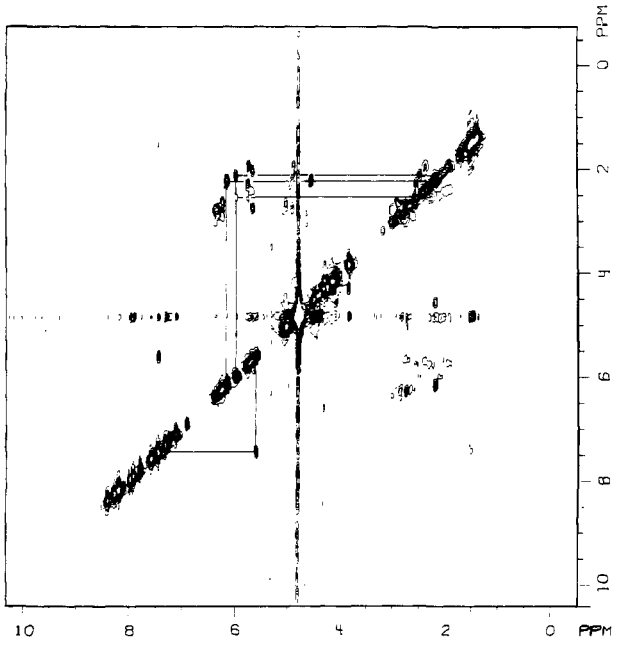

Figure 2. 360-MHz COSY spectrum (contour plot) of d(ATATCGATAT)$_2$ at 29 °C. Sample was the same as in Figure 1. The spectral width was ±2000 Hz. The data set consisted of 1024 points in the t_2 dimension and 128 points in the t_1 dimension. 96 FIDs were accumulated for each value of t_1, with a 4-s delay between acquisitions, and the total accumulation time was ~15 h. Axial peaks were suppressed by a 16-step phase-cycling routine. A 90° pulse (13.5 μs) was used for P_1, but 9.5 μs for P_2. The resulting data matrix was processed with a phase-shifted sine-bell in both dimensions and was zero-filled in the f_1 dimension. The absolute value mode is used. Connectivities manifested as cross peaks between the CH6 and CH5 resonances are indicated by the solid lines (bottom, left). Connectivities between some H1′ resonances (T_{10}, T_4) and the corresponding H2′,H2″ resonances are shown (top). The terminal T_{10} nucleoside shows only one cross peak between H1′ and H2′,H2″ since these latter resonances have the same chemical shift.

the cross peaks.[14] In the absence of second-order NOEs, the appearance of a pair of cross peaks located at (f_1, f_2) and (f_2, f_1) implies a short internuclear separation (probably less than 3.5 Å) between the two protons at (f_1, f_1) and (f_2, f_2).[6] A detailed analysis of these cross peaks in the NOESY spectrum is beyond the scope of this communication, but certain features merit discussion.

Some of the largest cross peaks in the NOESY spectra are between the H2′,H2″ proton resonances and the H1′ as well as the aromatic AH8, GH8, TH6, and CH6 resonances. There are strong cross peaks between each of the four methyl resonances and the four TH6 resonances resulting from intrabase interactions between TH6 protons and rotating methyl protons. Significantly, there are also three or four (two of the AH8 resonances overlap) interbase cross peaks between AH8 and TCH_3 protons. The existence of these interbase cross peaks indicates that the AH8 protons must be located in space near to the thymine methyl protons, and the fact that the intensities for at least two of the TCH_3–AH8 cross peaks are comparable to the intensities of the TCH_3–TH6 cross peaks implies that these interproton distances are similar.[14] Analysis of the assignments reveals that the weaker interactions are between the base pairs at the ends of the helix, and this is attributed to transient opening of the ends.

Examination of a model of B–DNA indicates that for an alternating AT sequence, the closest protons on the methyl group of a T base should be about 2.5 Å, on the average, from the H8 on the A base on its 5′ side (i.e., ApT), but quite distant (>5 Å) from the A base on its 3′ side (i.e., TpA). The observation of strong cross peaks between the AH8 and the methyl protons on a neighboring T base indicates that the base pairs are in the correct spatial configuration for a right-handed B–DNA helix. Furthermore, comparison of the relative magnitudes of the base (purine-H8 or pyrimidine-H6) cross peaks with H1′ and H2′,H2″ at shorter (60–100 ms) mixing times establishes that the bases are in the anti nucleotide conformation. This information, combined with measured coupling constants for the H1′ protons ($J_{1'2'} + J_{1'2''} \simeq 14$ Hz)[10] which indicate a predominantly S-type sugar pucker for the molecule,[15] is consistent with the expectation that d(ATATCGATAT)$_2$ is in the B conformation. The NOESY experiments also provide information that makes it possible to complete the assignments of the base proton resonances and to assign the H1′ sugar resonances. These assignments are discussed in detail elsewhere.[10]

A contour plot of a 2-D *J*-correlated (COSY) spectrum of d(ATATCGATAT)$_2$ is given in Figure 2. The diagonal spectrum is similar to the regular one-dimensional spectrum and off diagonal cross peaks connect homonuclear *J*-coupled proton resonances.[12,16] Interactions between all the *J*-coupled protons in DNA (i.e., sugar protons and CH5–CH6) are seen in the contour plot, although for the coupled sugar protons only the H1′–H2′,H2″ cross peaks are resolvable. The large cross peak connecting resonances at 7.45 and 6.23 ppm is due to coupling between C_5H6 and C_5H5. Analogous cross peaks should be valuable in assigning these resonances in other DNAs.

The preliminary results presented here, and elsewhere,[10,17] indicate that through the use of one- and two-dimensional NMR techniques it should be possible to completely assign the spectra of short DNA molecules and to investigate their solution state structural and dynamic properties at a level of detail heretofore impossible.

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Lifetime of $O_2(^1\Delta_g)$ in Liquid Water As Determined by Time-Resolved Infrared Luminescence Measurements

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The chemical and kinetic properties of singlet molecular oxygen in liquid phase have occupied the attention of chemists for almost 20 years as indicated by numerous reviews on the subject.[1-9] This transient entity, however, has evaded direct observation until very recently when the 1.27-μm luminescence from the forbidden transition $O_2(^3\Sigma_g^-) \leftarrow O_2(^1\Delta_g)$ was detected via photosensitization

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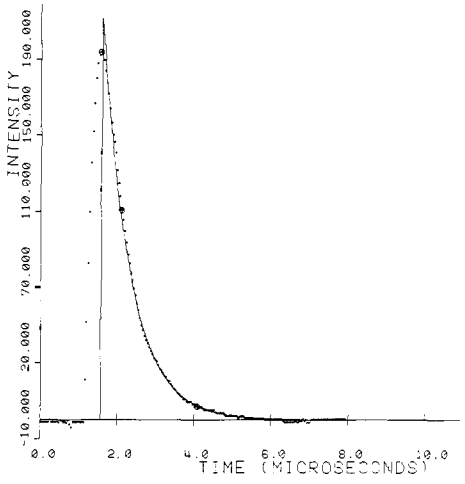

Figure 1. Time response of the detector–amplifier combination to 532-nm light scattered from an 11-ns (FWHM) laser pulse. Each dot represents 10 digitizer channels averaged together. The full curve is a computer-fitted exponential with a 0.76-μs lifetime. The experimental curve is an average of 10 individual experiments.

in solution, initially in steady-state experiments[10-11] and subsequently by time-resolved methods.[12-16] Improvements in these latter techniques have been brought about by using germanium photodiodes (with much greater sensitivity in the infrared than the visible region, in contrast to photomultiplier tubes) coupled to fast, high-gain amplifiers resulting in time resolution of ca. 10 μs.[14-17] In spite of these improvements the natural lifetime of singlet oxygen (τ_Δ) in light water (H_2O) has never been measured directly. Since much photobiological activity is thought to proceed via $O_2(^1\Delta_g)$ intermediates, it is clearly necessary to make a direct measurement of τ_Δ in water, the fundamental biological medium. This communication describes a detection system with a response time of less than 1 μs that has for the first time enabled the determination of τ_Δ in H_2O to be made directly.

The method for generation and detection of the 1.27-μm luminescence is based on those reported recently.[14,16,17] Excitation was by pulses of 532-nm light (10 ns) from a frequency-doubled Nd:YAG laser (Quantel YG 481). The unfocused beam (8 mm diameter) was incident on one face of a 10 mm × 10 mm fluorescence cuvette. Energies of no greater than 50 mJ/pulse were employed. Emitted radiation was detected at right angles to the laser direction by a 5-mm^2 germanium photodiode (Judson). The cuvette and diode window were close-coupled but separated by a silicon metal filter (5 mm thick, A-R coated; II-VI Inc.) and two layers of gelatin filter (Kodak Wratten 87A). This combination minimized scattered 532-nm radiation and transmitted ca. 80% of light at $\lambda > 1.15$ μm. In some experiments a 1.27-μm interference filter (Baltzer) was added to the combination. This attenuated the signal significantly but did not change its profile. The diode output was applied to the 50-Ω input connector of a Biomation 8100 digitizer via a 50 dB amplifier (Judson 000) and impedance-matching amplifier (Tektronix AM502) operating at unit gain. The rise and fall times of the diode were improved by applying a reverse-bias voltage. This was achieved by connecting a 50-Ω resistor between the bias pin of the amplifier and ground.

With pure water in the cuvette and the beam at normal incidence, a small residual scattered light signal (ca. 50 mV) could be registered by the detector circuitry. Larger-scattering intensities were obtainable by rotating the cuvette slightly out of normal incidence. In this manner a scatter signal of ca. 300 mV was used to test the response characteristics of the detector combination. As shown in Figure 1, this rises rapidly and decays exponentially with an e^{-1} time constant (τ_r) of 0.76 μs.[18] Signals of approx-

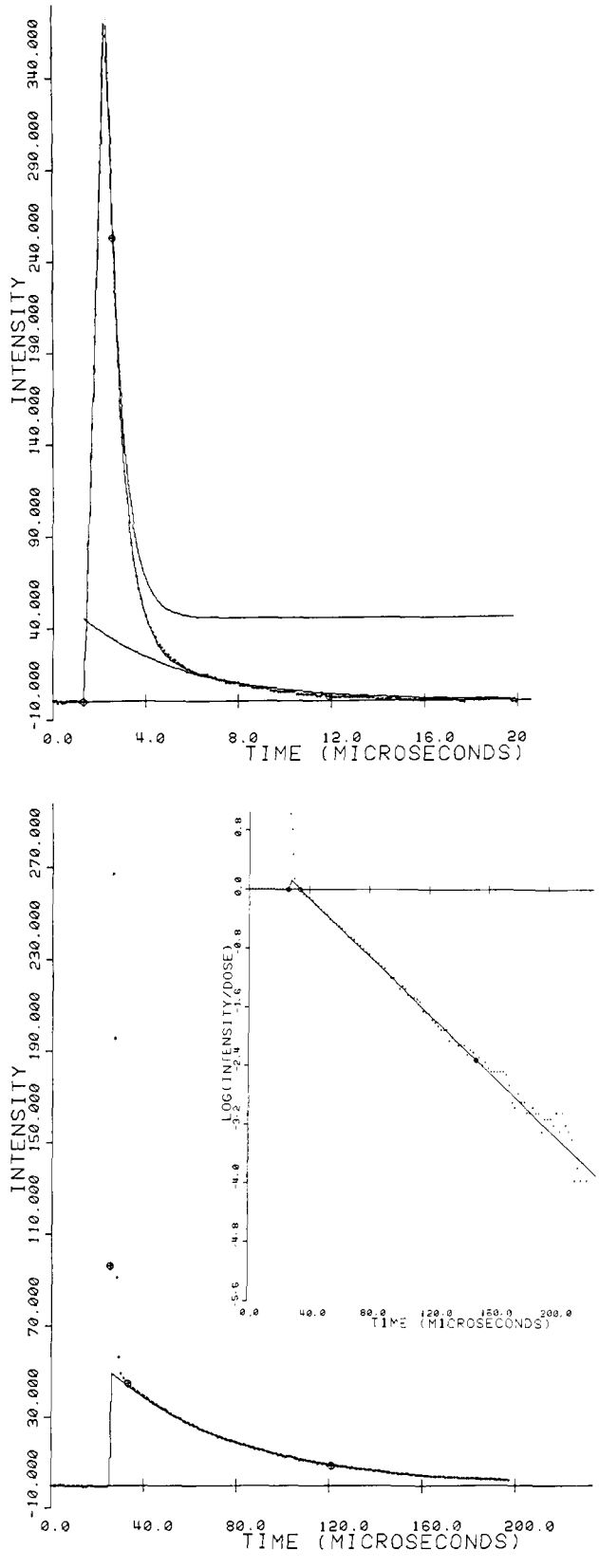

Figure 2. (Top) time profile of infrared light emitted from TPPS solution in H_2O. The curve through the points (10 digitizer channels) is the sum of the two exponential curves also displayed. (Bottom) same for TPPS in D_2O. (Inset): log (intensity) vs. time plot of the data in the main figure.

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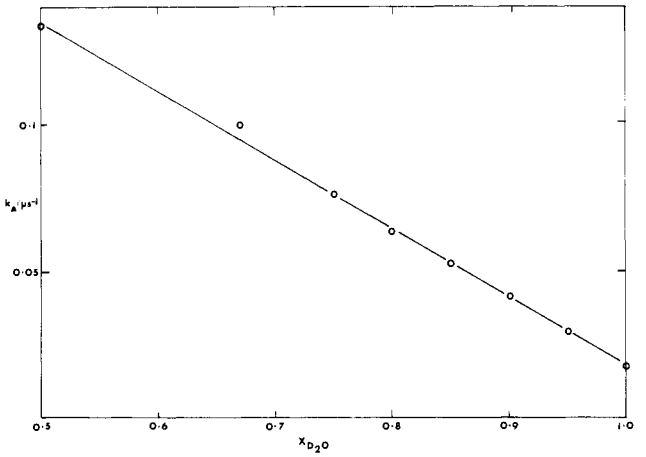

Figure 3. First-order decay rate constant of $O_2(^1\Delta_g)$ luminescence as a function of D_2O mole fraction in H_2O. The correlation coefficient from a linear regression analysis was 0.999.

imately this initial intensity were employed throughout. All lifetimes measured were corrected for this time constant according to

$$\tau_\Delta^2 = \tau_m^2 - \tau_r^2 \quad (1)$$

where τ_m is the reciprocal of the measured first-order decay constant (k_m) of the luminescence. In H_2O and D_2O solutions containing sensitizer [tetrakis(4-sulfonatophenyl)porphine, TPPS], the signal showed an intense early component followed by the weaker (ca. one-tenth) delayed luminescence of $O_2(^1\Delta_g)$. The initial amplitude of the fast component was about 5 times that observed to be scattered when pure H_2O (or D_2O) only was in the target cuvette in normal geometry. This intense early component was relatively very much less when CH_3OH (or CD_3OD) was the solvent and absent when dimethyl hematoporphyrinate (HPDME) was used as sensitizer in dielectric liquids such as benzene. Its origin in aqueous media is not certain but it is clearly related to the presence of TPPS in the target.

Figure 2, top and bottom, shows the luminescence time profiles from a TPPS (A_{532} 0.6) solutions in oxygen-saturated H_2O and D_2O, respectively. The nonexponential behavior is clearly apparent, unlike the profile of the scattered light. An iterative least-squares analysis was used to separate two first-order components.[19] No evidence was found of any second-order behavior of the early part of the decay. The lifetime of the early component was near 0.8 μs, which is the instrument response lifetime. The slower component (ca. one-tenth of the total signal amplitude) showed $k_m = 0.22\ \mu s^{-1}$ ($\tau_m = 4.5\ \mu s$). On correction for instrument response (eq 1) this yields $\tau_\Delta^{H_2O} = 4.4\ \mu s$.[20] This slow component was removed by saturating with nitrogen gas and is assigned to the infrared luminescence from $O_2(^1\Delta_g)$.

To verify that this residual luminescence was in fact not due to a system artifact, we examined a series of mixtures of H_2O and D_2O containing TPPS (A_{532} 0.64). Whereas the decay constant of the early component remained unchanged, that of the slow component was linearly dependent on the molar composition of the solvent systems (Figure 3). At $X_{D_2O} = 1$, $\tau_\Delta = 56\ \mu s$ was observed. The extrapolated value of k_Δ at $X_{H_2O} = 1$ was $2.54 \times 10^{-2}\ \mu s^{-1}$ or $\tau_\Delta = 3.9\ \mu s$ (correlation coefficient = 0.999), in close agreement with that observed directly. The value for $\tau_\Delta^{H_2O}$ measured here agrees well with a value (4 μs) obtained earlier by an indirect photobleaching method[21] but is somewhat larger than the value of 2 μs reported by Merkel and Kearns,[22] again by extrapolation from indirect measurements. The present data lead to a value of $\tau_\Delta^{D_2O}/\tau_\Delta^{H_2O} = 13$.

In conclusion, the ease, convenience and precision of time-resolved infrared luminescence measurements of τ_Δ allows the generation of a reliable data base from which a critical examination of the current theory[22] of solvent and isotope effects can proceed.

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Registry No. H_2O, 7732-18-5; O_2, 7782-44-7.

(18) At a referee's suggestion we measured the rise time of the detector response to a 10-μs duration square-wave light pulse from a red light emitting diode. The rising edge of the output wave form was exponential with an e^{-1} rise time of 0.82 μs, in good agreement with the scattered laser light measurement.

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Molybdenum Catalysts for Allylic Alkylation

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The ability to selectively activate relatively inert leaving groups toward substitution using palladium templates has generated a number of useful synthetic reactions and sequences.[1-6] The extraordinary chemo- and regioselectivity and stereocontrol exhibited by these templates led us to search for complementary reactivity, especially with respect to stereochemical control. The high coordination number of molybdenum, the ready availability of π-allylmolybdenum complexes, and the paucity of information regarding their susceptibility toward nucleophilic attack turned our attention toward π-allylmolybdenum complexes.[7] In this paper, we report stoichiometric and catalytic allylic substitution reactions involving molybdenum complexes and the sensitivity of regioselectivity toward the nature of the ligands on molybdenum.

Except for a single example of the alkylation of the cationic complex $CpMo(CO)(NO)(\pi\text{-allyl})^+$ with an enamine[8] to yield

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