Coherent 2D Resonance Raman Spectroscopy Simulation for C_2

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Coherent 2D resonance Raman spectroscopy is a method used to distinguish the vibrational-rotational peaks that are usually congested in 1D spectroscopy. Here we simulate the transitions for C_2 in the Swan band and generate the wavelengths in the range $500 \le \lambda_3 \le 515$ (nm) and $458 \le \lambda_3 \le 475$ (nm).

I. INTRODUCTION

Coherent 2D resonance Raman spectroscopy (C2DRRS) is a technique that allows the separation of rotational-vibrational peaks to curves according to vibrational sequence, rotational quantum number, and selection rules. This is a great advantage over 1D spectroscopy, since the electronic spectra of gaseous molecules turn out to be very congested with overlapping energy transitions. This is a result of the large number of transitions that exist between different rotational-vibrational energy levels. Also, even where one can resolve the necessary peaks, it is very difficult to assign them transitions. Hence, by using 2D spectroscopy overcomes many of these problems due to its capabilities of distinguishing between transitions.

In this paper, we will explain the theory behind 2D resonance Raman spectroscopy and display the results of simulations that were done for C_2 in the Swan band. We will derive the necessary formulae for the energies of transitions from the individual energies of the levels of transitions. Since we are interested in the transitions between states $d^3\Pi_g$ and $a^3\Pi_u$, the necessary constants were taken from the NIST chemistry database.

II. THEORY

In C2DRRS, we investigate transitions between states $d^3\Pi_g$ and $a^3\Pi_u$. In Figure 1, the energy levels can be seen, where level c is a virtual level and the 3rd arrow is the narrowband light, while the others are for the broadband lights. Level b represents a rotational-vibrational level in the lower electronic state, whereas d is a rotational-vibrational level in a higher electronic state.

The energies of these states are given by

$$E = T_e + G(v) + F(J)$$

where

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e (v + 1/2)^2 + ...$$
$$F(J) = B_v J(J + 1) - D_v J^2 (J + 1)^2 + ...$$
$$B_v = B_e - \alpha_e (v + 1/2) + ...$$
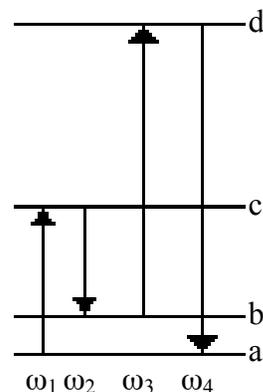
Figure 1. Energy transitions in C2DRRS. Level c is a virtual energy level.

The selection rules are that $\Delta J = 0, \pm 2$ for rotations and $\Delta v = \pm 1$ between vibrations in the same

electronic state. These selection rules arise from the rigid rotor and harmonic oscillator models. Hence if we ignore the D term in $F(J)$ –as it is very small compared to the B term - the energy difference between two levels becomes

$$\Delta E = T_e' - T_e'' + \omega_e'(v'+1/2) - \omega_e x_e'(v'+1/2)^2$$
$$- \omega_e''(v''+1/2) + \omega_e x_e''(v''+1/2)^2$$
$$+ (B_e' - \alpha_e'(v'+1/2))J'(J'+1)$$
$$- (B_e'' - \alpha_e''(v''+1/2))J''(J''+1)$$

The difficult part of preparing the simulations was figuring out between which energy levels the transitions are occurring. The notation used in the paper written by Chen et al.[1] was, at first look, quite difficult to decipher. However, through correspondence with Professor Peter C. Chen, certain details were illuminated enough for a physicist to understand chemists' notation.

In Table 1, the basic derivations of the ω_3 and ω_4 rotational components of the energies can be seen. The important fact to know about the derivations is the rotational quantum number J is taken as the ground state (level a in Figure 1) rotational quantum number and all other levels are marked with rotational quantum numbers according to the selection rules. For example, in the case of $\Delta J = -2$, we have for the ω_3 transition: level a is J, level d is J - 1 and level b is $J - 2$ (Figure 2)[2]. This information is listed in Table 1 for all types of transitions.

The J numbers alone are capable of giving us the wide parabolas that are associated with the $\Delta J = \pm 2$ transitions and will give us straight lines forthe $\Delta J = 0$ transitions. This is a good first approximation. However to observe the actual shapes of the narrow parabolas, one needs to figure out between which vibrational levels these transitions are occurring, too. For the Swan band we picked the $v = 0'' \rightarrow 1'' \rightarrow 1' \rightarrow 0''$ transition. This notation denotes a transition from level a to b to d and back down to a. This is skipping the transition between a and c, and c and b. Hence,

for all ω_3 components we have $v'=1, v''=1$ and for all ω_4 components, $v'=1, v''=0$.

Figure 2. The rotational quantum numbers of the energy levels of the transition $\Delta J = -2$.

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Once all the quantum numbers are determined, using the constants given in the NIST Chemistry Database, we can plot the ω_3 values against ω_4. All these values are in cm^{-1}s, which chemists use as an energy unit. This is simply the reciprocal of the wavelength that is measured. Hence by taking the

reciprocal of our final calculated values, we can get the wavelengths and plot λ_3 versus λ_4.

$\Delta J = -2$	$a = J$	$\omega_3 = F'(J-1) - F''(J-2)$
	$d = J-1$	$\omega_4 = F'(J-1) - F''(J)$
	$b = J-2$	
$\Delta J = 0$	$a = J$	$\omega_3 = F'(J+1) - F''(J)$
(R R)	$d = J-1$	$\omega_4 = \omega_3$
	$b = J$	
$\Delta J = 0$	$a = J$	$\omega_3 = F'(J-1) - F''(J)$
(P P)	$d = J+1$	$\omega_4 = \omega_3$
	$b = J$	
$\Delta J = +2$	$a = J$	$\omega_3 = F'(J+1) - F''(J+2)$
	$d = J+1$	$\omega_4 = F'(J+1) - F''(J)$
	$b = J+2$	

Table 1. Column 1: Transition rotational selection rules. Column 2: Rotational quantum number assigned to the energy levels a, d and b from Figure 1. Column 3: The rotational energy components for ω_3 and ω_4 transitions.

III. SIMULATIONS

Figure 3 (a) and (b) show the results of the simulation for the Swan band of C_2. Two separate parabolas are observed. The wide parabola belongs to the $\Delta J = \pm 2$ transitions, whereas the narrow parabola belongs to the $\Delta J = 0$ transitions. J_{max} was set to 40.

The addition of the α term of B_v to the energy calculations allows the formation of the narrow parabola; without this term, there would be a straight line rather than a parabola for the $\Delta J = 0$ transitions.
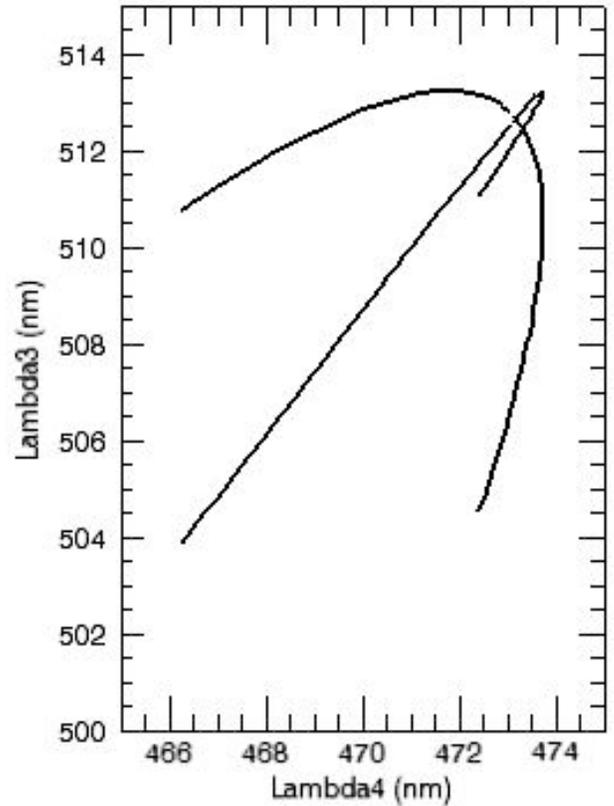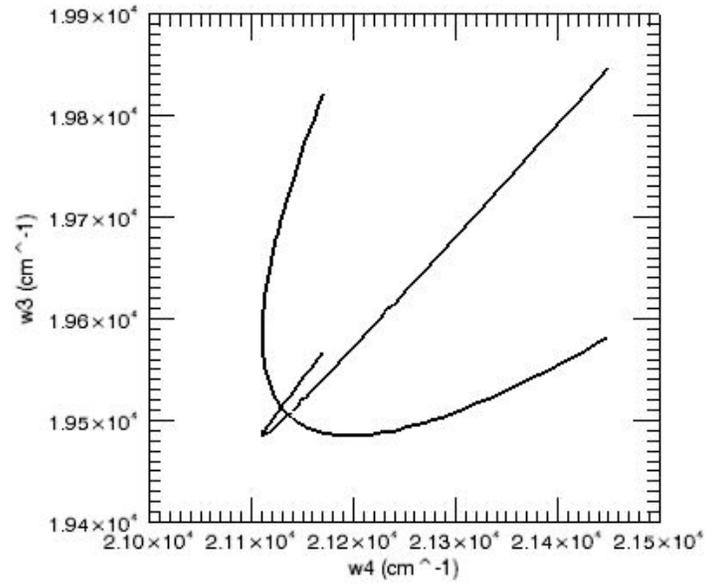
Figure 3. Top: Graph of ω_3 vs. ω_4. Bottom: Graph of λ_3 vs. λ_4.

The D term of $F(J)$ is on the order of 10^{-6}, hence very small compared to the B term. So they have been ignored in our calculations.

$d^3\Pi_g$	$a^3\Pi_u$
$T_e = 20022.50$	$T_e = 716.2$
$\omega_e = 1788.22$	$\omega_e = 1641.35$
$\omega_e x_e = 16.440$	$\omega_e x_e = 11.67$
$B_e = 1.7527$	$B_e = 1.6324$
$\alpha_e = 0.01608$	$\alpha_e = 0.01661$

Table 2. The constants used in simulations.[3]

IV. RESULTS

The simulations we have shown the results of have the capability of separating overlapping peaks of common spectroscopy. We have seen that rovibrational peaks form the same vibrational sequence are on the same parabolas, with increasing J values starting from the point of intersection between curves.

The simulations that were prepared successfully reproduced the results of Chen et al. (2005). It can be seen that this method allows to successfully predict the spectrum of C_2 and separate the transition peaks according to vibrational sequence, rotational quantum number and selection rules.

[1] Chen, P. C.; Joyner, C. C. *Anal. Chem.* **2005**, *77*, 5467-5473.
[2] Correspondence with Prof. Peter C. Chen.
[3] Huber, K.P.; Herzberg, G. Constants of Diatomic Molecules. In *NIST Chemistry WebBook*; NIST Standard Reference Database 69; Linstrom, P.J.,Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, March 2003 (http://webbook.nist.gov).