A short table of important distances and angles for the dimer **2** is given in Figure 2. It is interesting to compare the lithium–lithium distance (2.34 Å) in **2** with the structures of other organolithium derivatives.[3] The complex **2** incorporates the shortest lithium–lithium distance yet seen. This distance is significantly shorter than the Li–Li bond in tetrameric methyllithium (2.57 Å)[9] or the Li–Li bond in Li_2 (2.67 Å).[10] The lithium atoms in **2** are separated by a distance that approximates that found in hexameric cyclohexyllithium (2.40 Å).[11] It is tempting to consider a bonding interaction between the two lithium atoms in **2**. This structure then represents two pentacoordinate lithium atoms surrounded by a distorted trigonal bipyramid and is perhaps the first example of such a pentacoordinate organolithium compound.

We would like to focus on one additional aspect of the dimer **2**. In this associated dimer, the two lithium atoms are located symmetrically above and below (±0.80 Å) an approximate plane formed by the six nuclei N(1)–C(1)–C(2) and N(1′)–C(1′)–C(2′). However, the doubly bridging sp^2 carbon atoms (C(2) and C(2′)) are unexceptional and have an analogy in the structures of ferrocenyllithium–PMDT[12] and the tetramer of *o*-$LiC_6H_4(CH_2N(CH_3)_2)$.[7]

The crystal structure of **1** represents the first experimental evidence for an out of plane lithium atom in the structure of a vinyllithium derivative.

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Supplementary Material Available: Full crystallographic parameters including unit cell parameters, atomic coordinates, thermal parameters, bond lengths and angles, and standard deviations for compound **1** (5 pages). Ordering information is given on any current masthead page.

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Near-Infrared Emission in the Catalase–Hydrogen Peroxide System: A Reevaluation

Jeffrey R. Kanofsky

Medical Service, Edward Hines, Jr. Veterans Administration Hospital Hines, Illinois 60141

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Chemiluminescence near 1268 nm has recently been demonstrated in a number of peroxidase–H_2O_2–halide systems and evidence has been presented supporting the assignment of this emission to singlet oxygen ($^1\Delta_g$).[1-5] Khan has reported another near-infrared band at 1640 nm in the catalase–H_2O_2 system, which he attributed to a chemiluminescent process, either an environmentally perturbed singlet oxygen or an energy-transfer process from singlet oxygen to an iron–heme coordination complex.[4] An alternative hypothesis is that this emission is the result of thermal radiation. The high concentration of H_2O_2 (2.5%) used in Khan's experiments could have resulted in as much as a 17 °C temperature rise during the course of the reaction. Further, this emission would appear to be an emission band, since the sensitivity of the germanium detector used by Khan decreases rapidly for wavelengths greater than 1600 nm.[6] Evidence is now presented demonstrating that the near-infrared emission in the catalase–H_2O_2 system is due to thermal radiation.

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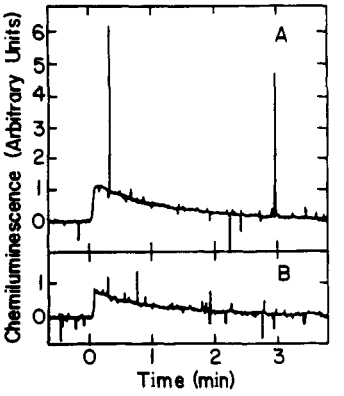

Figure 1. Near-infrared emission of the catalase–H_2O_2 system and of heated H_2O. (A) Injection of 1.5 mL of H_2O_2, 1.5 M, into an equal volume of catalase, 70 μg/mL. Both reactants were in 0.1 M sodium phosphate buffer, pH 7.6. (B) Injection of 1.5 mL of 51 °C H_2O into an equal volume of 24 °C H_2O. Emission was measured through a 1680-nm interference filter. Many noise spikes are seen on each tracing.

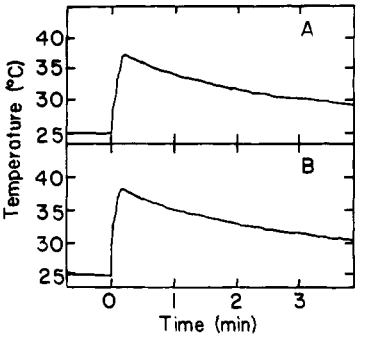

Figure 2. Time course of temperature in the catalase–H_2O_2 system and in heated H_2O. (A) Injection of 1.5 mL of H_2O_2, 1.5 M, into an equal volume of catalase, 70 μg/mL. Both reactants were in 0.1 M sodium phosphate buffer, pH 7.6. (B) Injection of 1.5 mL of 51 °C H_2O into an equal volume of 24 °C H_2O.

Table I. Spectral Distribution of Infrared Emission in the Catalase–H_2O_2 System and in Heated H_2O

	filter[a]	
nm	catalase–H_2O_2,[b] relative emission[d]	heated H_2O,[c] relative emission[d]
1070	−0.01 ± 0.01	0.02 ± 0.02
1170	0.00 ± 0.01	0.00 ± 0.01
1268	0.01 ± 0.01	−0.01 ± 0.01
1370	0.02 ± 0.01	−0.02 ± 0.02
1475	0.06 ± 0.01	0.09 ± 0.01
1580	0.46 ± 0.01	0.41 ± 0.02
1680	1.00 ± 0.02	1.00 ± 0.02
1761	0.47 ± 0.03	0.62 ± 0.03
1880	0.01 ± 0.01	0.03 ± 0.01
1968	0.01 ± 0.01	0.00 ± 0.02

[a] Spectral distribution obtained with a set of 10 band-pass interference filters with center frequencies as shown and band widths of 40–50 nm. [b] Catalase, 33 μg/mL; H_2O_2, 0.74 M; 100 mM sodium phosphate buffer, pH 7.6. Emission recorded for 2 min after the initiation of the reaction. [c] Emission from injection of 1.5 mL of 51 °C H_2O into an equal volume of 24 °C H_2O. Emission recorded for 2 min after the injection. [d] Normalized so the peak emission is 1.00 for both systems. Measurements were done in triplicate and reported as the mean ± standard error.

(6) Data from manufacturer's specifications for Model 403L germanium photodetector (Applied Detector Corp., Fresno, CA) used by Khan.

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The infrared chemiluminescence spectrometer used has been described previously.[1] It used a liquid-nitrogen-cooled germanium detector similar to that used by Khan. The reaction temperature was measured with a glass thermmistor probe. Catalase (11 800 Sigma units/mg) was obtained from Sigma Chemical Co., St. Louis, MO. All experiments were done at an ambient temperature of 24 °C.

Figure 1 shows the time course of the infrared emission through a 1670-nm interference filter. It is similar in half-life and intensity to that resulting from the injection of 1.5 mL of H_2O heated to 51 °C into an equal volume of H_2O at 24 °C. Figure 2 shows the time course of the temperature is similar in both systems. The half-life of the temperature decay is of the same order of magnitude as the half-life of the infrared emission. Table I presents the spectral distribution of the observed radiation in both systems, corrected for the transmission curves of each interference filter. The emission spectrum is the same for each system and consistent with thermal radiation. The absence of detectable emission through the 1880- and 1968-nm filters is due to steep decline in detector sensitivity for wavelengths greater than 1600 nm. Consistent with past studies excluding singlet oxygen as a product of the catalase–H_2O_2 system, no emission near 1268 nm was detected.[7] Using the H_2O_2 + HOCl reaction as a calibrating source of singlet oxygen emission, an upper limit of 0.02% can be placed on any singlet oxygen produced.[3]

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Real Two-Dimensional NMR Solvent Suppression Technique

E. Guittet, M. A. Delsuc, and J. Y. Lallemand*

Laboratoire de R.M.N.
Institut De Chimie Des Substances Naturelles
91190 GIF sur YVETTE, France

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Suppression of the solvent signal in ^1H NMR is of utmost importance, particularly in the studies of biological molecules and for in vivo applications. Although many different techniques have been recently reported, their applicability in two-dimensional (2-D) NMR has not been investigated. We present here a COSY-type experiment wherein two-dimensional solvent peak elimination permits us to observe signals obscured by the solvent or protons in slow exchange with the solvent. This technique is extendable to most 2-D experiments.

In order to run NMR experiments in the presence of strong solvent signals two different problems have to be faced. The undesired signal has to be attenuated at an early stage of the acquision, in order to enhance the acquisition dynamics, limited mainly by the analog-to-digital converter. This is generally achieved by the nonexcitation of the solvent signal (Redfield "2-1-4",[1,2] soft pulses,[2] composite pulses[3]) or alternatively by the attenuation of its resonance (saturation, WEFT[4]). On the other hand the residual acquired signal can be canceled by use of further suppression techniques such as DSA, ADA,[5] or filtering.

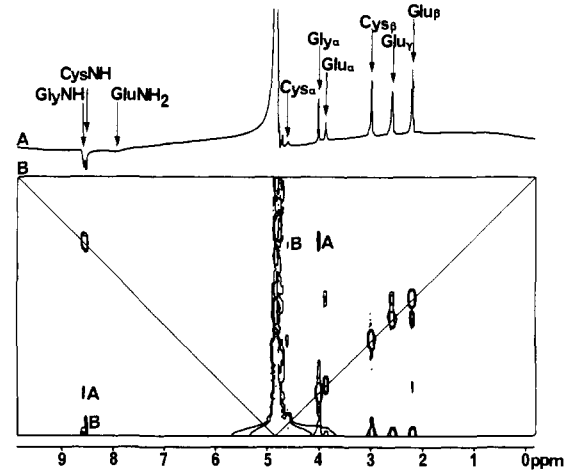

Figure 1. Spectra of glutathione 65 mM in H_2O (10% D_2O, pH 3.00, 19 °C), acquired on a BRUKER WM 400 spectrometer. (A) JR spectrum showing the characteristic phase inversion of this technique. (B) The modified JR sequence COSY spectrum shown in magnitude. A 64*1024 data matrix was acquired, 128 scans per FID for a total time of 8 h. A saturation pulse of 1 s was applied after each scan followed by a relaxation time of 2 s.

The need in 2-D experiments of hard pulses with definite flip angles leads to the preferential use of attenuation techniques such as WEFT or saturation.[6,7] However, their use is restricted to nonexchangeable protons or long T_1 molecules. The use of semiselective pulses in 2-D has been restricted for the moment to the read pulse in the NOESY experiment.[8,9] However, in this very special experiment, the mixing pulse and the read pulse are distinct and significant decay of the transverse H_2O magnetization takes place during the mixing period.[8]

In order to develop one-scan solvent suppression techniques that would be operative for 2-D applications, we therefore turned to those that use hard pulses and whose structure itself could be included as such in the pulse sequence. The jump and return (JR[10]) and the COSY pulse sequences present the required correspondence. The JR experiment consists in applying two $\pi/2$ pulses and making the phase of the second pulse such as to bring back the solvent magnetization to its original equilibrium state. The 2-D extension presented here also uses only two $\pi/2$ pulses and is based on increasing the time between these two pulses by the usual incremented time of the COSY experiment. This leads to the nonexcitation of the solvent diagonal line of the 2-D spectrum. It is worth noting that since all resonances experience the preparation pulse and the mixing pulse, a true two-dimensional solvent suppression is achieved. In fact the zero signal area is a hole centered at the point on the spectrum at $w_1 = w_2 = w_{solvent}$ coordinates and not a furrow lying along $w_2 = w_{solvent}$ as in the other solvent suppression techniques. As a consequence a proton under the solvent line will show its correlation peaks with other protons at their full intensity. It should be noted that the phase of the second pulse is fixed by the phase of the first, which hampers any quadrature detection in the w_1 dimension and leads to folding in this dimension. The only disadvantage of this method would be for a situation in which two coupled signals are symetrically placed on each side of the solvent. In this case correlation peaks would be lost.

Figure 1B shows the COSY spectrum of glutathione (Glu-Cys-Gly) 65 mM in H_2O. A saturation pulse has been introduced that randomizes the spin distribution and thus allows shortening of the necessary relaxation time. Although this ensures a better

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