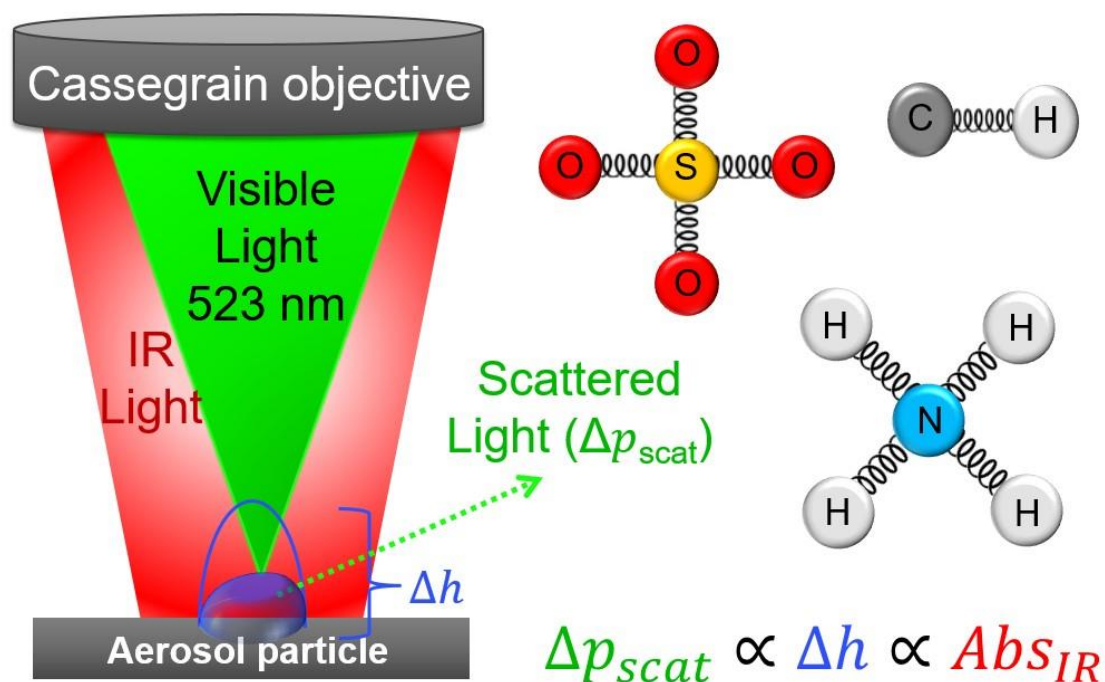


## Simultaneous Optical Photothermal Infrared (O-PTIR) and Raman Spectroscopy of Submicrometer Atmospheric Particles

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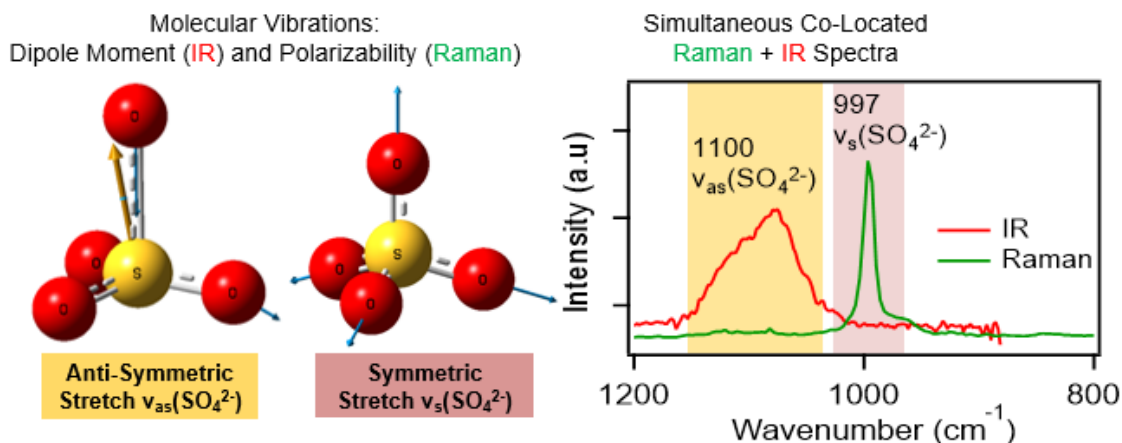
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Atmospheric aerosol particles impact climate by scattering or absorbing solar radiation, nucleating clouds and ice crystals, and participating in heterogeneous reactions with atmospheric gases. Physicochemical analysis of atmospheric aerosols at the most abundant sizes in the atmosphere ( $< 1 \mu\text{m}$ ) is analytically challenging due to their small size. Spectroscopic detection of species present at attogram to femtogram levels provides additional analytical challenges. Furthermore, the development of aerosol measurement techniques under ambient conditions is limited, as traditionally used microspectroscopy techniques are performed under vacuum conditions which distort the physical properties of aerosol particles and induce loss of volatile organic species. Herein, we show the first application of optical photothermal infrared spectroscopy (O-PTIR) to detect physicochemical properties of individual aerosol particles down to  $1 \mu\text{m}$  at ambient temperature and pressure. With this technique, localized IR absorption and Raman spectra are obtained after aligning a visible laser and a tunable IR laser on the sample and measuring the induced photothermal expansion that occurs when the incident frequency of the IR laser matches the vibrational absorption of the sample. The resulting photothermal expansion causes a change in the scattered Raman signal, which can then be extracted to obtain an IR spectrum. The photothermal IR spectra generated resemble Fourier-transformed IR (FTIR) absorbance spectra, but can achieve submicron resolution. When coupled to optical microscopy images of individual particles, this technique provides detailed information about the physical and chemical properties of aerosol particles. Microscopy substrates were tested for optimal sample signal and minimal interference with IR and Raman spectra. Organic and inorganic functional groups were characterized in laboratory-generated standards and ambient aerosol particles. Mapping was performed on complex, multi-component particles to determine the spatial variation of chemical species. The novel application of this new analytical microspectroscopy method to atmospheric samples enabled detection of organic and inorganic vibrational modes in samples that have previously been unstudied by vibrational spectroscopy. The results presented herein highlight the capability of O-PTIR to analyze particles well below the diffraction limit of traditional spectroscopy techniques and show the power of this analytical method to study physicochemical properties of aerosol particles. The information obtained provides key insight into atmospheric particles in a critical size range for climate and human health implications.



**Figure 1.** Schematic of optical photothermal infrared (O-PTIR) spectroscopy. Infrared and visible light are focused on the sample through a Cassegrain objective, inducing a photothermal response and expansion of the aerosol particle. The light scattered from the sample ( $p_{scat}$ ) is proportional to the height expansion of the particle ( $h$ ) and the absorbance of IR light ( $Abs_{IR}$ ). Here, we illustrate some of the vibrational modes detected in atmospheric aerosol particles.

## Optical Photothermal Infrared Spectroscopy



**Figure 2.** With optical photothermal infrared spectroscopy (OPTIR), simultaneous IR and Raman spectra are obtained from a single point, illustrating the various vibrational modes observed. We show the symmetric and anti-symmetric stretches of sulfate molecules as an example.