## Laser-Enhanced NMR Spectroscopy

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Experimental studies show that optical irradation far from any absorption bands can shift the resonances in a nuclear magnetic resonance (NMR) spectrum without significant heating. This effect may lead to increased dispersion in NMR studies of complex molecules.

MR SPECTROSCOPY HAS BECOME an extraordinarily powerful method for probing the structure of molecules, particularly with the development over the last decade of multidimensional techniques (1). These techniques have effectively enhanced spectral resolution to the point that solution-state conformations of 20-kD proteins can be measured, despite the obvious problem that such proteins have many duplicated amino acids with nearly identical proton resonances. Still, resolution enhancement is a fundamental and important quest in this field and is essential for studies of more complicated molecules.

For this reason we were interested in a recent paper (2) which claimed that a circularly polarized laser could raise the NMR resonance frequency into the gigahertz range, even if the laser was not resonant with any optical transitions. Clearly such a field increase would be tremendously useful. The dramatic prediction comes from second-order perturbation theory and is explained (2) in terms of coupling to a new quantum number related to optical phase conjugation in chiral media; in fact, however, the mechanism is actually equivalent to the inverse Faraday effect. (The Faraday effect uses a magnetic field on a noncentrosymmetric crystal to rotate the polarization of light; the inverse Faraday effect implies production of bulk magnetization by polarized light.) Unfortunately, this effect has been measured (3) and is extremely small. Perhaps a 1-Hz frequency shift of all resonances could be induced by an enormous laser, but this has no practical value for NMR spectroscopy, and the gigahertz frequency shifts discussed in (2) almost certainly require lasers which would turn the sample into a plasma.

On the other hand, even small changes in the resonance frequency would be useful, if the changes are localized (different for dif-

27 MARCH 1992

ferent positions in a molecule). Such localized shifts could, for example, disperse resonances from identical amino acids in different positions of a polypeptide chain or could remove accidental degeneracies. Shifts from the inverse Faraday effect would not be localized, but we show experimentally here that localized resonance frequency changes are possible with modest laser powers and with little heating of the sample. We call this a LENS experiment, for laser-enhanced NMR spectroscopy.

The absorption spectrum and 270-MHz NMR spectra of an organic test molecule, p-methoxyphenyliminocamphor, is shown in Fig. 1. The molecule is chiral (both enantiomers were synthesized) (4) and displays substantial circular birefringence-an important point, as we discuss below. In this experiment 514-nm light from a Coherent Innova 200 argon-ion laser propagated ~10 m and traveled directly down a 5-mm capillary tube spinning in a commercial (JEOL GX-270) NMR spectrometer. The laser beam had a diameter of  $\sim 10$  mm at the sample and was apertured to provide uniform irradiation. At this wavelength the solution has almost no absorption.

Our preliminary experimental results show both bulk and local frequency shifts. The magnitude of the typical shifts we observe are shown in Fig. 2, and Fig. 3 summarizes the power dependence of the differential shifts (solute peak minus solvent) used to separate out the bulk effects. Quantitative interpretation of the data in Figs. 2 and 3 is difficult; the observed shifts probably reflect a complicated interplay of different mechanisms. However, the dextrorotatory [derived from (1S)-(+)-camphorquinone] and levorotatory molecules in achiral solvents have identical spectra in normal NMR spectroscopy.

Great care had to be taken to minimize heating effects. We designed a special capillary NMR tube that coupled light out of the probe through the capillary walls, and we gated the laser with a shutter, which was controlled by the spectrometer's pulse programmer. The power dissipated in the sample itself is at most a few percent of the applied light, far too small to significantly change the temperature of this large a thermal mass; an estimate based on thermal conductivity of the tube and solution predicts a maximum temperature jump of 3°C. This estimate was confirmed by comparing the data in Fig. 3 to data with linearly polarized irradiation, which produced root-mean-squared differential shifts of 0.2 Hz at the maximum power for all peaks except for the "high-field ring" peaks; these peaks are shifted by -0.5 Hz. We estimate that our measurements of the center frequencies of the resonances have an uncertainty of  $\pm 0.2$  Hz. If the temperature is increased 7°C in the absence of irradiation, the "high-field ring" peaks move -2 Hz, and all other peaks change frequency by <0.2 Hz. We thus infer that the temperature increase is less than 2°C and that the differences in Fig. 3 are too large to be thermal.

The simplest explanation for a site-dependent shift only requires first-order perturbation theory. For an ensemble of chiral molecules in a laser field (5),

$$\mathbf{P}(\omega) = N \left[ \alpha'(\omega) + i\alpha''(\omega) \right] \mathbf{E}(\omega) - N\beta(\omega) [d\mathbf{B}(\omega)/dt]$$
(1)

where **P** is the polarization,  $\omega$  is the frequency, N is the number of molecules,  $\alpha'$ and  $\alpha''$  are the real and imaginary parts of the molecular polarizability, respectively, **E** is the electric field,  $\beta$  is the chiral response parameter, **B** is the magnetic field, and t is



Fig. 1. Visible and ultraviolet absorption spectrum (top) and 270-MHz NMR spectrum (bottom) of p-methoxyphenyliminocamphor. Note that the solution is essentially transparent at the irradiation wavelength of 514 nm.

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time. Normally one thinks of a laser as supplying an electric field, but  $|\mathbf{E}(\omega)| \propto |\mathbf{B}(\omega)|$  from Maxwell's equations. Thus  $\alpha''(\omega)$  gives absorption and  $\alpha'(\omega)$  gives dispersion and is broader. Far from resonance it is possible to induce polarization without substantial heating or absorption  $[|\alpha'(\omega)| >> |\alpha''(\omega)|]$ , which of course is the origin of the index of refraction of trans-

Fig. 2. Typical LENS spectra. These resonances are the methyl groups of the levorotatory enantiomer; insertion of the half-wave plate reverses the sense of the circular polarization. The beam diameter is  $\sim 1 \text{ cm}^2$  at the sample. At these modest intensities, resonances are shifted by several hertz from their unirradiated positions.

parent media. The quantity  $\beta(\omega)$  is experimentally measurable; the net rotation  $\Delta\theta$ after passage through a medium of length *l* is  $\Delta\theta = \omega^2 \beta(\omega)Nl/c^2\varepsilon_0$  (where *c* is the speed of light and  $\varepsilon_0$  is the dielectric constant of free space). If the light is circularly polarized, this induced circular polarization corresponds to a very small fractional charge oscillating at a distance of



**Fig. 3.** Differential line shifts (solute resonance shifts minus solvent resonance shift) as a function of laser power for the two enantiomers and opposite senses of circularly polarized light. The effects of linearly polarized light are far smaller (see text) and verify that these shifts are not simply thermal.

the size of the chromophore. In a two-level approximation, the field creates a steadystate superposition of the ground-state  $\psi_0$  and an excited-state  $\psi_1$ :

$$\psi(t) \approx \psi_0 + C \exp(i\omega_0 t) \psi_1, C \ll 1$$
 (2)

where  $\omega_0$  is the resonance frequency and C is a constant, and hence the charge distribution is given by:

$$\begin{aligned} |\psi(t)|^2 &\approx |\psi_0|^2 + C \exp(i\omega_0 t)\psi_0^*\psi_1 + \\ C^* \exp(-i\omega_0 t)\psi_0\psi_1^* + |C^2||\psi_1|^2 \end{aligned} (3)$$

This oscillatory charge distribution generates a current, which induces a dipole magnetic field. Either  $\alpha(\omega)$  or  $\beta(\omega)$  can produce this polarization and current. It is possible to calculate this effect quite precisely for hydrogen atoms irradiated near the  $1s \rightarrow 2p$ transition as a test case; irradiation with 100 V/cm (15 W/cm<sup>2</sup>), 10,000 cm<sup>-1</sup> off resonance, would generate an effective shift of ~2 Hz at a distance of 4 Å from the nucleus. Thus one would expect realistic laser intensities to be capable of producing measurable shifts.

Bulk shifts are seen in solvent and solute resonances alike. In addition, the lock circuitry changes the resonance frequency unless its input signal is overridden when the laser is on, which indicates that the deuterium resonance in the CDCl<sub>3</sub> solvent is shifted as well. The shifts generally go in the direction of decreased shielding (higher  $\delta$ ) independent of the sense of circular polarization. The shifts are solventdependent, as verified by comparing spectra in benzene or CDCl<sub>3</sub>. We believe that solvent absorption bands in the ultraviolet are creating these bulk shifts. Local shifts are also observed, and these shifts depend in a complicated way both on the molecular site and on the handedness of the enantiomer.

These observations do not agree with any existing theoretical treatment. Nevertheless, they demonstrate frequency changes that may be large enough to be useful. More recently, Evans and co-workers have derived a mechanism that depends on the product  $|\mathbf{E}(\omega)|^2 B_0$  and that might produce shifts in achiral molecules on the order of 0.1 Hz for our field intensity and magnetic field strength (6.4 T) (6). We believe that there are multiple competing processes because the dependence of the shift on laser power and molecular position is not simple.

We have shown experimentally that an off-resonance laser beam can shift NMR resonances, which implies that it is possible to enhance NMR resolution without heating. Irradiation in combination with more conventional techniques to improve dispersion (such as multidimensional NMR) is likely to be particularly useful; for example, in two-dimensional (COSY) spectra with the laser on in one time domain, we have verified that peaks are shifted in one dimension by the laser. Generalizations to multiple irradiation frequencies and other nuclear spins are also straightforward experimentally. However, much remains to be explored both theoretically and experimentally to determine the ultimate utility of this technique.

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# The Breakup of a Meteorite Parent Body and the Delivery of Meteorites to Earth

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Whether many of the 10,000 meteorites collected in the Antarctic are unlike those falling elsewhere is contentious. The Antarctic H chondrites, one of the major classes of stony meteorites, include a number of individuals with higher induced thermoluminescence peak temperatures than observed among non-Antarctic H chondrites. The proportion of such individuals decreases with the mean terrestrial age of the meteorites at the various ice fields. These H chondrites have cosmic-ray exposure ages of about 8 million years, experienced little cosmic-ray shielding, and suffered rapid postmetamorphic cooling. Breakup of the H chondrite parent body, 8 million years ago, may have produced two types of material with different size distributions and thermal histories. The smaller objects reached Earth more rapidly through more rapid orbital evolution.

ORE THAN 10,000 ANTARCTIC meteorites have been collected (1, 2), some of them very rare and surprising types of meteorites, including meteorites from the moon (3). It has been suggested that there are differences, even in the most common ordinary chondrites, between Antarctic meteorites and those currently falling elsewhere in the world (4). These differences include elemental and isotopic composition (5) and the frequency of various classes and types of meteorites (6, 7). The interpretation of these differences is difficult, mainly because of the problems of pairing and the effects of weathering on the Antarctic meteorites, many of which have been on Earth for 300,000 years or more (8, 9). It has, however, been argued that differences between Antarctic and non-Antarctic meteorites should not be present, because the existence of such differences requires that the flux of meteorites impacting Earth changed, either in terms of average numbers or types, in the 10<sup>5</sup>-year terrestrial age of the meteorites (10).

Another significant difference between

the Antarctic and non-Antarctic collections is found in the H5 chondrites. H5 chondrites are among the most common ordinary chondrites in both collections; however, a significant proportion of the Antarctic H5 chondrites has distinctly different induced thermoluminescence (TL) properties. The induced TL properties of meteorites are determined by the amount of feldspar present and the degree of its crystallographic ordering, and hence these properties may be used as an indicator of metamorphism (feldspar growth) and extreme shock (feldspar destruction) (11). Figure 1 shows induced TL peak temperature versus peak width for Antarctic H5 chondrites. The Antarctic data form two distinct clusters, one at relatively high peak temperatures (hereafter referred to as the ">190°C group"). The other cluster, with lower peak temperatures (the "<190°C group"), is similar to modern non-Antarctic meteorites, which plot along the dashed line (12). The presence of the >190°C group among Antarctic H5 chondrites is independent of weathering and pairing (12). This unusual group is present only in the H5 chondrites; the other classes of ordinary chondrites (the L and LL chondrites) do not differ from their modern non-Antarctic equivalents in terms of induced TL data.

The >190°C group is not present at all the collection sites in the Antarctic. Rather, the group is best represented at sites with a significant number of meteorites with old terrestrial ages (generally >200,000 years), but the number is relatively small or absent at sites with meteorites with relatively young terrestrial ages (<100,000 years) (Fig. 2). The Allan Hills Main ice field has a large number of meteorites with old terrestrial ages [up to 300,000 years (13)], and natural TL data indicate that the upper ice tongue at Lewis Cliff likewise has a high proportion of meteorites with old terrestrial ages (14). The meteorites from the Allan Hills Farwestern ice field have not been examined in great detail, but natural TL data indicate that their average terrestrial age is similar to that of the meteorites from the Lewis Cliff upper ice tongue. The meteorites from the Yamato site have fairly young terrestrial ages [<140,000 years (13)]. Natural TL data indicate that meteorites from the lower ice tongue and meteorite moraine at Lewis Cliff have fairly young terrestrial ages; dating of ice bands at the former site gives ages of <30,000 years [see references in (14)]. These data show that the frequency of the >190°C group meteorites decreased with time and that the >190°C group is essentially absent in modern falls.

The presence of the >190°C group of meteorites in the Antarctic collection, and the reason for its unexpected temporal decay, should provide new insights into the origins of meteorites. Members of the >190°C group have cosmic-ray exposure ages of <20



**Fig. 1.** Induced TL peak temperature versus peak width for Antarctic H chondrites (12). Exposure age: filled squares, <18 Ma; open squares, >18 Ma;  $\times$ , no data. The dashed line is the trend for non-Antarctic H chondrites (see Fig. 2). These properties are determined by the structural state of feldspar and therefore by the cooling rate after metamorphism. Two distinct groups, which have experienced different thermal histories, are apparent. Cosmic-ray exposure ages (16) are also different for the two groups.

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