Published in final edited form as:

J Magn Reson. 2014 July ; 244: 64–67. doi:10.1016/j.jmr.2014.04.021.

Remote sensing of sample temperatures in nuclear magnetic resonance using photoluminescence of semiconductor quantum dots

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Abstract

Knowledge of sample temperatures during nuclear magnetic resonance (NMR) measurements is important for acquisition of optimal NMR data and proper interpretation of the data. Sample temperatures can be difficult to measure accurately for a variety of reasons, especially because it is generally not possible to make direct contact to the NMR sample during the measurements. Here I show that sample temperatures during magic-angle spinning (MAS) NMR measurements can be determined from temperature-dependent photoluminescence signals of semiconductor quantum dots that are deposited in a thin film on the outer surface of the MAS rotor, using a simple optical fiber-based setup to excite and collect photoluminescence. The accuracy and precision of such temperature measurements can be better than ± 5 K over a temperature range that extends from approximately 50 K (-223° C) to well above 310 K (37° C). Importantly, quantum dot photoluminescence can be monitored continuously while NMR measurements are in progress. While this technique is likely to be particularly valuable in low-temperature MAS NMR experiments, including experiments involving dynamic nuclear polarization, it may also be useful in high-temperature MAS NMR and other forms of magnetic resonance.

It is often difficult to know sample temperatures with sufficient accuracy during nuclear magnetic resonance (NMR) measurements because one generally can not attach a temperature sensor directly to the sample. Most often, sample temperatures are inferred from the temperature of heated or cooled gas that flows around the sample within the NMR probe. Temperature gradients within the probe and sample heating from applied radio-frequency (rf) pulses can render such temperature inferences inaccurate, as can the frictional heating that occurs in magic-angle spinning (MAS) NMR experiments at moderate or higher spinning frequencies. Alternatively, sample temperatures can be determined more accurately from measurements of previously-calibrated, temperature-dependent NMR properties of material within the sample, such as temperature-dependent NMR frequency shifts or spin-lattice relaxation (T_1) times. As examples, temperature-dependent ^1H chemical shifts of

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H₂O and CH₃OH in solution [1, 2], temperature-dependent ²⁰⁷Pb chemical shifts of Pb(NO₃)₂ in the solid state [3], and the temperature-dependent T₁ of ⁷⁹Br in KBr powder [4] have been used in this way. However, materials with suitable temperature-dependent NMR properties are not always present within the sample of interest. Moreover, such temperature-dependent NMR properties generally can not be measured while the NMR experiment on the real sample is in progress.

Sample temperatures are particularly problematic in solid state MAS NMR experiments at low temperatures because temperature gradients within the NMR probe can be large. For example, the low-temperature MAS NMR probes developed in our laboratory use cold helium to cool the sample, located near the center of a long MAS rotor, and much warmer nitrogen gas for MAS drive and bearings at the ends of the rotor [5, 6]. Although we can determine sample temperatures with good accuracy when KBr powder is included within the sample volume [4], it is not always feasible to include KBr. Sample temperatures may also drift during long MAS NMR experiments at low temperatures. Relatively small changes in sample temperature can affect the NMR signal strengths significantly when signals are enhanced by dynamic nuclear polarization (DNP) [7, 8]. Thus, new methods are needed for measuring sample temperatures and for monitoring them during NMR measurements.

Semiconductor quantum dots (also known as nanoparticles or nanocrystals) are clusters of 10³–10⁶ atoms with chemical compositions and crystal-like structures similar to those of bulk semiconductors, but with altered electronic and optical properties due to their small diameters (5–50 nm). Colloidal quantum dots, originally developed by Louis E. Brus and colleagues at AT&T Bell Laboratories [9, 10], are now commercially available and inexpensive. Experiments described below used two different CdS_xSe_{1-x}/ZnS quantum dots purchased from Sigma-Aldrich as colloidal suspensions in toluene (0.865 g/ml, catalog numbers 753777 and 753793), with nominal diameters of 6 nm and different values of x that lead to nominal photoluminescence (PL) wavelengths of 540 nm and 630 nm. Aliquots of the two quantum dot suspensions were mixed. A small quantity (roughly 5% by volume) of VGE-7031 varnish (Lake Shore Cryotronics) was dissolved in the mixture to produce a quantum dot “paint” that can be applied to any surface, such as the surface of an MAS rotor or NMR tube. After drying, the surface remains coated with a thin film (typically <10 μm thick) of quantum dots embedded in varnish.

Figure 1a shows PL spectra of a quantum dot film on the surface of a sapphire block, mounted on the cold finger of a Janis Supertran ST-200-NMR continuous flow cryostat. This cryostat design, which has been used in several previous temperature-dependent solid state NMR experiments [8, 11–14], allows sample temperatures to be controlled to within roughly ±0.1 K over a temperature range that extends from above room temperature to below 4 K. PL was excited with 450 nm-wavelength light from a battery-powered laser (Z-Bolt Duet Sapphire, Beam of Light Technologies), carried into the cryostat by an optical fiber (Spectran Specialty Optics, 130 μm diameter). Laser light was coupled into the fiber with a fiber coupler (Newport model F-91UB) and objective lens (25 mm focal length). PL from the quantum dots (as well as reflected excitation light) was carried out of the cryostat by a second fiber, which was connected to a spectrophotometer (StellarNet BLACK-Comet C-200). The ends of the two fibers were approximately 2 mm away from the sapphire

surface. Strong PL peaks near 540 nm and 630 nm were readily observed with signal acquisition times of 10 s or less. The peak positions were found to be temperature-dependent, shifting by about 18 nm from the highest temperature (323 K) to the lowest temperature (10 K). Figures 1b and 1c shows the full temperature dependences of the PL peak wavelengths λ_{PL} (determined by fitting the PL peaks to log-normal functions with Origin 8.6 software, OriginLab Corp.), measured both in zero field and in a 9.4 T NMR magnet. Both quantum dots exhibit monotonically increasing λ_{PL} values from approximately 50 K to the highest temperature measured (323 K). Similar data for CdSe/ZnS quantum dots have been reported by Valerini *et al.* [15]. Below 50 K, λ_{PL} values in Figures 1b and 1c are relatively insensitive to temperature, possibly exhibiting shallow minima near 30 K that may reflect negative coefficients of thermal expansion at low temperatures, as observed for certain bulk semiconductors [16]. Values of λ_{PL} from both quantum dots are also observed to be weakly dependent on the external magnetic field, especially at the lowest temperatures. Over the measured temperature range, temperature dependences of λ_{PL} can be fit empirically with the expression $\lambda_{\text{PL}} = aT + b \exp(-cT^d)$ where T is absolute temperature. Best-fit values of a, b, c, and d are given in Table 1.

To verify that quantum dot PL can be used to determine sample temperatures under MAS NMR conditions, experiments were performed at 9.4 T with a commercial cryogenic MAS NMR probe (Revolution NMR, LLC) that uses liquid helium for sample cooling and nitrogen gas for MAS drive and bearings, as in probes developed in our laboratory [5, 6]. Quantum dot “paint” was applied to the outer surface of a 4.0 mm MAS rotor, which contained a mixture of KBr powder and uniformly ^{15}N , ^{13}C -labeled L-valine powder. After drying, the resulting thin film of quantum dots embedded in varnish (approximate 10 μm thickness) did not interfere with MAS or NMR measurements and adhered to the rotor surface throughout the measurements. Optical fibers (Thorlabs FT-400-UMT, 400 μm diameter) were inserted into the MAS assembly as shown schematically in Figure 2a. The same laser, coupler, objective lens, and spectrophotometer were used to transmit 450 nm excitation light into one fiber and detect the PL collected by the other fiber. Although the ends of the fibers were outside of the rf coil of the MAS NMR probe and roughly 4 mm away from the MAS rotor surface, strong PL was observed as long as the fibers were aimed between turns of the coil, as shown in Figure 2b. In this case, PL spectra were recorded with 1 s acquisition times.

With continual MAS at 6.5 kHz, the sample was cooled from room temperature to approximately 30 K by stepwise incrementation of the liquid helium flow to the NMR probe. After each step, the ^{79}Br T_1 was measured with the saturation-recovery method. During acquisition of the saturation-recovery curve, a PL spectrum was also recorded. Figure 3a shows examples of the saturation-recovery curves. Sample temperatures were then determined from the ^{79}Br T_1 values, using the previously-calibrated temperature dependence of the ^{79}Br T_1 in KBr powder [4] shown in Figure 3b. Sample temperatures were also determined from the values of λ_{PL} , using the empirical fits described above (Table 1, 9.4 T parameters).

Figure 4 compares sample temperatures determined from quantum dot PL signals with those determined from ^{79}Br T_1 values. Between 50 K and 250 K, the two methods agree to within

5 K. Worse agreement at higher temperatures is attributable to inaccuracy of the ^{79}Br -based temperatures, which are not well calibrated above 250 K. Agreement below 50 K is limited by the reduced sensitivity of λ_{PL} values to temperature for the quantum dots used in these experiments.

Strictly speaking, temperatures derived from λ_{PL} values are temperatures of the MAS rotor surface, while temperatures derived from ^{79}Br T_1 values are temperatures within the MAS rotor. When rf heating is significant, which is not the case in the current experiments, the two temperatures can differ significantly.

Results in Figure 4 required subtraction of 4.2 nm and 2.6 nm, respectively, from all λ_{PL} values of PL peaks 1 and 2 (Figure 2b) before comparison with the fitted calibration curves in Figures 1b and 1c. It appears that λ_{PL} values from two independent sets of measurements can differ by a temperature-independent constant. Although this observation is not yet understood, it does not interfere with the determination of sample temperatures from λ_{PL} values, since the appropriate constant correction can be determined readily from a PL spectrum at room temperature.

In conclusion, quantum dot PL measurements are a method for measuring sample temperatures in MAS NMR experiments with two important advantages: (i) temperatures can be monitored while NMR experiments are in progress; (ii) no extraneous material is required within the NMR sample. This method is likely to be useful in many low-temperature MAS NMR experiments, including DNP-enhanced experiments above 50 K. With a different choice of photoluminescent materials, it may be possible to extend this method to lower temperatures. For example, CdSe quantum dots embedded in bulk ZnSe have been shown to exhibit temperature-dependent λ_{PL} values below 20 K [17]. Application in high-temperature MAS NMR, other types of magnetic resonance, and other spectroscopic measurements are readily envisioned.

Acknowledgments

This work was supported by the Intramural Research Program of the National Institute of Diabetes and Digestive and Kidney Diseases of the National Institutes of Health.

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Highlights

- Semiconductor quantum dots are readily applied to surface of MAS rotor or NMR tube
- Quantum dot photoluminescence wavelengths are temperature-dependent down to 50 K
- Sample temperatures can be measured quickly and continuously during NMR experiments

Figure 1.

(a) PL spectra of $\text{CdS}_x\text{Se}_{1-x}/\text{ZnS}$ quantum dots with nominal PL wavelengths of 540 nm (peak 1) and 630 nm (peak 2), applied to the surface of a temperature-controlled sapphire block in a variable-temperature cryostat. Intense peak at 450 nm is reflected light from the PL excitation source. The two quantum dots were mixed in an approximate 1:2 molar ratio. (b, c) Temperature dependences of PL peak wavelengths λ_{PL} from the same sample in zero field and in a 9.4 T field. Solid lines are empirical fits as described in the text.

Figure 2.

(a) Schematic representation of the setup for simultaneous acquisition of low-temperature MAS NMR spectra and PL spectra. The orange region represents a quantum dot film on the surface of the MAS rotor, within the rf coil. Blue and red lines represent optical fibers for exciting and collecting PL signals. (b) PL spectra of $\text{CdS}_x\text{Se}_{1-x}/\text{ZnS}$ quantum dots applied to the surface of a MAS rotor containing a mixture of KBr powder and uniformly ^{15}N , ^{13}C -labeled L-valine powder, obtained in a 9.4 T field with MAS at 6.5 kHz. In this case, the two quantum dots were mixed in an approximate 1:1 molar ratio. Indicated temperatures were determined from ^{79}Br T_1 values.

Figure 3.

(a) Examples of saturation-recovery data used to measure ^{79}Br T_1 values. Solid lines are fits with single-exponential curves. (b) Calibration curve for determination of sample temperatures from ^{79}Br T_1 values, as reported previously [4].

Figure 4.

Comparison of sample temperatures determined from simultaneous measurements of quantum dot λ_{PL} values and $^{79}\text{Br } T_1$ values. Error bars represent temperature ranges due to uncertainties in fits to PL lineshapes and saturation-recovery data. When error bars are not shown, they are smaller than the symbol sizes.

Best-fit parameters determined by fitting experimental measurements of PL peak wavelengths to the empirical expression $\lambda_{PL} = aT + b \exp(-cT^d)$, as shown in Figures 1a and 1b.

Table 1

nominal PL wavelength of quantum dot (nm)	magnetic field (T)	a (nm/K)	b (nm)	c (K)	d
540	0.0	0.08612	536.26	0.012207	0.2
540	9.4	0.08724	538.73	0.013702	0.2
630	0.0	0.11244	609.63	0.001821	0.5
630	9.4	0.10926	610.34	0.001790	0.5