**Characterization of Gas-Aerosol Interaction Kinetics
using Morphology Dependent Stimulated Raman Scattering**

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A> Original Project Summary

An experimental research program aimed at characterizing the influence of aerosol surface structure on the kinetics of gas-aerosol interactions is proposed. In brief, the experiments involve measuring changes in gas phase chemical reaction rates as a function of exposure to a specific aerosol. Aerosols with differing surface properties will be generated by changing the composition and/or temperature of the material making up the aerosol. The kinetic data generated in these experiments can be used directly in atmospheric modelling calculations. The surface structure of the aerosol will be measured, both before and after reaction, using morphology-dependent enhancement of stimulated Raman scattering (MDSRS). Information about the detailed dynamics of gas-aerosol interactions can be obtained by correlating the change in the reaction rate with change in surface structure and by monitoring the change in aerosol surface structure during the course of the reaction. This dynamics information can be used to generate kinetic data for systems which are similar in nature to those studied, but are not amenable to laboratory investigation.

Studies will focus on the condensation and oxidation of sulfur species (sulfur dioxide and dimethyl sulfide) on water aerosols, and on the condensation and transformation of nitric acid on water/ice and sulfuric acid aerosols. These particular systems have been chosen because recent balloonsonde and airborne geochemical investigations show that these gas-aerosol systems play a vital role in determining the global atmospheric chemical budget.

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Final Technical Report for Fiscal Year 91 - 92

Grant # DE-FG02-91ER61204

I. Introduction

Recent field studies have shown that gas-aerosol interactions play a fundamental role in determining global atmospheric chemical balance and change. For example, ozone depletion in the stratosphere is now attributed to reactions between HCl, ClONO₂, and H₂O on sulfate, nitrate, and water aerosols, and oxidative chemical processes, which are responsible for tropospheric chemical balance, are now thought to occur primarily within cloud droplets.^{1,2} In addition chemical species contained within aerosols strongly determine cloud albedo (reflectivity) and as such effect the earth's radiation budget and ultimate global warming.

The long term goal of our proposed research is to characterize and categorize the influence that aerosol surface structure (i.e. chemical composition) has on the kinetics of gas-aerosol reactions. To perform research of this genre it is necessary that a spectroscopic method that can accurately determine aerosol surface structure be available. A technique which shows great promise in this regard is morphology dependent stimulated Raman scattering (MDSRS), and part of our first year's research has focussed on developing this technique so that it can be applied to the systems of interest. In addition to characterizing aerosol surface structure, the proposed kinetics studies also require that all gas phase species consumed or created in the reactions be monitored. Coherent anti-Stokes Raman scattering (CARS) spectroscopy is ideally suited for these latter studies, and the second half of our research has focussed on determining the absolute sensitivity limits and general applicability of a CARS apparatus we have constructed in our laboratory.

The progress we have made in developing these two nonlinear laser Raman spectroscopies is reported below. The report is split into two sections. The first section outlines the MDSRS experiments. The second section reports on the CARS studies. Since the general community is unfamiliar with nonlinear Raman effects, we also provide a brief description of the phenomenology of these two spectroscopic probes.

II. Morphology Dependent Stimulated Raman Scattering (MDSRS)

Stimulated Raman scattering (SRS) is a nonlinear optical process which is most easily understood by looking at Fig. 1a. If two light waves, at frequencies ν_0 and ν_s , are simultaneously incident on a sample, then the ν_s wave, called the Stokes wave, becomes amplified by one quantum while the ν_0 wave, the excitation wave, is depleted by one quantum. For propagation of the two incident waves along some length of sample, l , the Stokes wave becomes amplified by,

$$I_s(l) = I_s(0) \exp [(G_R - \alpha) l],$$

where α is the attenuation (absorption) coefficient at ν_s , and G_R is the gain factor for stimulated Raman scattering, given by;

$$G_R \sim (16 \pi^2 c^2 / \hbar \omega_s^3 n_s^2 \Gamma) N (d\sigma/d\Omega) I_0.$$

In this latter equation, c is the speed of light, $\hbar$ is Planck's constant, ω_s is the angular frequency of the Stokes emission, n_s is the refractive index of the material at the Stokes wavelength, Γ is the halfwidth of the transition (in frequency units), N is the density of molecules cm^{-3} , I_0 is the intensity of the ν_0 beam (W cm^{-2}), and $(d\sigma/d\Omega)$ is the Raman scattering cross section in $\text{cm}^2 \text{sr}^{-1}$.

It has recently been shown that the light intensity thresholds required to generate stimulated Raman scattering in small, micrometer sized particles (both solid and liquid) are orders of magnitude lower than the thresholds required to generate SRS in bulk samples.³ This reduction in intensity is a result of two processes. First, the particle interface acts just like lens and focuses the incident light to a small spot located just inside the shadow face of the particle (see Figure 1b). This focussing causes the internal intensity to increase by a factor of 200 or more, and since $I_s \propto \exp(G_R l)$ and $G_R \propto I_0$, then the 200-fold increase in intensity allows SRS to be generated in a sample 200 times shorter in length. For example, a 50 μm dia. droplet generates as much SRS intensity as does a 1 cm long sample.

Intensity thresholds are additionally reduced because the internally generated Stokes light gets trapped inside the particle by total internal reflection (see Figure 1c). When the

Trapping of SRS by total internal reflection

FIGURE 1.

wavelength of the trapped light is an integral number of the droplet circumference one of the particle's natural electromagnetic modes becomes excited (this is exactly analogous with the standing wave patterns set up in a laser resonator cavity), and the Stokes light will continue to propagate inside the particle for the lifetime of the mode excited (determined by the mode Q factor, $\Gamma = \omega/Q$). Extra gain for the SRS process is thus provided by the continued spatial overlapping of the Stokes light wave with the incident light wave at the particle shadow and front faces. Calculations and experiment show that the particle modes that participate in this process are located close to the surface of the particle.^{4,5} Hence MDSRS probes the surface, or more exactly the outer crust, structure of an aerosol particle.

Previous studies have shown that MDSRS can be used to detect sulfate and nitrate anions contained within water-based aerosols, however anion concentrations only down to about 0.2 M could be detected.⁶ This concentration limit is not sufficiently sensitive for our proposed gas-aerosol kinetics studies, but theoretical studies and experiments done in our laboratory this year show that the sensitivity can be improved markedly, by an estimated factor of 10^6 , simply by optimizing the geometry of the experiment and taking advantage of preresonance Raman enhancement by shifting the excitation wavelength to the UV. These experiments are described below.

i) MDSRS Experiments

The procedure associated with MDSRS of aerosols is extremely straightforward. A schematic of our laboratory apparatus is shown in Fig. 2. A train of aerosols (with diameters between 5 and 200 μm) is generated by passing a solution containing the species of interest through a vibrating orifice. A 90° incident laser beam of modest power is focussed and directed at the droplet. The driving conditions of the vibrating orifice are set to ensure that the spacing between the droplets is sufficiently large such that only a single droplet is illuminated by the laser at any one time, and a trigger system developed in this laboratory ensures that the incident beam targets a specified position on a droplet every time the laser is fired. The MDSRS signal arising from the droplet is collected by a lens, located

MDSRS APPARATUS

FIGURE 2.

90° to the input laser beam, imaged onto the entrance slit of a monochromator, dispersed, and detected by an optical multichannel analyzer (OMA).

Our first experiments have focussed upon improving the sensitivity of MDSRS. If one examines the equation for G_R given above one sees that there are two ways to effectively increase the value of the gain factor, and thus lower the anion concentration required to reach SRS threshold. The first is to increase the value of I_0 , the amount of incident light coupled into the droplet, and the second is to increase the Raman cross-section, $(d\sigma/d\Omega)$.

It is a fairly trivial exercise to increase I_0 , the amount of light coupled into the droplet. Theoretical studies show that I_0 can be enhanced by factors as large as 10^5 if the incident light can be made to excite one of the droplet's MDRs.⁵ To excite a droplet MDR it is necessary that the $\mathbf{k}$ vector of the incident light match the $\mathbf{k}$ vector of the droplet MDR. This can be accomplished if the incident light comes in grazing the droplet surface (see Fig. 3a). Results obtained in our laboratory indicate that the theoretical predictions are correct and reasonable. Fig. 3b contains two MDSRS spectra, one for focussed center illumination, the other for equatorial edge illumination. These spectra correspond to illumination of 1 M 190 μm dia. ammonium sulfate droplets using 20 mJ/pulse 532 nm incident light, focussed to a spot dia. of 33 μm . The spectra correspond to a 10 second data acquisition time (100 laser shots, 100 droplets). The increase in I_{MDSRS} is rather spectacular and by working back through the gain equation and making reasonable assumptions about light collection efficiency, the results show that I_0 in these experiments has been increased by at least 10^4 . The focussing conditions for these experiments were not as tight as could be. By improving this we can increase I_0 by at least another 100 fold, allowing anion concentrations at least as low as 1×10^{-6} M to be detected.

The results of this study emphasize the importance of being able to spatially target the droplet with the input laser beam in a reproducible fashion. In the early stages of our research we discovered that our biggest source of spatial variance was oscillation of the

a) Coupling input light into a droplet MDR

b) 1 M Ammonium Sulfate, 532 nm excitation, 20 mJ/pulse

FIGURE 3.

droplet stream. We subsequently redesigned the vibrating orifice aerosol generator and our new version now produces a stream of droplets that has a radius of oscillation $< 35 \mu\text{m}$ at the point where the laser is focussed on the droplet. With the improved stream stability we can now quantify our MDSRS measurements, and we have started a series of experiments aimed at determining absolute MDSRS sensitivity limits for sulfate and nitrate, and the exact analytic relation between MDSRS signal size and anion concentration.

With the improved droplet stream stability we have noticed that we can reduce the 532 nm input laser intensity and obtain an MDSRS signal that is significantly larger than the one generated earlier using 20 mJ/pulse laser intensity. Figure 4 contains two sulfate MDSRS spectra generated after our design improvements. The spectrum in 4a corresponds to illumination of 1 M 190 μm dia. ammonium sulfate droplets using 3 mJ/pulse 532 nm incident light focussed to a spot dia. of 33 μm , and a 5 second data acquisition time (50 laser shots). The peak height intensity in Figure 4a is 12,240 counts, as compared to the peak height intensity of 6400 counts measured earlier (see the upper spectrum in Figure 3b). The data acquisition time in Figure 4a is one-half that in Figure 3. Our sensitivity has therefore increased by a further factor of 2.

The spectrum in Figure 4b corresponds to illumination of 0.5 M 190 μm dia. ammonium sulfate droplets with 5 mJ/pulse 532 nm incident light focussed to a spot dia. of 33 μm , and a 5 second data acquisition time (50 laser shots). The peak height is 9,370 counts. The ratio of the MDSRS peak heights shown in Figures 4 a and b, $12240 / 9,370$ is 1.30. This ratio agrees, within experimental error, with the ratio predicted using the MDSRS gain equations given previously, i.e. $I_{\text{MDSRS}} \propto \exp N I_0 (d\sigma/d\Omega) = \exp 1 \text{ M} \times 3 \text{ mJ} / \exp 0.5 \text{ M} \times 5.5 \text{ mJ} = 1.28$. (Note $(d\sigma/d\Omega)$ is the same in these two experiments). This result shows that the gain equation for MDSRS is a quantifiable identity, and confirms our hypothesis that MDSRS can be used for analytic studies of gas-aerosol kinetics.

As mentioned earlier, MDSRS sensitivity can be further improved by increasing the Raman cross section, $d\sigma/d\Omega$. To increase the Raman cross section one need only take

FIGURE 4

advantage of the phenomenon of preresonance enhancement which shows that the Raman cross section increases as one shifts the excitation source to the blue (i.e. as one accesses an electronic transition in the system of interest). We have investigated the influence of changing the incident wavelength on MDSRS sensitivity and find that the gain in the droplet is indeed enhanced upon shifting the excitation source from the green (532 nm) to the UV (289 nm). Fig. 5 shows an MDSRS spectrum arising from center face illumination of 2 M 190 μm dia. ammonium sulfate droplets with 1.2 mJ/pulse 290 nm incident light focussed to a spot dia. of 33 μm , and a 10 second data acquisition time (100 laser shots). On this day in the laboratory, we were unable to generate MDSRS spectra using 532 nm incident wavelengths with intensities less than 6 mJ per pulse. (These experiments were done before we modified the aerosol generator, hence the reason for the poor signal response to decreased 532 nm intensity). The spectrum in Figure 5 shows that the gain in the droplet has been increased by a factor of at least 5 simply by changing the incident wavelength. This result, when combined with the result obtained in the edge vs center face illumination study, suggests that sulfate anion concentrations at least as low as 2×10^{-7} M can be detected using MDSRS.

We continued our studies of investigating the influence of changing incident wavelength on MDSRS signal intensity using our improved aerosol generator. The results proved to be quite surprising. The spectrum shown previously indicates that MDSRS achieves threshold (i.e. the peak starts to lift out of the background noise) with 1.2 mJ/pulse incident light intensity. To accurately quantify the signal improvement, relative to 532 nm excitation, we needed to generate UV light with an intensity around 5 mJ/pulse. This was accomplished by scanning the dye laser, the output of which is doubled to generate the UV, to the peak of the R590 dye curve. 5.5 mJ/pulse of 281.5 nm light was generated, and the resultant MDSRS spectrum of 1 M 190 μm dia. ammonium sulfate droplets (15 sec data acquisition time) is shown in Figure 6. Two peaks are present in this spectrum, one at 311 nm and one at 327 nm. The first peak is the first order Stokes

2 M Ammonium Sulfate, 289 nm excitation, 1.2 mJ/pulse

FIGURE 5.

MDSRS signal from water. The second corresponds to fifth order Stokes scattering from sulfate! To achieve 5th order MDSRS, the intensity of the 1st order MDSRS must be sufficiently large to pump the 2nd order MDSRS, etc., etc, to the 5th order. We have never seen multiorder Stokes scattering using 532 nm excitation, so clearly the 281.5 nm pump is a far more efficient wavelength for effecting MDSRS in sulfate aerosols. We do have to reduce the UV power however in order to obtain analytically meaningful results. These experiments are currently underway.

III. Coherent anti-Stokes Raman Scattering (CARS) Spectroscopy

To monitor changes in gas phase species created or depleted in gas-aerosol interactions we have chosen to use coherent anti-Stokes Raman scattering (CARS) spectroscopy primarily because the technique is extremely sensitive and is very versatile -all molecules have at least one Raman active mode, hence all molecules can be detected. CARS is a coherent nonlinear spectroscopic technique that basically involves mixing two beams at frequencies, ω_{pump} and ω_{Stokes} , to generate a new coherent frequency at $\omega_{\text{anti-Stokes}} = 2\omega_{\text{pump}} - \omega_{\text{Stokes}}$. The phenomenology behind CARS is best understood by looking at Figure 7a. When $\omega_{\text{pump}} - \omega_{\text{Stokes}} = \omega_{\text{Raman}}$, where ω_{Raman} is the frequency associated with an allowed Raman transition between two molecular energy levels, the nonlinear mixing is greatly enhanced, and a coherent signal at $\omega_{\text{anti-Stokes}}$ is generated. This technique can be quite sensitive and gas phase species concentrations as low as 10^{11} - 10^{12} molec cm⁻³ can be detected. The sensitivity can be improved further if the technique of background suppression is incorporated.

i) CARS Experiments

A schematic of the CARS apparatus we have assembled in our laboratory is shown in Figure 7b. ω_{Stokes} (~ 8 mJ/pulse) is generated by passing the second harmonic output of a Nd:YAG laser (532 nm) through a tunable dye laser. A small portion of the original 532 nm beam (16 mJ/pulse) is split off before it enters the dye, sent through an optical delay line to compensate for the delay in the dye laser, and then used directly as ω_{pump} .

a) Coherent anti-Stokes Raman scattering

ω_{Stokes} and ω_{pump} are expanded in a telescope, combined on a dichroic, and focussed down to a spot size of $\sim 200 \mu\text{m}$ dia. in the CARS spectroscopy cell. The resultant anti-Stokes signal is isolated from the Stokes and pump beams by a series of dichroics, further filtered by passage through a double monochromator, and detected by a 1P28 photomultiplier tube.

In preparation for the gas-aerosol kinetics studies we have spent time calibrating our CARS apparatus, determining absolute sensitivity levels, and optimizing the apparatus so that triatomics and polyatomics can be detected with ease. Our first experiments revolved around detecting N_2 and O_2 . CARS spectra corresponding to 10 Torr total pressure are shown in Figures 8a and b. The strongest features in these spectra are the Q-branch ($\Delta J = 0$) transitions; the smaller peaks on the right are the O branch ($\Delta J = 2$) transitions. Spectra have been generated for much lower pressures, and our absolute sensitivity limits for N_2 and O_2 are 2×10^{11} and 8×10^{11} molecules cm^{-3} , respectively.

Our second set of experiments have focussed on using CARS to detect polyatomic species. Our rationale for these experiments is to prove to the scientific community that molecules different from O_2 and N_2 are amenable to CARS probing. A CARS spectrum of CO_2 at 3×10^{-4} Torr (corresponding to a sensitivity limit of 1×10^{13} molec cm^{-3}) is shown in Figure 9. The resolution of the current apparatus, 2 cm^{-1} , is sufficient to separate the ν_1 and $2\nu_2$ vibrational modes, but not the individual rotational lines. With the addition of the new laser we have ordered, the latter lines can be resolved.

We have just started a series of CARS experiments aimed at detecting larger polyatomics, specifically the CH_xCl_y chloromethane series, HNO_3 , SO_2 , and $(\text{CH}_3)_2\text{S}$.

IV. Conclusions

In the past six months we have assembled and gotten working two very complex nonlinear laser Raman spectroscopic experiments. The preliminary MDSRS experiments show that increased sensitivity levels can be achieved by optimizing the geometry and excitation wavelength of the apparatus. Results indicate that anion concentrations as low as $2 \times 10^{-7} \text{ M}$ can be detected. The CARS experiments show that our apparatus is sensitive

FIGURE 8.

FIGURE 9.

enough to detect diatomic and triatomic gas phase concentrations in the 10^{11} to 10^{12} molecule cm^{-3} range. Sensitivity limits for larger polyatomic molecules are now being determined.

Two PhD graduate and one undergraduate students have participated in the research outlined in this report. Alan S. Olson (graduate) and Tony Jorgensen (undergraduate) have been working on the MDSRS experiments. Jiang-Xiang (Jane) Zhang is responsible for the CARS spectroscopy.

We are currently writing up our results on the MDSRS experiments and plan to submit a letter to the Journal of Physical Chemistry by the end of February 1992.

V. Bibliography

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