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Single Airborne Dust Particles using Plasmonic Metal Films with Hole Arrays

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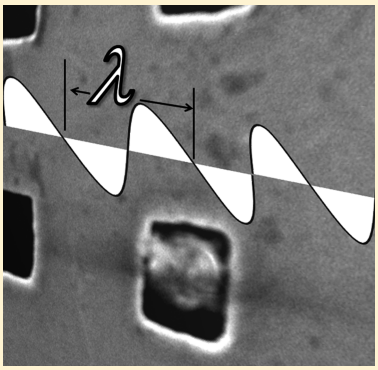
ABSTRACT: An airborne dust particle is trapped in the hole of a plasmonic metal film with a patterned array of holes (mesh) by pumping air through the mesh. Both scatter-free infrared spectra and scanning electron images are obtained on the same individual airborne dust particle, showing the feasibility of multiple, nondestructive experiments on a single, subwavelength particle. Ultimately, this may help to elucidate the effect of shape, orientation, and crystallinity on IR dust particle spectra.



SECTION: Atmospheric, Environmental and Green Chemistry

Plasmonic[1−3] metal films with subwavelength hole arrays (mesh)[4−12] can be used to capture an individual subwavelength particle[13,15] (or cell[14]) in a hole of the mesh. A number of interesting effects occur due to trapping a subwavelength particle in a similarly sized metal channel. The mesh exhibits "extraordinary transmission"[6] and can be considered a high-tech infrared (IR) window even though it is made of metal. Meshes have been described as inside−out fiber optics,[16−18] meaning that light is made to run along the surface of the mesh. The light is moved around on a subwavelength scale; in this case, light from a larger area is manipulated to be concentrated at the hole where the particle is positioned. An individual subwavelength particle can be examined by recording a scatter-free, IR absorption spectrum using an imaging IR microscope,[13−15] even though free and isolated particles of similar size as that of the wavelength usually exhibit severe scattering effects.[19,20] In a crude sense, our method is like simultaneously getting an attenuated total reflectance (ATR) spectrum[21,22] of the particle from the four sides of the hole, which reduces the ATR calibration problem for variable sample penetration with wavelength and angle.

Our previous work on a library of IR spectra of 63 dust particles from our laboratory air[13] offered no imaging of the subject dust particles. This work demonstrates that one can obtain an SEM image of the same particle for which one has obtained a scatter-free IR spectrum, revealing details not available with an optical microscope. The most important difference between our single dust particle work and the spectra of bulk dust samples is a large set of narrow, crystalline peaks that apparently get averaged away in bulk samples. It is well-known that the shape, orientation, and crystalline nature of a single particle affect the intensity, position, and line shape of IR phonon bands. The ability to independently address shape, orientation, and crystalline nature will no doubt be critical in the interpretation of single-particle spectra. Unlike most literature studies of crystal IR spectra, the experimentalist does not get to choose the orientation of a dust particle; therefore, a large challenge for quantitative analysis of single-particle spectra will deal with predicting spectra at arbitrary orientation. The job of making the connections between the shape/orientation of a particle and its spectrum is underway in our lab. This work shows that the job is feasible.

In addition to enabling scatter-free IR absorption spectra, the metallic mesh enclosure of a dust particle stores it for further incisive experiments. Interestingly, the metal keeps a dielectric dust particle from charging too much, allowing reasonable SEM images to be recorded without the necessity of gold coating. Other single-particle techniques[23] abound and include electron microscope and X-ray methods,[24−27] mass spectrometry,[28−31] and Raman spectroscopy,[32,33] but in many methods, the particle is lost or destroyed in the course of analysis. Single-particle infrared (IR) spectroscopy[34] (with either synchrotron[35−37] sources, ATRs,[21,22] or mesh[13−15]) can serve as a quick and nondestructive method that identifies individual particles for further study with the more intensive, complementary methods.

Plasmonic Transmission Resonances of Mesh. Consider the transmitted diffraction pattern of spots[10,38,39] produced by shining a visible laser pointer through a piece of mesh. As one shifts to a longer wavelength and into the IR, the spacing between the spots gets larger, and fewer spots are seen, that is, the spots come out at larger angles. Transmission resonances

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are observed at wavelengths where diffraction spots are bent so far that they come out parallel to the surface and are no longer transmitted. The evanescent waves run along the surface, interacting with the conducting electrons of the metal, producing surface plasmon polaritons (SPPs),[40−42] a mixed state of light, and conducting electrons.[41] At holes, the SPPs may either pass over or couple back out through the holes as light, without scattering from the incident beam. Transmission resonances are usually labeled by the diffraction spots that they would be at much shorter wavelengths. Particles in mesh holes experience a situation more like the evanescent wave of an ATR crystal,[43,44] in contrast to the well-known Mie scattering of an isolated particle.[19,20,45] The IR spectrum is described as scatter-free, which means that it does not show the broad and intense Mie scattering[19] peak nor does it exhibit scattering distortions of vibrational line shapes[15,46,47] (the Christiansen effect). However, these spectra still have difficulties associated with particle orientation[48] (birefringence) and particle saturation effects[19,20] (vibrational cross section bigger than the physical cross section).

Motivation for Studying Dust. Microparticles have great significance in health and science. The EPA sets a 24 h standard of 35 $\mu g/m^3$ for particulate matter (PM) smaller than 2.5 μm ($PM_{2.5}$) and 150 $\mu g/m^3$ for PM smaller than 10 μm (PM_{10}),[49] although this standard is only 50 $\mu g/m^3$ in the EU. More information in the size range between 2.5 and 10 μm ($PM_{10-2.5}$) would be particularly useful in light of conflicting studies.[50−52] $PM_{10-2.5}$ includes the largest particles that get past our noses and throats, making it into our lungs.[53] Because the airborne lifetime of particles decreases as the particle diameter increases, particles of ∼4 μm in diameter are expected to be more correlated with the local environment and particularly important in health as they are breathed into the lungs. Substances like elemental carbon, calcium, vanadium, and organic carbon material[51] in PM have shown strong positive correlations with respiratory health effects; therefore, it is desirable to know the chemical identity of these elements, an area where IR spectroscopy can be very useful. Increases in particulate matter are correlated with asthma, bronchitis, silicosis, asbestosis, pneumonia, lung cancer, and cardiovascular diseases.[54] A dramatic illustration of this is the "London Smog" of Dec. 4−9, 1952, in which approximately 300 times the normal amount (7000 $\mu g/m^3$) of particulate matter is thought to have killed 12 000 people.[54] Airborne particles are mostly natural, but 6−23% are anthropogenic[54] and, therefore, diagnostic for human effects on the environment. Particulate matter abounds in space, our atmosphere, our houses, water, and soil and includes contributions from pollen, bacteria, spores, organic debris, sea salt, wind-raised soil, and pollutants (insecticides, tire rubber, car exhaust, fuel combustion, coal dust, paint chips, etc.). Dust is even collected and studied from interstellar space.[33,34,55,56]

The capture of a dust particle in a mesh hole is described in Figure 1 and the Experimental Section at the end. The infrared spectra of the previously airborne particles, called Abby1 and Abby2, are shown in Figures 2 and 3, respectively. Astronomers tend to name the particles for which they made great efforts to obtain IR spectra, so one of us, Matthew McCormack, named our particles after his beloved dog. The IR spectra were taken with a Perkin-Elmer Spotlight 300 IR microscope, which is equipped with an array of 16 liquid-nitrogen-cooled mercury−cadmium−telluride (MCT) detectors. The spectral data were acquired in image mode, which means that a full FTIR spectrum was acquired at each 6.25 μm square pixel within the imaging region, as shown with a pink box on the left side of

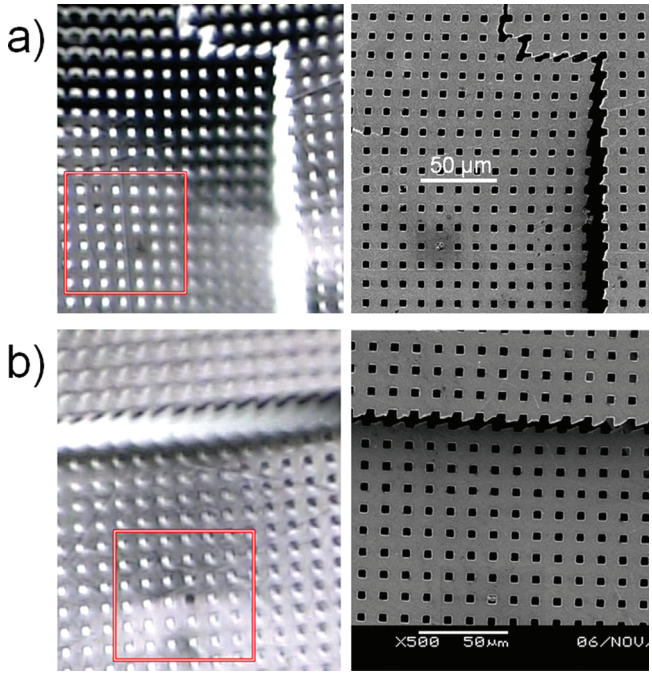

Figure 1. (a) Optical microscope image (left) and corresponding SEM image (right) of the region with the previously airborne dust particle Abby1. The region in which IR spectra were recorded with an IR imaging microscope is shown in pink on the left. (b) Optical microscope image (left) and corresponding SEM image (right) of the region with the previously airborne dust particle Abby2. Characteristic rips are shown near each particle, which enabled the particle to be located in different microscopes.

Figure 1. The box for Abby1 was 81 × 81 μm^2, corresponding to 169 separate spectra, and it was 81 × 75 μm^2 for Abby2, corresponding to 156 separate spectra. Each spectrum had 4 cm^{-1} resolution and 512 scans. False color maps of absorption (chemimaps) at 1033 cm^{-1} (with a 2 point baseline) for each spectra are shown in the middle inset of Figures 2 and 3, identifying the particles. Boxes of 3 × 3 pixels (as shown in the top middle inset of Figures 2 and 3) were constructed about each particle and an empty hole nearby. The average of the nine transmission spectra within the particle box (sample) were ratioed to that of a nearby empty box (background) to obtain the absorption spectra at the bottom of Figures 2 and 3. After the IR spectra were recorded, the mesh containing the particles was transported to a JEOL JSM 550 SEM. The particles were located by characteristic rips, as shown in Figure 1. A zoomed SEM image of each particle is inset at the top right of the corresponding single-particle IR spectra in Figures 2 and 3.

Abby1 is globular, ∼4.5 μm in diameter, and appears as an agglomeration of multiple smaller particles (note the hole at the particle center). The large broad IR peak at 1033 cm^{-1} with broad water-like OH stretching (3200−3700 cm^{-1}) and sharper OH^- bands from 3616 to 3696 cm^{-1} suggests that the largest component is clay. The sharp bands at 710 and 869 cm^{-1} with stronger bands at 1413 and 1441 cm^{-1} suggest carbonate. The peaks at 2852 and 2924 cm^{-1} are characteristic of CH_2 chains of organic material and may be correlated with the band at 1618 cm^{-1}. The peak just out of range to the low wavenumber and the peculiar rise increasing at 2000 cm^{-1} are similar to

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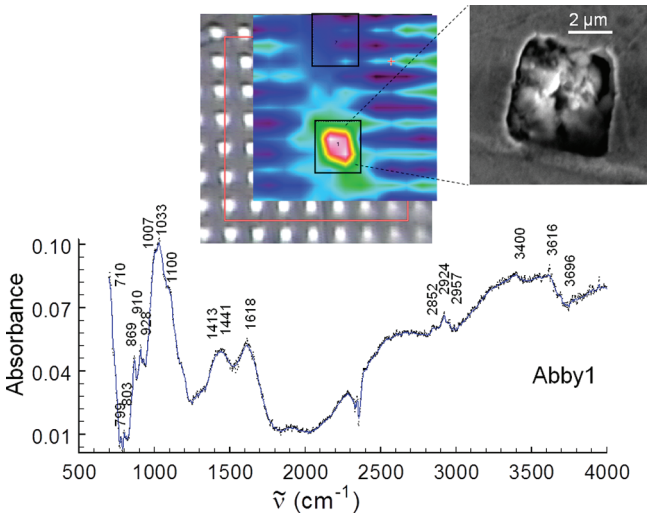

Figure 2. The bottom shows an IR spectrum of the previously airborne dust particle called Abby1. The top middle inset shows the IR imaging region (see the top left of Figure 1) overlaid with a chemimap of absorption at 1033 cm^{-1} (red is the most intense; blue is the least intense). The single particle in the imaging region clearly defines the offset of the optical and IR paths. The inset at the top right is the SEM image of the same particle (Abby1) showing details of its shape, size, and crystallinity. The mesh hole is 5 μm wide.

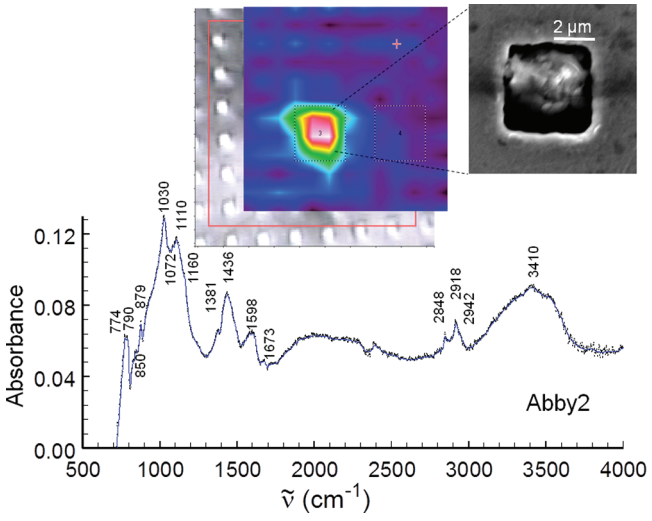

Figure 3. The bottom shows an IR spectrum of the other previously airborne dust particle called Abby2. The top middle inset shows the IR imaging region (see the bottom left of Figure 1) overlaid with a chemimap of absorption at 1030 cm^{-1} (red is the most intense; blue is the least intense). The inset at the top right is the SEM image of the same particle (Abby2) showing details of its shape, size, and crystallinity.

those of Fe_2O_3, although more work would be needed to make a definitive assignment. Therefore, Abby1 is a clay particle with some carbonate and possibly Fe_2O_3, as well as a small amount of organic carbon material. As our work on the 63 particle dust library has shown,[13] few airborne dust particles are alike; most are mixtures of multiple components, and a majority contain an organic component. We now know that this particle is very typical of the airborne dust found in our lab.

Abby2 is more elliptical, ~4.5 μm in its longest dimension and ~3 μm in its shortest. The pair of narrower peaks at 774 and 790 cm^{-1} with a very broad band centered at ~1070 cm^{-1} suggest a large component of quartz. The narrow peak at 879 cm^{-1} with a broad peak at 1436 cm^{-1} suggests some dolomitic carbonate. The organic component of Abby2 is more apparent than that with Abby1. In addition to the characteristic CH stretching bands at 2848, 2918, and 2942 cm^{-1}, there are protein-like amide I and II bands at 1673 and 1598 cm^{-1}, as well as a NH stretching band (3410 cm^{-1}) on top of the broad water-like OH stretching band. This is biological material that has started to decay. Again, Abby2 is a very typical airborne dust particle.

In order to better understand the scatter-free spectra of single dust particles, our future work will involve recording spectra of pure particles of known components of dust for calibration. There are two interesting spectral aspects that must be incorporated into the analysis before volume fractions of components can be quantified. (1) Many common mineral components of dust are birfringent or trirefringent. For example, quartz is birefringent and has a different IR spectrum for the ordinary and extraordinary beams. The peaks at the literature[48] frequencies of 778 (extraordinary) and 797 cm^{-1} (ordinary), which are seen in Figure 3, change their intensity with different orientations of the quartz particle. (2) Particles of this size (~4 μm) can have strong bands that have vibrational absorption cross sections that are larger than the physical cross section of the particle. This leads to particle saturation effects including broadening and distortion of the line shape (multiple peaks when there should only be one). In Figure 3, this is apparent for the asymmetric SiO_4 stretch that is observed at around 1030 cm^{-1}. The peak has literature values of 1072 cm^{-1} in the extraordinary beam and 1080 cm^{-1} in the ordinary beam but is split into a complicated line shape with maxima at 1030 and 1110 cm^{-1}. The calibration spectra may be as interesting as the single-particle airborne dust spectra themselves.

EXPERIMENTAL SECTION

Mesh from Precision Eforming of Cortland, NY (www.precisioneforming.com) was used. It is nickel with a square lattice of square holes (5.0 μm wide square holes, 12.6 μm lattice parameter, and a thickness of ~2 μm). To collect the airborne dust particles, mesh was placed over a 3.18 mm hole in a circular piece of stainless steel shim-stock with a diameter of approximately 25 mm. This size fits the mesh/shim-stock piece in a standard inline Derlin filter holder made by SKC. In early November 2010, dust was collected from the air in Evans Lab Room 0055 on The Ohio State University, Columbus campus. Obtaining an SEM image and IR absorption spectrum of the exact same subwavelength particle is not a trivial task as this involves two separate instruments, one of which requires vacuum. Our IR imaging microscope (Perkin-Elmer Spotlight 300) has a Cassegrain optical system that maintains a healthy vertical working space (~5 cm) and a broad range of in-focal-plane scanning, but these features produce only a modest optical microscope with a fixed and low magnification (effectively ~×24). Using both reflection and transmission optical modes, it can be discerned that the particle is contained in the hole, but little else. In order to find the particle in an SEM microscope, a landmark was applied to the mesh in order to find the particle under the different orientation and much higher magnification of the SEM. Observing particle positions under an Olympus BX50 microscope, an attempt was made to scratch the mesh near particles with an X-ACTO knife; however, rips were made instead. Figure 1 shows corresponding optical and SEM images of two different individual dust

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particles trapped in a hole of plasmonic mesh. The characteristic rips from the X-ACTO knife allowed location of the particle in both microscopes.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Maier, S. A. Plasmonics: Metal Nanostructures for Subwavelength Photonic Devices. *IEEE J. Sel. Top. Quantum Electron.* **2006**, *12*, 1214.

(2) Ozbay, E. Plasmonics: Merging Photonics and Electronics at Nanoscale Dimensions. *Science* **2006**, *311*, 189.

(3) Van Duyne, R. P. Physics: Molecular Plasmonics. *Science* **2004**, *306*, 985.

(4) Bravo-Abad, J.; Martin-Moreno, L.; Garcia-Vidal, F. J.; Hendry, E.; Rivas, J. G. Transmission of Light through Periodic Arrays of Square Holes: From a Metallic Wire Mesh to an Array of Tiny Holes. *Phys. Rev. B* **2007**, *76*, 241102.

(5) Maier, S. A. Plasmonics—Towards Subwavelength Optical Devices. *Curr Nanosci.* **2005**, *1*, 17.

(6) Ebbesen, T. W.; Lezec, H. J.; Ghaemi, H. F.; Thio, T.; Wolff, P. A. Extraordinary Optical Transmission through Sub-wavelength Hole Arrays. *Nature* **1998**, *391*, 667.

(7) Ghaemi, H. F.; Thio, T.; Grupp, D. E.; Ebbesen, T. W.; Lezec, H. J. Surface Plasmons Enhance Optical Transmission through Subwavelength Holes. *Phys. Rev. B: Condens. Matter* **1998**, *58*, 6779.

(8) Schroter, U.; Heitmann, D. Surface-Plasmon-Enhanced Transmission through Metallic Gratings. *Phys. Rev. B: Condens. Matter* **1998**, *58*, 15419.

(9) Gordon, R.; Brolo, A. G.; Sinton, D.; Kavanagh, K. L. Resonant Optical Transmission through Hole-Arrays in Metal Films: Physics and Applications. *Laser Photonics Rev.* **2009**, *4*, 311.

(10) Coe, J. V.; Heer, J. M.; Teeters-Kennedy, S.; Tian, H.; Rodriguez, K. R. Extraordinary Transmission of Metal Films with Arrays of Subwavelength Holes. *Annu. Rev. Phys. Chem.* **2008**, *59*, 179.

(11) Coe, J. V.; Rodriguez, K. R.; Teeters-Kennedy, S.; Cilwa, K.; Heer, J.; Tian, H.; Williams, S. M. Metal Films with Arrays of Tiny Holes: Spectroscopy with Infrared Plasmonic Scaffolding. *J. Phys. Chem. C* **2007**, *111*, 17459.

(12) Williams, S. M.; Rodriguez, K. R.; Teeters-Kennedy, S.; Shah, S.; Rogers, T. M.; Stafford, A. D.; Coe, J. V. Scaffolding for Nanotechnology: Extraordinary Infrared Transmission of Metal Microarrays for Stacked Sensors and Surface Spectroscopy. *Nanotechnology* **2004**, *15*, S495.

(13) Cilwa, K. E.; McCormack, M.; Lew, M.; Robitaille, C.; Corwin, L.; Malone, M. A.; Coe, J. V.; Scatter-Free, I. R. Absorption Spectra of Individual, 3−5 Micron, Airborne Dust Particles Using Plasmonic Metal Microarrays: A Library of 63 Spectra. *J. Phys. Chem. C* **2011**, *115*, 16910.

(14) Malone, M. A.; Prakash, S.; Heer, J. M.; Corwin, L. D.; Cilwa, K. E.; Coe, J. V. Modifying Infrared Scattering Effects of Single Yeast Cells with Plasmonic Metal Mesh. *J. Chem. Phys.* **2010**, *133*, 185101.

(15) Heer, J.; Corwin, L.; Cilwa, K.; Malone, M. A.; Coe, J. V. Infrared Sensitivity of Plasmonic Metal Films with Hole Arrays to Microspheres In and Out of the Holes. *J. Phys. Chem. C* **2010**, *114*, 520.

(16) Ulrich, R. Far-Infrared Properties of Metallic Mesh and Its Complementary Structure. *Infrared Phys.* **1967**, *7*, 37.

(17) Ulrich, R.; Martin, R. J. Geometrical Optics in Thin Film Light Guides. *Appl. Opt.* **1971**, *10*, 2077.

(18) Ulrich, R.; Tacke, M. Submillimeter Waveguiding on Periodic Metal Structure. *Appl. Phys. Lett.* **1973**, *22*, 251.

(19) van de Hulst, H. C. *Light Scattering by Small Particles*; Dover: New York, 1981.

(20) Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; Wiley-VCH Verlag GmbH: New York, 2007.

(21) Maskey, S.; Geng, H.; Song, Y.-C.; Hwang, H.; Yoon, Y.-J.; Ahn, K.-H.; Ro, C.-U. Single-Particle Characterization of Summertime Antarctic Aerosols Collected at King George Island Using Quantitative Energy-Dispersive Electron Probe X-ray Microanalysis and Attenuated Total Reflection Fourier Transform-Infrared Imaging Techniques. *Environ. Sci. Technol.* **2011**, *45*, 6275.

(22) Maskey, S.; Kang, T.; Jung, H.-J.; Ro, C.-U. Single-Particle Characterization of Indoor Aerosol Particles Collected at an Underground Shopping Area in Seoul, Korea. *Indoor Air* **2011**, *21*, 12.

(23) Kirchner, U.; Vogt, R.; Natzeck, C.; Goschnick, J. Single Particle MS, SNMS, SIMS, XPS, and FTIR Spectroscopic Analysis of Soot Particles during the AIDA Campaign. *J. Aerosol Sci* **2003**, *34*, 1323.

(24) Flynn, G. J.; Keller, L. P.; Wirick, S.; Jacobsen, C.; Sutton, S. R. Analysis of Interplanetary Dust Particles by Soft and Hard X-ray Microscopy. *J. Phys. IV* **2003**, *104*, 367.

(25) Flynn, G. J.; Keller, L. P.; Jacobsen, C.; Wirick, S. Elemental Mapping and X-ray Absorption near-Edge Structure (XANES) Spectroscopy with a Scanning Transmission X-ray Microscope. *Meteorit. Planet. Sci.* **1999**, *34*, A36.

(26) Johansso, S. A. E. Particle Induced X-ray Emission and Complementary Nuclear Methods for Trace Element Determination. Plenary Lecture. *The Analyst* **1992**, *117*, 259.

(27) Laskin, A.; Cowin, J. P.; Iedema, M. J. Analysis of Individual Environmental Particles Using Modern Methods of Electron Microscopy and X-ray Microanalysis. *J. Electron Spectrosc. Relat. Phenom.* **2006**, *150*, 260.

(28) Murphy, D. M.; Cziczo, D. J.; Froyd, K. D.; Hudson, P. K.; Matthew, B. M.; Middlebrook, A. M.; Peltier, R. E.; Sullivan, A.; Thomson, D. S.; Weber, R. J. Single-Particle Mass Spectrometry of Tropospheric Aerosol Particles. *J. Geophys. Res., [Atmos.]* **2006**, 111.

(29) Thomson, D. S.; Schein, M. E.; Murphy, D. M. Particle Analysis by Laser Mass Spectrometry WB-57F Instrument Overview. *Aerosol Sci. Technol.* **2000**, *33*, 153.

(30) Murphy, D. M.; Thomson, D. S. Laser Ionization Mass-Spectroscopy Of Single Aerosol-Particles. *Aerosol Sci. Technol.* **1995**, *22*, 237.

(31) Lee, S. H.; Murphy, D. M.; Thomson, D. S.; Middlebrook, A. M. Chemical Components of Single Particles Measured with Particle Analysis by Laser Mass Spectrometry (PALMS) during the Atlanta SuperSite Project: Focus on Organic/Sulfate, Lead, Soot, And Mineral Particles. *J. Geophys. Res., [Atmos.]* **2002**, 107.

(32) Widmann, J. F.; Aardahl, C. L.; Davis, E. J. Microparticle Raman Spectroscopy. *TrAC, Trends Anal. Chem.* **1998**, *17*, 339.

(33) Wopenka, B. Raman Observations On Individual Interplanetary Dust Particles. *Earth. Planet. Sci. Lett.* **1988**, *88*, 221.

(34) Wopenka, B.; Swan, P. D. Micro-FTIR Measurements On Individual Interplanetary Dust Particles. *Mikrochim. Acta* **1988**, *1*, 183.

(35) Smith, G. D. Infrared Microspectroscopy Using a Synchrotron Source for Arts-Science Research. *J. Am. Inst. Conserv.* **2003**, *42*, 399.

(36) Dumas, P.; Jamin, N.; Teillaud, J.; Miller, M.; Beccard, B. Imaging Capabilities of Synchrotron Infrared Microspectroscopy. *Faraday Discuss.* **2004**, *126*, 289.

(37) Raynal, P. I.; Quirico, E.; Borg, J.; Deboffle, D.; Dumas, P.; d'Hendecourt, L.; Bibring, J. P.; Langevin, Y. Synchrotron Infrared Microscopy of Micron-Sized Extraterrestrial Grains. *Planet. Space Sci.* **2000**, *48*, 1329.

(38) Williams, S. M.; Coe, J. V. Dispersion Study of the Infrared Transmission Resonances of Freestanding Ni Microarrays. *Plasmonics* **2006**, *1*, 87.

(39) Vigoureux, J. M. Analysis of the Ebbesen Experiment in the Light of Evanescent Short Range Diffraction. *Opt. Commun.* **2001**, *198*, 257.

(40) Kretschmann, E.; Raether, H. Radiative Decay of Nonradiative Surface Plasmons Excited by Light. *Z. Naturforsch., A: Astrophys., Phys. Phys. Chem.* **1968**, *23*, 2135.
(41) Raether, H. *Surface Plasmons on Smooth and Rough Surfaces and on Gratings*; Springer-Verlag: Berlin, Germany, 1988.
(42) Ritchie, R. H.; Arakawa, E. T.; Cowan, J. J.; Hamm, R. N. Surface-Plasmon Resonance Effect in Grating Diffraction. *Phys. Rev. Lett.* **1968**, *21*, 1530.
(43) Wilford, N. H. Expanded Formulas for Attenuated Total Reflection and the Derivation of Absorption Rules for Single and Multiple ATR Spectrometer Cells. *Spectrochim. Acta* **1965**, *21*, 815.
(44) Harrick, N. J. Surface Chemistry from Spectra Analysis of Totally Internally Reflected Radiation. *J. Phys. Chem.* **1960**, *64*, 1110.
(45) van de Hulst, H. C. *Light Scattering by Small Particles*: John Wiley and Sons: New York, 1958.
(46) Christiansen, C. Untersuchungen über die optischen Eigenschaften von fein vertheilten Körpern. *Ann. Phys.* **1884**, *259*, 298.
(47) Dunder, T.; Miller, R. E. Infrared Spectroscopy and Mie Scattering of Acetylene Aerosols Formed in a Low Temperature Diffusion Cell. *J. Chem. Phys.* **1990**, *93*, 3693.
(48) Spitzer, W. G.; Kleinman, D. A. Infrared Lattice Bands of Quartz. *Phys. Rev.* **1961**, *121*, 1324.
(49) *Particulate Matter*. http://www.epa.gov/airquality/particlepollution/standards.html (2011).
(50) Peng, R. D.; Chang, H. H.; Bell, M. L.; McDermott, A.; Zeger, S. L.; Samet, J. M.; Dominici, F. Coarse Particulate Matter Air Pollution and Hospital Admissions for Cardiovascular and Respiratory Diseases Among Medicare Patients. *J. Am. Med. Assoc.* **2008**, *299*, 2172.
(51) Bell, M. L.; Ebisu, K.; Peng, R. D.; Samet, J. M.; Dominici, F. Hospital Admissions and Chemical Composition of Fine Particle Air Pollution. *Am. J. Respir. Crit. Care Med.* **2009**, *179*, 1115.
(52) Dominici, F.; McDermott, A.; Zeger, S. L.; Samet, J. M. National Maps of the Effects of Particulate Matter on Mortality: Exploring Geographical Variation. *Environ. Health Persepect.* **2003**, *111*, 39.
(53) Hinds, W. C. *Aerosol Technology: Properties, Behavior, And Measurement of Airborne Particles*; J. Wiley: New York, 1982.
(54) Eastwood, P. *Particulate Emissions from Vehicles*; John Wiley & Sons: Chichester, England; Hoboken, NJ:, 2008.
(55) Sandford, S. A.; Walker, R. M. Laboratory Infrared Transmission Spectra Of Individual Interplanetary Dust Particles From 2.5 To 25 Microns. *Astrophys. J.* **1985**, *291*, 838.
(56) Flynn, G. J. Interplanetary Dust Particles Collected From The Stratosphere — Physical, Chemical, and Mineralogical Properties and Implications For Their Sources. *Planet. Space Sci.* **1994**, *42*, 1151.