Development of CARS spectroscopy
for the studies of transient molecules

Wong Ling Keong, Li Peng and Fan Wai Yip

Abstract

Collinear CARS (Coherent Anti-Stokes Raman Scattering) Spectroscopy experimental system was developed for the detection of gaseous stable and transient molecules. Gaseous molecules such as ammonia and chloroform were first used for optimization of the system. The 266 nm pulsed laser photodissociation of cyanogen isothiocyanate, NCNCS in a static cell was investigated leading to the first detection of the gas phase Raman spectra of NCNCS and its photolysis product, isocyanogen, CNCN. We are also making attempts to synthesize other important transient species that possess intense Raman signals for the vibrational modes.

Introduction

The study of free radicals and transient molecules is important and difficult since most of them exist only as short-lived intermediates in many chemical reactions. The identification and characterization of these intermediates are crucial for the understanding of reactions mechanism and modeling purposes. Raman spectroscopy serves as a complimentary technique to IR spectroscopy in characterizing vibrational spectral features of molecules. Conventional gas phase Raman spectroscopy has not been performed extensively due to very weak signals. However, with CARS (Coherent Anti-Stokes Raman Scattering) spectroscopy, which is one of the most sensitive Raman techniques, it is possible to study these gas phase species more extensively. Important transient species such as CH₃ and CF₃, which could be generated efficiently by laser flash photolysis, have been detected by the CARS method.

Two laser beams of different energies are used for the CARS method, where the frequency of CARS signal is given by the following:

$$2w_1 - w_2 = w_3$$

Where $$w_3$$ is CARS signal, $$w_1$$ is of fixed energy and $$w_2$$ is of tunable energy, $$w_1 > w_2$$
The molecules at the ground state energy a are excited to a virtual state c by the laser 1. The molecules are then stimulated back to a vibrationally excited state b by the laser 2. These vibrationally excited molecules are actually pumped again by laser 1 to another virtual state d since both lasers 1 and 2 overlap spatially and temporally. The CARS signal denoted by 3 would be seen when the excited molecules relax back to the ground state, a from d. Usually, the CARS wavelength falls within the blue region of the electromagnetic spectrum. The difference between the frequencies, w\(_1\) and w\(_2\) gives the vibrational band of the molecule. (Fig.1)

**Experimental**

The experimental setup for the CARS experiment is shown in Figure 2. A frequency-doubled YAG laser beam at 532nm was used. The beam was split by a beamsplitter in a ratio of 80:20 in which the main part of the beam was used to pump a dye laser to provide w\(_2\) and the other beam was used as the Raman pump beam, w\(_1\). The frequency of the dye laser is tunable, depending on the type of dye used. The two beams were then focused and combined collinearly with a dichroic mirror before entering the sample cell. If the CARS signal were generated, a third beam, w\(_3\) will be produced after the sample cell. Suitable optics were assembled before the photomultiplier to allow only the CARS beam, w\(_3\) to reach the photomultiplier tube (PMT) while at the same time, rejecting w\(_1\) and w\(_2\). A boxcar integrator was used to collect the signal from the PMT.
before being digitized and displayed on a computer. For preliminary testing, stable gaseous molecules such as ammonia and chloroform in a static cell were used to optimize the system before the detection of transient molecules was attempted. AgNCS was used as a precursor for the production of NCNCS. The compound was heated to about 300°C and precautions were being made to remove impurities and side products such as CS₂ and CO₂. NCNCS was collected in a glass cell and identified using FTIR spectroscopy. NCNCS was then photolysed for 10 minutes, using a 266nm laser beam, to produce CNCN transient molecules. The CARS spectra of both NCNCS and CNCN were then detected.

**Results and Discussions**

A reasonably large CARS signal was observed for the ammonia N-H stretching at 3337 cm⁻¹ (Fig.3). In fact the overtone of the N-H bend was also observed around 3330 cm⁻¹. CARS signal was also observed for the C-H stretch of chloroform vapour as well. These observations indicated that CARS spectrum due to transient species may be detectable and indeed, the Raman-active CN stretches were observed for NCNCS and its transient molecules NCNC (Fig 5) at 2267 cm⁻¹ and 2309 cm⁻¹ respectively. These marks the first time the Raman spectra of both molecules have been observed. The CNCN spectrum was much weaker as it has a shorter lifetime about 30 minutes and is a product of the 266 nm photodissociation of NCNCS to form NCNC and S (³P)

![CARS spectrum of ammonia gas](image)

**Fig. 3. CARS SPECTRUM OF N-H TRETCHING OF AMMONIA GAS AT 50 TORR**

![CARS Spectrum of NCNCS at 2261 cm⁻¹ recorded.](image)

**FIG. 4. The CARS spectrum of NCNCS at 2261 cm⁻¹ recorded. The CARS spectra of atmospheric nitrogen (2330 cm⁻¹) as well as the HCN impurity (2100 cm⁻¹) were recorded during the same scan.**

![CARS Spectrum of CNCN gas at 2 Torr recorded.](image)

**Fig. 5. CARS Spectrum of C-N Stretching OF NCNC gas at 2 Torr recorded. (CNCN 2309 cm⁻¹)**
**Current work**

Determination of transient and stable molecules that show strong Raman signals, were carried out using computational methods such as MP2/6-311+G** in Gaussian 98. Table 1 shows the calculation of active Raman peaks of NCNCSe, HNO, ketenimine, CH₂CNH and HCOBr. We designed the synthesis of HNO by carrying out the photodissociation of HBr using 266 nm laser in the presence of NO. However, instead of HNO that was being produced, another transient molecule, NOBr, was detected. IR spectrum of the product showed a peak at 1799 cm⁻¹ that could be assigned to the NO stretch of NOBr. Computational calculations were carried out but unfortunately this particular vibration only has a very weak Raman signal. (Table 1)

<table>
<thead>
<tr>
<th>Type of Molecule</th>
<th>Ketenimine</th>
<th>HCOBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequencies (cm⁻¹)</td>
<td>3359</td>
<td>3453</td>
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<tr>
<td>Raman active</td>
<td>120.35</td>
<td>76.84</td>
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<tr>
<td>IR intensity</td>
<td>7.73</td>
<td>0.20</td>
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<tr>
<td>Type of vibrations</td>
<td>Unsym CH stretching</td>
<td>Sym CH stretching</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Type of Molecule</th>
<th>NCNCSe</th>
<th>NOBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequencies (cm⁻¹)</td>
<td>2196</td>
<td>2378</td>
</tr>
<tr>
<td>Raman active</td>
<td>136.43</td>
<td>992.89</td>
</tr>
<tr>
<td>IR intensity</td>
<td>2760.35</td>
<td>1132.35</td>
</tr>
<tr>
<td>Type of vibrations</td>
<td>CN stretching</td>
<td>CN stretching</td>
</tr>
</tbody>
</table>

Table 1- any peak that shows >50 in Raman active section is considered strong.

NCNCSe was calculated to have strong CN stretch Raman signals and the production of it in a similar manner to NCNCS, is still being carried out at this moment. Excess amount of KNCSe was used to produce AgNCSe precipitate for the purpose of conducting thermal pyrolysis on the silver compound to produce NCNCSe. As there was no IR spectrum available, the identification of the pyrolysis product could not be determined. One way that could be employed to justify that NCNCSe is being produced is by photolysing the product under 266 nm laser. It is assumed that the photoproducts should also be CNCN as in the NCNCS case.

**Reference**