Multiphonon Decay Rates in Rare Earth Doped Chalcogenide Glasses

B.N. Samson, T. Schweizer*, J.R. Hector, W.S. Brocklesby, D.W.Hewak

Optoelectronics Research Centre
University of Southampton
Southampton
SO17 1BJ
U.K.

* corresponding author
Tel +44 (0)1703 593141
Fax +44 (0)1703 593142
Email: TS@ORC.SOTON.AC.UK

Abstract

The optical properties of rare earth doped chalcogenide glasses have received a considerable amount of interest in recent years, primarily because of their very low multiphonon decay rates when compared with other glass hosts. In this letter we compare the measured multiphonon decay rates for rare earth doped gallium lanthanum sulphide (GaLaS) glass with results obtained previously [1,2] and find significant discrepancies. Our results indicate that the multiphonon decay rate across energy gaps in the important 3-5μm wavelength range is considerably lower than previously calculated and we provide a more accurate set of parameters to describe this process in rare earth doped chalcogenide glasses.

Keywords: chalcogenide glass, rare earth doping, multiphonon decay

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1. Introduction

The optical properties of rare earth doped chalcogenide glasses is currently of interest for possible applications in mid-infrared lasers [3,4], optical fiber amplifiers [5,6] and other applications that utilise the low phonon energy inherent in this family of glasses. As a consequence of their low phonon energy these hosts exhibit excellent mid-infrared transmission with a low loss window extending as far as 10μm in some cases [7]. However, a further consequence of the low phonon energy is a much reduced multiphonon decay rate when compared with that found in oxide and fluoride glasses [1,2]. Since the multiphonon decay is essentially a competing process to the fluorescence, a low multiphonon decay rate can lead to an increased fluorescence efficiency for many important rare earth transitions. This, when coupled with good environmental properties and ease of fiberization, make these glasses of interest for fiber applications and indeed the first chalcogenide glass fiber laser has recently been demonstrated [8].

The theory of multiphonon decay rates in rare earth doped phosphors is well documented and has been applied to numerous crystal and glass systems [1,2]. Experimentally the multiphonon decay rate (W_{mp}) is obtained from a combination of the measured fluorescence lifetime (τ_m) and the radiative lifetime (τ_r), which may be estimated from a Judd-Ofelt analysis of the rare earth doped glass absorption spectrum:

$$W_{mp}=\frac{1}{\tau_m}-\frac{1}{\tau_r} \qquad (1)$$

The multiphonon decay rate is normally assumed to be independent of the rare earth ion, and seen to follow an exponential dependence with the size of the energy gap (ΔE) between the excited energy level and the next lowest lying level. At temperatures above 0K the multiphonon decay rate may be expressed[2];

$$W_{mp}=B[n(T)+1]^{p}\exp(-\alpha\Delta E) \qquad (2)$$

where the constants α and B are usually derived from fitting equation 2 to the experimental W_{mp} against ΔE data. The parameter p is simply the number of phonons required to bridge the energy gap:

$$p=\frac{\Delta E}{\hbar\omega} \tag{3}$$

and n(T) is the thermal occupancy for the phonon mode of energy $\hbar\omega$.

Obviously hosts with a low phonon energy tend to have a low multiphonon decay rate, but a quantitative evaluation of this process requires an accurate estimate of the parameters α and B for any particular host. Experimentally, this is usually done by measuring the fluorescence lifetimes for a number of rare earth ion transitions spanning a wide range of energy gaps and fitting equation 2 to the experimental multiphonon decay rates. Typically the energy gaps are chosen such that $2<p<7$ which for a typical chalcogenide glass (eg for GaLaS glass $\hbar\omega=425cm^{-1}$ [9]) puts ΔE in the range 1200-2500cm-1(ie 4-8μm). The lower limit for ΔE is where the radiative decay rate is negligible compared with the multiphonon rate, making detection of the weak fluorescence in the mid-infrared inpracticle. The upper energy limit is the case where the measured lifetime is dominated by the radiative rate and the multiphonon decay rate is a small fraction of the total lifetime. Since the radiative rate is an estimated quantity based on a Judd-Ofelt anaysis with typically ±20% error and in some cases even larger errors, it is pointless to estimate multiphonon decay rates for transitions where this nonradiative rate is only a few percent of the measured lifetime. We believe this is partly the reason that ref [10,11] obtained a fit between their measured multiphonon decay rates in chalcogenide glasses and the calculated value based on the parameters previously published in Ref [1,2]. The graphs presented in references [10,11] contain too many unreliable data points with $\Delta E>3000cm^{-1}$ and hence negligible multiphonon decay rate. Furthermore these authors failed to include the temperature dependence of the multiphonon decay rate, making the mistake of comparing a simplified form of equation 2 only valid for T=0K with lifetime data collected at room temperature. The aggreement between their experimental data and the correct form of equation 2 for T=300K, is in actual fact quite

poor.

In the case where the host glass phonon energy is small, comparable or even smaller than the Stark splitting of the energy levels under study, great care must be taken in defining the energy gap (ΔE) since variations corresponding to several quanta of phonon energy can easily occur in the definition of this parameter. In this paper most of the rare earth doped samples included in the study have a measurable mid-infrared fluorescence spectrum across the energy gap under study, and we simply define ΔE as the peak of this fluorescence. In most cases this corresponds closely to the energy difference between the two peaks as measured from the ground state absorption spectrum. An example of this is shown in figure 1a,b for Ho^{3+} doped GaLaS glass. In the few cases were fluorescence could not be measured across the energy gap under study, we have used this peak-peak definition as an alternative estimate of ΔE.

The parameters α and B for rare earth doped GaLaS glass have previously been published [1,2] and recently been applied to other chalcogenide glass systems in order to estimate the multiphonon decay rates in new sulphide glass systems [9,10,11]. However, the non-radiative properties of chalcogenide glasses have recently been shown to depend strongly on the oxide impurity levels present in the glass [12]. Thus the measured optical properties of the glass are strongly dependent on the details of the glass processing along with the purity of starting materials used in the fabrication of the samples. In this paper we present experimental data that suggests the multiphonon decay rates in rare earth doped chalcogenide glass is significantly different from that previously estimated. Importantly, we find that the multiphonon decay rate is as much as an order of magnitude less than previously thought, particularly in the critical 3-5μm range of interest for device applications. Using our measured multiphonon decay rates in a variety of rare earth doped samples we derive a new set of parameters that accurately describe this non-radiative decay process in GaLaS glass.

2. Experimental

The glass samples were all made from high purity starting powers and the gallium to lanthanum ratio was 70:30. These samples also contain very low levels of OH and oxide impurities, important since both can increase the non-radiative decay rate for rare earth ions in chalcogenide

glasses. In most cases the rare earth doping level was kept as low as possible in order to prevent ion-ion interactions from affecting the measured fluorescence lifetimes and typically the rare earth concentration was around 500ppm/wt (~$5.7x10^{18}$ ion/cm^3). The exception is the sample containing terbium which required a higher doping level in order to measure the mid-infrared fluorescence (~5μm) and lifetime. In this case the rare earth concentration was around 2000ppm/wt.

The measured lifetimes were obtained by exciting the glass sample with an argon ion pumped Ti:sapphire laser or diode pumped Tm-YAG laser operating at 2μm. The incident light was chopped by an acousto-optic modulator or mechanical chopper and the resulting fluorescence focused onto a small area InGaAs detector or liquid nitrogen cooled InSb detector, depending on the fluorescence wavelength. The measured decay curves were averaged using a digital oscilloscope and a single exponential decay curve fitted to the resulting data. Wavelength discrimination was provided by either a monochrometer or filters and the system response was 1μs with the InGaAs detector and 20μs with the InSb. Care must be taken in many of these experiments to prevent re-absorption from distorting the measured lifetime and where ever possible we have used resonant excitation of the energy level to be measured. Unfortunately this is not possible for some of the mid-infrared transitions under investigation and in these cases care must be taken that populations in higher lying energy levels do not distort the measured lifetime of the level under investigation.

3. Results

Estimates of the radiative rates for all of the energy levels under investigation were made using Judd-Ofelt analysis on heavily doped samples and details of this have been published previously for dysprosium [13], erbium [14], praseodymium [9], thulium and terbium [15] doped GaLaS glass samples. Our results for holmium doped samples have not been published but are largely in agreement with other results on holmium doped chalcogenide glasses. A summary of the measured lifetimes, radiative rates and resultant multiphonon decay rates obtained using equation 1 are listed in table I. In most of these cases the magnitude of the energy gap is simply taken as the peak fluorescence energy, the few exceptions (indicated with *) are the energy gaps <2000cm-1 which are beyond the sensitivity of our detection equipment. As already discussed above, in these cases the energy gap is taken as the energy difference between the two ground state

absorption peaks.

The resultant graph of W_{mp} versus ΔE is shown in figure 2 and clearly shows the exponential dependence between multiphonon decay rate and energy gap and that this process is largely independent of the rare earth ion used. The worst discrepancy is the high concentration Tb^{3+} doped sample which appears to have a higher multiphonon decay rate than expected probably due to cross relaxation effects increasing the overall non-radiative decay rate, not too surprising given the doping level used for this sample. The other possible exception is the Pr^{3+}-doped sample which we believe might also be effected by a cross relaxation process even at the low concentration used in this sample.

4. Discussion

Also included in figure 2 is a fit to the experimental data obtained using the parameters $\alpha=7x10^{-3}$ cm^{-1} and $B=2.5x10^{9}$ S^{-1} in equation 2, along with the results generated using the α and B parameters previously published for rare earth doped GaLaS glass [1,2]. Clearly the previous set of parameters does not accurately describe the multiphonon decay rate measured in the present set of GaLaS glass samples and a comparison of the two sets of parameters is shown in table II. In particular the parameter α is considerably higher in our glass samples resulting in a much reduced multiphonon decay rate in the region where p=4 to 7 phonons, $\Delta E=1800\text{-}3500cm^{-1}$ (3-5μm). Furthermore the parameter B is almost 3 orders of magnitude greater in our fit. We believe the much reduced multiphonon decay rate measured in our present study may be related to the increased purity of the chalcogenide samples used here, in particular the very low levels of oxide impurities which can significantly increase the measured non-radiative decay rates [12]. Another explanation may be related to the high number of transitions in the previous study [1,2] that occurred very close to the glass absorption edge, thus providing another non-radiative decay mechanism and hence shortening the measured lifetime [16]. In the present study we have avoided the use of energy levels at wavelengths <700nm, hence removing the possibility of energy transfer between the rare earth ion and the glass host. As already discussed, we believe the fit between theory and experiment demonstrated in ref [10,11] to be partly due to the incorrect form equation 2 used in the paper. The agreement between the correct form of equation 2 and their room temperature experimental data is acually rather poor providing further evidence that the

previous set of multiphonon decay rate parameters are not applicable to the chalcogenide samples currently being fabricated. Indeed, the data presented in references [10,11] for $\Delta E<3000cm^{-1}$ agree rather well with our data. As explained above, we believe the experimental data is unreliable for energy gaps greater than this value.

The physical interpretation of the α and B parameters is rather unclear due to the empirical nature of the formula but previous studies [1] have related the α parameter directly to the electron-phonon coupling constant (ϵ) which is also listed in table II:

$$\epsilon = \exp(-\alpha \hbar\omega) \tag{4}$$

Indeed the small value for α previously obtained in GaLaS glass has been taken to indicate a very large value for the electron phonon coupling strength in chalcogenide glasses [1] explained by the strong degree of covalent bonding inherent in this family of glasses. From the parameters previously used to describe the electron-phonon coupling strength in GaLaS glass, ϵ=0.36, this is almost a factor of 10 greater than that found in any other glass host. However, it is noticeable from table II that our set of parameters brings the values for GaLaS glass into broad agreement with those obtained in other glass hosts. Furthermore the large variations found when comparing the parameter B in various glass hosts can largely be removed by defining the parameter B* rather than B [17]:

$$\log(B*) = \log(B) - 0.86\,\alpha\hbar\omega \tag{5}$$

where essentially the energy gap has been reduced by a factor of twice the phonon energy. The tabulated values for B* and ϵ for our GaLaS samples are listed in table II and suggest that the multiphonon decay rate parameters for chalcogenide glasses are very similar to those found in various other glass hosts, and not the rather unique set of parameters as suggested by the previous set of measurements [1,2].

An accurate description of the multiphonon decay rate for doped chalcogenide glass is important in estimating the radiative quantum efficiencies for 'new' transitions potentially of interest in applications as mid-infrared lasers. From the results presented in this paper, the multiphonon decay rates in the critical wavelength range 3-5μm (ie energy gap 3300-2000cm-1) are as much as an order of magnitude lower than previously estimated in doped chalcogenide glasses. This is important, since the estimated quantum efficiencies for transitions in this wavelength range will actually be limited by the relative branching ratios rather than the non-radiative properties of the glass [9,10,14]. As a consequence there would be little advantage in seeking a glass host with a lower multiphonon decay rate (eg lower phonon energy) particularly since the branching ratios are relatively insensitive to the glass host. One example is the 1.3μm transition in Pr^{3+}-doped GaLaS ,which has an energy gap $\Delta E=3000cm^{-1}$, where the new set of parameters suggest a negligible multiphonon decay rate and indicate the radiative quantum efficiency is limited by the branching ratio. This result is broadly in line with recent quantum efficiency measurements on this transition [18], but in contradiction with that obtained using a Judd-Ofelt analysis [9].

5. Conclusion

In this paper we have provided experimental results on the multiphonon decay rate of rare earth ions in GaLaS glass which indicate that the previous estimates [1,2,10,11] of this process in chalcogenide glasses have been over estimated. In the critical wavelength range (3-5μm) for mid-infrared transitions the measured rate is almost an order of magnitude lower than previously found. This has consequences for calculations of the radiative quantum efficiencies for many important transitions and improves the prospects for mid-infrared chalcogenide glass fiber lasers operating in this wavelength range. The measured decay rate is seen to be largerly independent of the rare earth ion used and we provide a new set of multiphonon decay rate parameters which more accuratly describe this non-radiative process in doped chalocogenide glasses. This new set of parameters are seen to be largely in line with those obtained in other glass hosts.

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Figure captions

Figure 1a. Absorption spectra for Ho^{3+} doped GaLaS glass showing the energy gap under study. The magnitude of the gap is estimated from the peak-peak energy.

Figure 1b. Mid-infrared fluorescence for Ho^{3+} doped GaLaS across the energy gap indicated in 1a. The peak fluorescence wavelength agrees well with estimated peak-peak energy measured from absorption spectra.

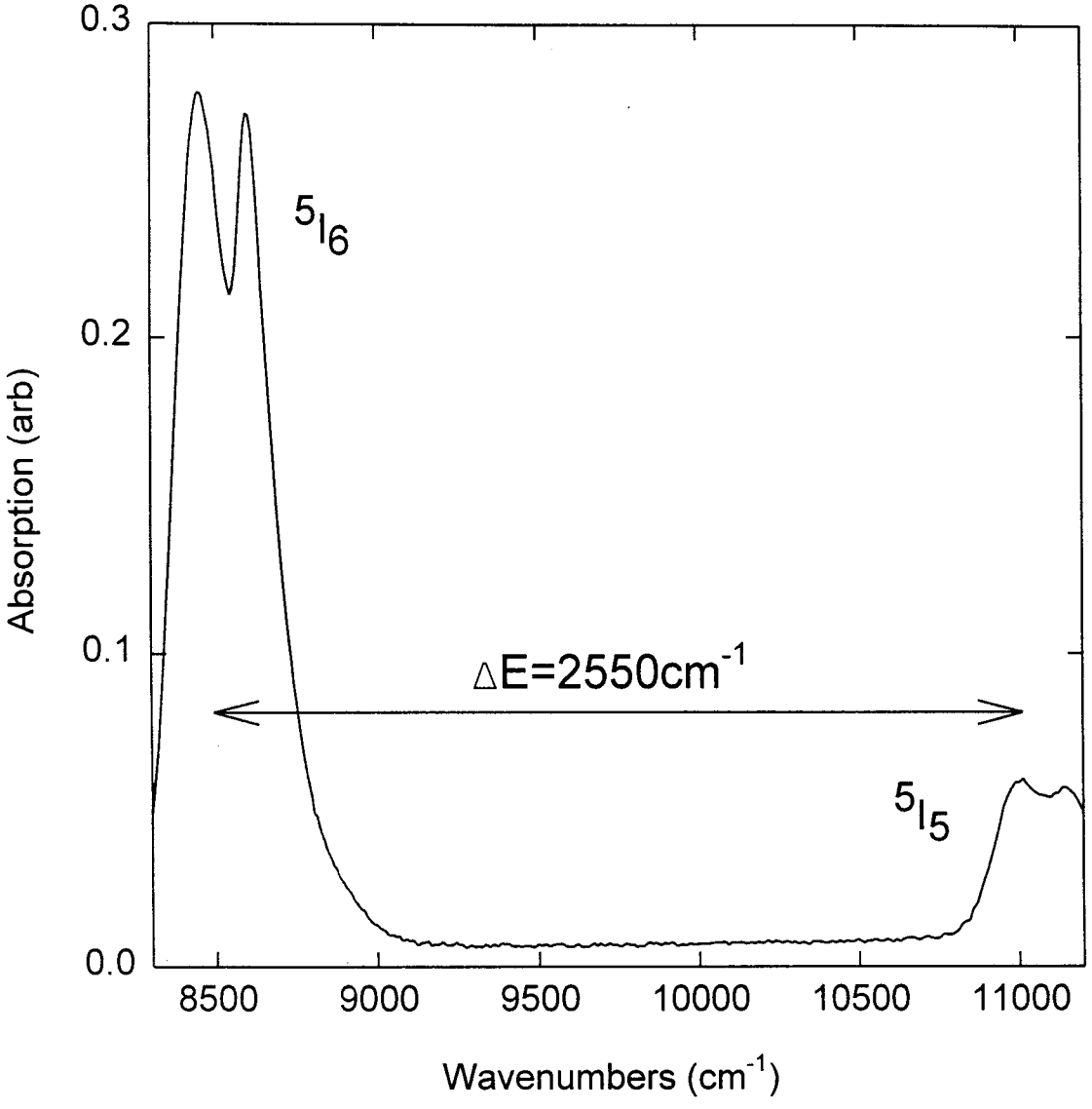
Figure 2. Measured room temperature multi-phonon decay rate against energy gap for rare earth doped GaLaS glass along with a fit to the experimental data using equation 2 (full line). Also shown (dashed line) is a plot generated using the set of parameters previously measured in GaLaS glass from reference [1].

Table I: Measured fluorescence lifetimes for rare earth doped GaLaS glass. The energy gap has been obtained from the peak fluorescence wavelength except those indicated by*

R.E	Wavelength	Energy Level	Energy Gap (cm^{-1})	τ_{meas}	τ_{rad}	W_{mp} (s^{-1})
Dy^{3+}	800nm	$^6F_{3/2}$	1400*	5μs	310μs	196800
Dy^{3+}	1300nm	$^6H_{9/2}$, $^6F_{11/2}$	1850*	55μs	440μs	14930
Dy^{3+}	1700nm	$^6H_{11/2}$	2350	1.3ms	2.6ms	385
Ho^{3+}	760nm	$^5I_4$	2040	500μs	3.5ms	1714
Ho^{3+}	900nm	$^5I_5$	2550	1.7ms	2.1ms	110
Tm^{3+}	700nm	$^3H_5$	1850*	27μs	60μs	20370
Tm^{3+}	1200nm	$^3F_2$, $^3F_3$	2575	730μs	780μs	88
Er^{3+}	800nm	$^4I_{9/2}$	2210	650μs	1.2ms	705
Pr^{3+}	4450nm	$^3H_5$	2100	220μs	16ms	4480
Tb^{3+}	4500nm	$^7F_5$	2080	100μs	17ms	10000

Table II: Multiphonon decay rate parameters for rare earth doped glasses

Host glass	α (cm^{-1})	B (s^{-1})	phonon energy(cm^{-1})	ϵ	log (B*)
GaLaS (Our Data)	$7x10^{-3}$	$2.5x10^9$	425	0.051	6.9
GaLaS [ref 1]	$2.9x10^{-3}$	$1x10^6$	350	0.36	5.1
ZBLA [ref 1]	$5.8x10^{-3}$	$1x10^{10}$	500	0.056	7.5
Tellurite [ref 1]	$4.7x10^{-3}$	$6.3x10^{10}$	700	0.037	8.0
Germanate [ref 1]	$4.9x10^{-3}$	$3.4x10^{10}$	900	0.013	6.7
Silicate [ref 1]	$4.7x10^{-3}$	$1.4x10^{12}$	1100	0.006	7.7


0.3
0.2
0.1
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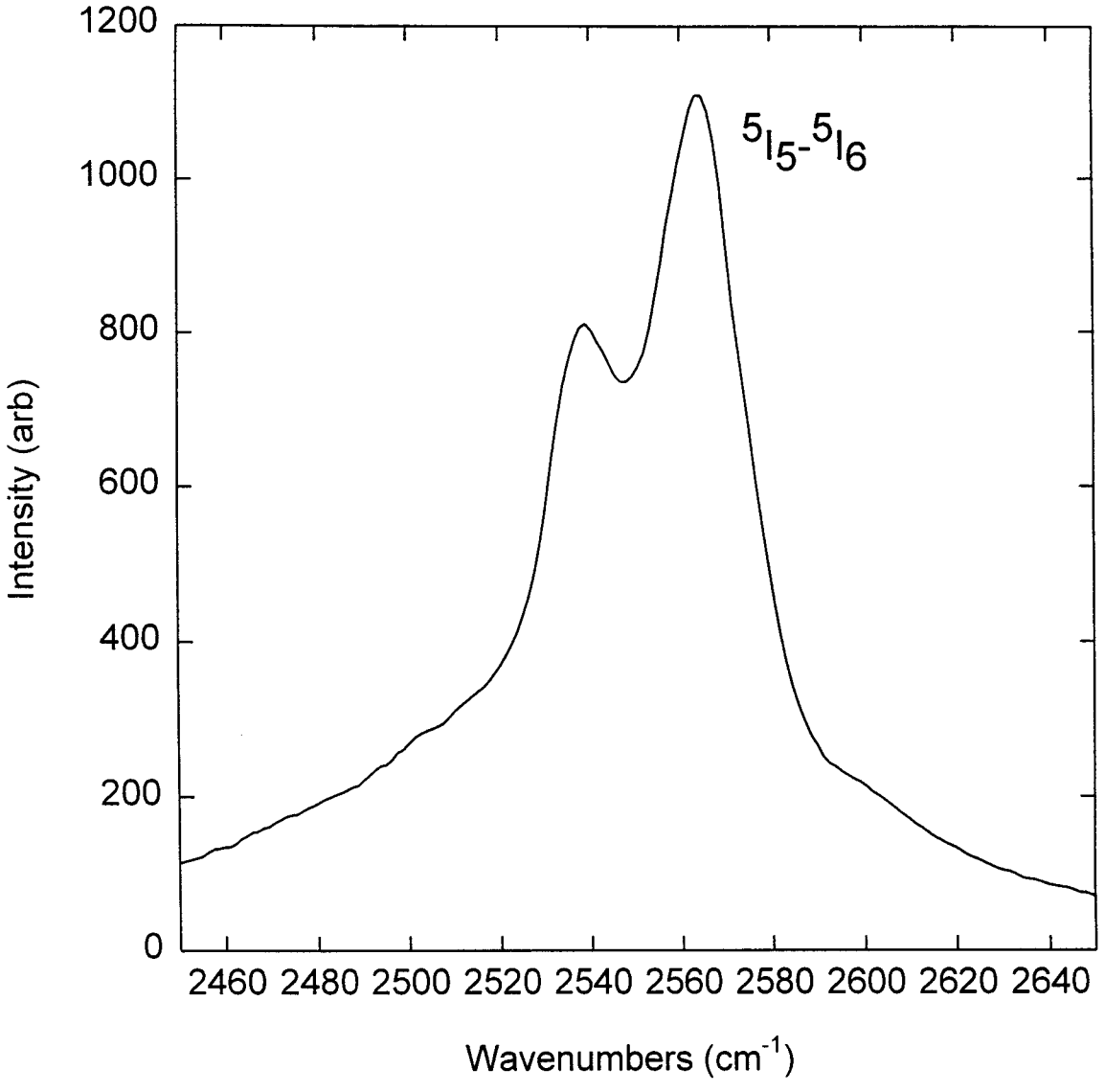
Absorption (arb)
$^5I_6$
$\Delta E=2550cm^{-1}$
$^5I_5$
8500
9000
9500
10000
10500
11000
Wavenumbers (cm^{-1})


1200
1000
800
600
400
200
0
Intensity (arb)
$^5I_5$-$^5I_6$
2460 2480 2500 2520 2540 2560 2580 2600 2620 2640
Wavenumbers (cm^{-1})