Resonance CARS in Br_2 molecules and Br atoms

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Abstract : Resonance-enhanced CARS processes were studied in molecular bromine. On the basis of the known spectroscopic constants of the two electronic states involved, the features in the spectra could be identified. CARS signals from Br-atoms produced from dissociation of Br_2 were obtained by tuning (ω_1 - ω_2) in resonance with the $^2P_{1/2}$ - $^2P_{3/2}$ spin-orbit splitting (3685 cm^{-1}). Different hyperfine components were resolved in the spectrum.

In this study (resonance-enhanced) CARS features were observed using a two-color set-up with a fixed-frequency pump-wave ω_1 (18788 cm^{-1}) and a tunable Stokes-wave ω_2 (13800 - 18300 cm^{-1}). A generated wave at frequency $\omega_3 = 2\omega_1 - \omega_2$ was detected. Strong overtones are observed in resonance-enhanced CARS spectra, similar to the appearance of overtones in Resonance Raman (Rousseau et al 1976). All distinct lines in the resonance-enhanced CARS spectra of Br_2, shown in the case of Δv=7 in fig.1, are produced by coincidental enhancement of the signal.

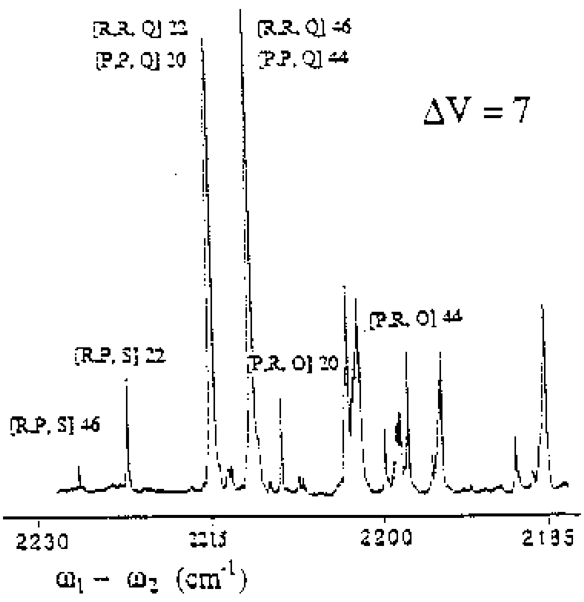

Fig. 1. Resonance-enhanced Δv = 7 CARS spectrum of Br_2.

The intensity of the CARS signal is proportional to the square of the tensor elements of the third order susceptibility tensor $\chi^{(3)}$ which can be written as (Oudar et al 1981):

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

N = number density of molecules,

ω_{ij} = transition frequency from state j to state i,

μ_{ij} = transition moment between states i and j,

$\rho_{ii}^{(0)}$ = initial population of state i,

Γ_{ij} = relaxation parameter.

In this expression the summations over |0>, |v>, |n> and |n'''> refer to all possible rovibronic states of Br_2. From the denominator of $\chi^{(3)}$ it follows that enhancement of the CARS signal is achieved for states |0> for which the fixed frequency ω_1 is in near resonance with an allowed transition in the molecule. As the frequency ω_1 is in near resonance with just a few absorption lines in Br_2, this introduces a certain selectivity in the overall CARS process leading to distinct lines in the spectra as shown in fig. 1. The Stokes frequency ω_2 is tunable and a resonance on $(\omega_1 - \omega_2)$, corresponding to the second frequency factor in the denominator of $\chi^{(3)}$, may always be achieved. The generated anti-Stokes wave at ω_3 is in resonance with a continuum state, related to the repulsive $^1\Pi_{1u}$ state and the dissociative continuum above the $B^3\Pi_{u0}{}^+$ state. This continuum effectively enhances the signal but again does not introduce any extra coincidental enhancement of the signal. So the distinct features in the resonance-enhanced CARS spectra of Br_2 can all be explained by the coincidental enhancement of the signal at the fixed frequency ω_1.

The assignment of the lines used in fig. 1 indicates the four-photon sequence of the total CARS process. P- and R- (ΔJ = -1 or + 1) denote one-photon discrete ω_1- and ω_2-resonances, whereas O-, Q- and S- are used for the continuum-enhanced two-photon resonances (ΔJ = -2, 0 or + 2). The assignments given in fig. 1 all concern the $^{79}Br_2$ molecule.

In the same set-up strong CARS signals from Br-atoms were observed. The atoms were produced from dissociation of Br_2 by the pump-wave ω_1. As $(\omega_1 - \omega_2)$ is tuned into resonance with the fine-structure splitting $^2P_{1/2}$ - $^2P_{3/2}$ of 3685 cm^{-1}, a generated wave at $\omega_3 = 2\omega_1 - \omega_2$ is observed. This signal is not electronically resonance-enhanced as there are no discrete energy levels in Br-atoms corresponding to frequencies ω_1 or ω_3. Different hyperfine components in the Br-atoms were probed shown in fig. 2 due to the use of an injection seeded Nd:YAG laser ($\Delta\omega_1$ = 0.005 cm^{-1}) and a narrow-band dye-laser ($\Delta\omega_2$ = 0.05 cm^{-1}).

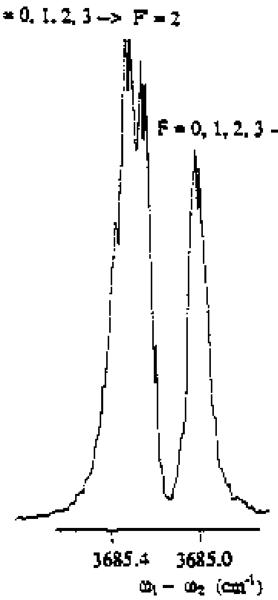

Fig. 2. CARS spectrum of Br-atoms.
F denotes the hyperfine quantum number.

References :

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