Raman detection of single airborne aerosol particles of isovanillin

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Single airborne aerosol particle of isovanillin were detected using a compact Raman spectroscopy system. The Raman system consisted of a 10 W, 532-nm cw laser, a 50x aerosol concentrator, an aerosol flow cell, an f/1.0 single-sided collection optics, an f/1.8 Raman spectrometer with a spectral range of 400-1400 cm^{-1}, and a low-noise CCD camera (1340 x 400 pixels; 20 x 20 μm/pixel). The combined collection and detection efficiency of the Raman system was 1.0%. The diameters of eleven particles were determined to be 3.4, 3.1, 3.5, 3.4, 2.3, 3.1, 2.5, 2.6, 2.5, 3.0, and 3.1μm based on the fundamental Raman equation. The accuracy of the particle diameter is estimated to be ±0.1 μm using measured concentration of the atmospheric CO_2. [http://dx.doi.org/10.1063/1.4984226]

INTRODUCTION

Raman spectroscopy of trapped single aerosol particles has been reported previously.[1–4] However, detection of single aerosol particles via Raman spectroscopy in a flowing system has not been yet reported. In this paper, we describe the first detection of single 3 μm flowing airborne aerosol particles flowing through a Raman system, which is a simplified version of the previously reported system[5] with a 532-nm, 10W cw double-pass laser, 532-nm isolator, and double-sided collection optics. The current system has single-pass laser, no 532-nm isolator, and single-sided collection optics. Previous Raman detection of single aerosol particles has been made using *trapped* particles.[6–8]

EXPERIMENTAL

Isovanillin aerosol particles were generated with a small household blender. Details of the Raman collection system have been given previously.[5] The laser power was 10 W in the laser beam waist of 50 μm, which was determined by the power transmitted through a pinhole. The transit time τ of the aerosol particle through the laser beam is equal to the diameter of the laser beam waist divided by the aerosol particle speed v. The value of v was determined to be 2.4 cm/s as the ratio of the flow rate of 10 mL/min or 1/6 mL/s and the input cross section of 0.071 cm^2 corresponding to the 3 mm diameter of the inlet into the flow cell. The value of τ is then equal to 2.1 ms.

Figure 1 shows a schematic of the current Raman system used for the present experiment.

The collection efficiency of the current system is about ½ of that in Ref. 5. The detection sensitivity of the current system is about ¼ of that in Ref. 5. The Raman signal scales as the cube of the particle diameter. Therefore, the detection sensitivity of the current system in terms of the particle diameter is only $(1/4)^{1/3} = 0.63$ of that in Ref. 5.

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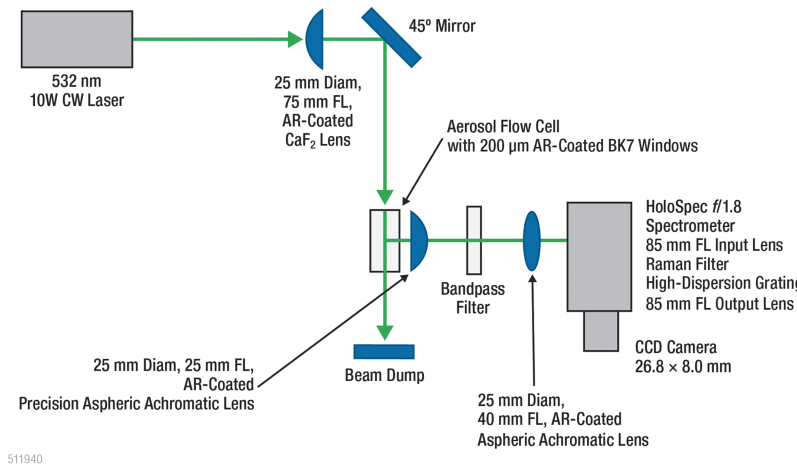

FIG. 1. Schematic of the Raman system.

RESULTS AND DISCUSSION

Figure 2 shows two single isovanillin aerosol single particles, which were observed in a 1340x240-pixel region of interest of the CCD camera in an integration time of 10 s. The integration time of 10 s is the acquisition time of the CCD. However, the Raman signal from each particle is only coming from an exposure time of 2.1 ms. Only two particles were observed in the acquisition time of 10 s using a cw laser and a CCD camera but not a fast camera or a single laser pulse. The input mass concentration of isovanillin, as measured by the TSI (Shoreview, MN 55126, USA) optical particle sizer (OPS) model 3330, into the Raman system was ~ 36 pg/cm^3. Raman spectra were collected in the low concentration range of isovanillin in order to avoid the overlap of single particles on the CCD in the high concentration range. Raman modes of isovanillin are observed as bright dots at x-pixel #124 (507 cm^{-1}), #875 (1116 cm^{-1}), #1058 (1242 cm^{-1}), and #1110 (1275 cm^{-1}). Raman modes of CO_2[9] are observed as slightly curved lines at x-pixel #1094 (1265 cm^{-1}), 1125 (1285 cm^{-1}), and #1291 (1388 cm^{-1}). Raman modes of H_2O vapors[10] are also observed as slightly curved lines at x-pixel #55 (443 cm^{-1}), #70 (457 cm^{-1}), #101 (485 cm^{-1}), #123 (506 cm^{-1}), #179 (557 cm^{-1}), #234 (606 cm^{-1}), #288 (653 cm^{-1}), and #345 (702 cm^{-1}).

Figure 3 shows the Raman spectrum of isovanillin particle #1and atmospheric CO_2 at y-pixels in the #109-123 region centered at pixel #116. The background-corrected Raman signal R_s of the 1116 cm^{-1} mode of isovanillin is 918 photons integrated over the 1110.5-1121.1 cm^{-1} region. The background-corrected Raman signal of 1285 cm^{-1} mode of CO_2 is 2090 photons integrated over the 1280.5-1288.9 cm^{-1} region.

The diameter of isovanillin particle can be determined using the Raman signal of the 1116 cm^{-1} mode and the basic Raman equation

$$R_S = (\eta_c \eta_d T_s)\, \sigma_R N_m \,(P_L \tau / h\nu_L) \quad (1)$$

Here η_c is the collection efficiency; η_d is the CCD detection efficiency; T_s is the Raman system transmittance; σ_R (cm^2) is he Raman cross section of the 1116 cm^{-1} mode of isovanillin; N_m is the number of isovanillin molecules (cm^{-2}); P_L is the laser power incident upon the isovanillin particle; τ is the transit time of the isovanillin particle through the laser beam; $h\nu_L$ is the laser photon energy. Using

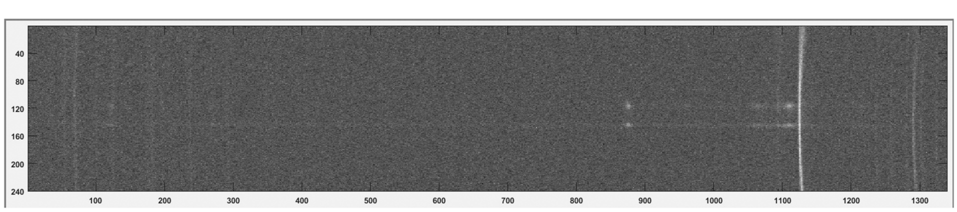

FIG. 2. Two isovanillin aerosol single particles observed in an integration time of 10 s.

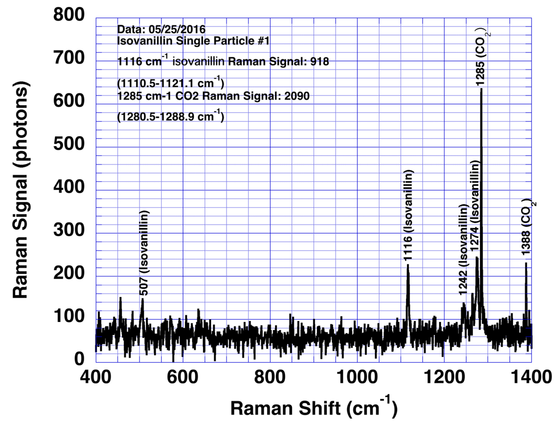

FIG. 3. Raman spectrum of isovanillin particle #1 and atmospheric CO_2.

values of 5.1x10^{-2} for η_c for $f/1.1$ single-sided collection, 0.42 (measured) for η_d, 0.48 (calculated) for T_s, 3.3x10^{-28} cm^2 for σ_R, 3.18x10^{17}d cm^{-2} for N_m (d is the diameter of the isovanillin particle in units of µm), 4.0x10^{-3}d^2 W for P_L, 2.1x10^{-3} s for τ, and 3.73x10^{-19} J for $h\nu_L$, Eq. (1) becomes

$$R_s = 24.3d^3 \tag{2}$$

Using a value of 918 photons for R_s, we obtain a value of 3.4 µm for the diameter d of particle #1.

Figure 4 shows the Raman spectrum of particle #2. The value of R_s for particle #2 is 738 photons, which yields a value of 3.1 µm for its diameter.

Figure 5 shows the Raman spectrum of particle #3. The value of R_s for particle #3 is 1035 photons, which yields a value of 3.5 µm for its diameter.

Figure 6 shows the Raman spectrum of particle #4. The value of Rs for particle #4 is 947 photons, which yields a value of 3.4 µm for its diameter.

Raman spectra of other particles #5-11 are similar to those of Figs. 2–5. The diameters of particles #4-11 were determined to be 2.3, 3.1, 2.5, 2.6, 2.5, 3.0, and 3.1 µm, respectively. Table I lists the values of R_s for the 1116 cm^{-1} mode of isovanillin and particle diameter for all the eleven particles reported here.

The accuracy of the particle diameter is estimated to be ±0.1 µm based on the accuracy of the measurement of the CO_2 concentration as discussed below. The accuracy of d is similar in magnitude based on the angle-and size-dependent characteristics of Raman scattering by microspheres.[11]

The basic Raman equation for the 1285 cm^{-1} mode of CO_2 is

$$R_S = (\eta_c \eta_d T_s)\, \sigma_R N_m L\, (P_L \tau / h\nu_L) \tag{3}$$

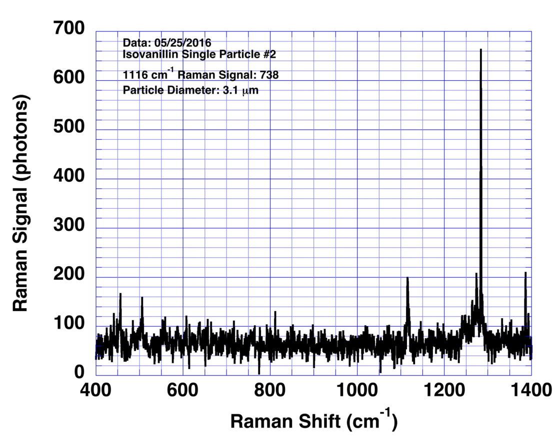

FIG. 4. Raman spectrum of isovanillin particle #2 and atmospheric CO_2.

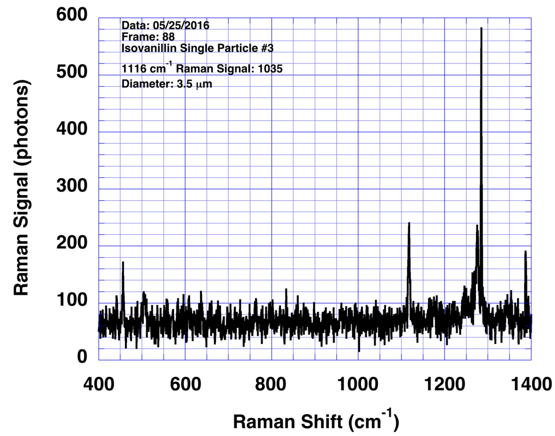

FIG. 5. Raman spectrum of isovanillin particle #3 and atmospheric CO_2.

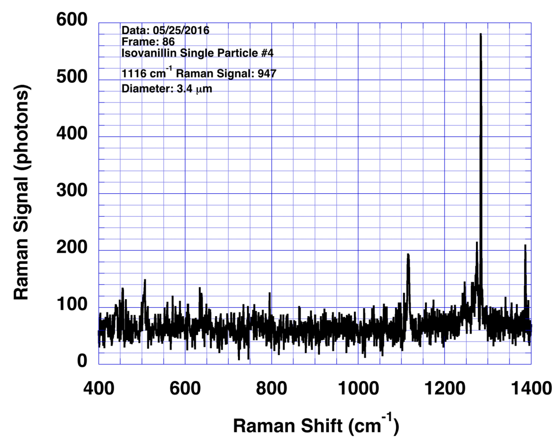

FIG. 6. Raman spectrum of isovanillin particle #4 and atmospheric CO_2.

Here σ_R (cm^2) is the Raman cross section of the 1285 cm^{-1} mode of CO_2; N_m (cm^{-3}) is the molecular concentration of CO_2; L is the length of the laser beam that is used in Fig. 2. Using values of 5.1x10^{-2} for η_c, 0.42 for η_d, 0.48 for T_s, 4.5x10^{-30} cm^2 for σ_R, 187.5 μm for L, 10 W for P_L, 10s for τ, and 3.73x10^{-19} J for $h\nu_L$, Eq. (3) is written as

$$R_s = 2.32 \times 10^{-13} N_m \tag{4}$$

TABLE I. Raman signal and diameter of eleven isovanillin particles.

Particle #	1116 cm^{-1} Raman Signal (Photons)	Particle Diameter (μm)
1	918	3.4
2	738	3.1
3	1035	3.5
4	947	3.4
5	290	2.3
6	692	3.1
7	383	2.5
8	404	2.6
9	369	2.5
10	649	3.0
11	744	3.1

Using the value of 2090 for R_s in Fig. 2, Eq. (4) yields a value of $9.0\text{x}10^{15}$ cm^{-3} for N_m, which corresponds to 367 ppm compared with the value of 470 ppm measured by a CO_2 probe located outside the Raman system. The Raman concentration of 367 ppm is 22% lower than the value of 470 ppm measured by the CO_2 probe. We assume the accuracy of the CO_2 concentration to be ±22%, which corresponds to an accuracy of ±2.8% in the diameter of the isovanillin aerosol particles because the Raman signal of a particle scales as the diameter of the isovanillin particle. Hence, the accuracy in the diameter of the aerosol particles is estimated to be ±0.1 µm. The estimated accuracy of the particle diameter is independent of the accuracy of the collection efficiency η_c, CCD detection efficiency η_d, and the Raman system transmittance T_s because the same values of η_c, η_d, and T_s are used both in the determination of the particle diameter and the concentration of CO_2.

The mass concentration of isovanillin may also be determined with the basic Raman Eq. (3) as used for CO_2. Using values of $3.3\text{x}10^{-28}$ cm^2 for σ_R of isovanillin, and 0.3 cm for L, the volume concentration of isovanillin is given by

$$R_s = 2.73 \times 10^{-10} N_m \tag{5}$$

Using the value of 1656 for R_s photons, which is equal to the sum of the Raman signals of 918 and 738 photons for particles #1 and #2, respectively, Eq. (5) yields a value of $6.06\text{x}10^{12}$ molecules/cm^3 for the concentration of isovanillin in the Raman system. The mass of an isovanillin molecule is $2.53\text{x}10^{-10}$ pg. The mass concentration of isovanillin inside the Raman system was $1.53\text{x}10^3$ pg/cm^3, which corresponds to the input mass concentration of 31 pg/cm^3 considering the aerosol concentration factor of ~ 50 for the aerosol concentrator in the Raman system. This value of 31 pg/cm^3 is consistent with an input mass concentration of ~36 pg/cm^3 measured by the OPS. This implies that the diameters of the isovanillin particles measured by the Raman system are consistent with those measured by the OPS.

SUMMARY

One, two, or three single particles of isovanillin were detected in 10 s by Raman scattering spectroscopy. The diameters of eleven particles were determined to be 3.4, 3.1, 3.5, 3.4, 2.3, 3.1, 2.5, 2.6, 2.5, 3.0, and 3.1µm with an accuracy of ±0.1 µm using the basic Raman equation. Also, the concentration of CO_2 inside the Raman system was determined to be 367 ppm, which is 22% lower than the value 470 ppm measured by a CO_2 probe located outside the Raman system.

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