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Aerosol particle mass spectrometry with low photon energy laser ionization

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Abstract

The problem of excessive ion fragmentation observed in the mass spectra of organic aerosols is addressed by varying the photon energy used to ionize the vaporized particles. Oleic acid aerosols are vaporized by either an IR CO_2 laser or by impaction on a heater and ionized by pulsed laser radiation produced by either third harmonic generation in Xe (118 nm; 10.48 eV) or by resonance difference frequency mixing in Kr (142 nm; 8.75 eV). The use of the lower energy laser light greatly reduced the fragmentation of the oleic acid ions. However, spectra of oleic acid particles taken at several different CO_2 laser powers showed that the internal energy of molecules in the vapor plume vary in time so that the appearance of the mass spectrum is a function of the delay time between CO_2 and VUV laser pulses. Hot molecules produced in the early stages of vaporization generated large amounts of fragment ions, whereas the mass spectra of colder molecules consisted predominantly of parent ions. Vaporization with the heater on the other hand, shows a more uniform heating of the particle, with very little ion fragmentation. The ionization energy (8.6 ± 0.1 eV) and the fragment ion appearance energy (9.0 ± 0.1 eV) of oleic acid were determined by photoelectron photoion coincidence spectrometry.

Keywords: Oleic acid; RDFM; Laser; Heater

1. Introduction

Mass spectrometric analysis of aerosol particle constituents has become an essential tool not only for laboratory studies of model aerosols [1–8] but also in field studies, where rapid detection and identification of aerosols is highly desirable [9–16]. Atmospheric aerosols contain a wide range of substances including inorganic salts, metals, dust, soot, and organic species [17]. The ideal analysis tool should be able to identify each molecule, and provide a quantitative measure of its concentration. Unfortunately, current instruments are far from achieving this goal. This paper deals with the analysis of organic species in aerosol particles. The difficult issue in their analysis is the ease with which they fragment upon ionization. If a particle contains a large range of organic molecules, the identification is clearly impeded by extensive fragmentation, which results in a broad range of ion peaks whose identity is then difficult to establish.

Current aerosol mass spectrometers use either continuous or pulsed ionization schemes. The former generally employs electron impact [18,19], or chemical ionisation [20,21]. The pulsed ionization approach depends on lasers that are fired whenever a particle appears in the ionization region. This has the advantage that the laser photons are efficiently used when an aerosol particle is in the ionization region. The pulsed laser approach is ideal for large particles (0.2–5 μm in diameter) because their arrival at the ionization region can be determined by light scattering from continuous lasers [4,22,23]. The continuous ionization scheme is clearly advantageous for the detection of a large number of small particles whose arrival time cannot be detected by laser light scattering, and whose arrival at the ionization region is in any case quasi-continuous.

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Fragmentation of ions is a result of internal energy imparted to the ion during the vaporization or ionization process. Ionization by a pulsed UV laser, in which ionization is achieved by multiphoton excitation, results in particularly high ion internal energies because, once formed, the ion continues to absorb photons during the 5–10 ns photon pulse. It is not unusual to detect mostly C^+ ions and the observation of parent ion peaks is rare [8]. For this reason, a single laser ablation/ionization scheme does not work for organic species. In response to that, Worsnop and co-workers [19] have developed a two stage vaporization/ionization scheme in which the particles are directed at a heater located in the ionization region, where the vaporized molecules are ionized by electron impact. This provides excellent sensitivity and reduced fragmentation in comparison to the UV laser ablation/ionization scheme. However, ion fragmentation by electron impact of organic mixtures remains a difficult problem. Reducing the electron energy from 70 eV to lower energies would reduce fragmentation, but would also reduce the ionization efficiency.

Our approach to reducing ion fragmentation has been to use pulsed vacuum UV laser radiation [4], which has now also been implemented by Oektem et al. [24]. The aerosol particles are vaporized either by the absorption of infrared radiation from a pulsed CO_2 laser, or by impinging on a heater. Once vaporized, the molecules are ionized by 118 nm (10.48 eV) radiation generated by the frequency tripling of a 355 nm Nd:YAG laser pulse in a Xe/Ar mixture. This approach has dramatically reduced ion fragmentation because the 10.48 eV photon is close to the ionization energy of many molecules such as benzene, nitrobenzene, aniline, etc. However, we have found that as larger molecules with lower ionization energies are investigated, the 10.48 eV photon energy is too high and thus results in considerable ion fragmentation. This was a particular problem with the analysis of reaction products from the reaction between ozone and oleic acid aerosol particles [25]. The mass spectra of the reacted oleic acid particles vaporized by the CO_2 laser and ionized by the 10.48 eV VUV photons were characterized by a broad range of lower mass peaks that prevented identification of reaction products [25]. Thus, a softer ionization approach would be highly desirable.

As stated before, ion fragmentation is a result of high internal energy, which is caused both by heating of the neutral molecules with, for instance the CO_2 laser or the heating element, and by the VUV laser. Unfortunately, heating of the oleic acid cannot be avoided if sufficient material is to be vaporized for a strong ion signal. Thus the question arises; can we reduce ion fragmentation by reducing the energy of the VUV photon, or is the fragmentation an inevitable consequence of the vaporization process? For instance, Amirav [26] and Amirav and Danon [27] concluded that the fragmentation in electron impact could be dramatically reduced by cooling the sample in a molecular beam, thereby suggesting that the molecule's internal energy is a decisive factor in the fragmentation process. LaFranchi and co-workers have recently employed photoelectron resonance capture ionization (PERCI) to reduce fragmentation [28,29]. A similar reduction is possible with chemical ionisation [20,21]. In this paper, we address this issue by generating light at 8.75 eV, which is nearly 2 eV lower than the previously used 10.48 eV. The nature of the vaporization method of oleic acid particles is also explored to better understand how different vaporization conditions affect the oleic acid mass spectrum.

2. Experimental approach

The current experimental set-up can be seen in Fig. 1. The oleic acid particles in this study were generated by atomizing a 1:10 oleic acid:isopropanol mixture with a glass nebulizer (Meinhard). The particles were then sent into an aerodynamic lens as described by Liu et al. [30,31], where they were focused and accelerated by gas expansion into the vacuum. The particle velocity, and thus their size, was determined by detecting scattered light as they passed through two green, continuous laser beams. The scattered light signals were sent into a timing circuit, which triggered the CO_2 laser to fire as the particle reached the TOF extraction region. After a variable delay between 2 and 20 μs, the vapor plume was ionized via VUV irradiation ($\lambda = 142$ nm).

The VUV radiation was generated by resonance difference frequency mixing (RDFM) as shown in Fig. 2 [32]. The 355 nm output from a Nd:YAG laser (Continuum) pumped a dye laser (Continuum) with an Exalite 428 dye to produce 425 nm light. This light was doubled with a BBO crystal in an Inrad Autotracker III, yielding $\lambda = 212.5$ nm light. The $\lambda = 425$ nm (2 mJ) and 212.5 nm (10 mJ) pulses were steered through a series of prisms, and directed into a Kr cell ($P_{Kr} = 10$ Torr) where RDFM produces the desired 142 nm (8.75 eV) light. The exit of the mixing cell was terminated by a LiF lens with a focal length of 20 cm, which causes the 142 nm light to slightly converge, leaves the 212 nm light nearly parallel, and the 425 nm light slightly divergent. This arrangement minimized the absorption of the 212.5 and

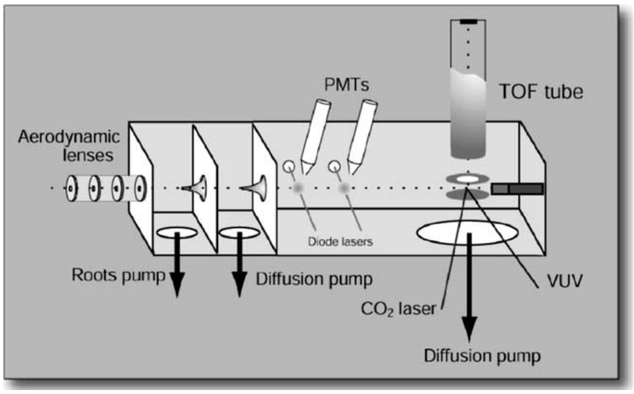

Fig. 1. Schematic of single aerosol particle laser TOF instrument. Particles are focused in the aerodynamic lens, detected and sized in the two light scattering regions, then vaporized and ionized in the extraction region of the TOF-MS.