FINAL TECHNICAL REPORT

MASTER

CO₂ Laser Absorption and Saturation Studies
of Molecular Impurities in Alkali Halide Crystals

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I. Summary

The objective of this research program has been to explore the equilibrium and non-equilibrium dynamical properties of ReO_4^- molecules embedded in alkali halide lattices using electromagnetic radiation. Both incoherent sources and CO_2 laser radiation have been used to explore the full dynamic range of the molecular vibrational modes. To achieve this objective stable molecular dopant--alkali halide combinations have been fabricated which have vibrational modes near the CO_2 laser frequencies. In order to uncouple the molecular modes from the lattice modes, to simplify the analysis as much as possible, low temperature spectroscopic measurements were required. In general, we found that the molecular vibrational modes in the low temperature quiescent lattice had extremely narrow linewidths (less than 0.1 cm^{-1}) so that most of the coincidences with the CO_2 laser lines were eliminated. In order to understand the dynamics of these systems, it was paramount to restore low temperature coincidences with the IR pump. To this end we developed a CO_2 pumped spin flip Raman laser which can be continuously tuned over the 0.6μ laser branch and which can be used for both the low temperature saturation studies and transient experiments alike.

II. Scientific Progress

A. Spectroscopy of tetrahedral molecules in ionic crystals

A.1. Double doped crystals

In last year's proposal we described the spectra of KCl, KBr, and KI doped with KReO_4 . The threefold degenerate ν_3 internal mode is observed in low resolution at 300°K as a single absorption line with a linewidth of 1 cm^{-1} . At liquid helium temperature this linewidth becomes extremely small and a coincidence with the P branch of the CO_2 laser is no longer possible (Chraplyvy and Sievers [1978]). In order to improve the likelihood of a low temperature coincidence we have investigated this year the spectral properties of double doped crystals. A variety of new spectral features have been observed and understood.

When the tetrahedral molecule ReO_4^- is doped into an alkali halide crystal, the molecule replaces a halogen ion in the crystal. The site symmetry in the crystal remains cubic but the local lattice undergoes a compression because the ReO_4^- molecular ion is larger (the radius is $3.09 \text{ \AA}$) than the halogen ion it replaces. The elastic misfit caused by the foreign molecule can be simulated by replacing this molecule by an elastic sphere different in radius from the halogen ion hole radius. In this elastic continuum approximation the hole and the sphere surfaces are then imagined to be glued together. From this construction it is obvious that the

symmetry of the strain field is radial and that compression is produced. Since the system is isotropic the strain field can only depend on the magnitude of the distance from the impurity. It can be shown that the strain field has the same form as given by Coulomb's law for electric charges, i.e. the field varies with the inverse square of the distance from the defect. The same strain field behavior occurs if the defect ion is much smaller in size than the lattice ion it replaces; however, now instead of a compression, a dilation of the lattice occurs. If the alkali halide lattice contains both a large impurity such as an ReO_4^- molecule and a small impurity such as an Li^+ ion then at high temperatures while the crystal is being grown these two ions attract each other, not because of the ionic charge since that is neutralized by the charged alkali halide ions but, instead, because of the two spherical strain fields of opposite sign. Although small concentrations of these impurities are doped in the crystal, the resultant impurity centers are not random throughout the crystal, since the strain energies favor coupled $\text{ReO}_4^- : \text{Li}^+$ pairs. The resultant symmetry for the ν_3 vibrational mode can be seen most easily by inspecting Fig. (A.1). At the top of the Figure is shown the substitutional ReO_4^- molecules with O_h symmetry in the crystal. If a nearest neighbor K^+ ion is replaced by Li^+ then the molecule is in a site of C_{4v} symmetry. The threefold degeneracy of the ν_3 transition is removed and a twofold and a single fold transition result. If two Li^+ ions are nearest neighbors, the resultant symmetry depends on the position of the two Li^+ 's in the nearest neighbor octahedron. For example, if the Li^+ 's

Figure A.1 Two dimensional representation of a KCl lattice containing different molecular impurities. The impurity at the top of the Figure represents an ReO_4^- molecule which has replaced a Cl^- ion in the lattice. The spherical top molecule does not lower the local lattice symmetry. The impurity at the bottom of the Figure shows a Ca^{2+} ion and its associated vacancy as nearest neighbors to the ReO_4^- ion. This defect pair lowers the local symmetry from O_h to C_2 . The resultant crystalline electric field completely removes the threefold degeneracy of the ν_3 vibration in the ReO_4^- molecule.

are on opposite sides of the ReO_4^- molecule then the resultant symmetry is D_{4h} and again the ν_3 vibration is split into a doubly degenerate and a singly degenerate mode while if the two Li^+ 's occupy any other two positions the symmetry is C_{2v} and all three ν_3 modes are nondegenerate.

Another possible dopant combination which makes use of similar analysis is shown at the bottom of Fig. (A.1). An alkali halide is double doped with ReO_4^- and Ca^{2+} . Since the Ca^{2+} by itself does not satisfy charge neutrality a vacancy is always associated with the Ca^{2+} impurity. The configuration shown in Figure (A.1) is one that minimizes both the local strain field and the resultant electric field between the Ca^{2+} and its vacancy. The resultant symmetry is C_2 and all three ν_3 modes are nondegenerate.

A.2 Fourier transform spectroscopic measurements of double doped crystals

The Fourier multiplex spectrometer is the ideal instrument for precise measurements of the infrared properties of molecules in alkali halide crystals. Our interferometer is built around a Michelson cube and mirror drive unit obtained from Idealab Inc. Laser fringes are used to monitor the mirror position in the Michelson cube. The entire assembly is contained inside an aluminum vacuum chamber which contains a number of modules. Our high intensity broad band source in the 10 micron region is a glowbar. A liquid nitrogen temperature transmission cryostat is placed between the interferometer and the infrared detector and a variety of tetrahedral molecule-alkali halide combinations have been measured in this single

beam configuration. A reference spectrum of the cryostat transmission without the sample is measured, next the sample is moved into the beam and the spectrum is recorded again. This second spectrum is then divided by the first one to give a transmission ratio or transmissivity of the doped sample. Since the pure alkali halide is transparent in this frequency region, molecular absorption lines are represented by dips in the transmission ratio. Typically, a transmissivity is recorded first at room temperature and then the sample is cooled with liquid nitrogen to about 100°K, where a second transmissivity is obtained. The resolution of the instrument is maintained at its minimum value, 0.5 cm^{-1} , for the transmissivity curves which are presented in this section.

Figure A.2 Transmission spectra between 880 and 1000 cm^{-1} of $\text{KCl} + 0.3\text{ mole \% KReO}_4 + 0.01\text{ mole \% CaCl}_2$ at 300°K and 100°K . The strong absorption line near 936 cm^{-1} is associated with the threefold degenerate ν_3 transition for isolated ReO_4^- molecules in the crystal. The other three lines of equal strength are associated with the three non-degenerate ν_3 modes of an ReO_4^- molecule and the nearest neighbor Ca^{2+} -vacancy pair. The resultant symmetry is C_2 . Notice that all four linewidths decrease as the temperature is decreased. The sample, cleaved from the top of boule #7803245W, is 1.13 cm thick.

Figure A.3 Transmission spectra between 880 and 1000 cm^{-1} of KBr + 0.1 mole % KReO_4 + 0.2 mole % LiBr at 300°K and at 100°K. The weak absorption line at 930 cm^{-1} is due to isolated ReO_4^- molecules while the two strong lines at 907.5 and 953.5 cm^{-1} are due to $\text{ReO}_4^-:\text{Li}^+$ pairs. The assignment is consistent with C_{4v} symmetry. The three linewidths decrease as the temperature is decreased. Notice that the high frequency line is always wider than the other two. The instrument resolution is 0.5 cm^{-1} . The sample, cleaved from the top of boule #7903056W, is 0.9 cm thick.

Figure A.4 Transmission spectra between 880 and 1000 cm^{-1} of KBr + 0.1 mole % KReO_4 + 0.2 mole % NaBr at 300°K and at 100°K. The weak absorption line at 930 cm^{-1} is due to isolated ReO_4^- molecules while the two strong lines at 908 and 953 cm^{-1} are due to $\text{ReO}_4^-:\text{Na}^+$ pairs. The assignment is consistent with C_{4v} symmetry. The three linewidths decrease as the temperature is decreased. The sample, cleaved 0.5 cm from the bottom of boule #7902195W-1, is 0.6 cm thick. Notice that this spectrum is almost identical to that found for the Li^+ double doped crystal shown in Figure (A.3).

Figure A.5 Transmission spectra between 880 and 1000 cm^{-1} of KI + 0.2 mole % KReO_4 + 0.2 mole % LiI at 300°K and 100°K. The strongest absorption line at 922 in the 300°K spectrum is due to isolated ReO_4^- molecules while the two weaker lines at 906 and 947 cm^{-1} are due to $\text{ReO}_4^- : \text{Li}^+$ pairs. The assignment is consistent with C_{4v} symmetry. The three linewidths decrease as the temperature is decreased; in addition, a large number of weak satellite lines appear. These weaker lines could be due to motional states of the $\text{ReO}_4^- : \text{Li}^+$ complex or could represent simple vibrational shifts due to $\text{Li}^+ : \text{ReO}_4^- : \text{Li}^+$ trimer centers. The sample, cleaved from the top of boule #7903136W-1, is 0.29 cm thick.

A.3 Coincidence of ν_3 with CO_2 laser lines.

An Apollo line tuneable CO_2 laser has been used to search for coincidences with ν_3 in double doped crystals. A large number of coincidences are found at room temperatures but as the material is cooled to lower temperatures the absorption lines narrow and in most cases fall between the CO_2 laser lines. Our experimental results are summarized in Table (A-1). The room temperature coincidence is labeled in column 2 while column 3 shows the low temperature coincidence and the corresponding temperature where it is observed.

TABLE (A-1) Coincidences of ν_3 with CO_2 laser lines

Crystals	Room T Absorption	Low T Absorption
$\text{RbCl} + 0.001 \text{ mole\%KReO}_4$	P(34)	None
$\text{KBr} + 0.2 \text{ mole\%KReO}_4$ + 0.2 mole%LiBr	P(36), P(4)	P(34) at 250°K
$\text{KBr} + 0.01 \text{ mole\%KReO}_4$ + 0.01 mole%LiBr	P(36)	None
$\text{KBr} + 0.1 \text{ mole\%KReO}_4$ + 0.1% CaCl_2	P(34), P(36)	None
$\text{KCl} + 0.3 \text{ mole\%KReO}_4$ + 0.1 mole% CaCl_2	P(28)	P(26) at 105°K
$\text{KBr} + 0.2 \text{ mole\%KReO}_4$ + 0.2 mole%LiBr	P(36), P(8)	P(6) weak
$\text{KI} + 0.005 \text{ mole\%KReO}_4$ + 0.1 mole%CsI	P(42), P(44)	P(42) at 90°K
$\text{KI} + 0.05 \text{ mole\%KReO}_4$ + 0.2%CsI	P(44), P(42)	P(42) (black)
$\text{KBr} + 0.2 \text{ mole\%KCrO}_3\text{Cl}$	P(38) (shallow)	None
$\text{KI} + 0.2 \text{ mole\%KReO}_4$ + 0.2 mole%Li	P(42), P(12), P(14)	P(42) black below 100°K P(18), P(30) P(10) - P(12)
$\text{KBr} + 0.1 \text{ mole\%KReO}_4$ + 0.2 mole%CuBr	P(36), P(18)	P(34) at 250°K
$\text{KI} + 0.2 \text{ mole\% KReO}_4$ + 0.05 mole% AgI	P(42) - P(44)	P(42) (black)

B. Saturation studies of $\text{KCl}:\text{ReO}_4^-$.

The effort described in this section has been done in collaboration with LASL, (Ahrenkiel, et. al. [1978]).

A large number of spectroscopic studies have been carried out on $\text{KCl}:\text{ReO}_4^-$. A high resolution Fourier transform spectrometer with a resolution of 0.06 cm^{-1} was used to resolve the isotope shift due to ^{185}Re and ^{187}Re at low temperatures. The data is shown in Figure (B.1). Although the ν_3 band appears to be a single line at room temperature it is resolved to be a doublet at 100°K . The absorption strength of the two peaks correlates with the relative abundance of the two isotopes. The line widths of the two absorption lines at 100°K are about 0.16 cm^{-1} .

The various processes contributing to the homogeneous line-width can be divided into two types: decomposition processes and scattering processes. Both can be regarded as broadening the absorption line by limiting the lifetime of the excited vibrational state.

In a decomposition process the internal vibration excited state decays into a number of phonons. The limiting temperature dependence for n-photon decay linewidths are

$$\Delta\nu_n \sim \text{const (low T)}$$

$$\Delta\nu_n \sim T^{(n-1)} \text{ (high T).}$$

Scattering processes broaden the absorption line by limiting the lifetime of the overall excited state. Using a Debye approximation for the phonons the scattering linewidth exhibits the limiting behavior:

Figure B.1 ν_3 vibrational mode isotope effect in ReO_4^- . The isotope effect due to the ^{185}Re - ^{187}Re mass change is resolved at low temperatures with a Fourier transform interferometer. The resolution is 0.06 cm^{-1} .

$$\Delta\nu_{sc} \sim T^7 (\text{low } T)$$

$$\Delta\nu_{sc} \sim T^2 (\text{high } T)$$

At least four KCl phonons are required to conserve energy for a decomposition process hence the high temperature linewidth should vary as T^3 . The scattering linewidth temperature dependence varies as T^2 independent of the relative size of the internal vibration energy and the phonon energy. Our measured temperature dependence of the linewidth agrees fairly well with the T^2 dependence associated with the scattering processes.

The room temperature saturation of a 5.5 cm long crystal of KCl: KReO₄ is shown in the data in Figure (B.2). The pulsed CO₂ source was operated on the 10.6 μ m, P(28) line which was coincident with the room temperature absorption peak. The beam had a gaussian profile in space and time with a FWHM of about 1.8 nsec. The solid curve evolves from a computer routine which calculates the total transmission of the space-time Gaussian pulse using a particular saturation model. The fit assumes homogeneous broadening and a 2-level energy system and the only independent parameter is I_s , the saturation parameter. This parameter was adjusted to optimize the fit to the data and a good fit was obtained using $I_s = 1.45 \text{ MW/cm}^2$.

The steady-state approximation ($T_1 < \tau$) is implicit in this model where T_1 is the population relaxation time and τ is the pulse width. The relaxation time is determined from the expression

Figure B.2 Saturation of the ν_3 transition in KCl + 0.2 mole % KReO₄. The 5.5 cm long crystal is at room temperature. The pulsed CO₂ source was operated on P(28) which was coincident with the room temperature peak. The saturation parameter is 1.45 MW/cm².

$$T_1 = \frac{h\nu}{\sigma(1 + \frac{g_0}{g_1})I_s} \quad (B-1)$$

where $h\nu$ is the photon energy in joules, g_0 and g_1 are the degeneracy of the ground and excited states, and σ is the absorption cross-section. The absorption cross-section at 300°K is $7.9 \times 10^{-17} \text{ cm}^{-1}$. Using the I_s values from the curve fit, we find $T_1 = 122 \text{ psec}$ at 300°K and 126 psec at 105°K. The decrease in saturation intensity at low temperature is compensated by a large increase in absorption cross-section. The steady state approximation ($T_1 < \tau$) is self consistent with these calculations.

An attempt to fit the data with an inhomogeneous broadening model was unsuccessful. As a homogeneous model describes the saturation at both 105K and 300K, the dominant line broadening mechanism is related to phonon interactions. This conclusion is consistent with our description of the temperature dependence of the linewidth described earlier.

C. Construction of a high resolution tunable source.

The previous work on the ReO_4^- alkali halide systems has clearly demonstrated the need for both high resolution spectroscopy (0.05 cm^{-1} or better) of these systems and a tunable source in the ν_3 frequency region whose output is capable of reaching saturation intensities for these systems. Presently the CO_2 pumped spin-flip Raman laser appears to hold the greatest promise of meeting both of these needs. Using a CO_2 TEA laser to pump large volumes of the InSb crystal Aggarwal et. al. [1971] were able to obtain Stokes output powers of $\sim 1 \text{ kW}$. Based on the work of Chraplyvy [1978] such power levels should allow us to obtain saturation intensities for these systems. As a high resolution spectrometer the spin-flip laser is also promising. Brueck and Mooradian [1976] have demonstrated linewidths of the order of 0.02 cm^{-1} using a CO_2 TEA pumped system.

Since much of the required equipment was already available, we have, for these reasons undertaken the development of a 10.6μ pulsed spin-flip Raman laser. Our progress is described in the remainder of this section. We begin with an introduction to the theory of spin-flip Raman scattering. From this we proceed to a discussion of the construction of the spin-flip system that has already been completed.

C.1 Spin flip Raman laser theory.

Much of this theory has been presented by R. Warner [1979].

The spin-flip Raman laser is a laser oscillator, the requisite

gain being provided by stimulated Raman scattering from conduction band electrons in InSb (or other semiconductors). The transition involved in this scattering process consists of a change in the spin quantum number, i.e., a spin-flip of a conduction band electron in the presence of a homogeneous magnetic field.

Recall that Raman scattering is an inelastic scattering process in which an incident photon of "pump" radiation at an angular frequency ω_p is scattered into a photon at new frequency ω_s , the energy difference being taken up by an excitation of the scattering medium. Conservation of energy thus requires that

$$E_f - E_i = \hbar(\omega_p - \omega_s) \quad (C-1)$$

E_i and E_f being the initial and final energy states of the scatterer. This process is shown schematically in Figure C.1. The scattered photon is called a Stokes photon if $E_f > E_i$ and an anti-Stokes photon for $E_f < E_i$. The energy spectrum for conduction band electrons in a semiconductor such as InSb is, to a first approximation, given by:

$$\epsilon_{l, k_z, m_s} \approx \hbar \omega_c (l + 1/2) + \frac{\hbar^2 k_z^2}{2m^*} + g^* \mu_B B m_s. \quad (C-2)$$

Here ω_c is the cyclotron frequency, $\frac{eB}{m^*c}$; k_z the momentum component along the field; m^* the effective mass; g^* the effective g factor of the electron; μ_B the Bohr magneton, $eh/2mc$; and B the applied magnetic field.

The transition of interest for spin-flip Raman scattering is that in which the spin quantum number m_s goes from $-1/2$ to $+1/2$, thus

Figure C.1 Illustrating the conservation of energy for Raman scattering.

giving $E_f - E_i = g^* \mu_b B$ and a scattered photon at

$$\omega_s = \omega_p - \frac{1}{h} g^* \mu_b B. \quad (C-3)$$

The frequency of the Stokes photon is thus seen to be shifted down from that of the pump by an amount proportional to the applied magnetic field. Since the effective g factors in semiconductors can be quite large ($g^* \sim -50$ in InSb) a tuning range of 150 cm^{-1} or more can be achieved with reasonable magnetic fields. The question of tunability of this device will be taken up in considerable detail later in this section.

C.1.a. Macroscopic theory of stimulated Raman scattering.

The macroscopic description of stimulated Raman scattering begins with the identification of the part of the phenomenological non-linear susceptibility which results in a non-linear polarization that oscillates at the frequency of the Stokes wave. The Fourier component of the polarization

$$P_s^{NL} = \chi |E_p|^2 E_s \quad (C-4)$$

is appropriate where E_p and E_s are the pump and Stokes wave electric field vectors. This non-linear polarization acts as a source term in the wave equation

$$\nabla \times \nabla \times \tilde{E}_s + \frac{\epsilon_s}{c^2} \frac{\partial^2}{\partial t^2} \tilde{E}_s = -\frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} P_s^{NL} \quad (C-5)$$

where ϵ_s is the linear dielectric constant at the frequency of the Stokes wave and μ_s has been taken as unity. Solving this equation with the usual slowly varying amplitude approximation and using the

fact that on resonance, the Raman susceptibility is essentially given by $\chi = -i\chi''$ we obtain

$$E_s(z) = E_s(0) \exp \left[\left(\frac{2\pi\chi''\omega_s}{n_s c} |E_p|^2 - \frac{\alpha}{2} \right) z \right] \quad (C-6)$$

In this expression α is the absorption coefficient and n_s is the refractive index at the frequency ω_s . Thus, we identify as the Raman gain

$$g = \frac{4\pi\chi''\omega_s}{n_s c} |E_p|^2 \quad (C-7)$$

such that

$$I_s(z) = I_s(0) \exp[(g-\alpha)z] \quad (C-8)$$

Clearly the ability to develop gain at ω_s in the scattering medium admits the possibility of an oscillator. By enclosing such a gain medium of length L in a cavity defined by a pair of mirrors of reflectivity R and resonant at ω_s , self oscillation will be obtained provided that

$$R \exp[(g-\alpha)L] \geq 1. \quad (C-9)$$

Most but not all spin-flip laser oscillators utilize a cavity formed by the plane, parallel, polished end faces of the crystal. The high refractive index of InSb ($n = 4$) provides a natural reflectivity of 36% at the crystal boundary. High resolution spectroscopy may require the operation of a spin-flip laser in which the crystal ends are appropriately coated and additional mirrors are employed to form the resonant cavity. The desirability of such operation will be discussed further in a later section.

The experimentally accessible quantity describing Raman scattering is the spontaneous cross-section, $d\sigma/d\Omega$, rather than the imaginary part of the non-linear susceptibility. It is therefore desirable to obtain an expression for χ'' and hence the Raman gain in terms of $d\sigma/d\Omega$. This may be accomplished by calculating the power delivered to each mode of the radiation field under the assumption of a single photon populating each mode, multiplying by the number of modes in the solid angle $d\Omega$ and normalizing with respect to the incident pump intensity. Taking the fields as

$$E_i = E_i \exp\{i(\omega t - \underline{k}_i \cdot \underline{r})\} + \text{c.c.} \quad (\text{C-10})$$

the power per unit volume delivered to the i^{th} mode of the Stokes field is given by

$$\text{Re} \left\{ \frac{dP_{si}^{\text{NL}}}{dt} \cdot E_{si} \right\} = 2\omega_s \chi'' |E_{si}|^2 |E_{pi}|^2 \quad (\text{C-11})$$

where $\text{Re} \{ \}$ implies the real part of the bracketed quantity. We obtain an expression for $|E_{si}|^2$ appropriate to a single photon occupying the i^{th} mode by equating the energy density to that of a single photon in the mode volume

$$n_s^2 |2E_{si}|^2 / 8\pi = \hbar\omega_s / V \quad (\text{C-12})$$

where V is the volume used in quantizing the radiation field, usually taken to be that of the crystal. Thus we obtain an expression for the rate at which energy is delivered to the i^{th} mode per photon in that mode as

$$dU_i/dt = \frac{4\pi\hbar\omega_s^2}{n_s^2 V} \chi'' |E_{pi}|^2 \quad (C-13)$$

The number of modes for one polarization in the solid angle $d\Omega$ and within the frequency interval $d\omega_s$, $N_{si} d\omega_s$ is given by

$$N_{si} d\omega_s = \frac{V}{(2\pi)^3} \left(\frac{n_s}{c}\right)^3 \omega_s^2 d\omega_s d\Omega \quad (C-14)$$

Finally, the pump intensity is given by

$$I_p = n_p c |2E_p|^2 / 8\pi \quad (C-15)$$

Combining Eqs. (C-14) and (C-15) with (C-13) we obtain an expression for the scattering cross section per electron, $d\sigma/d\Omega$, in the frequency interval $d\omega_s$, namely

$$N d\sigma/d\Omega d\omega_s = \frac{\hbar}{\pi} \frac{n_s}{n_p} \left(\frac{\omega_s}{c}\right)^4 \chi'' d\omega_s \quad (C-16)$$

We note that this is a small signal theory in that the total number density of electrons, N , is assumed to be available for scattering. The total cross section may be obtained by integrating this expression over all frequencies. To do this integration we assume that χ'' is Lorentzian with a linewidth, Γ , much less than ω_s and a peak height $\chi''_{\max}$. Under these conditions, the significant contribution to the integral comes from $\omega \approx \omega_s$ and we may simply replace $\int \chi''(\omega) d\omega$ by $\frac{\pi\Gamma}{2} \chi''_{\max}$ to obtain

$$N d\sigma/d\Omega = \frac{\hbar\Gamma}{2} \frac{n_s}{n_p} \left(\frac{\omega_s}{c}\right)^4 \chi''_{\max} \quad (C-17)$$

Finally, using this expression and equation (C-7) we write the peak small-signal gain in terms of the spontaneous cross section as:

$$g_{o,max} = \frac{16\pi^2 c^2 N}{n_s^2 \omega_s^3 \hbar \Gamma} \frac{d\sigma}{d\Omega} I_p \quad (C-18)$$

The macroscopic description of stimulated Raman scattering presented above allows the assessment of the possibility of obtaining a Raman laser using the start oscillator condition, equation (C-9), and experimentally accessible parameters. The description of a Raman laser, however, requires the extension of this small signal theory to include a saturation mechanism. To this end, following Wherrett and Firth [1972], we define the fractional population of excited (spin-up, $\uparrow$) electrons, f , such that

$$N^\uparrow = fN \text{ and } N^\downarrow = (1-f)N \quad (C-19)$$

when N is the total conduction band electron population available to take part in spin-flip scattering. (The qualifier, "available", used here will be discussed in detail in a subsequent section concerning quantum effects.) We then multiply the small-signal Raman gain g_o from Eq. (C-18) by the probability of scattering a pump photon to produce a Stokes photon, $(N^\downarrow - N^\uparrow)/N$;

$$g = g_o \frac{N^\downarrow - N^\uparrow}{N} = GI_p (1-2f) \quad (C-20)$$

where $G = \frac{16\pi^2 c^2 N}{\hbar \omega_s^3 n_s^2 \Gamma} \frac{d\sigma}{d\Omega}$ is dependent only on the crystal properties.

We may now write down a pair of rate equations for the Stokes intensity, I_s , and f . The expression for I_s is available immediately from (C-8) as

$$d/dt I_s = \frac{c}{n_s} (g - \alpha'_s) I_s \quad (C-21)$$

and we write

$$d/dt f = (\partial/\partial t f)_{\text{relax}} + (\partial/\partial t f)_{\text{scattered}} \quad (C-22)$$

The α'_s in Equation (C-21) is an effective absorption coefficient, which has been adjusted to account for the reflection losses at the mirrors, i.e., $\alpha'_s = \alpha_s - \frac{1}{L} \ln \sqrt{R_1 R_2}$. The relaxation of the electron spin population may be described by

$$(\partial/\partial t f)_{\text{relax}} = -f/\tau_s. \quad (C-23)$$

(Poscher et. al. [1976] have succeeded in a direct optical measurement of τ_s which they find to be of the order of 20-40 nsec at 4.2°K in samples of $N_e = 1.3 \times 10^{15} \text{ cm}^{-3}$.) The scattered contribution is determined by the rate at which electrons are transferred from the spin-down to the spin-up state by the Raman scattering process. Clearly for each scattered Stokes photon a spin is flipped. The rate at which photons are added to the Stokes field is given by $\frac{1}{\hbar\omega} \text{Re} \left\{ \frac{dP^{\text{NL}}}{dt} \cdot E \right\}$, which must be equated to $N \partial f / \partial t$, the rate of change of up-spin population density. Thus, using Eq. (C-11),

$$(\partial f / \partial t)_{\text{scattered}} = \frac{2\chi''}{\hbar N} |E_s|^2 |E_p|^2. \quad (C-24)$$

Now, expressing χ'' in terms of the gain, g , and the field intensities we obtain

$$(df/dt)_{\text{scattered}} = \frac{GI_p I_s}{N \hbar \omega_s} (1 - 2f) \quad (C-25)$$

The rate equation for the excited population thus becomes

$$(d/dt) f = \frac{GI_p I_s}{N\hbar\omega_s} (1-2f) - \frac{f}{T_s} \quad (C-26)$$

In the steady state we obtain an expression for the population fraction by setting the rate of the change of the Stokes intensity in equation (C-21) to zero, and using (C-20), we obtain

$$f = \frac{1}{2} \left(1 - \frac{\alpha'}{GI_p} \right) \quad (C-27)$$

Now, setting df/dt to zero and using Equation (C-27) we obtain an expression for the steady state Stokes intensity

$$I_s = \frac{N\hbar\omega_s}{2T_s \alpha'} \left[1 - \frac{\alpha'}{GI_p} \right] \quad (C-28)$$

This expression exhibits a definite threshold at $\alpha'/GI_p = 1$ which is equivalent to the start oscillator condition expressed in equation (C-9). The maximum Stokes intensity is determined by the population relaxation time as expected.

The expressions for I_s and f presented above are obtained in the approximation of plane waves for both the pump and Stokes fields and negligible pump depletion. This theory has been extended by Wherrett and Firth [1972] and Firth [1972] to include a gaussian beam profile and to account for pump depletion. These results although of practical importance do not significantly enhance our understanding of the basic physics of the spin-flip Raman laser and are not pursued further here.

C.1.b Tuning behavior and linewidth

One of the principal attractive features of the spin-flip Raman laser has been the prospect of its being a widely tunable, reasonably high power source of coherent radiation in the infrared region of the spectrum. As we have already pointed out (eqn. C-3) the Stokes frequency of the Raman oscillator is given by

$$\omega_s = \omega_p - \frac{1}{\hbar} g^* \mu_b B \quad (C-34)$$

The wide tuning range ($\approx 150 \text{ cm}^{-1}$), plus the use of higher order Stokes lines and different pump lasers (principally CO, CO₂ and NH₃) allows much of the spectral region between 5 and 20 μ meters to be covered. Most work to date has been concentrated on the spectral regions near 5 and 10 μ meters due primarily to the availability of reliable high powered CO and CO₂ pump lasers.

Deviations from the tuning behavior indicated by (C-34) were apparent at high fields in the first observation of spontaneous spin-flip Raman scattering reported by Patel and Shaw [1970]. This is not unexpected since the simple linear tuning behavior indicated by (C-34) is derived from a conduction band energy spectrum for the approximation in which the conduction band is decoupled from all other bands of the crystal. The departure from linearity is variously described as a field dependent g factor or effective mass, or as resulting from nonparabolicity of the energy bands. All of these effects result from the failure to account for the interband coupling in the Hamiltonian. Including this coupling we obtain the Stokes frequency shift $\delta\nu_{sf} = \nu_p - \nu_s$

to 3rd order in the applied field:

$$\delta v_{sf} = \frac{g^* \mu_B}{h} \left[1 - \frac{\hbar \omega_c}{E_g} + \frac{3}{2} \left(\frac{\hbar \omega_c}{E_g} \right)^2 + \frac{1}{2} \left(\frac{g^* \mu_B}{E_g} \right)^2 \right] \quad (C-35)$$

This expression is plotted as a function of applied magnetic field in Figure C.2. In this same figure the linear approximation of (C-34) is also plotted along with some data taken in our laboratory. The data presented here representing two different kinds of experiments (a Raman oscillator and a Raman amplifier) was taken on several different days using different crystals and several different pump wavelengths around 5.3μ meters.

The tuning behavior given by (C-35) and shown in Figure C.2 is the free tuning of the peak of the Raman gain, i.e., the spontaneous Raman scattering frequency. When the gain medium is enclosed in a cavity to produce an oscillation the resonant nature of the cavity is expected to modify this free tuning behavior. The oscillation frequency, in the plane wave approximation, is then given by the expression

$$v_{osc} = \frac{\Gamma_s v_c + \Gamma_c v_s}{\Gamma_s + \Gamma_c} \quad (C-36)$$

where the subscripts s and c refer to spontaneous and cavity respectively, Γ is the relevant linewidth and v the peak of the relevant resonance. One therefore expects the tuning rate to be less than that given by (C-35) by the fraction $\frac{\Gamma_c}{\Gamma_s + \Gamma_c}$ and to exhibit discontinuities as the oscillation shifts to new cavity modes. This behavior although not reported in the early observations of Patel and co-workers (see e.g., Patel and Shaw [1971]) was reported by Brueck and Mooradian [1971] in the operation of a single mode spin-flip laser. Patel's failure to

Figure C.2 The Stokes frequency shift as a function of applied magnetic field. The square points are from a Raman oscillator experiment and the circles from an amplifier experiment, $N = 10^{16}$ and 2×10^{16} respectively, $m/m^* = 72$.

observe this behavior can probably be explained as a failure to achieve single mode oscillation of the spin-flip laser.

The linewidth expected from a spin-flip Raman laser may be predicted by the well known Schawlow-Townes expression:

$$\Delta\nu_L = \frac{8\pi h\nu_L}{P} [\Delta\nu_c \Delta\nu_{sp} / (\Delta\nu_c + \Delta\nu_{sp})]^2,$$

P being the laser power output. This expression predicts a linewidth of the order 1 Hz. The extremely narrow linewidths to be expected from the spin-flip laser have resulted in considerable study, both experimental and theoretical, of the fine tuning behavior of these devices. Here we present a brief review of the relevant literature. Brueck [1971], Brueck et. al. [1973], and Brueck and Mooradian [1973] provide an in-depth study of the spontaneous spin-flip linewidth, Γ , and the line shape as a function of the sample carrier concentration, the magnetic field, and the polarization and propagation direction of both the pump and scattered radiation. They report spontaneous spin-flip linewidths as narrow as 0.005 cm^{-1} for $N_e \sim 8 \times 10^{15} \text{ cm}^{-3}$ at fields less than 1K Gauss in the commonly employed $E_p || B$ geometry. This linewidth increases approximately exponentially with field to the order of 0.2 cm^{-1} at 10 kG.

This exhaustive study of the spontaneous spin-flip linewidth forms the basis of subsequent work on the fine tuning of the spin-flip laser. Brueck and Mooradian [1974] report a detailed study of the fine tuning of the spin-flip laser. These experiments make use of a highly stabilized CO local oscillator against which the spin-flip output is heterodyned and then displayed on an rf spectrum analyzer.

The mode pulling and hopping described above is discussed in considerable detail together with the experimental conditions necessary for its observation. In the vicinity of a mode hop these authors report the simultaneous oscillation of two axial modes of the spin-flip laser, both of which show strong pulling of their frequencies toward the peak of the spontaneous gain curve. They also report in this work the achievement of spin-flip linewidth of 30 kHz. This is obtained using an elaborate system in which the spin-flip output is phase locked to a signal derived by mixing the CO local oscillator with a high harmonic of a klystron. Tuning is obtained by varying the klystron frequency, and thus the offset from the CO local oscillator frequency.

Additional studies of the tuning behavior of the spin-flip laser using the simpler experimental procedure of examining the output with a long path-length Fabry-Perot interferometer have been reported by MacKenzie et al. [1975]. The same mode pulling and mode hopping reported earlier is clearly visible in their data obtained with interferometer plate spacings of 25 cm and greater, but completely unresolved for interferometers significantly shorter than 25 cm. The failure of shorter interferometers in resolving this behavior is easily understood when one recalls that the resolving power of a Fabry-Perot is given by the ratio of its free spectral range, $c/2L$, to its finesse. Since, for a given pair of plates the finesse is nearly independent of the length, we find the resolving power to be inversely proportional to the length. Finally, Firth et al. [1975, 1976, and 1978] have pro-

vided a theoretical interpretation of this data in terms of a generalization of equation (3-36). The significant generalization provided by these authors is to include the effects of diffraction as manifested in the departure from plane waves propagating in the cavity for which (C-36) applies. They show these effects to introduce an asymmetry into both the tuning rate and the laser threshold about line center.

In our laboratory, with the exception of the observation of an occasional modulation of the output power whose periodicity correlates with tuning through a cavity free spectral range, these fine tuning effects have not been observed owing to the lack of sufficient resolving power in our instrumentation. That this is reasonable may be seen by using equation (C-36) to calculate the difference between the oscillation frequency and the spontaneous scattering resonance:

$$\nu_{osc} - \nu_s = \frac{\Gamma_s (\nu_c - \nu_s)}{\Gamma_c + \Gamma_s} \quad (C-38)$$

The difference frequency $(\nu_c - \nu_s)$ can never exceed half the free spectral range of the cavity, $\Delta\nu_c (= \frac{1}{nL} \text{ cm}^{-1})$ and Γ_c is given by

$$\Gamma_c = \frac{2\nu_c}{Q} = \frac{1}{\pi n} \left(\alpha + \frac{1}{L} \sqrt{R_1 R_2} \right) \quad (C-39)$$

where R_1 is the cavity reflectivity, L the length, α the absorption coefficient and n the refractive index. For a typical experimental configuration of a spin-flip laser cavity formed by the natural reflectivity of the polished ends of a crystal of InSb about 8 mm long we have $R_1 = R_2 = .36$, $\alpha = 2 \text{ cm}^{-1}$ and $n = 4$. Thus $\Delta\nu_c = 0.16 \text{ cm}^{-1}$, $\Gamma_c = 0.26 \text{ cm}^{-1}$ and taking as a representative value $\Gamma_s = .1 \text{ cm}^{-1}$, from

(C-37) we obtain a maximum difference from the spontaneous frequency,

$$|\nu_{\text{osc}} - \nu_s|_{\text{max}} = .02 \text{ cm}^{-1}.$$

The interactions between the spontaneous spin-flip resonance and the cavity resonance have led several investigators to consider providing the spin-flip laser with a cavity other than that formed by the natural reflectivity of the polished crystal faces. The use of an external cavity formed by a pair of separate mirrors into which an antireflection coated crystal is inserted offers the opportunity to design and control the cavity parameters independently of the gain medium. Certainly such a cavity could be constructed with a servo system to lock the cavity resonances to the peak of the spontaneous scattering resonance and thus eliminate the mode pulling and hopping effects. Several investigators, including ourselves, have reported successful operation of external cavity spin-flip lasers (see Brueck & Mooradian [1976], Scragg & Smith [1975], Scragg et. al. [1976], and Dutta et. al. [1976]).

C.1.c Quantum effects in spin-flip scattering

In the discussion to this point the scattering cross sections have been computed for a single electron under the tacit assumption that the total cross section per unit volume would be obtained by multiplying by the conduction band electron density. The conduction band electrons in InSb, however, form a degenerate Fermi gas with the result that this assumption is valid only for magnetic fields above the so called quantum limit. That is, only for fields sufficiently high that all but the spin-down sublevel of the lowest Landau level has been elevated above the Fermi level do all electrons participate.

The effects of Fermi statistics obeyed by the conduction band electrons on the operation of the spin-flip Raman laser are discussed below.

The effect of the conduction band electron statistics is to place restrictions on the summation over initial states which appears in the microscopic expression for the Raman cross section. The initial state cannot contribute to the cross section unless it is occupied by an electron and the Pauli principle prevents it from contributing unless the corresponding final state is simultaneously unoccupied. We may remove these restrictions if we first multiply the squared modulus of the transition matrix $|R|^2$ by a function $f_I(1-f_F)$. Here f_I and f_F are the probability of the initial and final states being occupied by an electron, i.e., the corresponding Fermi factors. The scattering cross section is therefore given by

$$d\sigma/d\Omega = \left(\frac{e}{mc}\right)^4 \left(\frac{\omega_c}{\omega_p}\right)^2 \left(\frac{n_s}{n_p}\right) \sum_i |R|^2 f_I(1-f_F) \quad (C-40)$$

where the summation is now taken over all initial states.

The significance of the Fermi statistics in reducing the scattering cross section for spin-flip Raman scattering was first recognized by Wherrett and Harper [1969] and has since been discussed by several authors. How this reduction comes about may readily be seen by reference to Figure C.3. In this figure we have sketched the conduction band energy level structure for two values of applied magnetic field, one below and one above the aumtum limit. At a sufficiently low temperature the states whose energy lies below the Fermi energy are occupied ($f = 1$), while those above are unoccupied ($f=0$).

Figure C.3 The effect of Fermi statistics on the spin-flip Raman cross section. The conduction band energy level structure is shown for two values of magnetic field, one below and one above the quantum limit. The levels are labeled with their Landau and spin quantum numbers and the Fermi energy is indicated. (After Patel and Shaw [1971].)

For fields below the quantum limit, as shown in Figure C.3a, only those electrons with z directed momenta lying in the indicated range can contribute to the scattering cross section. This is a small fraction of the total conduction band population density since it may be shown that the density of states contains singularities at the bottom of the Landau levels ($k_z = 0$). In contrast to this situation, Figure C.3b for fields above the quantum limit shows that all of the conduction band electrons may contribute to the cross section. Here the level ($\ell = 0$, $s = \uparrow$) has emerged above the Fermi energy and the total electron population is contained in the lowest energy level, thus $f_I = 1$ and $f_F = 0$ for all conduction band electrons.

These effects were reported by Patel and Shaw [1971] for the CO_2 pumped spin-flip Raman laser. The quantum limit was shown to represent a minimum magnetic field necessary to achieve oscillation. Below this field the cross section and hence the gain was insufficient to obtain laser oscillation. Since the position of the Fermi level is dependent upon the doping density of the crystal this leads to a threshold magnetic field which is a function of the doping density. This threshold field, the field at the quantum limit, is given by

$$B = \left(\frac{2(2\pi)^4 N^2 m}{m^* g^*} \right)^{1/3} \frac{\hbar c}{2e} \quad (\text{C-41})$$

where N is the doping density of the crystal. The threshold field is seen to increase as the density of doping atoms to the $2/3$ power.

C.2. Construction of the InSb spin-flip Raman laser

In this section, we will summarize the experimental apparatus that we have assembled for our spin-flip Raman laser system. In addition, we have performed some preliminary diagnostic experiments using crystals of InSb that were borrowed from Professor G. J. Wolga.

C.2.a. Spin-flip Raman cryostat

The central component in our spin-flip Raman laser system is a 100 kG superconducting magnet and its cryostat, borrowed from Prof. G. J. Wolga of Cornell University. The magnet, manufactured by Intermagnetics General Corporation, is of the split solenoid design which allows optical access to the sample along three mutually orthogonal axes. The laser crystals were mounted in the 1 1/2" bore of the cryostat on OFHC Cu sample mounts, yielding a sample temperature of $\sim 10^\circ\text{K}$. The dewar which houses the cryostat was manufactured by Janis Research Company and is of standard design. Forty-five liters of liquid He are required to initially cool and fill the He reservoir, and 25 liters per day are required to maintain magnet operation.

C.2.b. Pump lasers

We have used two pump lasers for our preliminary measurements. For high peak power pumping, we have a Tachisto Model 215G TEA CO_2 laser that can produce .1 - .5 joule pulses of 50-100 nsec width at 1 Hz repetition rate. This TEA laser is grating tunable to allow operation on many lines in the 9R, 9P, 10R, and 10P branches. (Here and hereafter, "9" stands for $(00^\circ 1)-(02^\circ 0)$ and

"10" stands for (00°1) - (10°0).) In addition, we have constructed an intracavity low-pressure gain section ("smoothing tube") that allows operation of the laser in a single longitudinal mode (see, for example, Loy and Roland [1977]).

For high repetition rate, lower power pumping, we have a grating tunable Apollo Lasers Model 550 CO₂ laser. This laser is Q-switched by a rotating mirror yielding ~ 1 KW peak power pulses of ~ 200 nsec duration at 100-300 Hz.

C.2.c. Experimental setup

In Figure C.4 we show a typical experimental setup for our spin-flip Raman laser system. We have chosen the standard collinear geometry, with $\vec{k}_p, \vec{k}_s \perp \vec{H}$ and $\vec{E}_p \parallel \vec{H}$, which yields a Stokes field polarization $\vec{E}_s \perp \vec{H}$. Our apparatus differs somewhat from previous experimenters in that the Stokes radiation is collected in the backward direction. Pump radiation is rejected when the Stokes radiation is reflected from the Ge flat oriented at Brewster's angle. Further pump rejection is performed by a Minuteman .5m low resolution monochromator, and the Stokes radiation is detected using a Ge:Cu photoconductive detector. The Stokes collection optics are aligned using a He-Ne beam retroreflected from the polished end face of the InSb crystal.

C.2.d. Results of preliminary experiments

Using borrowed crystals of carrier concentration $7.7 \times 10^{15} \text{ cm}^{-3}$ and $1 \times 10^{16} \text{ cm}^{-3}$, we observed Stokes radiation from a laser cavity formed by the polished natural reflectivity end faces of the crystal. We were able to quickly determine that crystals of

Figure C.4 Schematic of our preliminary spin-flip Raman laser system. The notation $\odot$ indicates that the vector in question is perpendicular to the page.

such high carrier concentration are unsuitable for our application in that they produce Stokes radiation of too low a frequency.

This problem and its proposed solution are discussed in detail in the second half of this proposal. Due to the questionable quality of the crystals, the peak powers we observed with TEA pumping were quite small, on the order of 1 watt. This problem will be remedied by ordering new crystals, according to the specifications described later in this proposal.

To summarize, we have constructed a complete spin-flip Raman laser system in our laboratory. We have observed tunable Stokes radiation in preliminary experiments.

III. Publications

1. CO₂ Laser Saturation of Internal-Vibrational Modes of Molecular Impurities in Alkali Halides, A.R. Chraplyvy and A.J. Sievers, Optics Letters 3, 112 (1978).
2. A New Saturable Absorber for the CO₂ Laser Using Doped KCl, R.K. Ahrenkiel, J.F. Figueira, C.R. Phipps, D.J. Dunlavy, S.J. Thomas and A.J. Sievers, Appl. Phys. Letters 33, 705 (1978).