Effects of spin–orbit coupling on resonant enhancement of stimulated electronic Raman scattering

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Abstract. The resonant enhancement and polarization properties of stimulated electronic Raman scattering by alkali metal atoms are investigated. Spin–orbit splitting of nearly-resonant intermediate levels results in a 90° rotation of the plane of polarization of the stimulated Stokes radiation. The relationship to two-photon absorption is also described.

1. Introduction

Resonant enhancement of stimulated electronic Raman scattering (SERS) is obtained when the incident (pump) radiation is close to resonance with an intermediate state (Rokni and Yatsiv 1967, Sorokin *et al* 1967, Sorokin and Lankard 1973, Carlsten and Dunn 1975, Cotter *et al* 1975, 1976). The polarization properties of the scattered radiation have been studied for a number of transitions between selected atomic sublevels in alkali metals (Barak and Yatsiv 1971, Arutyunyan *et al* 1974a, b). Raman transitions between substates of different or of the same $^2P_{1/2}$, $^2P_{3/2}$ manifolds were observed, and resonant enhancement was obtained by means of intermediate $^2S_{1/2}$ states.

In this paper we describe the resonance and polarization properties of SERS between $^2S_{1/2}$ states in the alkali metals, with the $^2P_{1/2}$ and $^2P_{3/2}$ states playing the role of resonant intermediate levels. Spin–orbit splitting of the intermediate levels leads to an antisymmetric term in the nonlinear susceptibility. The possibility of antisymmetric terms in Raman-effect tensors was pointed out by Child and Longuet-Higgins (1961) and Axe (1964), and asymmetry in spontaneous electronic Raman scattering by a trivalent rare-earth ion was observed by Kiel *et al* (1969). Here we present experimental evidence of antisymmetric stimulated Raman scattering in caesium. The relevance to some spectroscopic applications is indicated, and the relationship between the properties of SERS and two-photon absorption is described.

2. Theory

A general treatment of nonlinear atomic susceptibilities using irreducible spherical tensor techniques and Racah algebra has been given by Yuratich and Hanna (1976).

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Expressions for the susceptibilities were obtained in a form in which any angular momentum coupling mode can be incorporated and the interacting fields can take quite general polarizations. Using this approach one can derive an expression for the SERS susceptibility describing the transition from the $|n_g{}^2S_{1/2}\rangle$ ground state to a $|n_f{}^2S_{1/2}\rangle$ final state in an alkali atom when the effects of spin–orbit (LS) coupling are included:

$$\chi^{(3)}(-\omega_s; \omega_p, -\omega_p, \omega_s) = \frac{N}{6\hbar^3\epsilon_0(\Omega_{fg} + \omega_s - \omega_p + i\Gamma)}\overline{|\mathcal{M}_{SRE}|^2_{LS}} \tag{1}$$

where

$$\overline{|\mathcal{M}_{SRE}|^2_{LS}} = \frac{e^4}{3}\left|\sum_{n_2}\left[\tfrac{2}{3}\Phi(n_2 p \tfrac{3}{2} 0) + \tfrac{1}{3}\Phi(n_2 p \tfrac{1}{2} 0)\right]\right|^2\Theta^{(0)}$$

$$+ \frac{2e^4}{81}\left|\sum_{n_2}\left[\Phi(n_2 p \tfrac{3}{2} 1) - \Phi(n_2 p \tfrac{1}{2} 1)\right]\right|^2\Theta^{(1)} \tag{2}$$

and

$$\Phi(n_2 p J_2 K) = \langle n_f s \tfrac{1}{2}|r|n_2 p J_2\rangle\langle n_2 p J_2|r|n_g s \tfrac{1}{2}\rangle$$

$$\times\left(\frac{1}{\Omega_{n_2 p J_2 n_g s\frac{1}{2}} - \omega_p} + \frac{(-1)^K}{\Omega_{n_2 p J_2 n_g s\frac{1}{2}} + \omega_s}\right). \tag{3}$$

The incident (pump) field is of frequency ω_p, the scattered (Stokes) field of frequency ω_s, N is the atomic density, $\hbar\Omega_{ab}$ is the energy difference between two unperturbed atomic energy levels E_a and E_b, Γ is a phenomenological damping term and the other symbols take their usual meanings. The defining relations for the electric fields, nonlinear polarization and susceptibility given by Yuratich and Hanna have been adopted here. Equation (2) contains a summation over intermediate states $|n_2{}^2P_{J_2}\rangle$, and $\overline{|\mathcal{M}_{SRE}|^2_{LS}}$ has been calculated by summing over all degeneracies of the initial, final and intermediate states. It has been assumed that the amount by which the pump frequency is detuned from resonance with each of the intermediate levels is larger than the hyperfine splitting of these levels, and so only $K = 0$ and 1 terms appear in (2).

The geometrical terms in (2) are

$$\Theta^{(0)} = \tfrac{1}{3}|\epsilon_s^* \cdot \epsilon_p|^2 \tag{4}$$

and

$$\Theta^{(1)} = \tfrac{1}{2}|\epsilon_s^* \times \epsilon_p|^2 \tag{5}$$

where ϵ_p and ϵ_s are unit polarization vectors for the pump and Stokes waves respectively. Thus the nonlinear susceptibility can be evaluated for any particular polarization geometry. In this paper, we shall confine ourselves to the case for which the pump wave is linearly polarized, but treat the Stokes wave as having a general elliptical polarization. Since stimulated scattering is being considered, it is assumed that the two waves are collinear (propagating in the z direction). We define the x and y directions to be parallel and perpendicular to ϵ_p respectively. The major axis of the Stokes polarization ellipse is inclined at an angle β to x, and the ellipticity (ratio of minor axis to major axis) is ξ ($0 \leqslant \xi \leqslant 1$). Then from (2), (4) and (5) it can be shown that

$$\overline{|\mathcal{M}_{SRE}|^2_{LS}} = \mathcal{S}(\cos^2\beta + \xi^2\sin^2\beta) + \mathcal{A}(\sin^2\beta + \xi^2\cos^2\beta) \tag{6}$$

where the symmetric $(K = 0)$ and antisymmetric $(K = 1)$ terms are

$$\mathscr{S} = \frac{e^4}{81} \left| \sum_{n_2} [2\Phi(n_2 p\tfrac{3}{2}0) + \Phi(n_2 p\tfrac{1}{2}0)] \right|^2 \tag{7}$$

and

$$\mathscr{A} = \frac{e^4}{81} \left| \sum_{n_2} [\Phi(n_2 p\tfrac{3}{2}1) - \Phi(n_2 p\tfrac{1}{2}1)] \right|^2 . \tag{8}$$

The expressions for the SERS susceptibility are translated into the corresponding ones for two-photon absorption (TPA) by making the following simple substitutions:

$$\boldsymbol{\epsilon}_s \rightarrow \boldsymbol{\epsilon}_s^* \qquad \omega_s \rightarrow -\omega_s \qquad \Gamma \rightarrow -\Gamma. \tag{9}$$

Thus it follows that for linear polarizations the geometrical dependence of the TPA susceptibility is identical to that given here for SERS. When the two beams are linearly polarized in the same direction $(\xi = 0,\ \beta = 0)$, then it is clear from (6) that only the symmetric term contributes to the nonlinear susceptibility. Under these conditions, when the frequency of one beam is tuned between an intermediate doublet, destructive interference occurs and the TPA cross section vanishes at one particular frequency. A cancellation of this type has been observed by Bjorkholm and Liao (1974) for the $3s \rightarrow 4d_{3/2}$ two-photon transition in sodium.

The polarization properties of SERS differ from those of TPA in one important respect. For TPA, both beams are injected into the nonlinear medium and hence each have defined polarizations. In SERS, the stimulated Stokes radiation is generated within the medium and will therefore be observed to have that polarization for which the Raman gain is greatest. In that case, either or both of the $\mathscr{S}$ and $\mathscr{A}$ terms can contribute. Thus from (6) it follows that for a linearly polarized pump, the Stokes wave will be observed to be linearly polarized $(\xi = 0)$ in the x $(\beta = 0)$ or y $(\beta = \tfrac{1}{2}\pi)$ direction depending on whether the symmetric or antisymmetric term dominates. When these terms are equal $(\mathscr{S} = \mathscr{A})$ the Stokes radiation will have equal x and y components.

We have calculated the $\mathscr{S}$ and $\mathscr{A}$ components of the SERS susceptibility for the $6s \rightarrow 7s$ transition in caesium (figure 1), using the transition frequencies listed by
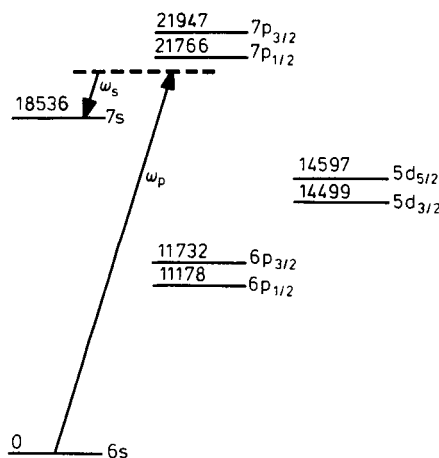

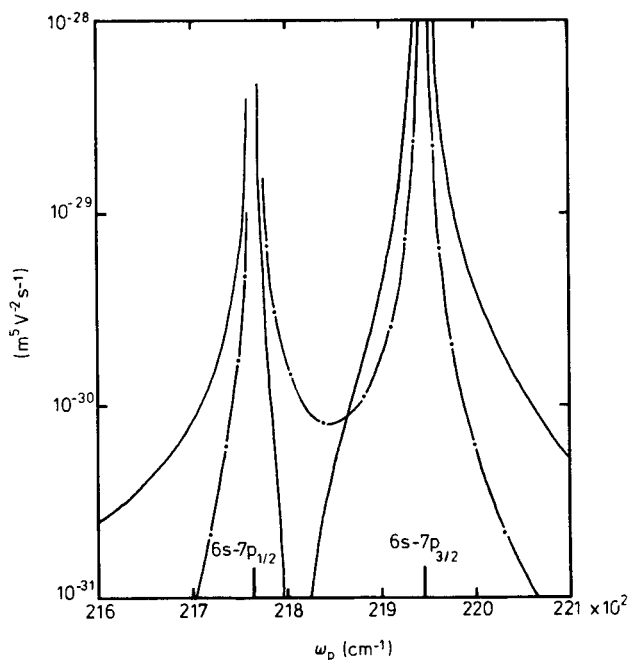**Figure 1.** Part of the energy level diagram of caesium.

Figure 2. Calculated values of the symmetric ($\mathscr{S}$) and antisymmetric ($\mathscr{A}$) terms of the SERS susceptibility for 6s → 7s Raman scattering in caesium. (———, $\mathscr{S}/6\hbar^3\epsilon_0$; —·—·, $\mathscr{A}/6\hbar^3\epsilon_0$.)

Moore (1958) and taking the theoretical oscillator strength values from Warner (1967). The results of the calculations shown in figure 2 indicate that the antisymmetric term is dominant for pump frequencies in the range extending from the lower resonance to about midway through the doublet interval, and should completely eliminate the destructive cancellation in the symmetric term†.

3. Experiment

A dye laser which could be tuned in the vicinity of the $6s–7p_{1/2}$, $6s–7p_{3/2}$ resonances in caesium was used to produce SERS. Using a 7-diethylamino-4-methylcoumarin/methanol solution pumped by a Molectron UV-300 nitrogen laser, the dye laser gave a linearly polarized output with an energy of 110 μJ in a 7 ns pulse. Approximately 80% of this energy was focused into a heat-pipe oven containing a ∼25 cm column of caesium vapour at ∼10 Torr. The SERS signal (around 3300 cm^{-1}) was detected using a pyroelectric detector placed after the oven. A germanium filter stopped the residual dye laser beam and an infrared grating monochromator was used to discriminate against any fixed frequency emissions from the vapour. The

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† In some earlier experimental work on the 6s → 9s electronic Raman transition in caesium (Cotter *et al* 1976), the SERS output was observed to pass through a minimum (although not to zero) when the pump frequency was tuned to ∼27653 cm^{-1} between the $6s–9p_{1/2}$, $6s–9p_{3/2}$ doublet. This was incorrectly attributed at the time to destructive cancellation in the Raman susceptibility. Using the theoretical oscillator strength data of Warner (1967) the calculated minimum in the antisymmetric term occurs at 27656 cm^{-1}, in quite good agreement with the observed minimum.
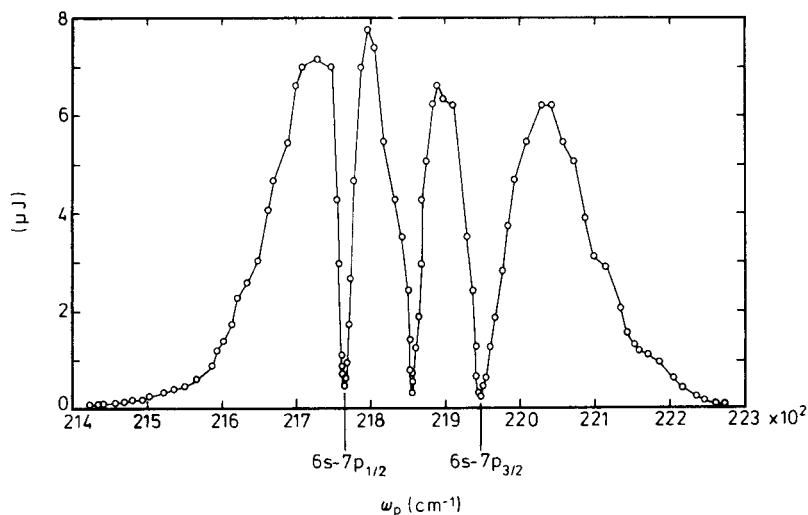
Figure 3. Measured SERS output energy.

observed SERS energy as a function of dye laser tuning is shown in figure 3. Three distinct minima in the SERS spectrum were observed. The outer two were accompanied by very weak transmission of the dye laser beam through the vapour, and correspond in frequency to the resonance doublet $6s–7p_{1/2}$, $6s–7p_{3/2}$. The central minimum at $\sim 21855\,cm^{-1}$ was not accompanied by any observable dip in transmission of the dye laser beam.

The SERS output was also analysed using an infrared grid polarizer having a 15:1 intensity discrimination for orthogonal polarizations at $\sim 3000\,cm^{-1}$. It is convenient to define a measurable polarization ratio

$$\mathscr{R} = \frac{W_x - W_y}{W_x + W_y} \tag{10}$$

where W_x and W_y are the mean detected energies of the SERS signal when the infrared analyser is aligned to transmit x and y polarizations respectively. The observed value of this ratio is shown as a function of dye laser tuning in figure 4. The SERS radiation was linearly polarized for almost all frequencies in the range of the measurements. (The maximum observed ratios $\mathscr{R} = \pm 0.88$ are less than unity because of the incomplete discrimination of the grid polarizer.) In agreement with the theory, the SERS polarization vector rotates rapidly through $90°$ as the dye laser is tuned through the $6s–7p_{1/2}$ resonance and rotates back again through $90°$ at a dye laser frequency almost exactly midway between the doublet.

The position of this upper polarization flip-over point was measured as $21855 \pm 2\,cm^{-1}$. When the dye laser intensity was attenuated by a factor of ~ 3, this frequency was found to be unaltered within the accuracy of the measurements. According to the calculations, this flip-over ($\mathscr{S} = \mathscr{A}$) should occur at $\sim 21866\,cm^{-1}$ and this does correspond very closely with a distinct dip in the observed polarization ratio (figure 4). However the actual flip-over point occurs some $10\,cm^{-1}$ lower in frequency and coincides exactly with the central sharp minimum in the Raman spectrum in figure 3. The origin of this minimum is not known. It does not seem likely that such a narrow, well-defined dip in the Raman spectrum would result from the
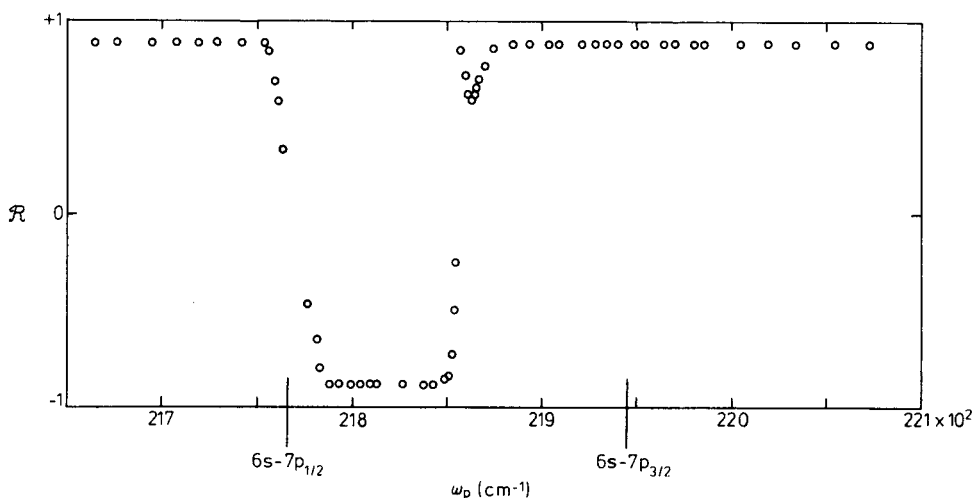
Figure 4. Measurements of the SERS polarization ratio defined in equation (10).

shallow minimum in the antisymmetric component of the Raman susceptibility (figure 2). However, when the dye laser is tuned to $\sim 21855 \, cm^{-1}$ the corresponding Raman frequency ($\sim 3320 \, cm^{-1}$) is in close resonance with the $6p_{1/2} \leftrightarrow 5d_{3/2}$ single-photon transition. Since strong amplified spontaneous emissions are observed at fixed frequencies corresponding to the transitions $7s \rightarrow 6p_{1/2}$ and $7p_{1/2} \rightarrow 5d_{3/2}$, amongst others, it appears likely that the $6p_{1/2}$ and $5d_{3/2}$ levels each become significantly populated during the laser pulse. The interference between this single-photon transition and the process of Raman generation is complex, and the detailed dynamics of the resulting absorption and emission processes and their polarization properties are beyond the scope of the present work.

4. Conclusions

A full treatment of the SERS susceptibility of an alkali atom which includes spin–orbit coupling leads to an expression containing a term which is antisymmetric in the two contributions from the resonance doublet, in addition to the usual symmetric term. It has been demonstrated here that the antisymmetric term is dominant over a large range of pump frequencies between the resonance doublet. This term results in a 90° rotation of the plane of polarization of the generated Stokes radiation.

The flip-over from one polarization direction to the other occurs at the pump frequency for which the symmetric and antisymmetric terms become equal. From (3), (7) and (8) it can be seen that a measurement of the frequency of this flip-over point could provide a novel technique for determining the ratio of the doublet oscillator strengths for otherwise inaccessible transitions $n^2S_{1/2} \rightarrow n^2P_{1/2}$, $n^2P_{3/2}$. For the particular case of $6s \rightarrow 7s$ SERS in caesium, however, we were not able to make this measurement with sufficient accuracy owing to the unfortunate proximity of a competing absorption process.

There is an interesting close similarity between the resonance and polarization behaviour of SERS and that of TPA. In particular, for the case of linearly polarized waves, the geometrical properties of the nonlinear susceptibilities describing the two processes are identical. By making the substitution $\omega_s \rightarrow -\omega_s$ from (9) into (3), it can be seen that in the case of degenerate TPA ($\omega_s = \omega_p \approx \frac{1}{2}\Omega_{rg}$), the antisymmetric

term ($K = 1$) makes no contribution. However in the nondegenerate case ($\omega_s + \omega_p \approx \Omega_{fg}$, $\omega_s \neq \omega_p$), the cancellation in the TPA susceptibility when tuning between the intermediate doublet should be eliminated when the two beams have *orthogonal* linear polarizations. The analysis presented here has described $^2S_{1/2} \rightarrow {}^2S_{1/2}$ SERS and TPA transitions, but can be readily extended to cover $^2S_{1/2} \rightarrow {}^2D_{3/2}$ and $^2S_{1/2} \rightarrow {}^2D_{5/2}$ transitions. The relevant geometrical factors are given by Yuratich and Hanna (1976). In the case of $^2S_{1/2} \rightarrow {}^2D_{3/2}$ transitions, both $^2P_{1/2}$ and $^2P_{3/2}$ are allowed intermediate states, and the SERS and TPA susceptibilities again contain symmetric and antisymmetric resonance terms. The cancellation in the TPA cross section which has been observed on the $3s \rightarrow 4d_{3/2}$ transition in sodium using beams having parallel polarizations (Bjorkholm and Liao 1974) would be eliminated by using *orthogonally* polarized beams. (SERS on $^2S_{1/2} \rightarrow {}^2D_{3/2,5/2}$ transitions has not been observed in alkali metal vapours because the $\langle s|r|p \rangle$ dipole matrix elements are generally greater than the corresponding $\langle p|r|d \rangle$ elements, and so the gain coefficients for stimulated scattering on $^2S_{1/2} \rightarrow {}^2S_{1/2}$ transitions dominate.)

Finally, the work described here has certain significance for practical applications. SERS in atomic vapours has recently been exploited as a simple method of converting the output of a dye laser to a source of tunable infrared radiation (Carlsten and Dunn 1975, Cotter *et al* 1975, 1976). The results here show that over a substantial part of the tuning range for which high conversion efficiencies are possible, it is the antisymmetric part of the nonlinear susceptibility that dominates in the process of Raman generation. In particular, the polarization flip phenomenon itself has obvious practical consequences for the performance of an infrared laser spectrometer based on SERS (Cotter *et al* 1975), since the beam-splitter used in the conventional dual beam ratiometer arrangement has a polarization-dependent reflectivity.

Acknowledgments

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