

Comment on "Laser Cooling in the Condensed Phase by Frequency Up-Conversion"

In light of our own work on the laser cooling of a solid [1], we read with great interest the recent Letter by Clark and Rumbles [2] on the laser cooling of a dye solution, a result the authors assert to be the first demonstration of laser cooling of a condensed sample. In this Comment we raise several objections concerning this work that suggest the authors' observations are spurious.

Most significantly, the authors claim that a 3-K temperature drop is observed for their 0.3-ml Rhodamine 101 dye solution after 4-h exposure to the 350-mW output of a dye laser tuned to 634 nm. However, the authors neglect to consider whether this temperature drop is consistent with the heat load delivered by a net absorption of RT blackbody radiation:

$$P_{\text{load}} = \sigma A(T_R^4 - T_S^4) \approx 4\sigma AT_R^3 \Delta T, \quad (1)$$

where P_{load} is the net absorbed power, σ is the Stefan-Boltzmann constant, A is the sample's surface area, T_R is the temperature of the surrounding RT radiation bath, T_S is the sample temperature, and $\Delta T \equiv T_R - T_S$. [Equation (1) assumes that the sample emissivity is unity over the wavelength range relevant to a RT blackbody, an assumption well justified for an ethanol sample contained in a fused silica cell.] Substituting values for the above quantities into Eq. (1), we find that for a 0.3-ml spherical sample at a temperature of 3 K below RT, the radiative load is 4.2 mW.

Such a value is significantly larger than the cooling power the authors could have at best obtained. This best-case cooling power is given by $P_{\text{cool}} = aP_{\text{laser}}\Delta E/E$, where P_{laser} is the laser pump power, a is the fraction of the pump power absorbed by the sample, and $\Delta E/E$ is the fractional change of the mean emitted-photon energy relative to the pump-photon energy. For $P_{\text{laser}} = 350$ mW, $a = 0.05$ (from the authors' calculation of the sample transmittance given in their Table I), and $\Delta E/E = 0.036$ (for a pump wavelength of 634 nm), we find that P_{cool} is only 0.63 mW. We conclude that under the experimental conditions specified by Clark and Rumbles, a temperature drop of 3 K is not possible. Moreover, we predict that the authors should have observed a temperature drop of merely ~ 0.5 K, a value on the same order as the noise in the temperature measurements implicit in their Figs. 2 and 3.

Another point is that Clark and Rumbles specify the heat capacity C of their sample as 3 J/K. We estimate a significantly smaller value from the data in their Letter. The volume of ethanol used is 0.3 ml; this corresponds to a heat capacity of only 0.6 J/K. The dimensions of the fused silica tube in which the liquid is sealed are not specified, but assuming an enclosed volume double that of the liquid, and assuming a wall thickness of 1 mm, we estimate the cell's heat capacity to be ~ 0.4 J/K. This gives an estimate

of the total heat capacity of 1 J/K, a factor of 3 less than the authors' quoted value.

The significance of the heat capacity lies *not* in the calculation of the temperature change of the sample, but rather in the time constant characterizing the liquid's rate of approach to its final, equilibrium temperature. This time constant τ can be easily estimated (for small departures in temperature from RT) with the help of Eq. (1) as

$$\tau = C/4A\sigma T_R^3, \quad (2)$$

which equals 13 min for $C = 1$ J/K. The observed temperature change due to the pump light should therefore have equilibrated within 40 min. In contrast, Clark and Rumbles observed a linear temperature change over a 4-h time span (cf. their Fig. 3), with no sign of equilibration. As a check on this highly unexpected behavior, it would be helpful to know how the fluorescence intensity changes when the dye laser is switched off at the end of each 4-h run: Does it return to its initial value exponentially and if so at what rate?

Finally, Fig. 3 includes a reference curve, which shows no temperature change over a 4-h time period. This appears to rule out the possibility that the authors' observed temperature changes arise from thermal drifts of the cryostat. However, this reference signal is measured with the dye laser shut off. It is no surprise that the system temperature does not vary in that case. A more meaningful reference measurement would be obtained by leaving on the dye laser but tuning its wavelength to that corresponding to the mean fluorescent-photon energy of 2.03 eV. At this pump wavelength, the absorbed and emitted powers exactly balance, so that the sample temperature should remain unchanged with time. Measuring the reference in this way, rather than in the manner of Clark and Rumbles, helps eliminate potential flaws in their radiative cooling experiment.

In light of this unmeaningful and potentially misleading reference measurement, the unexpected time dependence of the sample temperature, and, most significantly, the apparent impossibility of the sample having reached the temperatures claimed by the authors, we doubt Clark and Rumbles's assertion that they have directly observed laser-induced cooling of their sample.

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