Application of Cars Spectroscopy To the Detection of So2

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Experiments have been performed to investigate the possibility of detecting low concentrations of SO$_2$ using CARS spectroscopy. The experiments were also aimed at high-temperature investigations both in a heated cell and in a flame. During the cell measurements it was clearly revealed that the temperature has a dramatic influence on the shape of the CARS spectra, indicating a good potential for thermometry using SO$_2$ and CARS spectroscopy.

Index Headings: CARS; Flames; Sulphur dioxide; Spectroscopy.

INTRODUCTION

During the past two decades, the energy crisis and the growing awareness of our serious environmental situation caused by air pollution have encouraged increased research in basic combustion. The aim of this research has thus been to achieve a deeper insight into the phenomena which will ultimately increase the efficiency in industrial combustion processes at the same time that the emission of air pollutants is decreased. One of the key issues in understanding these phenomena is the use of nonintrusive diagnostic techniques, e.g., those utilizing lasers which give high spatial and temporal resolution.

Since the first demonstration of the application of laser techniques to combustion diagnostics—about twenty years ago—several techniques have emerged. For comprehensive reviews see, for example, Refs. 1–3. The technique which probably has the largest potential, at least in the practical sphere of measurements, is Coherent Anti-Stokes Raman Scattering, or CARS. Thanks to pioneering work by Taran and co-workers, the technique was introduced for studies of combustion phenomena in the early seventies.$^4$,$^5$ After these first demonstrations, the technique was extended to allow it to yield both high temporal and spatial resolution measurements, through the introduction of the broad-band CARS$^6$ and the BOXCARS$^7$ techniques, respectively. During the past decade CARS has been used in numerous combustion applications, including sooty flames,$^6$ internal combustion engines,$^8$ and large-scale furnaces.$^{10,11}$ CARS has mostly been utilized for temperature measurements using the temperature dependence of the spectra. Since N$_2$ is the most abundant species in air-fed combustion, this molecule has been of specific interest for thermometry. Other diatomic molecules that may be of interest are, for example, CO, O$_2$, and H$_2$. Three-atomic molecules that might be of interest for CARS investigations in a combustion environment are H$_2$O and CO$_2$, which also have been the subject of detailed investigations (see, for example, Refs. 12 and 13).

In the present paper, results are presented of CARS investigations concerning the potential for the detection of SO$_2$ molecules, and the use of its spectral shape for thermometry. There are several reasons why nonintrusive measurements of SO$_2$ would be of major importance. First, in industrial chemical plants (for example, those producing liquid H$_2$SO$_4$), SO$_2$ is present in concentrations of up to 20%, and thus in situ measurements of temperature and/or concentration, preferably on-line, could be used for process control and steering purposes. The second reason why SO$_2$ is of interest—and it may be the more important one—is the role SO$_2$ plays as a major air pollutant. There are both direct biological effects caused by SO$_2$ and also indirect effects when SO$_2$ acts as a precursor of acidic rain by its reaction with water vapor.

The conventional technique for measurements of SO$_2$ is IR absorption, where normally a gas sample is extracted from the unknown gas mixture with the use of a probe. Other techniques for measurement of SO$_2$ based on probe sampling are conductometric and coulometric techniques. All these probe techniques have drawbacks, in so far as they are somewhat perturbing in nature, and have temporal and spatial resolution that is not always adequate. It is, in principle, possible to make an in situ absorption SO$_2$ experiment which would yield a nonperturbing measurement; however, the spatial and temporal resolution would still be low, and problems could arise in a flame environment because of spectral interferences from other flame species. Several of the problems appearing with the conventional techniques described above

References:

The third-order susceptibility can be divided into a resonant and a nonresonant part
\[ \chi = \chi_R + \chi_{NR} \]  
where the nonresonant part, \( \chi_{NR} \), arises from electronic and remote Raman transitions, and \( \chi_R \) consists of one real and one imaginary part. For a Raman transition \( j \) we have
\[ \chi_R = \chi' + i\chi'' = \frac{2\pi c^4}{\hbar\omega_0^4} N\Delta b_j \left( \frac{dr}{d\Omega} \right) \frac{\omega_j}{\omega_j^2 - (\omega_p - \omega_s)^2 - i\Gamma_\omega (\omega_p - \omega_s)} \]  
where \( N\Delta_\omega \) is the population difference between the initial and final states, \( b_j \) is the line strength factor, \( \left( \frac{dr}{d\Omega} \right) \) is the Raman cross section for the molecular species, and \( \Gamma_\omega \) is the Raman linewidth.

From Eqs. 1–3 it follows that a CARS spectrum has a dependence on the magnitude of \( \chi_R \) and \( \chi_{NR} \), resulting in different line shapes for different concentrations of the species being studied.

Prior to running a CARS experiment, it is important to get familiar with the spectroscopy of the molecule which is to be studied. \( \text{SO}_2 \) is, strictly speaking, an asymmetric top molecule with all principal moments of inertia being different, with an O-S-O angle of 119.53°, and with an O-S distance of 1.432 Å, measured by microwave investigations. However, since the two larger moments of inertia are roughly equal, the \( \text{SO}_2 \) molecule can almost be regarded as a prolate, symmetric top, which facilitates spectral identification. \( \text{SO}_2 \) has three primary vibrational-rotational bands—\( \nu_1, \nu_2 \), and \( \nu_3 \) at 1151, 518, and 1362 cm\(^{-1}\), respectively—in addition to several combination and overtone-bands. The infrared spectrum of \( \text{SO}_2 \) has been studied in several investigations (see, for example, Ref. 19). The Raman spectrum of \( \text{SO}_2 \) has previously been investigated theoretically and experimentally—among others, by Murphy and by Brooker and Eysell, who made hot-band assignment and isotopic shift mea-

**BACKGROUND**

The basic theory of CARS is based on nonlinear optics and was outlined in the mid-sixties by Maker and Therune. Here, we will give only a brief phenomenological description of the process. For a more detailed description we refer the reader to, for example, Refs. 1 and 17.

In a CARS experiment at least two laser beams are required (see Fig. 1), here denoted as the pump beam at \( \omega_p \) and the Stokes beam at \( \omega_s \), where at least one must be tunable. By choosing the frequency difference between the two laser beams \( \omega_p - \omega_s \), so that this is equal to a Raman-allowed transition, \( \omega_R \), one generates a new laser beam from the region where the two primary laser beams cross at an angle given by the phase matching condition. This new beam, the CARS beam, is generated through the third-order nonlinear susceptibility \( x^{(3)} \). In the CARS process, one photon from the pump beam and one from the Stokes beam beat a Raman-allowed vibration, i.e., \( \omega_p - \omega_s = \omega_R \). Once the vibration is excited, a second \( \omega_p \) photon is scattered off, to form a blue-shifted CARS photon at \( \omega_s = 2\omega_p - \omega_s \). The intensity \( I_{as} \) in the CARS beam is given by
\[ I_{as} = \frac{4\pi^2\omega_{as}^2}{c^2} \frac{2}{I_p I_s} \left| \chi^{(3)} \right|^2 z^2 \]  
where \( I_p \) and \( I_s \) are the laser intensities of the pump and Stokes beam, respectively, and \( z \) is the pathlength from which the CARS signal is generated.

The chemistry of the formation of sulphur oxides is fairly straightforward, and the end product is almost invariably sulphur dioxide. A comprehensive review article describing the kinetics of the combustion of sulphur compounds has been published by Cullis and Mulcahy.

Although the production of sulphur oxides by combustion cannot easily be controlled, there are several ways to decrease the emission of this pollutant—for example, by scrubbers or by the injection of pulverized limestone. In conjunction with these sulphur oxide trap-devices there seems to be a great interest in the possibility for on-line, nonintrusive measurements of \( \text{SO}_2 \), which could be achieved by CARS spectroscopy.
Measurements of SO$_2$. The Raman technique has also been used for remote detection of SO$_2$ using lidar techniques.$^{22}$ In this work we have used the strongly Raman-allowed symmetric stretch, $v_1$, at 1151 cm$^{-1}$ with a Raman cross section of 5.4 times that of N$_2$.$^{1}$

**EXPERIMENTAL SETUP**

Throughout the measurements, the planar BOXCARS technique was used and the setup can be seen in Fig. 1. A Quantaray DCR-1A Nd:YAG laser produced ~8 ns laser pulses of 200 mJ at 10 Hz in the frequency-doubled radiation at 532 nm. Of this radiation, 10% was split off and used as the pump beam, ($I_p$) in the CARS process, while the rest was used to pump a Quantaray PDL-1 dye laser. Rhodamine 6G was used to produce wavelengths around 567 nm, which then served as the Stokes beam. Since this wavelength was at the edge of the dye curve, only 6–8 mJ per pulse was obtained, which, however, was quite enough in the measurements reported here. With the use of the beamsplitter (BS), the pump beam ($I_p$) was split into two beams. The yellow beam ($I_b$) was aligned and superimposed on one of the pump beams, with the dichroic mirror (DM). All beams were then focused in a planar BOXCAR arrangement inside a heatpipe furnace or a flame with the use of an f = 500 mm lens, where the crossing-angle between the laser beams was ~2°. The heat pipe was a Leybold-Heraeus, Model RoM 5/70, capable of reaching 1800 K, and the temperature was monitored with a chromel-alumel thermocouple placed inside the heatpipe. Here a quartz cell was placed, which was used to contain different SO$_2$/N$_2$ mixtures. The quartz cell limited the temperature measurements to 1200 K, as local high-temperature zones would cause cell deformation and, thus, problems in the generation of the CARS signal. Together with the created CARS beam, all laser beams were recollimated after the heatpipe, with the use of another f = 500 mm lens. The CARS beam was spectrally isolated from the green pump beam by two dichroic mirrors and an interference filter centered at 501 nm, corresponding to a Raman shift of 1151 cm$^{-1}$. In the heatpipe measurements, a photomultiplier (EMI 9558 QA) was used, and, in order to ensure a linear detector response, neutral-density filters were used to attenuate the CARS beam. The electric signal was then fed to a BOXCAR integrator, EG&G Model 4420 equipped with two Model 4422 gated integrators. The EG&G Model 4402 signal processor performed the necessary signal averaging, and the data were stored on floppy-disks for further processing. In the flame experiments the furnace was removed and SO$_2$ was introduced in a premixed C$_2$H$_6$/O$_2$/N$_2$ flame. A broad-band Stokes laser was used to permit single-shot CARS generation. As detector, an EG&G PARC OMA III unit with a 1421 detector head was used and was placed in the exit plane of a home-made 1-m spectrograph with a dispersion of ~3 Å/mm.

**MEASUREMENTS AND RESULTS**

In the nonflame experiments, the CARS spectra were all obtained by scanning the dye-laser wavelength. The resulting linewidth, ~0.5 cm$^{-1}$, of the spectra was limited by the dye laser, $\Delta \nu \approx 0.3$ cm$^{-1}$, since an etalon was used in the Nd:YAG pump laser, thus reducing this linewidth to $\Delta \nu \approx 0.15$ cm$^{-1}$. Normally, the wavelength of the dye laser was scanned at a rate of 0.015 cm$^{-1}$/s, resulting in approximately 100 laser pulses per channel in the EG&G signal processor. A typical scan of 30 cm$^{-1}$ thus required 30 min of data acquisition.

**Room-temperature Measurements.** CARS measurements of SO$_2$ at room temperature, 300 K, posed two problems. It turned out that at this low temperature an opaque deposit was formed on the walls of the quartz cell within an hour, with the use of 200 Torr of SO$_2$. Also, optical breakdown was induced at a lower laser intensity than during the high-temperature measurements. However, a moderate temperature increase, 100 K, immediately eliminated both problems.
The CARS spectrum from 200 Torr of SO$_2$ at 300 K shows only the expected peak at 1151 cm$^{-1}$, and the signal was quite strong, clearly visible to the naked eye when scattered off a piece of white paper. A calibrated gas mixture of 0.2% SO$_2$ in nitrogen was used to estimate the detection limit. Figure 2 shows the resulting spectrum (650 Torr, 300 K). The CARS spectral shape is essentially dispersive, caused by the interference of $X_{NR}$ and $X_R$, as described above. $I_b$ and $I_p$ are defined as shown in the figure, marking the background and the peak intensities of $X_{NR}$ and $X_R$, respectively. The ratio $\sqrt{I_p/I_b}$ was measured for a number of different SO$_2$/N$_2$ mixtures on several occasions, and the results are shown in Fig. 3. As can be seen, the plot is approximately linear to 10–15% SO$_2$. Up to this level of SO$_2$ in N$_2$, the decrease in $I_b$ by the replacement of N$_2$ by SO$_2$ is insignificant. However, at higher concentrations of SO$_2$ the background level is increasingly influenced by the dilution of N$_2$, and thus the values $I_p/I_b$ are expected to change in this region, since the total pressure was kept at 650 Torr.

Measurements at Elevated Temperatures. When capturing CARS spectra of SO$_2$ at elevated temperatures, we used a quartz cell containing 200 Torr of SO$_2$. Prior to each CARS-spectra-measuring sequence, the cell was filled at 300 K and then sealed off. In Fig. 4 the SO$_2$ CARS spectra at 300, 600, 900, and 1200 K can be seen. The measurements were always performed by starting at the lower temperature, since the heatpipe cooled off very slowly. By translating the thermocouple inside the cell, we found that the temperature variation along the quartz cell in the probed area was less than 5°C. From Fig. 4 it is clear that a number of additional peaks appeared when the temperature was increased. Also, the spectral widths were broadened at higher temperatures. The temperature dependence of the peak intensity was measured on several occasions over an extended period of time. The data are summarized in Fig. 5. As can be seen, the intensity varies by about a factor of 10$^2$ from 300 K to 1000 K, which is about the same factor as was previously found by Dreier et al. in measurements on N$_2$ and O$_2$.

From Fig. 4 it is clear that the different peaks in the CARS spectra have different dependence on the temperature. In Fig. 6 three different ratios are plotted vs. the temperature. Again this is a compilation of data from a large number of different experimental runs. The ratios show strong temperature dependence, and the ratio (a) seems to be particularly sensitive to temperature changes within the temperature interval in question.

In order to understand the origin of the hot SO$_2$ CARS spectra we made preliminary attempts to identify the structures appearing at higher temperatures. In Fig. 6 the CARS spectrum at 1200 K is inserted, and the four most prominent peaks are marked with arrows. The suggested identifications are based on calculations using the expression for vibrational energy in cm$^{-1}$ given by Shelton et al.
FIG. 6. Plot of different peak ratios as a function of temperature. Inserted in the figure is a spectrum at 1200 K where the different peaks are tentatively identified and labeled.

\[
G(v_1, v_2, v_3) = (v_1 + \frac{1}{2})\omega_1 + (v_2 + \frac{1}{2})\omega_2 + (v_3 + \frac{1}{2})\omega_3 + (v_1 + \frac{1}{2})^2X_{11} + (v_2 + \frac{1}{2})^2X_{22} + (v_3 + \frac{1}{2})^2X_{33} + (v_1 + \frac{1}{2})(v_2 + \frac{1}{2})X_{12} + (v_1 + \frac{1}{2})(v_3 + \frac{1}{2})X_{13} + (v_2 + \frac{1}{2})(v_3 + \frac{1}{2})X_{23}
\]

where \(v_1, v_2, \) and \(v_3\) are the vibrational quantum numbers associated with the fundamental vibrational frequencies \(\nu_1, \nu_2, \) and \(\nu_3,\) \(\omega_1, \omega_2, \) and \(\omega_3\) are the zero-order harmonic frequencies, and \(X_{ij}\) are anharmonic and interaction terms. These constants are also taken from Ref. 19.

The locations of the band centers corresponding to different vibration modes are calculated to be

\[
\begin{align*}
G(1,0,0) - G(0,0,0) &= 1151.7 \text{ cm}^{-1} \\
G(2,0,0) - G(1,0,0) &= 1143.8 \text{ cm}^{-1} \\
G(1,1,0) - G(0,1,0) &= 1149.7 \text{ cm}^{-1} \\
G(2,1,0) - G(1,1,0) &= 1141.7 \text{ cm}^{-1}
\end{align*}
\]

etc. These locations are in good agreement with the observed structure, and we conclude that the four most prominent peaks are due to the \( (1,0,0)-(0,0,0) \) and \( (1,1,0)-(0,1,0) \) transitions, together with the connected hot-bands \( (2,0,0)-(1,0,0) \) and \( (2,1,0)-(1,1,0) \).

Since it was not possible to go to higher temperatures in the heatpipe because of cell deformations starting at 1200 K, concluding measurements were performed that aimed at recording CARS spectra from \( \text{SO}_2 \) in a flame. Because of possible corrosion problems in the burner, as well as unwanted chemical reactions, \( \text{SO}_2 \) was not introduced in the premixed burner together with the fuel and oxidant. Instead, \( \text{SO}_2 \) was introduced in the post-flame region by a copper probe, which was not nonintrusive but gave a good possibility of allowing the study of the CARS spectrum from \( \text{SO}_2 \) at flame temperatures.

In Fig. 7 the \( \text{SO}_2 \) CARS spectrum is shown as obtained when corrected for the broad-band dye laser distribution.
As can be seen, the spectrum is now considerably broader than it is in the cell experiment, extending over ~150 cm$^{-1}$. The drop in intensity around 1000 cm$^{-1}$ is caused by the limited photo-sensitive area of the diode array. The spectrum shows several bands. However, no attempts have been made to analyze their origin. The temperature in the flame was not explicitly measured, but previous CARS experiments on this burner with the same gas flows and N$_2$ as the test species have given a temperature around 2000 K. It is difficult to compare the spectrum in Fig. 7 with those in Fig. 4, since the spectral resolution is different and because the temperature and concentration of SO$_2$ are not exactly known at the measuring point. However, by looking at the spectra in Fig. 4 and the strong temperature dependence of the spectral change, one could anticipate a very broad flame spectrum.

Since the SO$_2$ was introduced in the post-flame region and since the conversion into other sulphur-containing molecules is expected to be rather weak$^{24}$, one should not normally expect any spectral interference from these species. The species that might interfere is SO, which has a Raman shift interfering with that from SO$_2$ (SO, 1150 cm$^{-1}$; SO$_2$, 1151 cm$^{-1}$)$^{11}$. However, even under extreme conditions SO has a concentration about an order of magnitude lower than SO$_2$,$^{24}$ which, with the quadratic concentration dependence on the CARS signal, would strongly reduce interference even from SO.

**DISCUSSION AND CONCLUSIONS**

As has been demonstrated in this paper, CARS spectroscopy has a considerable potential for the detection of low concentrations of SO$_2$. In addition, the possibilities of using this species for temperature measurements also seem attractive. According to Fig. 4, the spectral changes from room temperature to 1200 K are considerable. This result should be compared to the temperature dependence of the N$_2$ CARS spectra, where the intensity of the hot-band transition, $v = 1 -> v = 2$, is barely seen below 1000 K ($<5\%$ of the fundamental band $v = 0 -> v = 1$). The temperature change in this case is, rather, seen as a broadening of the fundamental band, due to the increased population of higher rotational levels.

In this study the temperature dependence of the SO$_2$ CARS spectra was examined with no background, $x_{NR}$. However, in a measuring situation of an unknown composition the nonresonant background may change the calibration curves shown in Fig. 6. Clearly in this situation there might be a need for a model generating theoretical CARS spectra of SO$_2$ with $x_{NR}$ and $T$ as parameters, as in the case of most diatomic and some polyatomic molecules. To our knowledge no such model has been presented for SO$_2$. In addition to the problem that SO$_2$ is actually an asymmetric molecule, problems would arise due to lack of fundamental data, for example, for Raman linewidths. An alternative to this procedure could be to extend the measurement presented in this study to also include measurements at varying temperatures and concentrations, and in this way to build up a library of CARS spectra which could be of use in a real measurement situation. A third method, and probably the best one, is to use an experimental approach where the nonresonant background is rejected by using different polarization orientations of the laser beams in combination with a polarizer in the CARS beam.$^{25}$

Concerning the high-temperature measurements of SO$_2$, it is worth mentioning the quite drastic spectral changes at elevated temperatures, which have previously been seen both in the UV region (see, for example, Ref. 26) and in the infrared$^{27}$ and which are suggested to be the reversible formation of an isomer.$^{28}$ The structure of this isomer is not known exactly, but it has been suggested that the bond angle is more acute than it is in normal SO, and that the bond lengths are longer.$^{29}$ As was pointed out in Ref. 15, the question of an isomer is not only an academic one, since this factor would strongly influence the equilibrium composition of flame gases containing sulfur. Although there has been strong indication of the formation of an isomer of SO$_2$ at high temperature, other explanations for the spectral behavior at higher temperatures have also been put forward.$^{30}$ In our study we have not tried to contribute to this discussion, since our temperature range was limited to very hot gases ($\sim$2000 K) and gases with relatively low temperature ($<1200$ K).

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A Monte Carlo Study of the Effect of Noise on Wavelength Selection During Computerized Wavelength Searches

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The process of selecting wavelengths for performing quantitative analysis in the near-infrared is notorious for its instability. A Monte Carlo technique was used to investigate the sensitivity of the wavelength selection process to the noise content of the spectra. The random nature of the noise causes the wavelengths to be selected at random; this seems to be sufficient to explain the instability of the selection process. The statistics of the selection process are insensitive to error in the dependent variable, and, within limits, also insensitive to the amount of noise in the spectral data. The statistics are sensitive to the number of samples in the data set and to the nature of the distribution of the noise.

Index Headings: Computer applications; Reflectance spectroscopy; NIR analysis; Chemometrics; Calibration techniques.

INTRODUCTION

It has been many years since the initial development of the spectroscopic technique now called Near Infrared Reflectance Analysis (NIRA).1 In all that time, one of the most intractable problems in the use of this analytical technology has revolved around the question of developing a methodology for selecting the wavelengths to use for a given analysis.

In practice, many empirical methods have been developed for selecting the analytical wavelengths (see the discussion in Ref. 2 for an excellent review of the techniques currently in use). However, most of these methods are subject to a certain difficulty. This difficulty arises because an automatic computerized wavelength selection technique is almost invariably included in the method development process.

There are a number of excellent reasons for this, among them the fact that many of the analyses of interest are for powdered solid materials. Data from such specimens show an offset which is systematic across the wavelengths but random in direction and magnitude from pack to pack. Clearly, a measurement at some wavelength is needed to account for this extraneous variation of the spectral data, but just as clearly, “particle size effect” does not have a characteristic absorbance band, such as chemical constituents possess. Furthermore, many of the constituents in natural products, where this technology has its most widespread use, have at least some absorbance at virtually every wavelength in the near-infrared region. In many cases the desired analysis is for some characteristic of the sample defined by the process, such as “baking quality,” where the chemistry and spectroscopy of the analysis are ill-defined or unknown.

For all these reasons, automatic wavelength searches are used. One chooses the “best” wavelength so as to optimize the calibration by finding the wavelengths where one of the calibration statistics shows the calibration to be best. This optimum value could be either a maximum or a minimum value, depending upon the statistic used: if correlation coefficient, for example, is the chosen statistic, it would be maximized, while if Standard Error of Estimate (SEE) is the test statistic, it would be minimized.

The difficulty that arises when automatic wavelength selection methods are used is that, when such an experiment is done more than once (i.e., with a set of data from similar but not identical samples), the wavelengths that are chosen are rarely the same in the different experiments. Furthermore, the interactive nature of the data at different wavelengths in the NIR spectra causes large shifts in all the wavelengths that are chosen by such searches.

Currently there is a trend toward use of calibration methods, such as Principal Component Analysis (PCA) and Partial Least-Squares (PLS), that do not require wavelength selection because data at all available wavelengths are used. However, this is not a complete solution to the problem either. Not only are there already a large number of excellent reasons for this, among them the fact that many of the analyses of interest are for powdered solid materials.