

# Red Shift of the Raman (FBCARS) Excitation Profile of Iodine from the Absorption Spectrum(I)

Mu Sang Lee

Department of Chemistry, Teacher's College, Kyungpook National University, Taegu 635

L.A. Carreira

Department of Chemistry, University of Georgia, Athens, Georgia 30602, U.S.A.

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Folded Box coherent anti-Stokes Raman spectroscopy (FBCARS) spectra of the fundamental symmetric stretch(213 cm<sup>-1</sup>) and the first overtone(421 cm<sup>-1</sup>) of I<sub>2</sub> have been recorded over the pump wavelength range from 495 nm to 580 nm. The lineshapes were fitted using the least squares method and the A and C term of CARS were calculated. From the fitting of A and C terms, the real(R) and imaginary(I) term intensity of CARS were calculated using harmonic oscillator program. The calculated CARS excitation profile of I<sub>2</sub> with R and I term data was about 270 cm<sup>-1</sup> red shifted from the absorption spectrum.

## Introduction

The properties of excited molecular states can be obtained from the analysis of the absorption spectrum and Raman excitation profile. As a tool for interpreting the complex absorption spectra, comparisons are made between the absorption spectrum and the intensity of a given Raman mode versus the excitation frequency (excitation profile), and in some cases the agreement between the two is good.<sup>1,3</sup> On the other hand, some complex systems reveal that the peak of the excitation profile is red shifted from the absorption maximum.<sup>4,6</sup> These include studies of I<sub>2</sub><sup>5,8</sup>, Br<sub>2</sub>, and tetracyanoethylene charge transfer complexes.<sup>7</sup>

In this work we have studied the red shift of CARS excitation profile of I<sub>2</sub> from the absorption spectrum. FBCARS data and harmonic oscillator wavefunctions were used to calculate the excitation profile.

## Experimental

Iodine and cyclohexane were purchased from E. Merck and used without further purification. The spectra reported here were obtained at an Iodine concentration of 5 × 10<sup>-3</sup> M for the fundamental band and 10<sup>-2</sup>M for the first overtone band in cyclohexane, respectively. The absorption spectrum was measured with a GCA-Mcpherson scanning UV-Visible spectrometer (EU-700 series).

A diagram of the optical and electronic arrangement of FBCARS used in this experiment appears in Figure 1. In FBCARS ω<sub>1</sub> (pump beam) is split into two components and focussed onto the sample in a plane perpendicular to the optical table with an intersection angle of 2θ<sub>1</sub>. The probe beam, ω<sub>2</sub>, in a plane perpendicular to the ω<sub>1</sub> plane is focussed onto the sample at an angle θ<sub>2</sub> to the plane, producing a CARS signal ω<sub>3</sub> at the opposite side of ω<sub>2</sub> beam but in the same plane.<sup>9</sup> The major modification in FBCARS is the incorporation of a 25mm pellicle beam splitter in front of ω<sub>1</sub> of the CARS system.<sup>9,10</sup> The beam from a Moletron corporation UV-1000 pulsed nitrogen laser is split into two beams by a 2:1 beam splitter. These beams are used to pump two DL 200 dye laser; ω<sub>1</sub> (pump) and ω<sub>2</sub>(probe). While ω<sub>1</sub> is fixed, the ω<sub>2</sub> dye laser beams equipped with a stepping motor drive for continuous

scanning. The ω<sub>1</sub> and ω<sub>2</sub> beams are focussed on the sample and the FBCARS signal is isolated spatially, filtered with a JY DH-20S 1200 UV monochromator, and focussed on a RCA C31034 photomultiplier tube. The output is averaged using a BOXCAR averager (EG and G Princeton Applied Research model 162). The results (ω<sub>3</sub> intensity/reference intensity) are sent to an analog to digital converter where it is stored and processed by a PDP-11/34 digital computer.

## Results and Discussion

In order to study the lineshapes, the FBCARS spectra of the fundamental symmetric stretch (213 cm<sup>-1</sup>) and the first overtone (421 cm<sup>-1</sup>) of I<sub>2</sub> have been recorded. As can be seen in Figure 2, the spectra show a clear change from positive through dispersive to negative lineshapes for the fundamental. The spectra of the fundamental and first overtone were recorded and recorded spectra were fitted using the least squares method. These spectra are shown in Figure 2 and Figure 3. In order to understand the lineshapes one must obtain an expression for the third order susceptibility χ<sup>(3)</sup>. The χ<sup>(3)</sup> can be written as follows.<sup>10,11,12</sup>

$$|\chi^{(3)}|^2 = B + \frac{R + iI}{\delta r + iI r} \quad (1)$$

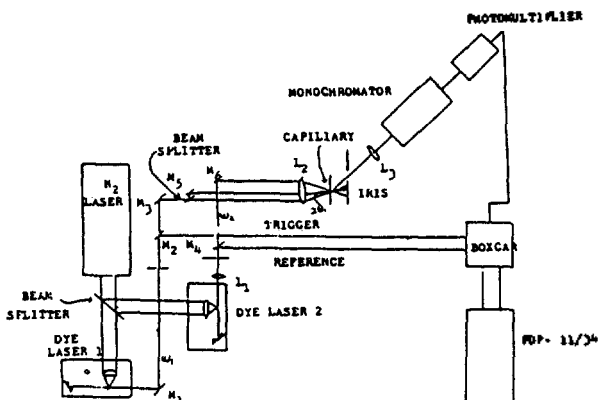


Figure 1. Folded BOXCARS (FBCARS) experimental set up. L1 - L3 are lenses, M1 - M7 are mirrors.

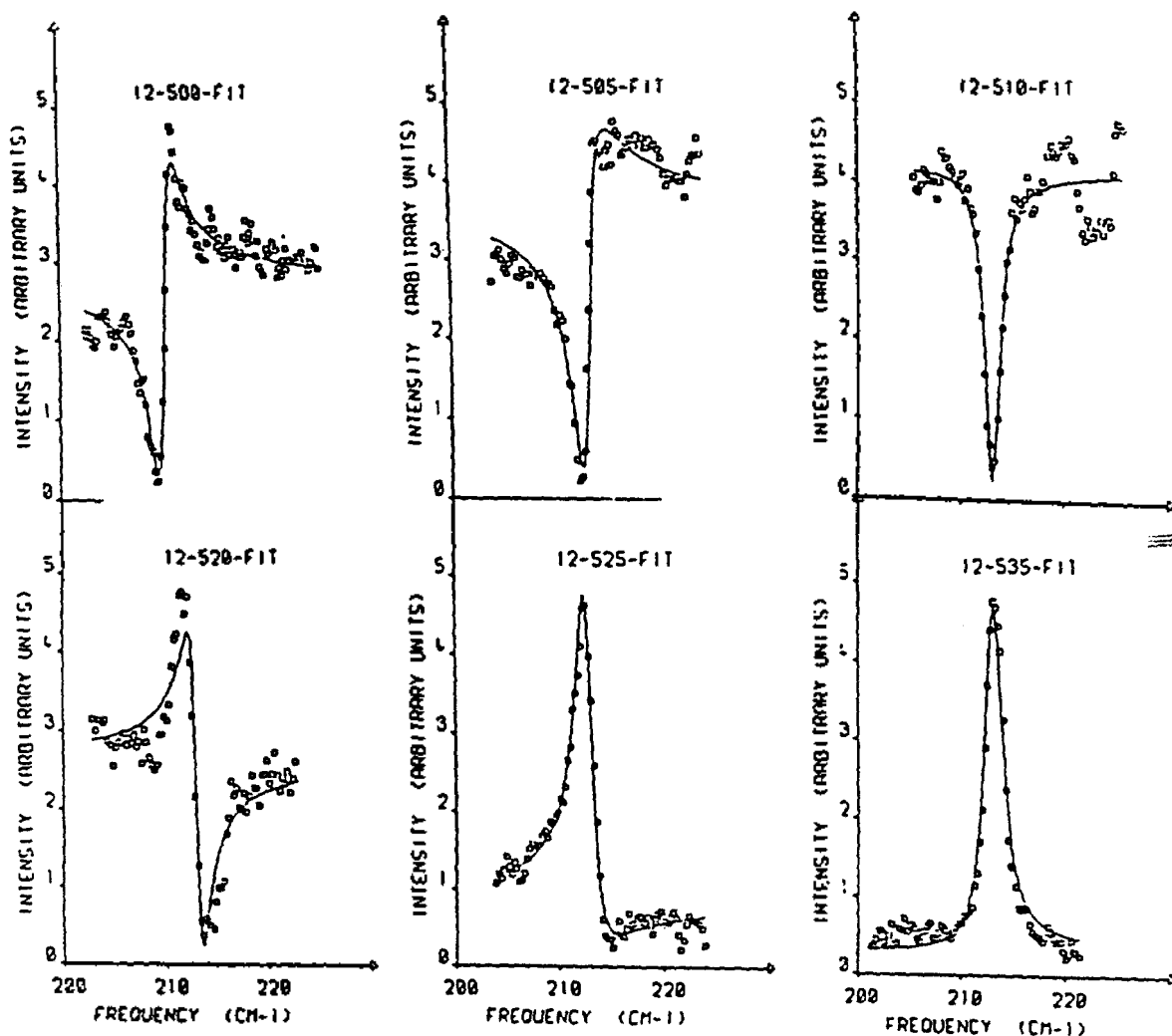


Figure 2. Original and fitted FBCARS spectra for the fundamental peak of  $I_2$ . Original data (square) and fitted (solid line) for the fundamental symmetric stretch of  $I_2$ . The pump frequencies are indicated above each spectrum (500 → 535 nm).

Table 1.  $I_2$  Parameters Extracted from Harmonic Oscillator fit.

0 - 0 transitions	541.6 nm
Electronic halfwidth	1628.6 $\text{cm}^{-1}$
Displacement parameter*	2.5
Ground state frequency (wavenumber)	213 $\text{cm}^{-1}$
Excited state frequency (wavenumber)	126 $\text{cm}^{-1}$
Raman halfwidth	1.07 $\text{cm}^{-1}$

\*Displacement(separation) parameter; displacement along the dimensionless coordinate between the ground and excited state potential functions.<sup>11</sup>

where  $\delta_r = \omega_r - (\omega_1 - \omega_2)$ , and  $\omega_r$  is a Raman allowed frequency of halfwidth  $\Gamma_r$ .  $B$  is the background(solvent) susceptibility,  $R$  and  $I$  are the real and imaginary part of the Raman susceptibility, respectively. The observed CARS intensity is proportional to the calculated value<sup>11</sup> of  $|\chi^{(3)}|^2$

$$|\chi^{(3)}|^2 = B^2 + \frac{R^2 + I^2}{\delta r^2 + \Gamma_r^2} + \frac{2BR\delta r}{\delta r^2 + \Gamma_r^2} - \frac{2BI\Gamma_r}{\delta r^2 + \Gamma_r^2} \quad (2)$$

The second term scales as the square of the solute concentration (positively shaped Lorentzian centered at  $\delta_r = 0$ ). The third and fourth terms are solute-solvent cross terms and scale

linearly with solute concentration. Both are centered at  $\delta_r = 0$  and the former(third) has a dispersive shape while the latter(fourth) is Lorentzian. These  $R$  and  $I$  components, expressed as functions of pump wavelength,<sup>13</sup> are calculated and fitted with experimental results using a harmonic oscillator program<sup>11</sup> to extract molecular parameters. In order to fit the experimental results, equation (2) is written as<sup>13</sup>:

$$|\chi^{(3)}|^2 = B^2 \left[ 1 + \frac{A}{\delta r^2 + \Gamma_r^2} + \frac{C\delta r}{\delta r^2 + \Gamma_r^2} \right]$$

$$\text{where } A = \frac{R^2}{B^2} + \frac{I^2}{B^2} - \frac{2\Gamma_r}{B}, C = \frac{2R}{B}$$

From the lineshape fitting of Figure 2 and Figure 3,  $A$  and  $C$  terms of experimental CARS intensities were extracted. These  $A$  and  $C$  terms of both the fundamental and first overtone were fitted in Figure 2 and Figure 3 using the harmonic oscillator program,<sup>11</sup> then  $R$  and  $I$  values obtained and molecular parameters extracted from these fits (Figure 4a - Figure 5b). The parameters obtained from these fits are listed in Table 1.

From Figure 4a and Figure 4b, one can see the fits are reasonably good for the fundamental. On the other hand, shown in Figure 5a and Figure 5b the fits are shifted about 10 nm from the experimentally extracted curves for the ov

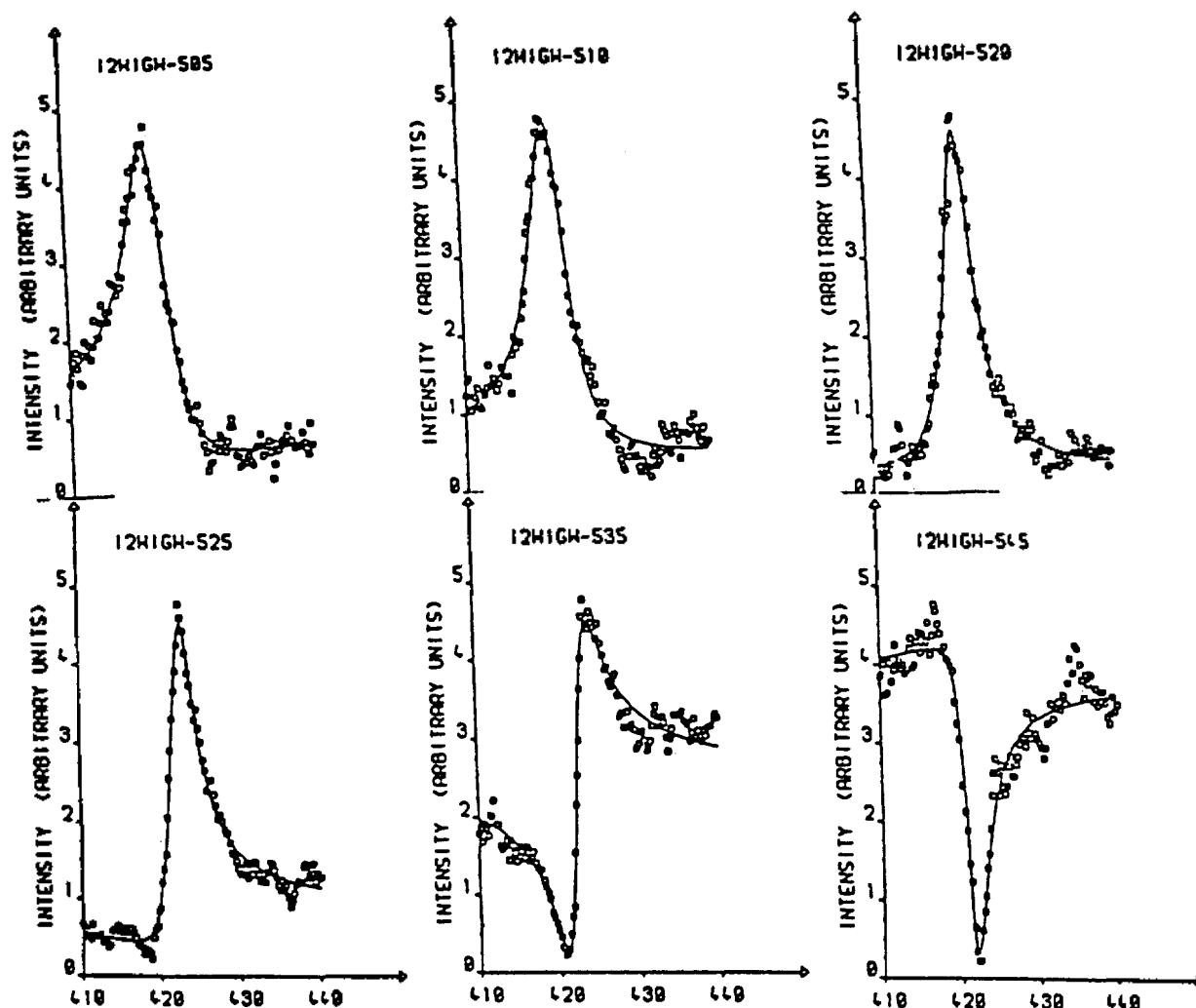


Figure 3. Original and fitted FBCARS spectra for the 1st overtone peak of I<sub>2</sub>. Original data(square) and fitted(solid line) for the 1st overtone of I<sub>2</sub>. The pump frequencies are indicated above each spectrum. (505 → 545 nm).

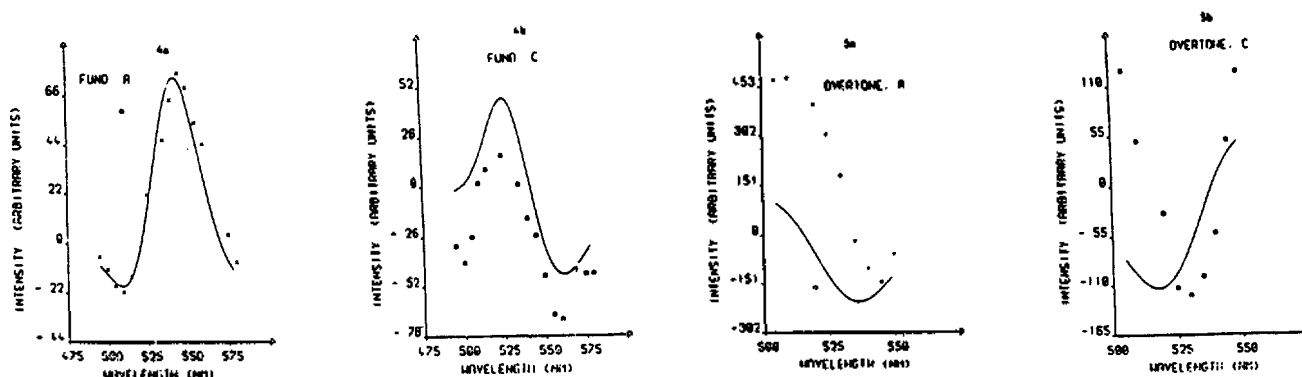
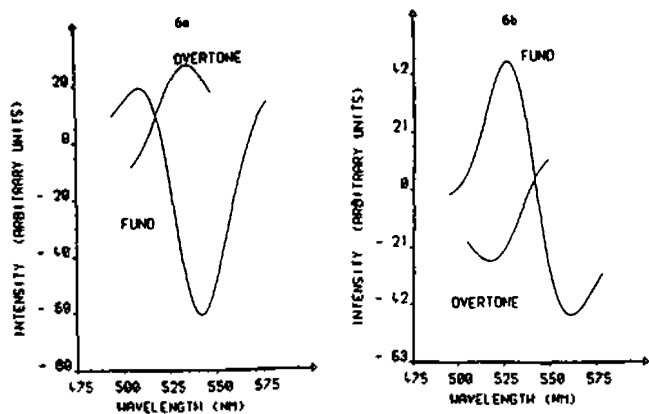


Figure 4. 4a; Observed(cross) and calculated(solid line) A terms of the fundamental symmetric stretch of I<sub>2</sub>. 4b; Observed (square) and calculated(solid line) C terms of the fundamental symmetric stretch of I<sub>2</sub>.

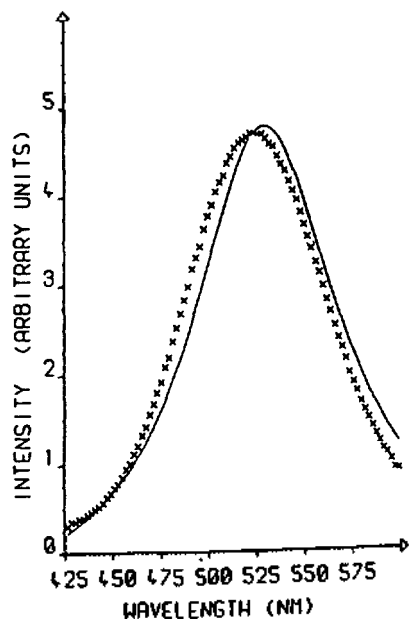
Figure 5. 5a; Observed(cross) and calculated(solid line) A term of the first overtone of I<sub>2</sub>. 5b; Observed(square) and calculated(solid line) C term of the first overtone of I<sub>2</sub>.

tone. The major part of these shifts may be due to the formation of very weak charge transfer complex (cyclohexane → iodine). From the lineshape fitting results, we can generate real(R) and imaginary(I) intensity terms for the fundamental and the first overtone bands. These results are shown in

Figure 6a and Figure 6b. The CARS(FBCARS) excitation profile was calculated by harmonic oscillator program<sup>14</sup> with R and I components and this was found red shifted by 270 cm<sup>-1</sup> from the absorption spectrum as shown in Figure 7. This calculated shift is in good agreement with others,<sup>4,5,8,15</sup> but



**Figure 6.** 6a; The extracted real components for the fundamental and overtone transitions in  $I_2$  using harmonic oscillator fitting data. 6b; The extracted imaginary component for the fundamental and overtone transitions in  $I_2$  using harmonic oscillator fitting data.



**Figure 7.** The absorption spectrum (cross) of  $I_2$  in cyclohexane and calculated (solid line) CARS excitation profile.

the amount of shift is still smaller than the experimental results.<sup>4,6,15</sup> This difference in shift is due to the results of harmonic oscillator calculations in Figure 4a through Figure 5b. Harmonic oscillator calculations are work well for the molecules which have high dissociation energies (potential well

is deep),<sup>1,14</sup> but one must be careful for the molecules which have low dissociation energies (potential well is shallow) like iodine. For iodine, the ground electronic potential well depth is about  $12,000 \text{ cm}^{-1}$  and that of the excited state is about  $4,300 \text{ cm}^{-1}$ .<sup>16</sup>

Morse wavefunction calculation for the iodine will be reported in next paper.

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