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**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 modeling 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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B) Progress Report for Fiscal Year 92 - 93

Grant # DE-FG02-92ER61480

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 research is currently focused 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 focused 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.

II. Morphology Dependent Stimulated Raman Scattering (MDSRS)

Results from our previous year's research showed that it was possible to use MDSRS to detect sulfate in aerosols at concentrations of 1.0 and 0.5 M. We showed that

an equatorial edge illumination geometry gave improved sensitivity, relative to a center f. illumination geometry, and we determined that the MDSRS signal was a quantifiable identity in that the gain equation roughly followed the form;

$$I_s(l) = I_s(0) \exp [(G_R - \alpha) l], \quad (1)$$

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

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

In this latter equation, c is the speed of light, h 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 lifetime of the droplet resonance (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 $\text{cm}^2 \text{sr}^{-1}$.

The focus of our second year's MDSRS studies was to further elucidate the gain equation for MDSRS and to determine absolute sensitivity limits for sulfate anion contained in water-based aerosols. Although we have been able to detect sulfate in aerosols at lower concentrations, specifically down to 0.1 M which is a record low, we have not been able to make much progress in quantifying the gain equation because of signal reproducibility problems incurred by a poorly designed laser trigger/data collection electronic circuit. This latter problem and the solution we have for it are discussed below, but first we will outline the gains we made in terms of being able to detect lower sulfate anion concentrations in water-based aerosols.

A substantial improvement in MDSRS sensitivity was achieved when we installed a new Nd:YAG laser in the experimental apparatus. Previously we had been using a Nd:YAG laser with a linewidth of $\sim 1.4 \text{ cm}^{-1}$ at 532 nm. The new laser has a narrower bandwidth, specifically 0.15 cm^{-1} and improved pulse-to-pulse and pointing stabilities. The influence that the new Nd:YAG has on MDSRS sensitivity is illustrated in Figure 1 which shows two MDSRS spectra which correspond to edge illumination of 0.5M 190 μm

dia. ammonium sulfate droplets with 5 mJ/pulse 532 nm incident light focused to a spot dia. of 33 μm . The MDSRS spectrum in the upper panel corresponds to 50 shots of the 1.4 cm^{-1} linewidth laser. The MDSRS spectrum in the lower panel corresponds to 5 shots of the 0.15 cm^{-1} linewidth laser.

The spectra differ quite substantially. First, the MDSRS signal intensity at 561 nm is substantially larger in the lower spectrum, and in fact after only 5 laser shots has saturated the detector. Saturation was not achieved in the upper spectrum, even after 50 laser shots. Second, the lower spectrum contains a large peak at 594 nm which is not present in the upper spectrum. The peak at 594 nm corresponds to second order MDSRS scattering and shows that the droplet internal intensity at 561 nm is large enough to be used as a stimulated Raman scattering pump (i.e. it is sufficiently large to compete with the incident 532 nm intensity).

The fact that we can see second order MDSRS with the new laser indicates that the gain in the nonlinear process has been increased substantially, and illustrates that it is the laser linewidth which essentially determines, or limits as the case may be, the lifetime of the droplet mode excited (represented by Γ in the equation (2) above). We cannot experimentally quantify the exact increase in the gain as a result of switching from a 1.4 to 0.15 cm^{-1} linewidth since our signal has saturated the detector, but in principal the increase should be a factor of 10 (i.e. 1.4/0.15).

The fact that it is the illumination laser linewidth that determines the Γ accessed in the MDSRS experiment will actually make it easier for us to quantify the exact form of the gain equation, since this eliminates one unknown in equation (2) above. This result also suggests that MDSRS signal size should be independent of the size of the droplet used in the experiment. Equation (1) shows that stimulated Raman intensity is proportional to l , the sample length. In a spherical droplet, the illumination light is trapped inside the droplet because there is total internal reflection at the liquid/gas interface. Thus l , the sample length, is simply determined by the number of times the light travels around the droplet

circumference, which is determined by the speed of light in the medium (c/n_s) time lifetime of the mode excited or the length of the illumination pulse, which ever is larger. With the 0.15 cm^{-1} resolution laser the mode lifetime is limited to 0.22 nsec, a time which is longer than the 0.02 nsec lifetime achievable with the 1.4 cm^{-1} resolution laser, but shorter than the pulse width which is 6 nsec FWHM. Hence the sample length is determined by the pulse width of the laser and MDSRS signal size should therefore be independent of droplet size.

We have done some experiments which show that MDSRS signal size is independent of droplet diameter but we emphasize that these results are very preliminary. As stated above, we have had technical problems with our laser trigger/data acquisition timing electronics; the upshot being that we essentially have not been able to accurately fire the laser such that the incident beam targets a specified vertical position on a droplet every time the laser is fired. As such, the results presented below correspond simply to brute force averaging, i.e. data was taken whether the laser hit the droplet or not, but it is not unreasonable to extrapolate trends in data taken in such a fashion, so long as the data is taken under equivalent conditions.

The table below lists that average signal intensities collected for two data sets corresponding to edge illumination of 0.5 M ammonium sulfate droplets of various sizes using two different illumination intensities.

	Droplet Dia. (μm)	Signal Intensity (Arb. Units)
0.5M Ammonium Sulfate	324	3796 ± 1596
7.3 mJ/pulse, 532 nm	272	4115 ± 2423
250 shots/data set	239	3490 ± 1586
0.5M Ammonium Sulfate	301	4790 ± 2478
5 mJ/pulse, 532 nm	272	4881 ± 2934
150 shots/data set	239	4353 ± 2106

The results show that MDSRS signal size is independent of droplet size, within the signal-to-noise variation. It is interesting to note that the signals collected for the 5 mJ/pulse experiment are larger than those for the 7 mJ/pulse experiment. This anti-intuitive result stems from the fact that there is less second order MDSRS signal generated (hence less depletion of the first order signal which was measured) at the lower laser power.

Although we have been unable to quantify the relation between MDSRS signal size and sulfate anion concentration, we have shown that it is possible to detect sulfate at concentrations lower than previously reported by our group and the Chang group.¹ Figures 2, 3, and 4 show MDSRS spectra collected for 0.2, 0.15 and 0.1 M sulfate droplets. The experimental parameters associated with the data collection are listed on the spectra. The 0.1 M MDSRS signal is quite small, anomalous if one compares it with the signals generated for 0.2 and 0.15 M sulfate droplets. But the data shows that the spectrometer filters were set incorrectly that day as evidenced by the large residual green scatter signal which appears at wavelengths shorter than ~ 555 nm. An improper setting of the filters will reduce the signal intensity at higher wavelengths. Unfortunately the person performing the experiment did not realize the error in his ways.

The spectra presented in Figures 2 to 4 are the first reported MDSRS spectra of sulfate at these concentrations. Previous studies showed that MDSRS could be generated in droplets containing sulfate at concentrations down to 0.4 M, but not lower than this, and it was concluded that once the sulfate mode SRS intensity dropped lower than the water asymmetric mode SRS intensity then the water SRS would dominate over all other possible nonlinear processes.¹ (This phenomenon does occur if one does stimulated Raman scattering using a linear sample). The results from our laboratory show that this conclusion is incorrect and suggest that the phenomenological principles developed for linear SRS do not necessarily apply to droplet MDSRS.

The difficulty with the laser trigger/data collection timing system started when we changed the Nd:YAG laser on the experiment. The previous laser had a simpler set of

FIGURE 2

Wavelength

FIGURE 3

Wavelength

FIGURE 4

commands associated with it, hence it was possible to build a trigger circuit with the technical resources available at the University of Wisconsin-Milwaukee. The circuit, however, has a more complicated series of commands associated with it, a problem for those who are electronically challenged, but a benefit for those doing nonlinear laser experiments for the laser's pulse-to-pulse stability specifications are excellent - $\pm 1.5\%$. (This is an important factor in experiment design for the MDSRS signal is proportional to $\exp I_{\text{laser}}$. A new circuit for the 0.15 cm^{-1} linewidth laser was designed at the University of Wisconsin-Milwaukee, but the electronic components used in the construction were not appropriate for what was required. The end result was that the laser was not triggered properly. Several adaptations were made over the space of several months, but we were unable to get the triggering circuit to work as it should have. This problem has been overcome by moving to the University of Pittsburgh for the technical resources to solve the problem are here and a better and more reliable circuit has been designed and is currently being constructed. We will therefore be able to continue with our gain equation studies.

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.

In preparation for the gas-aerosol kinetics studies we have spent time calibrating the CARS apparatus we have constructed, determining absolute sensitivity levels, and optimizing the apparatus so that triatomics and polyatomics can be detected with ease. Last year we reported sensitivity limits for detection of N_2 , O_2 , and CO_2 , three simple molecules that are amenable to CARS probing. This year we focused on detecting larger molecules, and specifically on detecting molecules containing chlorine as these molecules have not been previously detected using CARS.

We have just finished a series of CARS experiments aimed at detecting larger polyatomics, specifically the CH_xCl_y chloromethane series. We have been able to use

CARS to detect 2 fundamental modes of chloroform, specifically the ν_4 and ν_5 modes. These modes are degenerate and have e symmetry. The measured CARS spectra are shown in Figure 5, along with the corresponding detection limits. The ν_4 mode has been classified by linear Raman spectroscopy as having a moderate Raman cross section. Figure 5 shows that our CARS spectrometer can detect concentrations as low as 3 Torr with very adequate signal to noise. The ν_4 vibrational spectrum is rather broad, but we expect this, for the resolution of our CARS apparatus is only 2 cm^{-1} which is not sufficient to resolve the rotational lines for chloroform.

Our CARS sensitivity limit for the ν_5 mode is only 50 Torr. This mode has been classified as having a very large Raman cross section. A priori we expect our CARS sensitivity limits to be substantially better. But the region where we do the spectral probing is at the start of the Rhodamine 590 dye curve and so the CARS sensitivity is limited by the output intensity of the dye laser.

Using the same dye we have been able to detect the ν_6 mode of methyl chloride, CH_3Cl . This mode, like the ν_4 and ν_5 modes of chloroform is degenerate and has e symmetry. The CARS spectrum of the ν_6 mode of methyl chloride is shown in Figure 6. The Raman cross section associated with this mode has been classified as very small. Since the CARS signal scales with the square of the Raman cross section, we expect our sensitivity limit to be rather poor. This is born out by our experimental observations which show that we can only measure CARS CH_3Cl spectra at pressures greater than 200 Torr.

The CARS spectrum we measured for methylene chloride, CH_2Cl_2 is quite different from those measured for methyl chloride and chloroform. Figure 7 shows the CARS spectrum of the ν_2 mode. This mode is not degenerate and has a_1 symmetry and explains why the shape of the spectrum is quite different from that observed for the other two molecules. This mode has been classified as having a moderate Raman cross section. We can detect concentrations as low as 20 Torr with our CARS apparatus.

ν_1 mode of CHCl_3 CARS signal at 3 torr

ν_5 mode of CHCl_3 CARS signal at 50 torr

FIGURE 6

ν_2 mode of CH_2Cl_2 CARS signal at 20 torr

To summarize we have shown that it is possible to use CARS to detect polyatomic molecules with reasonable sensitivity. If we compare our results with ordinary Raman intensity measurements, which are only described in relative terms strong, moderate and weak, we see that a rule of thumb can be used to estimate CARS sensitivity limits. Specifically, strong bands can be detected at pressures much less than 3 Torr, moderate bands in the range between 3 and 50 Torr, and weak bands require concentrations in the hundreds of Torr before they can be detected.

IV. Conclusions

In the past year we have shown that increased MDSRS sensitivity is achieved by using an excitation laser source that has a narrow linewidth and we have been able to detect sulfate anion concentrations much lower than previously reported. We have shown that the linewidth of the MDSRS mode excited in a droplet is limited by the laser linewidth. This is a positive result for it eases our ability to quantify the MDSRS gain equation. This result also suggests that MDSRS signal size should be independent of droplet size, and preliminary experiments confirm this hypothesis.

Our CARS experiments show that it is possible to detect polyatomic molecules with high sensitivity and selectivity. We have measured CARS spectra for a series of chloromethane compounds and have developed a simple rule for determining CARS detection limits of polyatomics. Specifically our experiments show that modes classified by linear Raman spectroscopy as strong can be detected with CARS at pressures much less than 3 Torr. Modes classified as moderate can be detected at pressures between 3 and 50 Torr, and modes classified as weak require concentrations in the hundreds of Torr before they can be detected using CARS.

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