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Observation of Carbon–Carbon Connectivities in Rotating Solids

E. M. Menger, S. Vega,[†] and R. G. Griffin*

Contribution from the Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

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Abstract: ^{13}C NMR spectra of ^{13}C–^{13}C spin pairs in solids rotating at the magic angle exhibit intensity and line width contributions due to homonuclear dipolar couplings. These couplings provide a mechanism whereby ^{13}C–^{13}C connectivities can be observed; it should therefore be possible to use these spectra to establish structures in the solid state. Two approaches to obtaining these data are discussed and demonstrated. The first is based on the two-pulse Jeener experiment and the latter involves double-quantum filtering.

I. Introduction

The past few years has witnessed the development of a variety of new NMR techniques for the elucidation of the structure of complex molecules, the most powerful and generally applicable of these being the class of experiments known collectively as two-dimensional spectroscopy.[1,2] In these experiments, the spectral interactions are manipulated in two separate time domains and dispersed in two orthogonal frequency dimensions. In "resolved" two-dimensional experiments, two interactions such as chemical shifts and hetero- or homonuclear spin couplings are displayed in the two dimensions. A second category of methods consists of "correlation" experiments, and they differ from resolved experiments in that they contain a mixing period during which coherence is transferred or evolves in the spin systems.[3] The end result is a two-dimensional spectrum exhibiting connectivities, i.e., cross-peaks between lines from spins which are coupled to one another. This type of experiment was first performed for (^1H–^1H) couplings in solution spectra of small molecules[2] and more recently has been applied to small proteins.[4,5] In addition, connectivities have been observed in spectra of low natural abundance nuclei such as ^{13}C.[6-9] While the spectral display is slightly different from that used in the polypeptide experiments, the information obtained at the end of the experiment is not. Specifically, ^{13}C–^{13}C connectivities are established and therefore the bonding pattern of a complex hydrocarbon can be derived. The success of these experiments in solution suggests that they could also be quite valuable for solid-state studies, and in a previous publication we have demonstrated the feasibility of observing ^{13}C–^{13}C connectivities in the spectra of single crystals.[10] In this report we present results of preliminary experiments which show that ^{13}C–^{13}C connectivities can also be observed under other high-resolution conditions, i.e., in the spectra of rotating solids.

More specifically the purpose of the experiments described here is twofold: first to demonstrate that ^{13}C–^{13}C dipolar couplings are present in spectra of rotating solids and second to illustrate some techniques which are useful for obtaining double-quantum spectra. These goals are most readily realized by employing samples which are 90% double ^{13}C labeled so that the effects of ^{13}C–^{13}C dipolar couplings on, for example, sideband intensities are easily discernible. However, we emphasize that our use of 90% doubly labeled samples does not imply that these experiments require such high levels of enrichment. ^{13}C–^{13}C dipolar couplings in natural abundance samples were reported by Van der Hart[11] some time ago. More recently, dynamic nuclear polarization methods have been incorporated into solid-state ^{13}C experiments resulting in signal-to-noise enhancements of 40–50[12-14] which should raise natural abundance ^{13}C-^{13}C dipolar signal levels to approximately those currently available for single-quantum ^{13}C spectroscopy. Alternatively, a factor of ~75 increase in signal-to-noise is available by working at 4.2 K and using CH_3 groups to shorten the ^1H T_1.[15] These experiments indicate that double-quantum spectroscopy on natural abundance samples is clearly within the range of practicality. Finally, there are other nuclei such as ^{29}Si and ^{187}W where solution-state double-quantum experiments have been performed,[16] and these, too, should be susceptible to study with the techniques outlined here.

II. ^{13}C–^{13}C Dipolar Interactions in Rotating Solids

In order to establish connectivities between atoms in a molecule, there must exist a coupling between the spins of interest. In solution the indirect dipolar or *J* coupling, amounting to about 35 Hz,[6] is employed in connectivity experiments. In static solids the direct dipolar interaction, which ranges from 2 to 4 kHz for a typical ^{13}C–^{13}C bond,[17] is the dominant interaction. However, the size of this coupling is also the same size as the spinning speed employed in magic angle experiments, and thus, it is natural to inquire if a residual ^{13}C–^{13}C dipolar coupling exists in rotating solids.

In the case of two unlike spins, the heteronuclear dipolar interaction (of magnitude ΔD) is governed by the I_zS_z term of the whole dipolar Hamiltonian. Since this term is *inhomogeneous*, it contributes to the centerband and sidebands in the same way as the shift anisotropy, $\Delta\sigma$. Thus, for $\Delta\sigma < \nu_R < \Delta D$ the spectrum is a dipolar spectrum split into sidebands which collapses to a single line when the spinning speed is increased so that $\nu_R > \Delta D$. Because of this, ^{13}C–^{15}N dipolar couplings can essentially be removed by

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[†] Permanent address: Isotope Department, Weizmann Institute of Science, Rehovoth, Israel.

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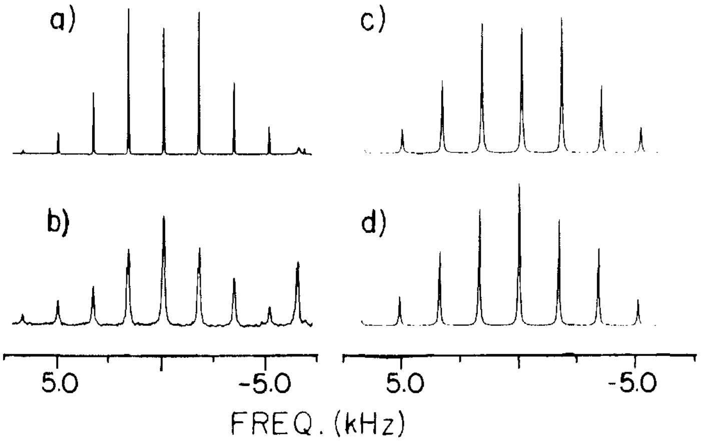

Figure 1. Comparison of ^{13}C MASS spectra obtained from singly and doubly labeled glycine samples illustrating the effects of $^{13}C-^{13}C$ dipolar couplings. $\nu_R = 2.0$ kHz, $\nu_{^{13}C} = 79.9$ MHz. (a) Spectrum of the carbonyl region of the singly labeled sample ($NH_3^+-CH_2-^{13}CO_2^-$) in which the line widths are ~60 Hz. (b) Spectrum of the carbonyl region of the doubly labeled sample ($NH_3^+-^{13}CH_2-^{13}CO_2^-$). The line widths have increased to ~150 Hz and the sideband intensities are noticably different due to the $^{13}C-^{13}C$ dipolar coupling. (c) Simulation of part a with use of principal values obtained from ref 12. (d) Simulation of part b with use of the same shift parameters plus a 4-kHz $^{13}C-^{13}C$ coupling.

2-3 kHz magic angle sample spinning (MASS).[18] In contrast, for homonuclear spins the flip-flop term of the dipolar Hamiltonian must be taken into account. This term does not commute with the $I_{zi}I_{zj}$ term and the chemical shift part of the Hamiltonian, and it will therefore lead to a broadening of the centerbands and sidebands in the spectrum.[19] However, for homonuclear spins in powder samples with nonoverlapping static chemical shift spectra, and for which the dipolar interaction strength is smaller than the difference in chemical shifts for all crystalline orientations, the flip-flop term can again be ignored.

An example of the intermediate case, where the dipolar interactions are of the order of or smaller than the chemical shift differences, is shown in Figure 1. Here, we show a sideband spectrum obtained from a sample of carboxyl labeled glycine ($NH_3^+-CH_2-^{13}CO_2^-$) which is due exclusively to the chemical shift anisotropy. Note that the lines are sharp, and at this spinning speed the first two rotational sidebands are more intense than the centerband. The effect of introducing a homonuclear $^{13}C-^{13}C$ dipolar coupling is illustrated in Figure 1b which is a spectrum of the carbonyl region of doubly labeled glycine, e.g., $NH_3^+-^{13}CH_2-^{13}CO_2^-$, obtained at the same spinning speed. Clearly, the sideband intensities are different, and the lines are noticably broader than those observed for the singly labeled sample. In glycine the difference in isotropic chemical shifts is 10.4 kHz while the dipolar interactions between the ^{13}C atoms in the molecules can maximally become 4.1 kHz.[17] In Figure 1c we show the calculated sideband spectrum of a rotating sample using only the chemical shift parameters of the CO_2^- carbon in glycine. The spectrum in Figure 1d was obtained by considering, in addition to the chemical shift parameters, the secular part of the dipolar interaction between the CO_2^- carbon and the CH_2 carbon. These calculated spectra are very similar to the experimental results in parts a and b in Figures 1 and suggest that the $I_{zi}I_{zj}$ term of the dipolar interaction is primarily responsible for the changes in the sideband and centerband intensities. We attribute the observed *line broadening* to the flip-flop term of the dipolar coupling.

III. Jeener Experiment

The simplest way to establish connectivities in solution spectra is the two-pulse Jeener experiment[1] which is commonly referred to as COSY.[2,4,5] The pulse sequence is shown in Figure 2a and it begins with the customary cross-polarization procedure, which serves the same function as the initial 90° pulse in a solution experiment. This is followed at a time t_1 by an additional 90° pulse which is phase-cycled for reasons to be discussed below. Following this pulse, data acquisition commences immediately.

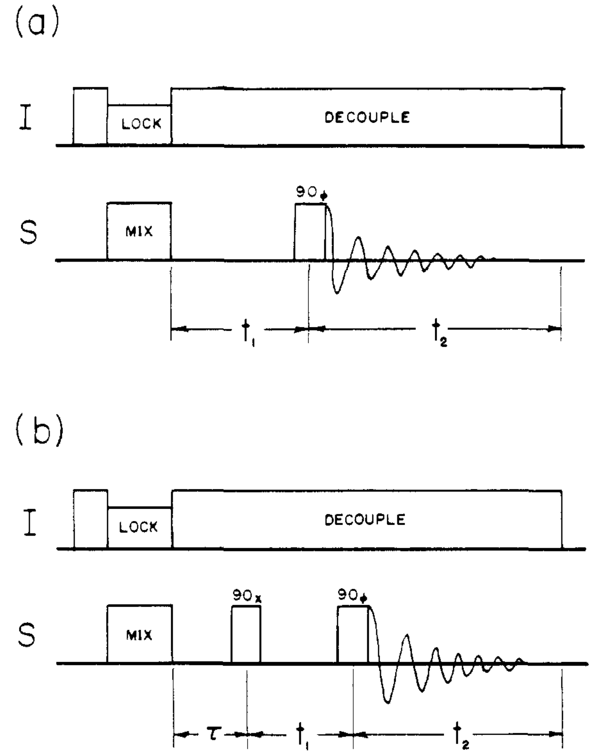

Figure 2. Pulse sequences for the Jeener experiment (a) and double-quantum experiment (b). I and S denote ^1H and ^{13}C pulses, respectively.

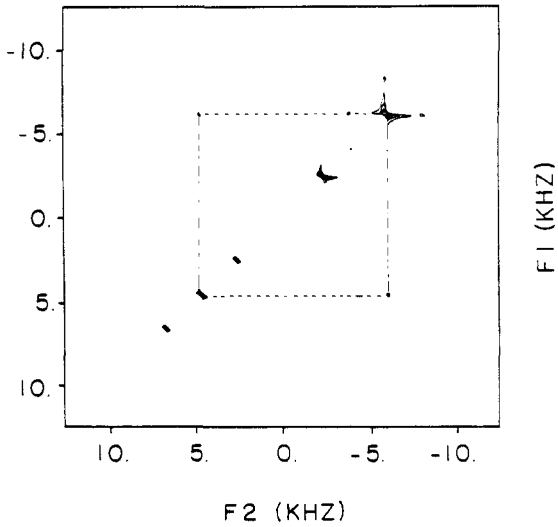

Figure 3. ^{13}C spectrum obtained from a sample of double labeled glycine with the Jeener experiment. The cross-peaks "connecting" the centerbands from the carbonyl group and the methylene group are shown with dashed lines. Notice that the Delrin line has no cross-peaks associated with it. Also visible are some "self-cross-peaks" associated with the methylene group which were not completely suppressed.

A two-dimensional contour spectrum obtained from $^{13}C_2$-Gly with use of the Jeener sequence is shown in Figure 3 and exhibits the expected centerbands and rotational sidebands on the diagonal. Specifically, the CH_2 and CO_2^- centerbands occur at −5 and +5 kHz, respectively, the Delrin line from the rotor is at −4 kHz, and the remaining diagonal lines are rotational sidebands. Also present in the spectrum are cross-peaks denoted by dashed lines which establish that the methylene and carboxyl carbons are directly bonded. In addition, there are some "self-cross-peaks" present in the methylene region which are absent in the carboxyl region.

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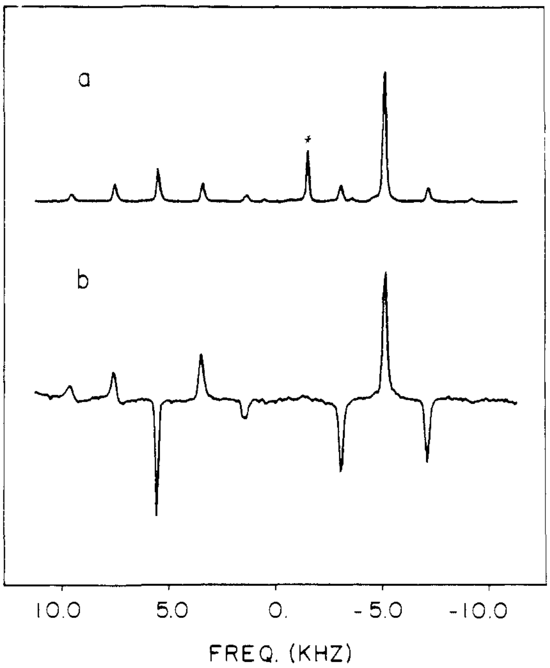

Figure 4. Comparison of ^{13}C spectra obtained from a doubly labeled glycine sample with (a) a normal MASS pulse sequence and (b) a double-quantum pulse sequence (Figure 2b) with τ = 200 μs. In addition, synchronous incrementation was employed during t_1. Approximately 64 scans were accumulated for each spectrum.

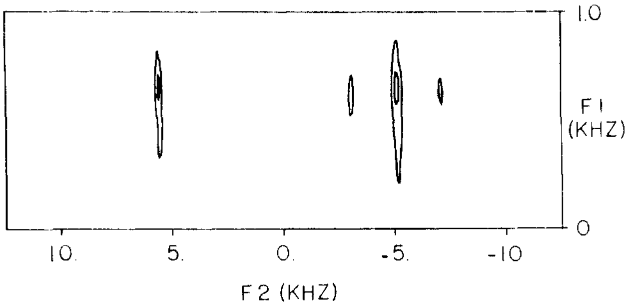

Figure 5. Two-dimensional ^{13}C spectrum obtained from a doubly-labeled glycine sample with use of the pulse sequence of Figure 2b; τ = 200 μs. In addition, synchronous incrementation (sampling) was employed during t_1. Since they occur at the same F_1 frequency, the spectral lines clearly show the connectivity between the carbonyl and methylene carbons.

Most of these peaks are suppressed by phase cycling the second pulse. However, the CH_2 has a small shift tensor, and the centerband is therefore quite intense. This leads to the residues present in Figure 3 which presumably arise from experimental imperfections.

The data in Figure 3 establish that ^{13}C–^{13}C connectivities can be obtained from MASS spectra. However, this exerimental approach suffers from the obvious disadvantage that the strong lines on the diagonal will swamp the weaker cross-peaks. This problem will be particularly acute when examining natural abundance ^{13}C samples and requires a method for suppressing these signals in the spectrum. This is conveniently done with multiple-quantum filtering techniques.

IV. Double-Quantum Filtering

A direct method for establishing connectivities is a double-quantum filtering technique used previously in liquids[6-9] and more recently in single crystals.[10] The pulse sequence employed in these experiments is shown in Figure 2b and it begins with the customary Hartmann–Hahn cross-polarization. Double-quantum coherence is excited by the second $\pi/2$ pulse after a time τ and is recalled to the single-quantum domain for observation after a variable time t_1. For systems with a well-defined dipolar or J coupling, e.g., single crystals or solutions, the pulse sequence of Figure 2b represents an efficient means to excite double-quantum coherence. In particular, when $\tau \simeq 1/\Delta$, where Δ is the size of the coupling, then there is an efficient transfer of coherence between the single- and double-quantum regimes. However, in the situation of interest here, the samples are rotating powders and the efficiency of the double-quantum excitation is lowered due to the complicated behavior of the spin systems during each rotor cycle. Because the double-quantum coherence is created by the inhomogeneous part of the dipolar interaction, the second pulse must be applied at a time τ shorter than the rotor period which is not necessarily of the order of $1/\Delta$. Notice that in the experiment of Figure 2b no refocusing 180° pulses are employed, since they would scramble the magnetization vectors of the nuclei in different crystallites of the powder and would make the detection of sideband spectra impossible.[20] For the results shown below we have employed τ = 200 μs which was found empirically to yield the optimum signal-to-noise.

Some typical results are shown in Figure 4, the top half of the figure being the normal single-quantum spectrum obtained from NH_3^+–$^{13}CH_2$–$^{13}CO_2$ rotating at 2.0 kHz. Note that a line marked with an asterisk is present and is due to the Delrin rotor. Application of the double-quantum sequence with t_1 = 0 and the proper phase cycling results in the spectrum shown in Figure 4b. In this trace, the signal-to-noise is much lower due to the low double-quantum excitation efficiency. In addition, we observe that the centerbands and sidebands are no longer in absorption mode. The intensities and the phases of the sidebands and centerbands are governed by a number of factors such as off-resonance values, chemical shift tensor magnitudes, and relative orientations. Note that the double-quantum excitation does remove the single-quantum signals from the spectrum—the Delrin line is absent.

Although the spectrum of Figure 4 indicates that ^{13}C–^{13}C dipolar couplings are present, it does not provide information on which ^{13}C's are coupled to one another. This information can be introduced by adding a second time dimension to the experiment. Specifically, t_1 of Figure 2b is stepped through a series of values and a two-dimensional spectrum is constructed in the normal fashion. Figure 5 is such a two-dimensional spectrum and clearly illustrates the connectivity between the CH_2 and CO_2^- in glycine, i.e., the lines occur at the same F_1 frequency. Note that rotational sidebands are present in the F_2 dimension of the CH_2 line but not on the CO_2^-. This is again due to the fact that the CH_2 tensor is smaller and more intensity is resident in the centerband. Sidebands in the F_1 dimension were suppressed by incrementing t_1 in steps of ν_R^{-1}—synchronous sampling which results in a reduced bandwidth in this dimension. In principle, chemical shift scaling[21] could be incorporated into either dimension if greater bandwidths are necessary. Concurrently, the signal-to-noise should increase since the intensity originally resident in the sidebands will now appear in the centerband. An alternative method for performing the double-quantum filtering is to fix t_1 and step τ through a series of values. This approach has recently been employed in ^{1}H liquid state experiments.[22]

V. Conclusions

We have demonstrated that ^{13}C–^{13}C dipolar couplings are present in the spectra of rotating solids. They manifest themselves as broadenings of the ^{13}C lines and as changes in the relative intensities of the centerbands and sidebands. Since these couplings are present, it is possible to excite ^{13}C–^{13}C double-quantum transitions and subsequently to extract information on carbon–carbon connectivities from the spectra. Thus, in principle, it should be possible to elucidate the structures of carbon skeletons in solids with these techniques. In the above, we have described methods to accomplish this goal and the simplest is the two-pulse Jeener

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experiment. With this method *single* lines appear on the diagonal of the two-dimensional plot and cross-peaks connect lines corresponding to dipolar coupled spins. The second approach involves double-quantum filtering and therefore single-quantum lines are removed from the spectra. A technique such as this (together with extensive phase cycling) is mandatory for natural abundance samples where the intensity of the double-quantum spectra is well below the single-quantum lines. The second method results in a display containing isotropic shifts in the F_2 dimension and sums and differences of shifts in F_1 as in the liquid-state INADEQUATE experiment.[6-9] It is clear that with improved signal-to-noise, available through dynamic nuclear polarization or low temperatures, these methods should be applicable to ^{13}C–^{13}C spectra and to a number of other systems, e.g., ^{187}W, etc. They should provide a powerful technique for elucidating the structure of solids.

VI. Experimental Section

The spectra discussed above were obtained on a home-built pulse spectrometer operating at ^{1}H and ^{13}C frequencies of 317 and 79.9 MHz, respectively. The ^{1}H decoupling field was 100 kHz and the ^{13}C field was 60 kHz. The glycine was 90% doubly labeled and was procured from Merck Isotopes. Rotors were of the Andrew-Beam design fabricated from Delrin.

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Registry No. NH_3^+–$^{13}CH_2$–$^{13}CO_2^-$, 67836-01-5.

Heats of Formation of Radicals and Molecules by a Photoacoustic Technique[1]

T. J. Burkey, M. Majewski, and D. Griller*

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Abstract: A photoacoustic technique was used to measure heats of free radical reactions. To illustrate the method, bond dissociation energies were measured for the Sn–H bond in *n*-Bu$_3$SnH, for the C$_3$–H bond in 1,4-cyclohexadiene, and for the C$_2$–H bond in diethyl ether. Heats of formation of *t*-BuO$\dot{\mathrm{P}}$Ph$_3$ and *t*-BuO$\dot{\mathrm{P}}$(Bu-*n*)$_2$ were determined, and the method was also used to measure quantum yields for the photolysis of di-*tert*-butyl peroxide and diphenyl disulfide.

Homolytic bond dissociation energies have proved to be particularly difficult to measure. Even in the simplest cases, experiments are fraught with problems as evidenced by the controversy surrounding values for primary, secondary, and tertiary C–H bond strengths.[2] Reliable data for organometallic compounds and for those of high molecular weight are particularly rare, because these materials are inappropriate for conventional gas-phase techniques. Under these conditions, any method that represents a new source of thermochemical information should obviously be welcomed and exploited to the full.

Recently, Peters and his co-workers described a photoacoustic technique for measuring heats of reactions that were photoinitiated.[3-6] For example, they studied the thermochemistry of ion-pair formation in triplet benzophenone quenching by aniline[3] and the heat of formation of diphenylcarbene,[4] a species that is particularly short lived in solution. With their help and encouragement, we have applied the technique to free radical reactions and now report measurements of some C–H and an Sn–H bond strengths. We have also used the method in situations where the radical thermochemistry was reasonably well-known and have thus been able to derive quantum yields for bond cleavage and heats of formation of molecules. In addition, we have measured the heat of formation of a short-lived phosphoranyl radical.

Experimental Section

Materials. All of the materials used in this work were commercially available. Benzene was purified by multiple washings with concentrated sulfuric acid. It was then washed with water, dried over sodium sulfate, and finally distilled from calcium hydride. Diethyl ether was distilled from sodium benzophenone. Triphenylphosphine and *o*-hydroxybenzophenone were recrystallized twice from ethanol. Di-*tert*-butyl peroxide was washed with an aqueous solution of silver nitrate and then with water. It was dried over magnesium sulfate and was finally passed through a column of neutral alumina. Tri-*n*-butyltin hydride and 1,4-cyclohexadiene were distilled under nitrogen before use.

Apparatus. The photoacoustic apparatus is shown schematically in Figure 1 and follows the design developed by Peters et al.[3-6] Pulses from a nitrogen laser (Molectron UV 24, λ = 337.1 nm; pulse width 10 ns; power, 10 mJ per pulse; repetition rate, 5 Hz) were used to photolyze solutions of photolabile substrates contained in a standard UV flow cell (Hellma 176). An iris ensured that only a very small part of the light passed as a fine beam through the center of the cell, and a low powered lens was used to correct for the slight divergence of the beam. Neutral density filters were often employed to further attenuate the light intensity.

The heat evolved as a result of the photoinitiated reactions caused a shock wave in the solution, which was transmitted at the speed of sound to the cell wall. Here, the primary wave and its many reflections were detected in a time-resolved mode by a piezoelectric transducer (Panametrics V110, response 0.2 μs, or Model V101, response 2.0 μs). The transducer signals were amplified (Panametrics ultrasonic preamplifiers) and were recorded on a storage oscilloscope (Tektronics 7020).

A quartz plate was used to reflect part of the laser beam to a reference device, so that corrections could be made for variations in the laser power. Several devices were tried, e.g., power meter, photomultiplier tube, photodiode. However, in our hands, the most reliable reference was a second photoacoustic arrangement consisting of a cuvette and a trans-

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