# Laser Cooling in the Condensed Phase by Frequency Up-Conversion

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Frequency up-conversion has been observed in fluid solutions of the laser dye, rhodamine 101, when excited at 1.96 eV into the low energy absorption tail 0.15 eV from the 0-0 band origin. The emission intensity is temperature dependent and is demonstrated to be an excellent measurement of the temperature of the sample. We show for the first time how intense laser irradiation in this spectral region leads to the removal of thermal energy by the frequency up-conversion process, and thus lowers the temperature of the sample. A decrease in temperature at a rate of 0.7 $\mathrm{K\,h^{-1}}$ is demonstrated for a sample with a 3 $\mathrm{J\,K^{-1}}$ heat capacity, when irradiated with 350 mW of laser light at 1.96 eV.

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Organic dyes can be excited in the long wavelength wing of the $S_0$-$S_1$ transition beyond the fluorescence emission peak where only a fraction of the molecules interact with the exciting laser light. The dynamics of such a $S_0$-$S_1$ relaxation has been successfully modeled [1]. In a recent study of both fluid and solid solutions of the dye, rhodamine B, irradiation in the red at 632.8 nm produced a very noticeable yellow emission [2]. There were a number of unusual observations associated with the luminescence, primarily that the excitation light was 0.28 eV lower than the absorption maximum of the rhodamine B dye and even 0.13 eV lower in energy than the emission maximum. Experimental measurements of the variation of the luminescence signal with input power eluded a linear proportionality implying a mechanism involving one photon for the up-conversion process. Finally, the luminescence disappeared when the sample temperature was reduced from 298 to 180 K. The frequency up-conversion process was attributed to excitation of dye molecules, populating high vibrational states, into the first excited state, i.e., hot band absorption. Rhodamine B has a high fluorescence quantum efficiency and consequently the majority of excited states fluoresced back to the ground electronic state and to vibrational states lower in energy than those prior to excitation. This simple interpretation was consistent with all of the observed data and it suggested a possible method of removing thermal energy from the sample, if it is considered to be a thermodynamically open system: If it is assumed that the absorbed photon accesses only the lowest vibrational states of the excited state, then fluorescence of higher energy than the absorbed light removes thermal energy and creates a local cooling, rather than heating. Rhodamine B has a luminescence quantum efficiency of only 0.7 and thus 30% of the absorbed light is lost nonradiatively, leading to a far more efficient heating effect than the cooling of the up-conversion process. However, for a dye with a fluorescence quantum efficiency of close to unity, there is no nonradiative decay route and a greater probability of observing the cooling effect. The xanthene dye, rhodamine 101, was chosen as a suitable candidate as the molecular fluorescence quantum efficiency is reputed to be close to unity [3]. This also has the beneficial effect of keeping the amount of triplet states to an absolute minimum and thus reduces the possibility of long term photodegradation of the dye. Rhodamine 101 is a well known laser dye, indicating the absence of any transient absorption in the spectral region of the emission spectrum. This is an important feature as two photon absorption into higher excited states would decay by a nonradiative internal conversion process back to the first excited state and hence lead to sample heating.

In this Letter, we report a cooling effect in the condensed phase of a thermodynamically open system, by creating an adiabatic, low heat capacity solution of rhodamine 101. The sample temperature is reduced by a single photon up-conversion mechanism via irradiation into the low energy tail of the absorption spectrum.

The sample consisted of 0.3 ml of a solution of $10^{-4}M$ rhodamine 101 in acidified ethanol ($10^{-2}M$ HCl) in a fused silica, cylindrical sample tube. The solution was degassed by freeze, pump, and thawing the sample at low pressure, sealed off, and then placed in a cryostat. The acidification of the ethanol ensures that the dye is in the cationic form only [4] and at these low concentrations has been shown not to aggregate [5]. Absorption spectra show a simple temperature dependence of a single, well solvated dye molecule with no evidence for the zwitterionic form of the dye with an isobestic point at 2.11 eV (589 nm) that determines the position of the 0-0 or band origin [6,7]. Light from a 1 mW, stabilized helium-neon laser was used to excite the sample at 632.8 nm (1.96 eV). Luminescence was collected perpendicular to excitation with a 5 cm focal length lens that focused the light onto the slits of a 1 m monochromator and was subsequently detected by a photomultiplier tube (Hamamatsu R955) connected to a gated photon counter (Stanford SR400),

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interfaced to a computer for data analysis. In an identical fashion to the previous work on rhodamine B, luminescence from the sample was readily observed, even though the excitation light was 0.20 eV lower in energy than the absorption maximum and 0.12 eV lower than the emission maximum. Once again, by lowering the temperature the luminescence intensity reduces and is negligible at ca. 160 K. A representation of these spectra is shown in Fig. 1, where the low energy absorption spectrum is also shown for comparison, along with the position of the excitation light. We conclude from these data that the origin of the luminescence is identical to the case of rhodamine B discussed above. The data, plotted in Fig. 2, show the temperature dependence of the luminescence intensity at 2.00 eV (620 nm), and can be modeled with a function of the form $\exp(-\Delta E/kT)$, where $k$ is the Boltzmann constant and $T$ is the temperature. $\Delta E$ was determined to have a value of $0.14 \pm 0.01$ eV in good agreement with the difference between the excitation energy (1.96 eV) and the band origin (2.11 eV) as predicted by the Boltzmann distribution function, which models the population of the vibrational state being excited. In addition to confirming the origin of the frequency up-conversion, these data also provide an ideal method for monitoring the temperature of the sample since any change in temperature will be manifested as an increase or decrease in luminescence intensity, depending on whether the sample was heated or cooled. This is very convenient as any other temperature measuring device would add to the heat capacity of the sample and, depending on the device used, may also absorb some light and lead to an unwanted heating effect.

To create the adiabatic environment, the sample cell was attached to a Teflon holder and suspended in the cryostat which was subsequently evacuated to $<10^{-4}$ mbar and the temperature controller disabled. The cryostat was then returned to the luminescence spectrometer described above and the helium-neon laser set up in a stable configuration to excite the sample luminescence and hence monitor any intensity changes. Light from a cw dye laser was focused onto the sample using a 5 cm focal length cylindrical length that counter propagated the He-Ne monitoring light. Up to 350 mW of light in the wavelength range 580–680 nm was available using either rhodamine 6G or Kiton Red as the laser gain dyes, pumped with the 3W all lines output light from an argon ion laser. In four separate experiments the sample was irradiated at 583 nm (170 mW), 605 nm (310 mW), 620 nm (250 mW), and 634 nm (350 mW) for periods of up to 4 h. At 15 min intervals, the dye laser light was blocked and the luminescence intensity monitored by the He-Ne laser. These sets of data, normalized to the luminescence intensity at time zero, are plotted in Fig. 3. In addition, luminescence from the sample was also monitored without any irradiating light from the dye laser, in order to provide a reference signal for comparison.

When irradiating at 620 and 634 nm, the luminescence intensity quite clearly decreases, while irradiating at 583 and 605 nm, the signal increases. The reference signal remains unaffected over the full 4 h period and in all four cases the signal eventually returns to the reference value after ceasing dye laser excitation, indicating no long term photodegradation of the sample. We therefore conclude that the change in luminescence intensity is a result of a change in temperature of the sample caused by laser irradiation. At 583 and 605 nm, the sample appears to heat up, while at 620 and 634 nm the temperature goes down. This is the first direct observation of cooling of a condensed phase sample with the use of laser light.

Comparison of the change in luminescence intensity with the calibration data shown in Fig. 2 suggests that the

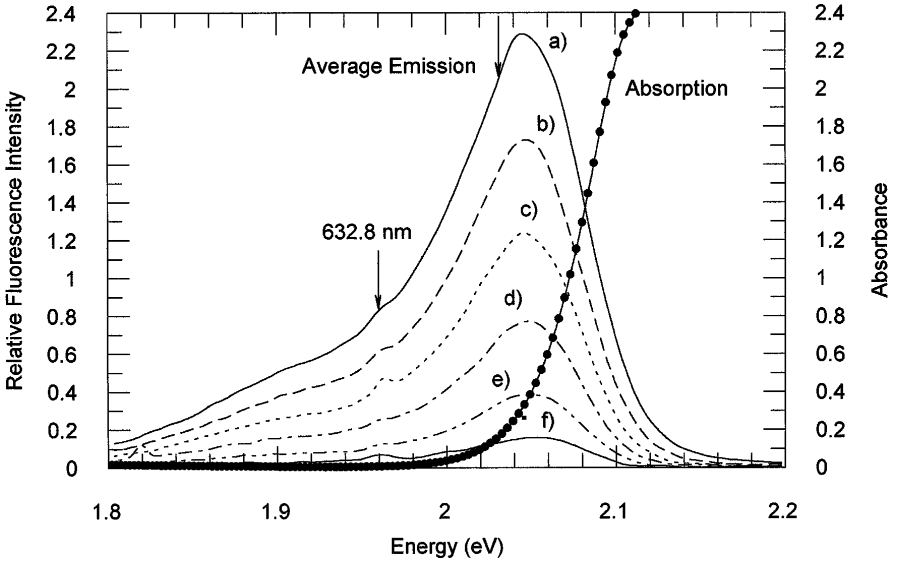

FIG. 1. Dispersed emission spectra for a $10^{-4}M$ solution of rhodamine 101 in acidified ethanol at (a) 310 K, (b) 290 K, (c) 270 K, (d) 250 K, (e) 220 K and (f) 200 K. Also shown for comparison is the low energy absorption tail of this sample, the He-Ne excitation wavelength, and the position of the average energy of the light emitted from this solution.

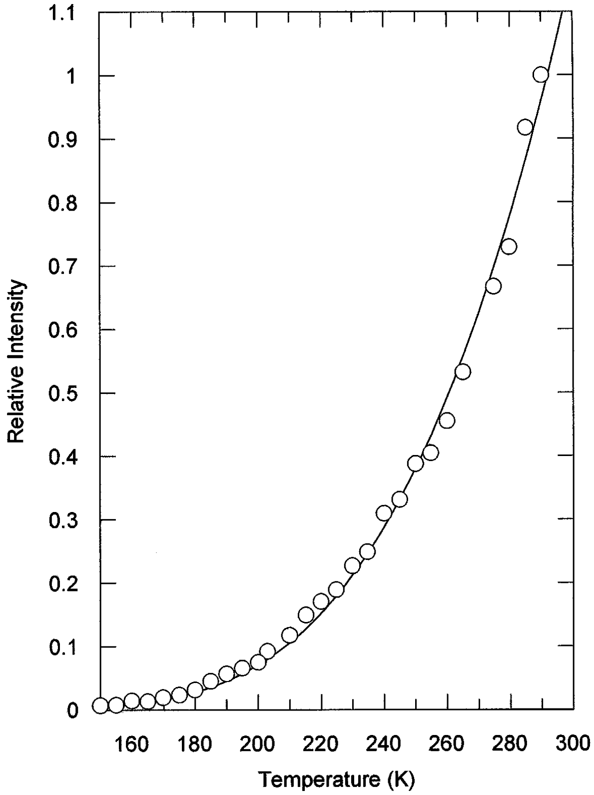

FIG. 2. Dependence of fluorescence intensity at 620 nm on temperature, for $10^{-4}M$ rhodamine 101 in acidified ethanol (○). The fluorescence intensity is normalized to that at room temperature (290 K) to allow for a direct relation with Fig. 3. The solid line represents an experimental fit to the function: Relative intensity, $I = 314 \exp(-2.32 \times 10^{-20}/\mathrm{kT})$.

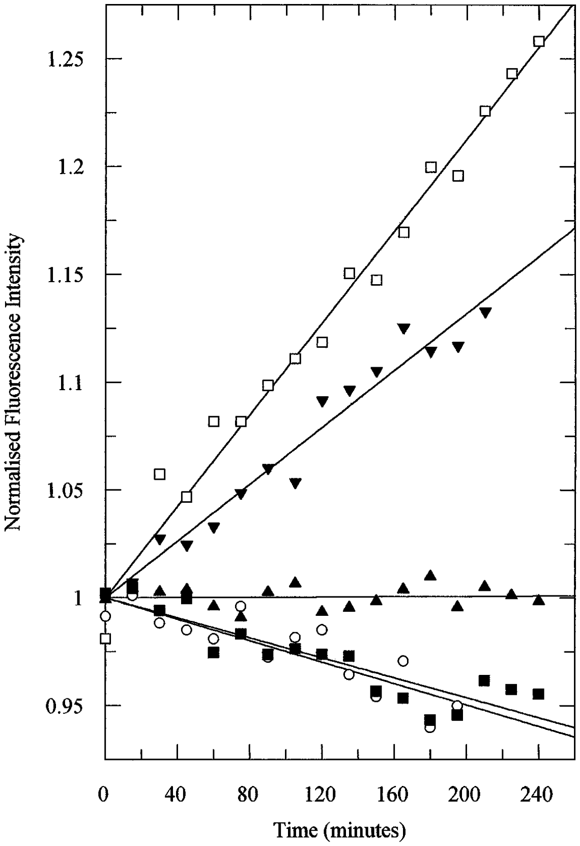

FIG. 3. The dependence of the emission intensity at 620 nm, monitored with time, when excited at (▼) 583 nm (170 mW), (□) 605 nm (310 mW), (▲) reference, (○) 620 nm (250 mW), and (■) 634 nm (350 mW). Solid lines are a linear fit to the data to act as a guide to the eye.

5% reduction is a result of a drop in temperature of 3 K, which is quite substantial. The average energy of the light emitted by the rhodamine 101 from the sample used is 2.03 eV, which is approximately 0.07 and 0.03 eV higher in energy that the energy of the incident photons at 634 and 620 nm, respectively, and therefore these two wavelengths would be predicted to cool the sample. However, it is 0.02 and 0.10 eV lower in energy than light at 605 and 583 nm, respectively; therefore, these wavelengths would be predicted to heat the sample. In both cases the predicted effect is observed, lending credibility to the hypothesis. The amount of thermal energy removed per absorbed photon at 634 nm is therefore 0.07 eV ($1.12 \times 10^{-20}$ J). The heat capacity of the sample is 3 $\mathrm{J\,K^{-1}}$ and thus $2.7 \times 10^{20}$ photons are required to be absorbed in order to realize a 1 K drop in sample temperature. The laser power used for this particular experiment was 350 mW, which is $1.12 \times 10^{18}$ photons per second. Since the sample temperature was reduced by 3 K in 4 h, this suggests that only 1 in every 18 photons is required to be absorbed, or a sample transmittance of 95%. The sample absorbance at 634 nm (see Fig. 1) was judged to be ca. 0.01, inferring a transmittance of 97%, and therefore the measured drop in temperature is within the predictions of a simple calculation. A summary of this calculation and similar analysis at the other excitation wavelengths is shown in Table I. Although the amount of thermal energy removed by irradiating at 620 is less than at 634 nm, the sample transmittance is lower and therefore more photons are absorbed leading to a more rapid cooling effect and so a lower excitation power effects the same decrease in temperature. On the high energy heating side of the average emission energy, the transmittance at 605 nm is lower still and therefore the small amount of heating far more rapidly raises the temperature as can be seen from the data in Fig. 3. Although these calculations are simplified, ignoring any vibrational relaxation in the excited state and assuming no other heating effects, the qualitative agreement between prediction and experiment is very good. The discrepancy between predicted and experimental observation for 583 nm light, where less heating is observed than is predicted, may be explained in terms of the large attenuation of the light. The simple model does not address the case of low transmittance and is thus inapplicable. The reabsorption effect is also less prevalent if all the light is absorbed close to the sample surface leading to an increase in average energy of emission and hence less heating. There is

TABLE I. Theoretical calculations for the required sample transmittances (%$T$) at all excitation wavelengths to effect the experimentally observed temperature changes $\Delta T$ from time zero. $\langle E_{ex} \rangle$ is the average energy of the light emitted by the rhodamine 101 sample used and is 2.03 eV.

| $\lambda_{ex}$ (nm) | $\Delta E$ from $\langle E_{ex} \rangle$ (eV) | $\Delta E$ from $\langle E_{ex} \rangle$ (J) | Irrad'n Power ($\mathrm{J\,s^{-1}}$) | No. irradiating photons $\mathrm{s^{-1}}$ | No. irradiating photons in 4 h | Observed $\Delta T$ (K) | No. photons req'd for observed $\Delta T$ | Calc'd %$T$ | Actual %$T$ |
|---|---|---|---|---|---|---|---|---|---|
| 634 | $-0.07$ | $-1.12 \times 10^{-20}$ | 0.35 | $1.12 \times 10^{18}$ | $1.61 \times 10^{22}$ | $-3.0$ | 1 in 18 | 95 | 97 |
| 620 | $-0.03$ | $-4.81 \times 10^{-21}$ | 0.25 | $7.80 \times 10^{17}$ | $1.12 \times 10^{22}$ | $-2.5$ | 1 in 7 | 86 | 90 |
| 605 | $+0.02$ | $+3.20 \times 10^{-21}$ | 0.31 | $9.44 \times 10^{17}$ | $1.36 \times 10^{22}$ | $+10.0$ | 1 in 1.5 | 31 | 41 |
| 583 | $+0.10$ | $+1.60 \times 10^{-20}$ | 0.17 | $5.00 \times 10^{17}$ | $7.18 \times 10^{21}$ | $+6.0$ | 1 in 6 | 83 | 0.3 |

a clear trade off between lowering the energy of the incident light to extract more energy per absorbed photon versus the number of absorbed photons. Other methods of enhancing the effect have been considered; perhaps the most obvious method would be to increase the concentration of the laser dye in the solution. However, large dye molecules are well known to readily form dimers and higher order aggregates at high concentrations that do not luminesce [1,5]. The rapid nonradiative, internal conversion processes in these species would therefore lead to sample heating and defeat the object of increasing the cooling effect. Another effect of increasing the dye concentration that is not as readily apparent is the problem of luminescence reabsorption caused by the large overlap of the luminescence spectrum and absorption spectrum in the region of the band origin [1,8,9] as seen clearly in Fig. 1. The measured peak of the emission from the rhodamine 101 at a concentration of $10^{-4} M$ occurs at 2.05 eV (605 nm), which is not the true maximum of the molecular emission. In undistorted luminescence spectra measured at low dye concentrations, the true peak occurs at 2.08 eV (597 nm). Based on this value, the amount of thermal energy removed per absorbed photon is in fact greater than the calculation allows for; however, it is the emission that is actually emitted by the sample that is significant in the cooling process. The reabsorbed emission will have an effect on the sample temperature, but this has been assumed to be a negligible contribution with respect to the amount of laser light absorbed. All these factors induce a delicate balance between sample concentration, quantum efficiency, pump wavelength and power, and the ability to effect a cooling of the sample.

Another method of enhancing the effect would be to reduce the heat capacity of the sample, by reducing the solution volume and the size of the container; however, the surface to volume ratio must be kept small as the fused silica surface enhances nonradiative decay for dye molecules in contact with, or near to the surface [10]. By embedding the dye in a polymer host, the container can be removed completely, although it is not clear whether the dye has a unit fluorescence quantum efficiency in this environment.

In conclusion, we have shown that irradiation of a solution of rhodamine 101 at energies lower than the 0-0 band origin results in a frequency up-conversion that leads to a cooling of the sample. Doppler cooling of atoms in the gas phase using laser radiation is well known [11] and, although the mechanism described here is similar, this is the first time that a cooling effect has been observed in a condensed phase system. An interesting feature of the effect is the saturable absorption phenomenon. As the sample cools, the population of the state being excited becomes less, leading to a limiting temperature and then no further cooling can occur regardless of the intensity of the radiation. This result may prove useful in exploiting large electronic resonance effects in nonlinear optics applications, without invoking the normal unwanted effects such as thermal lensing and sample destruction.

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