Measurements of ion concentration in gasoline and diesel engine exhaust

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Abstract

The nanoparticles formed in motor vehicle exhaust have received increasing attention due to their potential adverse health effects. It has been recently proposed that combustion-generated ions may play a critical role in the formation of these volatile nanoparticles. In this paper, we design an experiment to measure the total ion concentration in motor vehicle engine exhaust, and report some preliminary measurements in the exhaust of a gasoline engine (K-car) and a diesel engine (diesel generator). Under the experimental set-up reported in this study and for the specific engines used, the total ion concentration is ca. $3.3 \times 10^6 \, \text{cm}^{-3}$ with almost all of the ions smaller than 3 nm in the gasoline engine exhaust, and is above $2.7 \times 10^8 \, \text{cm}^{-3}$ with most of the ions larger than 3 nm in the diesel engine exhaust. This difference in the measured ion properties is interpreted as a result of the different residence times of exhaust inside the tailpipe/connecting pipe and the different concentrations of soot particles in the exhaust. The measured ion concentrations appear to be within the ranges predicted by a theoretical model describing the evolution of ions inside a pipe.
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1. Introduction

Due to their potential adverse health effects, nanoparticles (diameter < 50 nm) emitted by motor vehicles have received increasing attention (e.g., Kittelson, 1998; Shi and Harrison, 1999; Tobias et al., 2001). Increasing numbers of studies indicate that the toxicity of particles increases as their size decreases (e.g., Ferin et al., 1992; Oberdörster et al., 1995; Seaton et al., 1995; Donaldson et al., 1998, 2000; Maynard, 2000). Some studies also found that particle number, which is dominated by nanoparticles, correlated better than fine particle mass with increased symptoms for respiratory effects (e.g., Peters et al., 1997). A recent comparison of the health effects of ultrafine particles (diameter < 100 nm) with those of fine particles (diameter $< 2.5 \, \mu\text{m}$) indicates that ultrafine as well as fine particles are associated with mortality (Wichmann et al., 2000). Nemmar et al. (2002) conclude that inhaled nanometer carbon particles (5–10 nm) pass rapidly into the systemic circulation, and suggest that this process could account for the well-established, but poorly understood, extrapulmonary effects of ultrafine particle pollution.

In view of the strong adverse health effects associated with high concentrations of very small particles, future standards may be imposed on the number emissions of ultrafine particles (Kittelson, 1998). It is important to note that technologies needed to reduce particle number emissions may be quite different from the ones currently used to reduce mass emissions. Effective and low cost means of ultrafine particle emission reduction must be based on a firm physical understanding of the processes and parameters controlling formation and evolution of

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ultrafine particles in vehicle exhaust. Such an understanding is critical to helping establish criteria for engine design, operation, after-treatment, and fuel and lubricating oil compositional modifications that would effectively reduce ultrafine particle emissions. Such an understanding is also fundamental to developing aerosol emission inventories, which are important in the study of health, chemical, and climatic effects of aerosols.

In view of the difficulty of classical binary nucleation theory in explaining some key properties of observed nanoparticles in engine exhaust, Yu (2001) proposed that chemiions generated during fuel combustion might play an important role in the formation of these nanoparticles. The predicted nanoparticle properties based on the chemiion theory closely match measurements (in terms of total nanoparticle concentrations, and their sensitivity to fuel sulfur contents) that the classical binary nucleation theory fails to explain. Yu (2001) found that the total number of nanoparticles formed in motor vehicle exhaust is very sensitive to chemiion concentrations. Recently, Yu (2002) investigated the key parameters controlling the evolution of chemiions in a vehicle tailpipe or experimental sampling transfer line, and showed that the observed dependence of nuclei mode particles on transfer line residence time, soot concentration, and vehicular speed is consistent with the chemiion theory. Nevertheless, experimental studies are needed to verify—or rule out—the chemiion theory. Specifically, it is critical to know if the concentration of ions in the exhaust is high enough to explain the observed concentration of nucleated volatile nanoparticles.

In hydrocarbon flames, chemiionization is known to generate copious ions, and positive ion concentrations of up to 10^{10}–10^{11} cm^{-3} have been reported (e.g., Fialkov, 1997). Arnold et al. (2000) detected a positive ion concentration of $\sim 1.6 \times 10^8$ cm^{-3} at a distance 1.39 m behind a jet engine and concluded that the positive chemiion concentration at the exit plane should be at least 1×10^9 cm^{-3}. In this paper, we report an experimental design to measure the total ion concentrations in motor engine exhaust. Some preliminary measurements taken in the exhaust of a gasoline engine and a diesel engine are presented. The properties of ions in the exhaust inferred from the measurements are also discussed.

2. Experimental design

Our experimental design to measure ion concentrations in motor engine exhaust is shown schematically in Fig. 1. A conductive pipe (radius R, length L) is connected to the engine pipe with proper insulation. An adjustable electrostatic potential is imposed on the exhaust passing through the conductive pipe via a rod
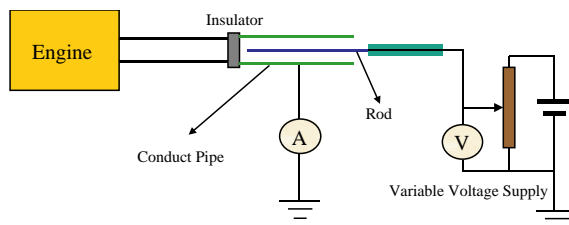

Fig. 1. A schematic showing the experimental design used in this study to measure ion concentrations in motor engine exhaust. A conductive pipe (radius R, length L) is connected to the engine pipe with proper insulation. An adjustable electrostatic potential is imposed on the exhaust passing through the conductive pipe via a rod (radius r_0) placed at the center of the pipe. A is the electrometer and V is the voltage source. Ion concentration can be estimated based on the current measured by the electrometer and the exhaust flow rate (see details in the text). For the measurements reported below, the values of R, r_0, and L are 2, 0.25, and 32 in, respectively.

(radius r_0) placed at the center of the pipe. A is the electrometer and V is the voltage source. The electronic probes such as the one used in this study have been widely used in the past to measure ion concentration (e.g., Fialkov, 1997; Arnold et al., 2000). For the measurements reported below, the values of R, r_0, and L are 2, 0.25, and 32 in, respectively. We used the Keithley electrometer Model 610B to measure the current. This electrometer has 28 current ranges from 10^{-14} A at full scale to 0.3 A and the accuracy $\pm 2\%$ of full scale on 0.3–10^{-11} A ranges. The variable voltage supply is from Glassman High Voltage Inc. (Model # ER3R100) which can provide voltage in the range of 0–3000 V.

As a result of electrostatic forces, ions in the exhaust are collected by the conductive pipe and rod. The relationship between the concentration of ions in the exhaust and the current (I) measured by the electrometer is straightforward. The current (I) measured by the electrometer is equal to the production of elementary charge and the number of ions collected by the probe per unit time, which is equal to the concentration of ions (already collected) multiplied by the exhaust flow rate. From the current (I) measured by electrometer, the average concentration of ions (of one sign) in the exhaust which have already been collected can be estimated as

$$[\text{ion}] = \frac{I/e}{\dot{V}}, \tag{1}$$

where $e = 1.6 \times 10^{-19}$ C is the elementary charge. $\dot{V}$ (l min^{-1}) is the exhaust flow rate, which can be estimated from fuel consumption rate and air fuel ratio. Generally speaking, smaller ions have higher mobility (M) and need lower imposed voltage (U) to be collected by the conductive pipe. I is expected to increase with increasing U as more ions are collected at higher U. If

the voltage is high enough, all ions in the exhaust can be collected and then I will not increase when U increases further.

The travel time of the exhaust inside the conductive pipe (t_c) is

$$t_c = \frac{\pi(R^2 - r_0^2)L}{\dot{V}}. \tag{2}$$

Based on Gauss's law, the electric field intensity inside the conductive pipe $E(r)$ is

$$E(r) = \frac{U}{\ln(R/r_0)}\frac{1}{r}, \quad r_0 < r < R, \tag{3}$$

where U is the voltage imposed. The drift velocity (v) of ions (with mobility M) under this imposed electric field is

$$v = E(r)M. \tag{4}$$

The time needed for ions with mobility M to drift from $r = r_0$ to R is

$$
\begin{aligned}
t_d &= \int_{r_0}^{R} \frac{1}{v}\, dr = \int_{r_0}^{R} \frac{\ln(R/r_0)}{MU} r\, dr \\
&= \frac{\ln(R/r_0)}{MU}\frac{(R^2 - r_0^2)}{2}
\end{aligned} \tag{5}
$$

and $t_c \leqslant t_d$ is the condition where all the ions with mobility M can be collected by the conductive pipe. Thus, the minimum voltage U needed to collect all ions of a certain mobility M as the exhaust passes thorough the conductive pipe U_M can be estimated as

$$U_M = \frac{\dot{V}\ln R/r_0}{2\pi LM}. \tag{6}$$

It is clear that U_M increases as the mass of ions increases and the ion mobility decreases. However, those ions in the exhaust close to the wall of the conductive pipe may also be collected even when the voltage is smaller than the U_M corresponding to their mobility. By studying the changes in current I observed by the electrometer as the imposed voltage U increases, we can obtain some useful information about the mass distributions of ions in the exhaust.

3. Measurements

Some preliminary measurements of ion concentrations have been carried out at the Automotive Emissions Laboratory in the Bureau of Mobile Sources and Technology Development of the Division of Air Resources of the NYS Dept. of Environmental Conservation. Fig. 2 shows a picture of the experimental set-up for measurements in the exhaust of (a) a gasoline engine (K-car) and (b) a diesel engine (diesel generator). The K-car used was a 1987 Plymouth Reliant LE 4 Door Wagon with a 4 cylinder, 2.21 97 hp gasoline engine. The
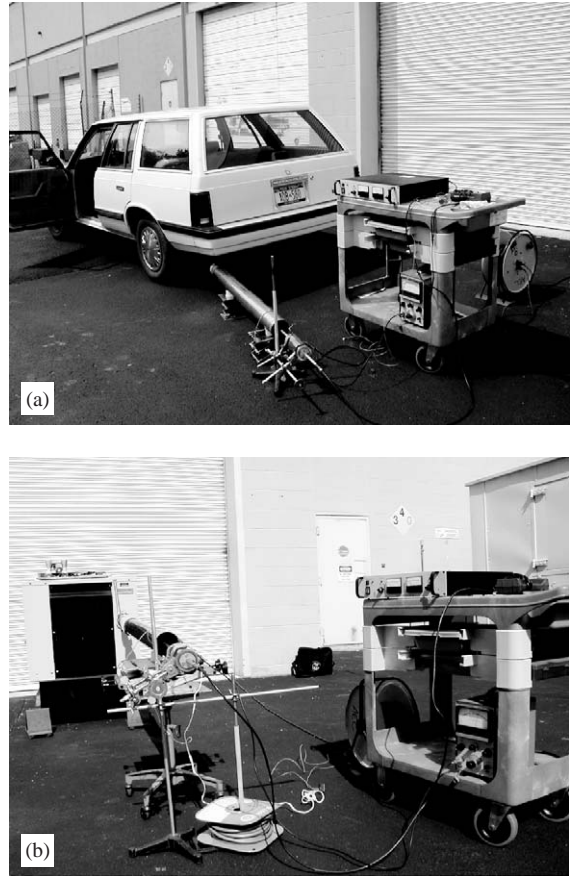
Fig. 2. Pictures of experimental set-up for measurements in the exhaust of (a) a K-car (gasoline engine), and (b) a diesel generator (diesel engine). The K-car used was a 1987 Plymouth Reliant LE 4 Door Wagon with a 4 cylinder, 2.21 97 hp gasoline engine. The Sentry-Pro 7.5 kW diesel generator is powered by a Kubota model Z482-E, 479 cc, 12.5 hp diesel engine. In this study, the K-car was running at ∼35 mph and the diesel generator was operating at 50% load. The conductive pipe was connected to the end of the tailpipe of the K-car, and to the exhaust manifold of the diesel engine.

Sentry-Pro 7.5 kW diesel generator is powered by a Kubota model Z482-E, 479 cc, 12.5 hp diesel engine.

In this study, the K-car was running at ∼35 mph and the diesel generator was operating at 50% load. For the K-car, the conductive pipe was connected to the end of the tailpipe. For the diesel engine, the conductive pipe was directly connected to the exhaust manifold. The residence time of the exhaust inside the tailpipe or connection pipe before entering the conductive pipe is ∼0.7 s for the K-car case and ∼0.15 s for the diesel engine. The residence time is estimated from the exhaust flow rate. The imposed voltage U was adjusted manually and the corresponding current I was recorded. Since the engine did not run in an absolute stable condition and the flow inside the pipe was turbulent, the measured I
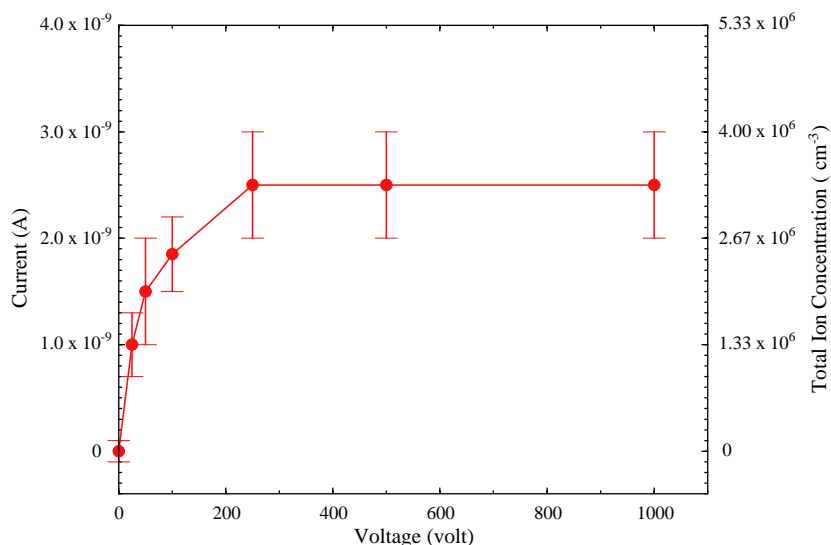
Fig. 3. The change in measured I as U increases from 0 to 1000 V in the exhaust of the gasoline engine (K-car, Fig. 2a).

values fluctuated at a given U. The error bars shown in the figures below indicate the range of these fluctuations.

Fig. 3 shows the changes in measured I as U increases from 0 to 1000 V in the exhaust of the K-car (Fig. 2a). The corresponding total ion concentrations (positive ions + negative ions = 2 × [ion] estimated using Eq. (1) are also given. The K-car was running at ~35 mph and the exhaust flow rate was ~560 l min^{-1}. When no voltage was imposed (i.e., $U = 0$ V), the values of I fluctuated between -1.0×10^{-10} and $+1.0 \times 10^{-10}$ A, suggesting that both positive and negative ions diffuse into the inner wall of the conductive tube. As U increases, the observed current increases, and when $U = 250$ V the measured current I reaches a maximum value of around $2.5 \pm 0.5 \times 10^{-9}$ A (corresponding to a total ion concentration of ~$3.3 \pm 0.66 \times 10^{6}$ cm^{-3}). When $U > 250$ V, I does not change as U increases, which suggests that all ions in the exhaust have been collected. Based on Eq. (2), all ions in the exhaust with mobility less than ~0.2 cm^2 v^{-1} s^{-1} should have been collected at $U = 250$ V. As discussed earlier, in general ions with larger sizes (lower mobility) are collected at higher voltage. The continuous increase in I as U increases when $U < 250$ V suggests that the size or mass of ions in the gasoline engine exhaust has a wide range. Since the corresponding diameter of ions with mobility of 0.2 cm^2 v^{-1} s^{-1} is ~3 nm, we can conclude that most of the ions in the exhaust of the K-car are smaller than ~3 nm.

Fig. 4 shows the I–U curve measured in the exhaust of the diesel engine (Fig. 2b). The corresponding total ion concentrations are also indicated. At $U = 0$ V, the values of I fluctuate between -4.0×10^{-9} and $+2.0 \times 10^{-9}$ A

with an average value of -1.0×10^{-9} A. Note that the magnitude of the fluctuation at $U = 0$ V in the diesel exhaust is more than one order of magnitude larger than that in the K-car exhaust, which suggests a much higher concentration of small ions in the diesel exhaust at the measurement point. The average negative current at $U = 0$ V indicates that the mean mobility of negative ions is higher than that of positive ions. When a positive voltage is imposed, a positive current appears and the current measured increases almost linearly with imposed voltage (0–2900 V). The observed currents in the exhaust of the diesel generator are ~$1.7 \pm 0.2 \times 10^{-8}$ A at $U = 250$ V and ~$2.0 \pm 0.1 \times 10^{-7}$ A at $U = 2900$ V, which correspond to a total ion concentration of $2.26 \pm 0.26 \times 10^{7}$ and $2.67 \pm 0.13 \times 10^{8}$ cm^{-3}, respectively (based on exhaust flow rate of 560 l min^{-1}).

Based on Eq. (2), the mobility of ions completely collected is estimated to be $\leqslant 0.2$ cm^2 v^{-1} s^{-1} (corresponding to a diameter of $\leqslant \sim 3$ nm) at $U = 250$ V and $\leqslant 0.019$ cm^2 v^{-1} s^{-1} (corresponding to a diameter of $\leqslant \sim 10$ nm) at $U = 2900$ V. While all ions/charged particles $\leqslant 10$ nm are expected to be collected at U of 2900 V, some particles > 10 nm may also have been collected if they were in the exhaust close to the wall. The diesel engine used in this study has a very high emission index of soot particles (on the order of 10^{8} cm^{-3}), and when a high voltage was imposed some charged soot particles were collected. The increase in the measured current as U increases when $U > 250$ V is likely due to the collection of these charged soot particles. In contrast to the diesel engine, the soot emission index of the gasoline engine (K-car) is much lower (the concentration of soot particles in the exhaust is on the order of
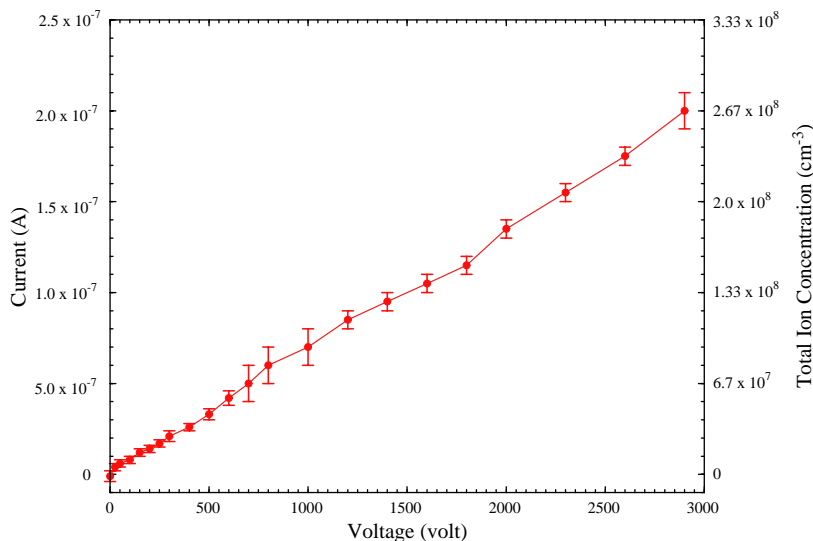
Fig. 4. The change in measured I as U increases from 0 to 3000 V in the exhaust of the diesel engine (diesel generator, Fig. 2b).

$10^4\,cm^{-3}$), which may explain why no visible change in the current is observed even when the voltage imposed on the K-car exhaust is increased from 250 to 3000 V.

When the imposed voltage is less than 250 V, the measured current (and hence the concentration of collected ions) in the diesel exhaust is about one order of magnitude higher than that in the K-car exhaust. This difference is likely due to the much shorter residence time ($\sim 0.15\,s$) of exhaust inside the pipe connecting the conductive pipe and the diesel engine. The residence time of exhaust inside the K-car tailpipe is $\sim 0.7\,s$. The concentration of small ions in the exhaust drops significantly in the first 0.5 s inside the tailpipe or connecting pipe as a result of ion–ion recombination, soot scavenging, and wall loss (Yu, 2002).

Fig. 5 shows the theoretically calculated evolution of total ion concentrations ($= 2 \times$ [ion]) inside the tailpipe or connecting pipe, along with the observed ion concentrations in the exhaust of the K-car ($U > 250$ V) and the diesel generator ($U = 250$ and 2900 V). We assume that the initial total ion concentration at the end of the expansion stroke ($\sim 0.01\,s$ exhaust age) is $2 \times 10^9\,cm^{-3}$ (Yu, 2002). The curves are calculated based on the equation derived by Yu (2002) at two different ion–ion recombination coefficients ($K_r = 2 \times 10^{-7}$, $1 \times 10^{-8}\,cm^3\,s^{-1}$) and four ion loss time constants ($\tau = 0.05$, 0.2, 1.0, 5.0 s). As we discussed earlier, ions in the engine exhaust have a wide range of masses. Ions of different masses have different values of K_r and τ. It is difficult to simulate a size-dependent evolution of ions inside the pipe since the initial size distributions of ions is unknown. Nevertheless, we can learn how ions of different masses may evolve and obtain the possible ranges of ion concentration by carrying out sensitivity studies. For each curve shown in Fig. 5, it has been assumed that all ions have fixed K_r and τ. Generally speaking, curves with larger K_r and smaller τ values correspond to smaller ions. The value of τ also decreases as the concentration of soot particles increases and/or the diameter of pipe decreases (Yu, 2002).

It may be seen from Fig. 5 that our measurements lie within the possible ranges of ion concentrations predicted by the theoretical model. Since the residence time of ions inside the K-car tailpipe is $\sim 0.7\,s$, it is likely that a significant fraction of small ions was lost inside the tailpipe. Thus, what were measured are those ions with relatively large mass that survived the diffusion loss and recombination inside the K-car tailpipe. For the diesel generator, though the soot concentration is much higher (τ of small ions is likely less than 0.1 s), the concentrations of small ions at the measurement point is still much higher than that in K-car exhaust due to the much shorter residence time.

The composition of these ions smaller than 3 nm is not known. They may be composed of elemental carbon, metal species, sulfuric acid, and low-volatile hydrocarbons (unburned lubricant oil, etc.). Some of the ions may be formed at the same time as the large soot particles were formed, while others may be a result of the growth of small ions by uptake of low volatile species when the exhaust cools down inside the pipe (the tailpipe and conductive pipe were directly exposed to the ambient air in our measurements). These ions can readily act as nuclei when emitted. The concentrations of small ions are expected to increase significantly when the residence time of the exhaust inside the tailpipe or connecting pipe decreases as a result of higher exhaust
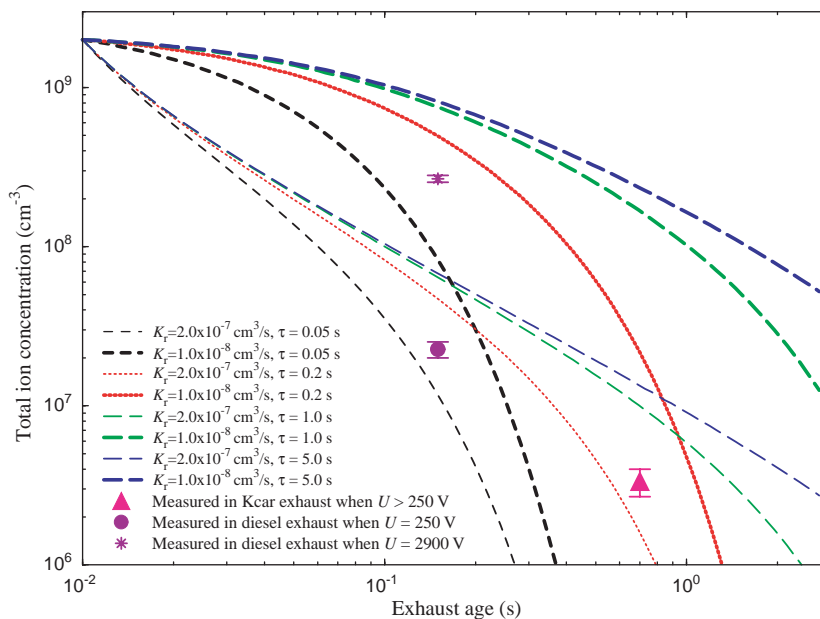
Fig. 5. Theoretically calculated evolution of total ion concentrations inside the tailpipe or connecting pipe at two different ion–ion recombination coefficients ($K_r = 2 \times 10^{-7}$, 1×10^{-8} cm^3 s^{-1}) and four ion loss time constants ($\tau = 0.05, 0.2, 1.0, 5.0$ s). The observed ion concentrations in the exhaust of the K-car ($U > 250$ V) and the diesel generator ($U = 250$ and 2900 V) are also indicated. The initial total ion concentration at the end of the expansion stroke (~ 0.01 s exhaust age) is assumed to be 2×10^9 cm^{-3}.

flow rate or shorter pipe. More detailed discussions of the parameters controlling ion concentrations in the vehicular exhaust can be found in Yu (2002).

4. Summary and discussion

Due to their potential health effects, volatile nano-particles emitted by diesel and gasoline engines have received increasing attention. Recently, Yu (2001, 2002) proposed that the chemiions generated during combustion play a key role in the formation of these nanoparticles. While very high concentrations of ions in hydrocarbon flames and in the exhaust of aircraft have been reported in the literature, direct measurements of ion concentration in motor engine exhaust are needed to either verify or rule out the chemiion theory. In this paper, we report an experimental design to directly measure the concentration of ions in engine exhaust. Our preliminary measurements in the exhaust of a gasoline engine (K-car) and a diesel engine (diesel generator) indicate the presence of high concentrations of ions.

Using the experimental set-up reported in this paper, the total ion concentration was found to be around 3.3×10^6 cm^{-3} with almost all of the ions smaller than 3 nm in the exhaust of the gasoline engine, and above 2.7×10^8 cm^{-3} with most of the ions larger than 3 nm in the exhaust of the diesel engine. The difference is likely

due to the different residence times of exhaust inside the tailpipe or connecting pipe and the different concentrations of soot particles in the exhaust. The residence time of exhaust is ~ 0.15 s inside the pipe connecting the conductive pipe and the diesel engine, and is ~ 0.7 s inside the K-car tailpipe. The concentration of small ions drops significantly in the first 0.5 s inside the tailpipe or connecting pipe as a result of ion–ion recombination and loss to the surface of the wall and soot particles. In the exhaust of the diesel engine, the concentration of soot particles is very high and small ions were likely to be scavenged quickly by these soot particles (lifetime of molecular ions is < 0.1 s). The total ion concentrations of $\sim 2.7 \times 10^8$ cm^{-3} at an exhaust age of ~ 0.15 s in the diesel exhaust and of 3.3×10^6 cm^{-3} at an exhaust age of ~ 0.7 s in the gasoline exhaust are within the ranges predicted by the theoretical model. The ions larger than 3 nm in the diesel exhaust are likely charged soot particles, while those ions smaller than 3 nm in both the gasoline exhaust and the diesel exhaust may be composed of elemental carbon, metal species, sulfuric acid, nitric acid, and low volatile hydrocarbons (unburned lubricant oil, etc.). The higher values of current at larger voltages are due to the collection of ions with larger masses, however our measurements could not provide the size distributions due to scavenging of ions near the wall. The small ions can readily act as nuclei for the formation of volatile nanoparticles when emitted. The concentrations of small ions are

expected to increase significantly when the residence time of the exhaust inside the tailpipe or connecting pipe decreases as a result of a higher exhaust flow rate or a shorter pipe. Further measurements are needed to study the concentrations and sizes of ions in the exhaust of different engines running under different conditions.

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