

## Multiresonance CARS spectra of quinizarin in chloroform solution

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**Abstract.** Some properties of multiresonance CARS spectra of polyatomic molecules in condensed phases are briefly discussed with reference to the possible effects of having a transfer of population under one-photon resonance conditions. Some experimental results are presented for the case of quinizarin in chloroform solution at room temperature. The observation of vibrational resonances of the first excited state as well as evidences of the participation of higher excited states to the multiresonant processes clearly indicate the need to go beyond the usual four level system description of the CARS spectra.

**Keywords.** Multiresonance CARS; four-wave-mixing spectroscopy; quinizarin.

### 1. Introduction

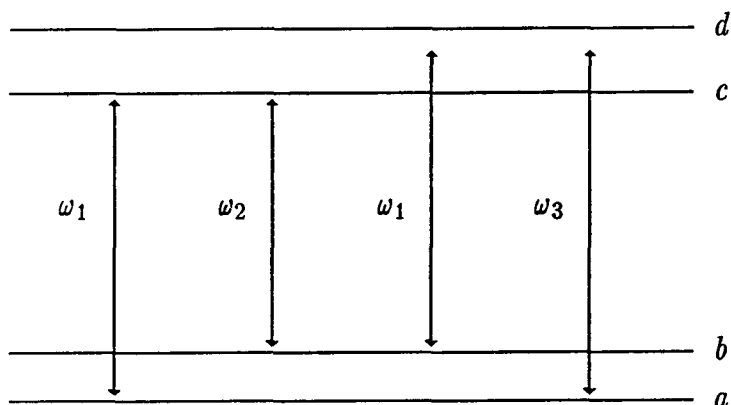
Multiresonance CARS (coherent anti-Stokes Raman spectroscopy) and in general all 4-WM (four-wave mixing) resonant techniques (Shen 1984) are very powerful methods for the study of ground and excited state properties of molecular systems, such as transition frequencies and linewidths of both vibrational and vibronic levels (Dick *et al* 1987).

In most theoretical work on multiresonance 4-WM processes the molecules are modelled by four level systems such as the one shown in figure 1. In the specific case of CARS, two input laser beams frequency  $\omega_1$  and  $\omega_2$  with  $\omega_1 > \omega_2$  are used and a coherent signal at the frequency  $\omega_3 = 2\omega_1 - \omega_2$  is generated. CARS spectra are obtained by varying the frequency of the  $\omega_2$  beam and recording the  $\omega_3$  signal.

The simplest description of multiresonance CARS spectra is obtained at the third order of perturbation theory, assuming that only the ground state (level *a* in figure 1) is populated. In this case the theory predicts that two resonances can be revealed by CARS spectra: the ground state vibrational one at  $\Delta = \omega_1 - \omega_2 = \omega_{ba}$  with a width typical of Raman transitions and the vibronic resonance at  $\omega_3 = \omega_{da}$  (that is  $\Delta = \omega_{dc} - d$  where  $d = \omega_1 - \omega_{ca}$ ) with a width typical of vibronic structures in absorption spectra.

If it is supposed that also the excited state (level *c* in figure 1) is initially populated (incoherent population), additional bands appear in the CARS spectra due to the vibrational resonance of the excited state at  $\Delta = \omega_{dc}$  and the vibronic resonance at  $\omega_2 = \omega_{cb}$  (that is  $\Delta = \omega_{ba} + d$ ) (Bozio *et al* 1983). The presence of these additional resonances is expected also when the CARS signal is calculated at the fifth order of perturbation theory starting with an initial population in the ground state only (Carlson and Wright 1987). In fact, in this case there is coherent population of the excited state *c* in the course of the CARS process itself. The two approaches result

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**Figure 1.** Level diagram representing a four level system in which  $a \rightarrow c$ ,  $b \rightarrow c$ ,  $b \rightarrow d$ , and  $a \rightarrow d$  are one-photon allowed transitions, whereas  $a \rightarrow b$  and  $c \rightarrow d$  are two-photon allowed transitions.

in a different dependence of the intensities of some bands of the CARS spectra on the pure dephasing rate and on the rate of population decay of the excited state (DICE effect) (Bogdan *et al* 1981; Andrews and Hochstrasser 1981). Four level systems have also been considered in developing non-perturbative calculations of 4-WM processes to which one must resort when strong resonant laser fields are used (see, e.g. Dick and Hochstrasser 1983).

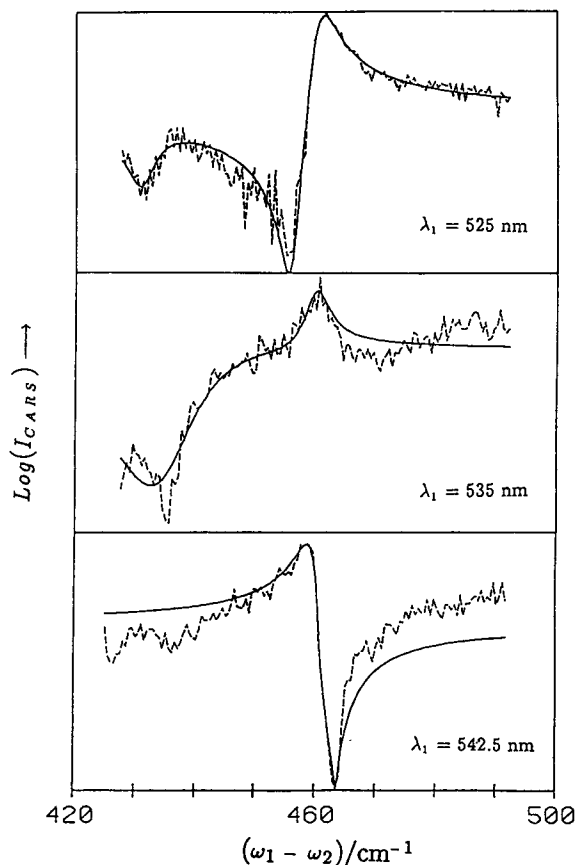
For large polyatomic molecules with dense manifolds of vibronic levels the four level system becomes clearly oversimplified. First of all, one has to introduce a sum over the states of the vibronic manifold to account for all possible simultaneous resonances or near-resonances of the input and output beams with molecular transitions. Furthermore, for certain systems one has to account for electronic transitions involving higher excited states.

The analysis of the variation of intensity and bandshape of vibrational resonances when the frequency of the  $\omega_1$  beam is varied inside the vibronic manifold can substantially contribute to our understanding of multiresonance CARS processes in polyatomic conjugated molecules (Lynch *et al* 1977; Carreira *et al* 1977; Watanabe *et al* 1987). As a prototype system for our multiresonance CARS studies we have chosen quinizarin (QIN) in chloroform (CHL) solution at room temperature.

### 3. Results and discussion

We have measured the CARS spectra of the vibrational mode of the ground state of QIN at  $460 \text{ cm}^{-1}$  and the  $365 \text{ cm}^{-1}$  mode of CHL, used as an internal standard, with  $\lambda_1$  in the 465–560 nm range, that is resonant or preresonant with absorption band peaked at 485 nm (Feis *et al* 1990). The spectra have been recorded at room temperature using low laser powers. The concentration of the solution was about  $1.3 \times 10^{-3} \text{ M}$ .

Figure 2 shows the behavior of the CARS band of QIN in the preresonance region. The striking variation of lineshape is well predicted by the four level model in the basic multiresonance CARS theory (Lynch *et al* 1977). It is due to the change of the

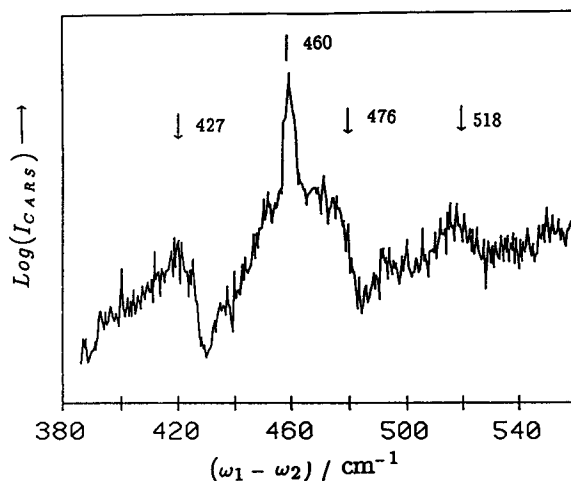


**Figure 2.** Experimental (dashed line) and calculated (full line) CARS band of the  $460\text{ cm}^{-1}$  mode of quinizarin  $1.3 \times 10^{-3}\text{ M}$  in chloroform at room temperature for different values of  $\lambda_1$ .

relative sign of the resonant and nonresonant part of the susceptibility which describes the CARS signal when  $\omega_3$  is tuned across the 0–0 transition. No such striking variations are observed when  $\omega_1$  is well within the absorption profile. In fact, in this case there are many resonances with vibronic levels contributing to the CARS process so that the interplay of their changing signs becomes less well defined.

Figure 3 shows the CARS spectra of QIN when  $\omega_1$  is inside the absorption profile. The presence of resonances at frequencies in good agreement with those previously assigned to vibrations of the first excited state ( $S_1$ ) (Friedrich and Haarer 1963) bears a clear indication that some transfer of population to the  $S_1$  state occurs during the nonlinear interaction process. The  $S_1$  population should be considered incoherent due to the fast dephasing processes which occur in solution at room temperature.

The possibility that higher excited states contribute to the CARS generation process when population is transferred to the excited state has been investigated by measuring a steady state differential transmittance spectrum of QIN under the same experimental conditions in which the CARS spectra were recorded. The data (Feis *et al* 1990) show that the excited state absorption ( $S_n \leftarrow S_1$ ) partially overlaps that of the ground state ( $S \leftarrow S_0$ ).



**Figure 3.** CARS spectrum of quinizarin  $1.3 \times 10^{-3}$  M in chloroform at room temperature with  $\lambda_1 = 510$  nm. Vertical bars and arrows indicate ground and excited state vibrational frequencies respectively.

All the above findings demonstrate that, to account properly for the multiresonance CARS processes in QIN, one must include consideration of the manifold of vibronic levels of  $S_1$  and of higher excited states. The latter should contribute both to the enhancement of Raman resonances of  $S_1$  and to two-photon resonances that determine a complex nature of the background signal. A complex background must in fact be assumed to obtain a satisfactory fit of the observed lineshapes.

We have measured the CARS excitation profile (CEP), i.e. the dependence on  $\omega_1$  of the square modulus of the fully resonant part of the CARS susceptibility at a constant value of  $(\omega_1 - \omega_2) = 460 \text{ cm}^{-1}$ . The CEP data were obtained from a least squares fitting of the CARS spectra of QIN at different  $\omega_1$  values and were normalized to the non-resonant signal of the  $365 \text{ cm}^{-1}$  mode of CHL. Details of the results are published elsewhere (Feis *et al* 1990).

The consequences of the complicated nature of the multiresonance CARS processes in QIN on the CEP are not fully evaluated at the present time. Comparison of the measured CEP data with calculations based on the transform relation that links CEP and the absorption profile in the standard vibronic model (Page and Tonks 1981) shows several unexplained features. A reasonable model for the analysis of our CEP data should account for the contribution to the ground state Raman resonance given by processes starting from the excited state population (Bozio *et al* 1983). However in these processes the  $S_n \leftarrow S_1$  transitions should not be involved so that the CEP of the ground state Raman resonance should carry information on the  $S_1$  state only.

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