

EXPERIMENTAL TEST OF A TIME-TEMPERATURE FORMULATION OF THE UNCERTAINTY PRINCIPLE

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ABSTRACT

A novel form of the Heisenberg uncertainty principle, as introduced by de Sabbata and Sivaram, $\Delta T \Delta t \geq \hbar/k$, was tested using laser-induced fluorescence of 30 nm particles of YAG:Ce. The temperature-dependent fluorescence decay lifetimes of this material were measured at thermal equilibrium over the range from ≈ 285 to 350 °K. The uncertainty in temperature of ≈ 4.5 °K (as derived from the relationship between temperature and lifetime) and the measured uncertainty in decay lifetime, ≈ 0.45 ns, yielded an “internal” estimate of $\Delta T \Delta t \geq 2.0 \times 10^{-9}$ °K s, which is ≈ 263 times larger than $\hbar/k = 7.6 \times 10^{-12}$ °K s. An “external” estimate of $\Delta T \Delta t \geq 4.5 \times 10^{-11}$ (which is ≈ 6 times \hbar/k) is derived from the measured uncertainty in the temperature of the sample and the measured uncertainty in lifetime. These results could be argued to increase by a factor of 5.6 if signal averaging is taken into account. If our approach is valid, then the findings are not inconsistent with the limitations predicted by this formulation of a time-temperature uncertainty principle and they imply the existence of a type of thermal quantum limit. The approach might thus open a path towards improved precision in the determination of the Boltzmann constant based on thermal squeezing techniques.

1. Introduction

The Heisenberg uncertainty principle is one of the fundamental tenets of quantum mechanics and many different interpretations of it have been developed, including number-phase [1], space-time [2] and information-entropy [3] versions, to list just a few. (Unnikrishnan and Gillies [4] are preparing a review of the topic which will survey the relevant literature.) In 1992, de Sabbata and Sivaram [5] developed still another formulation of it while investigating how torsion in general relativity links to defects in space-time topology. A model of the thermodynamics of the early universe served as a test bed for some of their predictions, and the general relationship between thermal energy and temperature, $E \sim kT$, led them to a phenomenological statement of the uncertainty principle of the form

$$\Delta T \Delta t \geq \hbar/k \quad (1)$$

where \hbar is the Planck constant and k is the Boltzmann constant. Further details of this calculation were provided later by de Sabbata [6]. Gillies *et al* [7] are in the process of examining this relationship from a quantum-mechanical as opposed to a dimensional-analysis perspective, and the work described below was motivated originally as a means of providing some experimental guidance for that theoretical effort.

Equation (1) is a rather surprising statement that predicts a fundamental limit on the precision with which temperatures may be measured. The question that arises immediately is, “the temperature of what?” In quantum mechanics, an uncertainty relation can be established between pairs of commutative variables, eg., displacement and momentum, energy and time, and so on, but is there a quantum mechanical role for temperature in that context? Kobayashi [8-10] has explored this point and has developed quantum mechanical descriptions of thermal equilibrium states and quasi-static processes in terms of eigenstates of relative phase interactions between particles or oscillators. While not placing temperature and time in the category of commutative quantum mechanical variables, his arguments do suggest that temperature can play a legitimate role in theoretical descriptions of physical phenomena at the quantum level. In a similar way, Ford and O’Connell [11] consider the effects of finite temperature on the spreading of a wave packet and show how this can lead to the calculation of decoherence rates.

Our approach to this question has been to carry out a laboratory study of a hybrid atomic/molecular process in which there is a well known coupling between time and temperature in a way that intermingles quantized atomic transitions with mesoscopic crystalline structures: the measurement of the temperature-dependent fluorescence decay lifetimes of rare-earth-doped ceramic oxides, which are often called thermographic phosphors. Fluorescence as referred to here is the emission occurring from electronic transitions and is usually in the visible region of the spectrum. It is generally true that the fluorescence spectral properties of any material will change with temperature. This is so in part because the Boltzmann distribution governs the partitioning of the populations in the various participating vibrational levels of the ground, excited and emitting states. A change in intensity distribution (including width and position of spectral lines) results since individual oscillator strengths vary in accordance with the selection rules and the Franck-Condon principle. The temperature dependence of these processes can be striking when there is competition with states which contend for nonradiative deexcitation pathways. The rate of change of the population of an emitting state, 2, to a ground state, 1, is the sum of a constant, purely radiative spontaneous emission, $A_{1,2}$, and a nonradiative component, $W_{1,2}$, which is temperature dependent. The decay rate, κ , is given by

$$\kappa = 1/\tau = A_{1,2} + W_{1,2} \quad (2)$$

where τ is the measured lifetime. One model for temperature dependence for some fluorescent materials is based on thermal promotion to a nonemitting electronic state followed by nonradiative relaxation. This is the “charge transfer state” (CTS) model and has been used by Fonger and Struck [12,13] to describe the thermal quenching of fluorescent materials. Depending on the temperature, the vibrational distribution in the excited state will be given by a Boltzmann distribution. At low temperature, states in resonance with the CTS are improbable. However, at higher temperature a significant fraction of the distribution will be at energies corresponding to the CTS and the transition to the CTS becomes likely. The rate is therefore

proportional to $\exp(-E/kT)$ where E is the energy difference between the excited electronic state of the dopant atom and the charge transfer state of the host ceramic matrix. Hence, equation (2) can be extended into an expression that predicts how decay time and temperature couple, which in simplest form [12,14] is

$$\tau = [(1/\tau_0) + b \cdot e^{(-E/kT)}]^{-1} \quad (3)$$

Here τ_0 is the unperurbed decay time and b is the rate to and from the CTS, which is on the order of the lattice vibration rate, $> 10^9 \text{ s}^{-1}$ [12,13]. A measurement of the fluorescence decay lifetime can thus be used to establish the temperature of the host lattice, with the uncertainty in the measured lifetime thus directly affecting the uncertainty in the resulting determination of lattice temperature. The measurement is intrinsically quantum mechanical in nature, in that a discrete atomic transition (or set of transitions) is being observed. One can then adopt the view that the resulting fluorescence lifetime and the associated lattice temperature are at least functionally commutative, in that a measurement of either one determines the other.

To explore what this might mean in terms of inter-related uncertainties, consider the following qualitative argument which, although non-rigorous, does illustrate a possible path toward an expression like equation (1). If the fluorescence lifetime and lattice temperature of a thermographic phosphor behave as discussed above, then the uncertainty in the energy (per dopant atom) coupled by the charge transfer state into the lattice vibrational mode, ΔE_{CTS} , would be related to the uncertainty in the measured fluorescence decay lifetime, $\Delta\tau$, via the standard uncertainty relation

$$\Delta E_{\text{CTS}} \Delta\tau \geq \hbar/2 \quad (4)$$

For a crystalline structure that is otherwise at thermal equilibrium with its surroundings, this uncertainty in CTS energy will manifest as an uncertainty in the thermal energy of the atom in the corresponding lattice mode. At room temperature, the lattice vibrational energy per atom per mode, E_v , would be

$$E_v = \frac{1}{2}kT \quad (5)$$

More generally, equation (5) would have a different numerical factor on the right hand side, depending on the specific solid state model that was employed. For example, the Heat Rule of Dulong and Petit [15] would require that $\frac{1}{2} \rightarrow 3$, and the models of Einstein [16], Debye [17], and Born and von Kármán [18] (and of course all of the more modern ones) would correct the functional form of the whole expression to take into account low temperature behavior, etc. However, our experiment was done in the range of room temperatures. Therefore, keeping to the simplest case for illustrative purposes, we then note that equation (5) leads to an uncertainty in the lattice vibrational energy of

$$\Delta E_v = \frac{1}{2}k \Delta T \quad (6)$$

It is then straightforward to relate the uncertainty in the energy of the lattice vibrational mode to the uncertainty in the CTS energy by rewriting equation (6) as

$$\Delta E_{\text{CTS}} = \frac{1}{2}k\Delta T \quad (7)$$

By combining equations (4) and (7), we then arrive at

$$\Delta T\Delta\tau \geq \hbar/k \quad (8)$$

which has the form of equation (1), but with the result now being at least heuristically motivated by standard considerations of solid state physics as applied to an experimental system that has a well known coupling between quantum and thermal effects. Equation (8) suggests that the Heisenberg uncertainty principle not only establishes the familiar quantum limits encountered, eg., in gravitational wave detection, but also fixes an unavoidable *thermal quantum limit* on atomic processes that are energetically coupled to a heat bath.

In what follows, we discuss the results of our recent measurements of the laser-induced fluorescence decay lifetime of 30 nm particles of YAG:Ce [19] and use the measured uncertainties in the lifetimes and in the YAG:Ce temperature to test the predictions of equation (8). The use of nanoscale particles is of particular interest, since for small enough particles the exact ratio of dopant atoms to host matrix atoms can either be measured or estimated precisely, and this would help lead to improved versions of the model discussed above. This work has been carried out within the broader context of our ongoing studies of remote thermometry with thermographic phosphors. An extensive review of the whole field is available elsewhere [20].

2. Experimental Arrangement

The thermographic phosphor used for this work was a powder of 30 nm particles of YAG:Ce, the specific stoichiometry of which was $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$. Two different samples of it were used; in both cases, a thin layer of it was bonded onto an aluminum substrate and placed in a Petri dish of water to help keep the sample in thermal equilibrium. The temperature of this assembly was adjusted by warming it on a laboratory hot plate. A nitrogen laser operating at 337 nm was used to excite fluorescence of the phosphor, which was subsequently detected by a photomultiplier tube. A 400 MHz waveform processing oscilloscope (Tektronix TDS3052) was used to capture the decaying exponential signals transduced by the photomultiplier, and the digitized data were then stored on a laboratory computer for subsequent analysis. Fiber optic cables were used to convey the excitation and fluorescence signals to and from the instrumentation. A 700 nm optical bandpass filter was used to prevent the shorter wavelengths from saturating the photomultiplier tube. To check for effects of wavelength selection, optical bandpass filters at 550 nm and 620 nm were also used in some of the experiments.

The thermometer used to measure the phosphor temperature was a Wahl 392MX platinum resistance thermometer with a Wahl 202 immersion-tip probe. It had a resolution of 0.1 °C and its calibration was traceable to the U.S. NIST. A measurement of its stability was obtained by placing the probe into one well of a Wahl IPR-4-110 ice point reference bath. The standard deviation of 32 measurements made at 30 s intervals was < 0.05 °C. During the fluorescence experiments, the tip of the probe was kept in mechanical contact with the aluminum substrate in the immediate proximity of the phosphor layer. The thermometer data were read and recorded manually.

The fluorescence decay lifetimes were extracted from the transduced photo-optical signals following acquisition and averaging of 32 individual waveforms at each temperature

tested. This was done to improve the signal-to-noise ratio and thus enable a more accurate determination of the waveform parameters. (The implications of the use of signal averaging within the context of testing the predictions of an uncertainty principle are discussed in Section 4 below.) Although the fluorescence decay signals were not pure single-exponential waveforms [19], such a fit was still good enough to permit the estimation of an equivalent single exponential decay time and the related uncertainty at each of the temperatures at which measurements were made. Further details about the preparation and use of the phosphor, and the performance characteristics of the measurement system are available elsewhere [19]. It is useful to note that the data obtained in these experiments are very similar in nature to those from many other such studies in our laboratories [20].

3. Results

The decay times measured as a function of temperature are plotted in Figure 1. Also shown there are curves of the calculated decay time estimates from equation (3), using 34.75 ns as the nominal value of the unquenched time constant and $E = 1090 \text{ cm}^{-1}$ as the electronic-state to charge-transfer-state energy difference. The standard error in the fit of the data to the model was $\Delta\tau/\tau \approx 1.3\%$, and the dashed lines show the range of models allowed by that uncertainty.

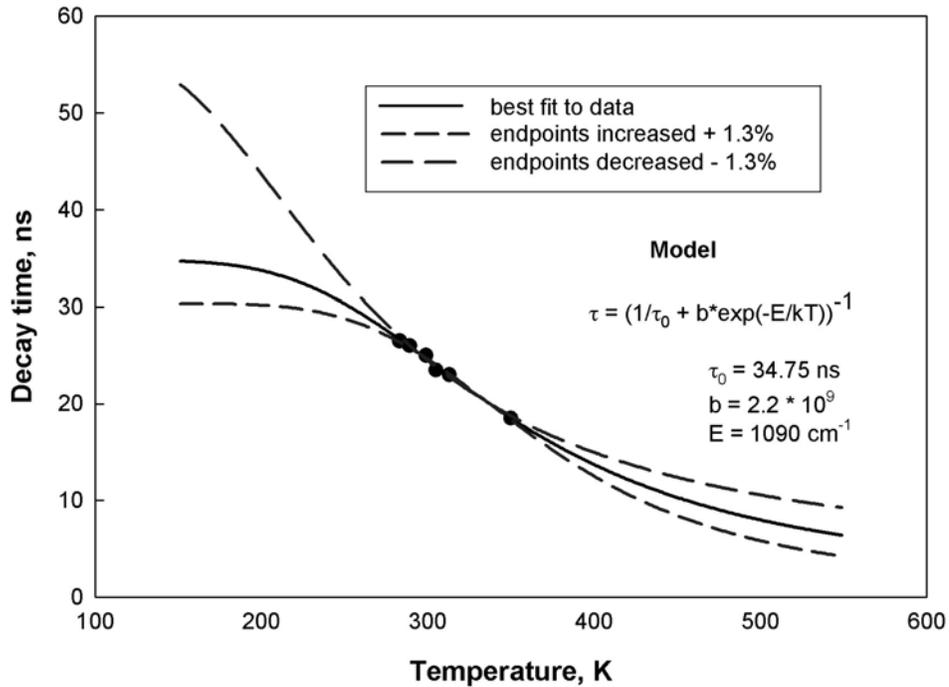


Figure 1. Decay time vs. temperature for 30 nm particles of YAG:Ce excited by a 337 nm pulsed nitrogen laser. The data are fit by equation (3) and the range of allowed models is shown by the dashed lines.

Over the range of temperatures at which the data were taken, one can approximate the roll-off in the thermal quenching with a straight line: from 285 to 350 °K, the decay time constant drops from ≈ 26 ns to ≈ 19 ns, yielding an equivalent slope having an absolute value of $n = 0.1 \text{ ns } ^\circ\text{K}^{-1}$.

Systematic uncertainties were not assigned to the data points in this preliminary study, but previous work in our laboratories has shown that detailed determinations of individual overall uncertainties for this type of measurement system are often as small as $\Delta\tau/\tau < 0.03\%$ [20,21]. Instead, we used the standard error relative to the fitted curve, 1.3%, to arrive at a conservative value of $\Delta\tau = 0.013 \cdot 34.75 \text{ ns} \approx 0.45 \text{ ns}$ as the uncertainty of the decay time constants. The associated uncertainty in the temperature, ΔT , was found by taking $\Delta T = \Delta\tau/n \approx 4.5 \text{ }^\circ\text{K}$. We refer to this as an “internal” estimate of the uncertainty in temperature, since it is derived directly from the uncertainty in the lifetime by way of the relationship between lifetime and temperature expressed in equation (3). The resulting product $\Delta T \Delta\tau = 2.0 \times 10^{-9} \text{ }^\circ\text{K s} > \hbar/k = 7.6 \times 10^{-12} \text{ }^\circ\text{K s}$, thus satisfying equation (8) by a factor of 263.

An alternative approach involves what we term an “external” estimate of ΔT . In this case, the uncertainty in temperature is given by the maximum measured departure from thermal equilibrium observed during a given set of lifetime measurements. During the course of our experiments, no such fluctuations larger than the resolution of the platinum resistance thermometer were observed, hence we take $\Delta T = 0.1 \text{ }^\circ\text{K}$ to be the external estimate. The uncertainty in the decay lifetime remains the same, thus $\Delta T \Delta\tau = 4.5 \times 10^{-11} \text{ }^\circ\text{K s} > \hbar/k = 7.6 \times 10^{-12} \text{ }^\circ\text{K s}$, which also satisfies equation (8), in this case by a factor of ≈ 6 . Of course, this is a much more debatable number in that it is not traceable to the quasi-commutative characteristic of the variables used to obtain the internal result. Even so, it does legitimately characterize the maximum thermal fluctuations present within the YAG:Ce sample.

4. Discussion

There is a time-honored axiom that an extraordinary claim requires extraordinary evidence to support it. We do not contend that the results presented here constitute sufficient experimental evidence to support explicitly the validity of a new form of the uncertainty principle, because of the assumptions and approximations made both in our own theoretical model and in the application of the data to it. However, the concept is intriguing and phosphor thermography does have the merit of linking the temperature of a crystalline specimen to the quantum physics of the fluorescence process. Hence we suggest that it is worth further investigation and offer the following comments and discussion.

The 30 nm crystals of YAG:Ce are an interesting material to use for this application because at a 1% dopant concentration, there is essentially one activator (Ce) atom per particle. This should simplify the modeling of the fluorescence process on the one hand, and also open the door to the application of single-atom spectroscopic methods on the other. The latter could be especially important in eliminating any competitive inter-particle effects that might act to modify the decay lifetimes. For instance, there was some evidence [19] that multi-photon processes were at work in our measurements, since the photo-optical decays were not purely single exponential. Ideally, this should be avoided and single nanocrystal spectroscopy would be a step in that direction. A number of other phosphors are also candidate materials including nanocrystalline $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, the particles of which are even smaller in size (8 to 12 nm) and which we have used in other applications [22].

Heating of the sample by the laser excitation is also a potential concern. The 337 nm

nitrogen laser used here was chosen because with it, we could maximize the brightness of fluorescence and thus reduce the reliance on signal averaging for extraction of the decay time constants (for the significance of this, see below). However, the cost of this in terms of effects on the nanoscale heat balance of the samples under illumination are yet to be determined. Fortunately, any such problems can be ameliorated significantly by using low intensity sources like blue LEDs which have recently been shown to fluoresce materials of this type at very low power levels [23]. Note, however, that a switch from laser-based illumination to use of an LED would eliminate the coherence of the excitation source, with ramifications for the phasing of the non-radiative decays via the CTS.

As mentioned above, the decay lifetimes were obtained via an algorithm that used as its input an average of 32 separate fluorescence signals. The signal-to-noise ratio improvement provided by the signal averaging reduces the uncertainty in τ , but it raises an important issue that is central to this approach. In a series of concise papers on the topic, Ramsey [24-26] explored the nature of quantum mechanical limitations in precision measurement, with emphasis on the application of the uncertainty principle. He points out there that the uncertainty principle is valid for “a single measurement on a single system” [25]. The question then becomes one of defining what it means to make a single measurement of fluorescence decay lifetime. Of course, values of τ and $\Delta\tau$ can be extracted from a single exponentially decaying fluorescence pulse. However, if the detection system’s shot noise on a single pulse is too large to permit extraction of a decay time constant, then signal averaging is needed. On the other hand, that does not (nor can it) mean that the intrinsic atomic decay time constant *per se* has been changed by the averaging. The central issue is really one of reducing the instrumentation system’s noise floor to the point where one can observe the variations in the decay time constant arising from the presence of the charge transfer state in the crystal, which is the mechanism through which the temperature dependence of the fluorescence process arises. We would argue that it is not until that noise floor is reached that one has actually made a meaningful measurement of the decay time constant, and the uncertainty in it at that point is what is of interest. If a sufficiently noiseless instrumentation system existed, this measurement could be made with a single atomic excitation. However, ambiguity arises when considering that 32 individual atomic excitations were needed to arrive at a determination of the lifetime and its uncertainty, yet the fluctuations in that lifetime should ideally not be different from those made with a single measurement with the sufficiently noiseless system (if the system’s noise is the only corrupting factor). One solution suggested by Ramsey is that the uncertainty principle’s limit is still valid in such a case, but that the equivalent numerical size of it be reduced by \sqrt{N} where N is the number of different systems that are measured [25]. It is not clear that this solution should be applied here, but if one does so, the right-hand side of equation (8) is reduced by a factor of ≈ 5.6 , or equivalently, our internal and external estimates of $\Delta T\Delta\tau$ become 1472 and 33.6 times greater than \hbar/k , respectively. We are continuing to investigate this issue.

An interesting conjecture that derives from equation (8) is the possibility of realizing thermally squeezed states in closed systems. Aharonov and Reznik [27] have shown that conserved observables within closed systems are generally subject to an uncertainty relation. The radiative plus nonradiative components of the energy from the fluorescence decay of the dopant atom’s excited state are a conserved quantity in that the sum of them must equal to the excitation energy. Therefore, in analogy with the generation of optically squeezed states of light, one should be able to generate thermally squeezed charge transfer states in the host matrix. An implication of that possibility might be the creation of phonon bundles in the lattice that have

phase-coherence with the optical excitation pulses. From a metrological perspective an interesting outcome of attaining thermal squeezing might be the creation of new techniques for determining the Boltzmann constant. The question would be this: can one manipulate the experimental conditions of an apparatus in such a way that the values of ΔT and Δt could be used to reduce the uncertainty in k since \hbar is presently known to within 80 ppb? As shown in our work, a value of < 1 ns for Δt ($\equiv \Delta \tau$) is not unusual in experimental settings. In a thermally isolated system, could one then employ suitable thermal squeezing and averaging schemes to obtain an uncertainty of 10^{-3} °K or less for ΔT ? If so, the right hand side of equation (8) might be re-established with a one-order-of-magnitude or more lower uncertainty, thus allowing a corresponding improvement in the knowledge of k . The ratio of the uncertainties of \hbar and k as stated in the most recent re-adjustment of the fundamental constants [28] is roughly 20:1, so the uncertainty in k could conceivably be improved by a factor of 20 before the uncertainty in \hbar further limits improvement in k . Any improvement in the value of the Boltzmann constant would automatically lead to an improvement in the value of the Stefan-Boltzmann constant, σ , since it is defined to be $\sigma = (\pi^2/60) \cdot (k^4 / \hbar^3 c^2)$, and presently known with an uncertainty of 7 ppm.

5. Conclusions

We have investigated the laser induced fluorescence of nanocrystalline YAG:Ce as a means of testing a novel time-temperature version of the Heisenberg uncertainty principle. If valid, our experimental approach to this problem leads to a value of $\Delta T \Delta t \geq 2.0 \times 10^{-9}$ °K s, which is approximately 263 times the limit called for by $\Delta T \Delta t \geq \hbar/k$ without consideration of signal averaging, and 1472 times it with \sqrt{N} averaging, where $N = 32$ in our case. A number of fundamental questions and unsettled issues make our result open to interpretation and possible invalidation, but if ultimately found to have a workable basis, such a technique might introduce a means of achieving thermally squeezed states, with implications for improved determination of the Boltzmann constant.

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