ROTATIONAL BAND STRUCTURES IN RESONANCE CARS OF I_2

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ABSTRACT

In discrete-continuum resonance CARS processes in I_2 irregular patterns of resolved rotational lines are observed which may be attributed to accidental enhancement by the pump wave. At increasing laser intensities however, satellite lines tend to grow in, developing into rotational band structures with some similarity to convential non-resonance CARS spectra.

1. Introduction

Electronic resonance enhancement of Coherent Anti-stokes Raman Scattering (CARS) was set on a thorough theoretical foundation in detailed papers by the ONERA-group[1,2]. Although expressions for the third-order nonlinear susceptibility $\chi^{(3)}$ were derived for all possible cases of electronic enhancement, experimental evidence was restricted to examples with pump and anti-Stokes wave in resonance with bound-bound transitions in the $B^3\Pi^+_{u0}$-$X^1\Sigma^+_g$ system of I_2: discrete resonance CARS. The group of Kiefer[3,4] focused on the effects of electronic enhancement by continuum states. These continuum resonance CARS processes were again observed in the prototype molecule for these kinds of studies: molecular iodine. Dimov *et al.*[5] presented evidence for a combination of pump-wave electronic enhancement by a bound-bound transition and anti-Stokes electronic enhancement by continuum states in I_2. Recently the latter discrete-continuum resonance CARS process was reinvestigated in detail by the present authors[6]. It was shown that the pump-wave enhancement acts as a mechanism for selecting particular rotational states to be probed in this form of resonance CARS. As in all resonance CARS processes strong Raman overtones are observed, the intensities of which are governed by Franck-Condon overlap integrals. In the previous investigation[6] peculiar asymmetrically broadened spectral features were observed in the resonance CARS spectra. These features are the subject of the present higher resolution study. They are identified as rotationally resolved Raman lines enhanced by transitions in the medium, slightly detuned from the pump frequency.

2. Experimental observations

The experiments were performed in a standard two-color CARS-setup with a colinear geometry for the incident beams. The frequency of the pump (ω_1=18788.30 cm^{-1}) was obtained from an injection seeded Nd-YAG laser and has an extremely narrow bandwidth ($\Delta\omega_1$=0.005 cm^{-1}). The width of the tunable Stokes-laser ($\Delta\omega_2$=0.07 cm^{-1}) was improved by a factor of four to the previous investigation[6]. The incident waves were focused (f=25 cm) in a cell with pure I_2 at room-temperature vapour pressure (0.3 torr). The generated blue anti-Stokes wave at frequency $\omega_3=2\omega_1-\omega_2$ was separated with a color filter and a monochromator and detected with a photomultiplier.

In Fig. 1 part of the Δv=6 Raman overtone spectrum is shown, once recorded at low laser intensities (lower spectrum) and once at fairly high laser intensities (upper spectrum). The observed features were attributed[6] to a process of discrete-continuum resonance CARS in I_2. In comparison to spectra[6] recorded with a Stokes-laser bandwidth of 0.3 cm^{-1}, the present spectra show much narrower resonances. The previously observed asymmetric line broadening and noisy background level at higher intensities appear to consist of well resolved narrow resonances. Close inspection of these features reveals that their spectral width equals the bandwidth of the Stokes-laser (0.07 cm^{-1}). The number of satellite lines was found to grow steadily with increasing laser intensity.

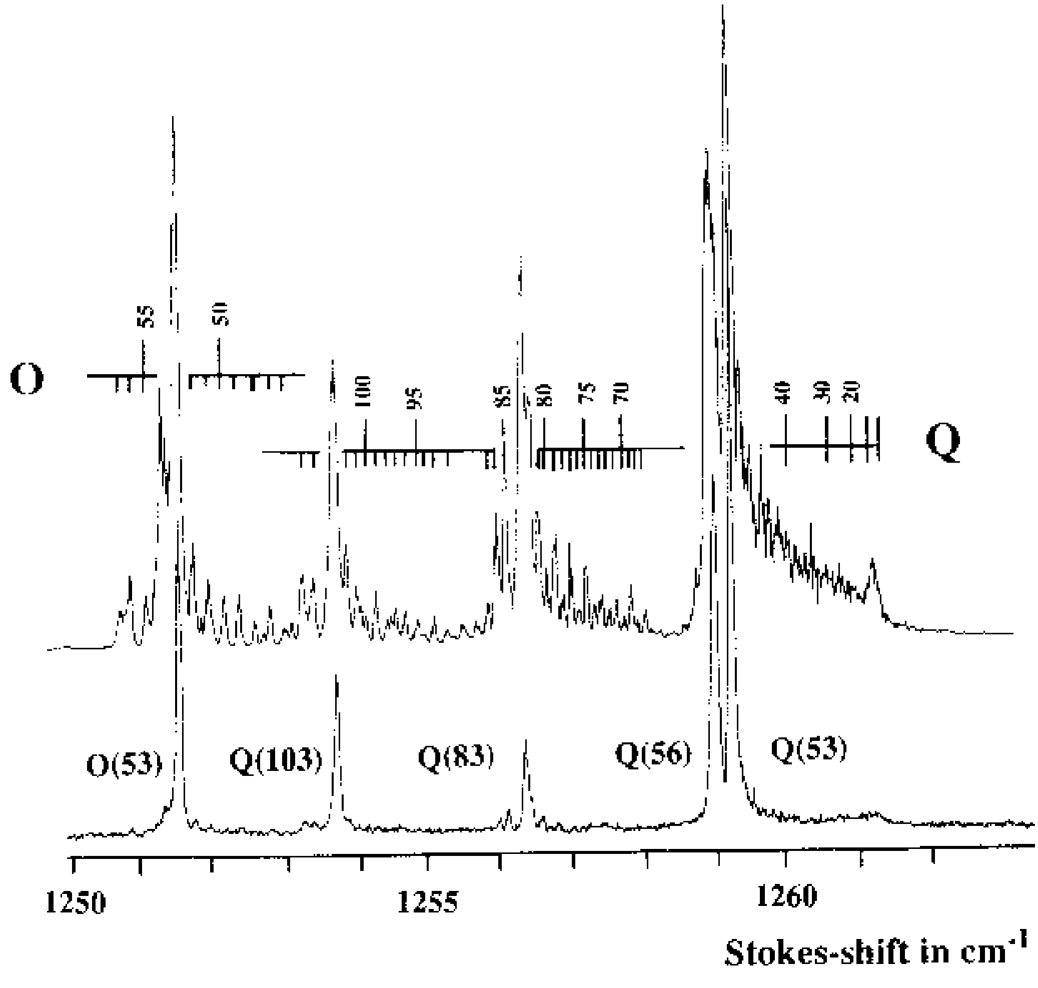

Fig.1 : Observed spectrum for the $\Delta v=6$ Raman overtone in discrete-continuum CARS in I_2. Lower spectrum recorded at 0.8 mJ/pulse for the pump and 0.1 mJ/pulse for the Stokes beam. Upper spectrum: 11 and 1.3 mJ for ω_1 and ω_2 respectively. The absolute intensity of the main resonances in the high power spectra is about a factor of 25 larger.

3. Interpretation

As a starting point for an interpretation of discrete-continuum resonance CARS spectra we consider the expression for the nonlinear susceptibility for this particular process[6]:

$$\chi^{(3)} \propto \sum_{0,n,v,c} \rho_{00}^{(0)} \frac{\mu_{0c}\mu_{cv}\mu_{vn}\mu_{n0}}{(\omega_{n0} - \omega_1 - i\Gamma_{n0})\,(\omega_{v0} - \omega_1 + \omega_2 - i\Gamma_{v0})\,(\omega_{c0} - \omega_3 - i\Gamma_{c0})}$$

Here |0> represents the populated rotational ground states, |n> the bound electronically excited states, |v> the vibrationally excited ground states involved in Raman transitions, and |c> the electronically excited continuum states, respectively. A generalized energy level scheme with the resonant interactions of the four waves is presented together with the relevant potential energy curves of I_2 in Fig. 2.

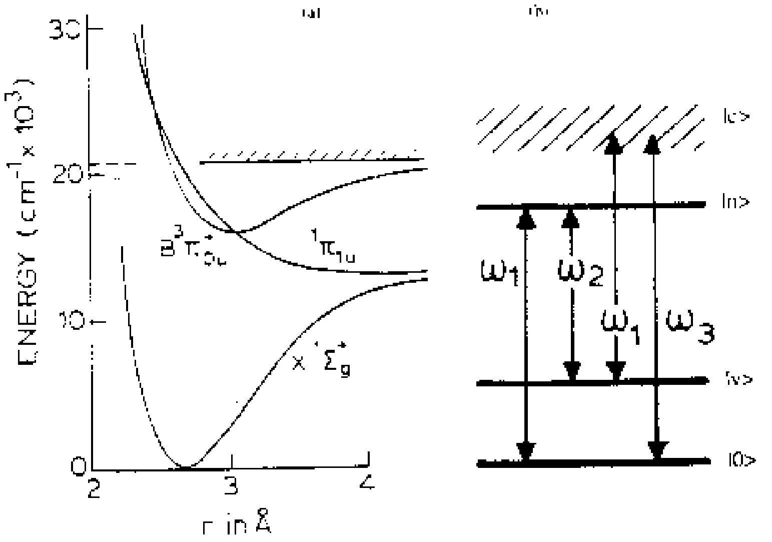

Fig. 2: (a) Potential energy curves for I_2; (b) Energy level scheme for discrete-continuum resonance CARS. In both parts the dashed region represents the dissociative continuum of the $B^3\Pi^+_{u0}$ state.

The first factor in the denominator selects particular states |0> for which an accidental resonance exists in the $B^3\Pi^+_{u0}$-$X^1\Sigma^+_g$ system with the fixed laser at ω_1=18788.30 cm^{-1} (estimated frequency of the pump wave). For all R(J) and P(J) transitions the detuning $\delta\omega_1=\omega_{n0}-\omega_1$ in the first resonance denominator may be readily calculated, by making use of the accurately known molecular constants[7] for I_2. These calculations were performed for the (32,0), (33,0) and (34,0) bands of the B-X system, and results are plotted in Fig. 3. In the (32,0) band $\delta\omega_1$ is close to zero for J=56 in the R-branch and J=53 in the P-branch. In the (33,0) a near-zero detuning $\delta\omega_1$ is found at J=86 and 83, and in the (34,0) band at J=106 and 103, in the R and P-branches respectively. Only three of these resonances, the P(53), R(56) and P(103) have a detuning smaller than 0.15 cm^{-1}.

The CARS resonances are predicted by the second factor in the denominator to be exactly located at the position of a Raman resonance $\Delta\omega=\omega_{v0}=\omega_1-\omega_2$. The observed strong features indeed coincide on the scale for the Stokes shift $\Delta\omega$ with the positions calculated for the Raman resonances: O(53), Q(53), Q(56) and Q(103). Outside the interval shown in Fig. 1 also the corresponding S-lines are found. In the B-X(33,0) band only detunings $\delta\omega_1$ > 0.5 cm^{-1} occur, which explains why the features near Q(83) are weak. Weak contributions of four one-photon resonances at J=82, 83, 85 and 86 are observed. The third factor in the denominator always produces continuum enhancement, as for all J-states the anti-Stokes wave is in resonance with a transition to the continuum. From these considerations we can understand the low intensity CARS spectrum: the fixed ω_l selects certain rotational transitions, whereas ω_2 determines the frequency position at which the resonance is found.

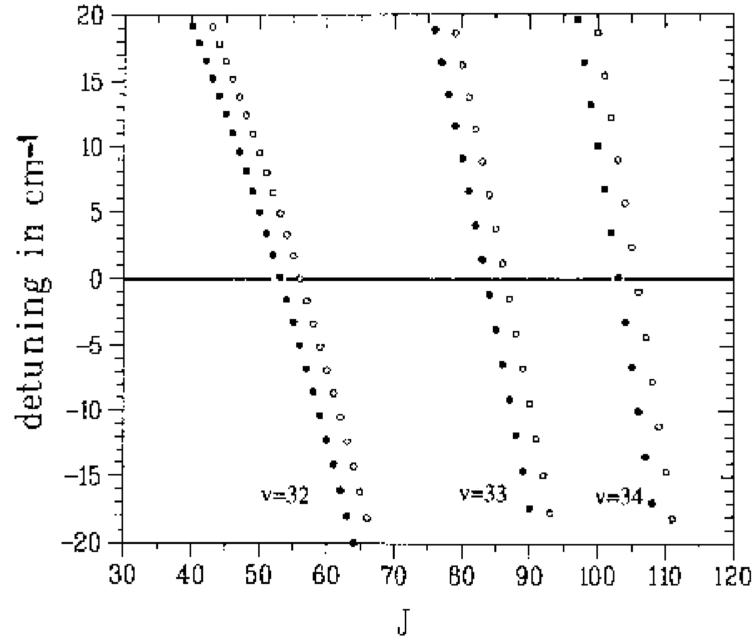

Fig 3: Detunings $\delta\omega_1=\omega_{v0}-\omega_l$ of rotational transitions from the pump frequency (ω_l= 18788.30 cm^{-1}) for the B-X (v,0) bands, for v=32, 33 and 34. Black circles: P(J)-lines; open circles: R(J)-lines.

For an interpretation of the higher laser intensity CARS spectrum we first note that the intensity increase on the strong resonances is only a factor of 25. Based on an intensity dependence relation for CARS of $I_3 \sim I_1{}^2 I_2$ one would expect an increase of about 2500. Thus the CARS resonances with the smallest detunings $\delta\omega_l$ are heavily saturated. In a qualitative sense one may argue that CARS lines with increased detuning $\delta\omega_l$ will be less influenced by saturation, so that at higher intensities satellite lines neighbouring the principal resonances will relatively gain in strength. The frequency positions of the narrow satellite lines were determined on a $\Delta\omega$-scale and compared with calculations[7] of Stokes shifts. Agreement within 0.03 cm^{-1} was found. A striking effect is the observation of off-resonance lines down to the lowest J-values in the Q-branch, where intensity is found to pile up. With the appearance of almost all J-values and the formation of O, Q and S-branches at high laser intensities the CARS spectrum of I_2 loses its particular signature of a resonance CARS spectrum with its characteristic occurence of accidental lines. In contrast it almost resembles a conventional off-resonance CARS-spectrum with regular band structures.

4. References

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