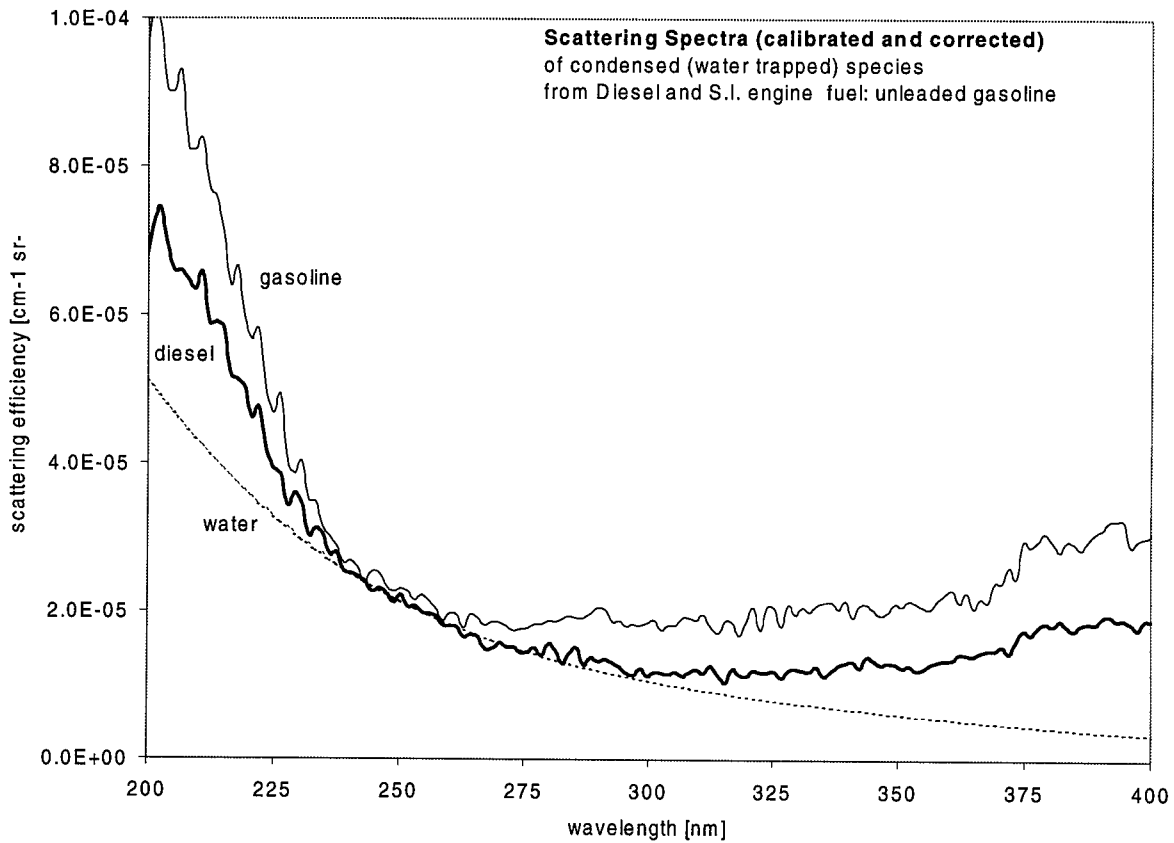


Figure 4: Scattering efficiencies , units of $\text{cm}^{-1} \text{sr}^{-1}$, as functions of the wavelength in the 190nm-400nm ultraviolet band, for pure water (bottom), ‘diesel’ WT samples (thick solid line), ‘gasoline’ WT samples (top). Also shown by dashed line is the scattering efficiency of water, as predicted by density fluctuation theory.

Table I -

Engine	Size [nm]	Volume fraction	$[C]_{\text{WT}}/[C]_{\text{Fuel}}$
S.I. Unleaded "Gasoline"	2 ± 0.5	30 ppm	$6 \cdot 10^{-5}$
Direct Injection "Diesel"	2 ± 0.5	85 ppm	$2 \cdot 10^{-4}$