

Observation of ^{13}C - ^{14}N dipolar couplings in single crystals of glycine

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The early work of Pake¹ on gypsum showed that one could employ dipolar splittings to determine internuclear distances and directions with nuclear magnetic resonance. However, the practical utility of this method has been limited because the large number of nuclear couplings usually present produces extensive broadening of the NMR lines, and consequently obscures the dipolar splittings of interest. Recently several methods have been developed for removing homo² or heteronuclear³⁻⁵ dipolar broadening and thus allowing observation of high resolution NMR spectra in solids. If one employs these methods on systems which contain additional nuclei in a magnetically dilute form, then resolvable dipolar splittings appear which can be utilized in the determination of internuclear distances and directions.

An example of such a system is the simplest of amino acids, glycine. Here one has two magnetically dilute spin reservoirs consisting of ^{13}C and ^{14}N nuclei, and an abundant spin reservoir consisting of protons. With rf fields of sufficient strength one can decouple³ the protons from the magnetically dilute nuclei and (in principle) observe dipolar splittings in either the ^{13}C or ^{14}N spectra. A spectrum illustrating such dipolar splittings is shown in Fig. 1 and is a ^{13}C spectrum obtained from a single crystal of glycine.⁶

Glycine crystallizes in a monoclinic lattice with four molecules per unit cell,⁷ and the symmetry of the cell allows one to observe lines from two different molecules. Thus, the two lines on the left side of the spectrum are due to the carboxyl groups of the two magnetically distinguishable glycine molecules. In an arbitrary orientation one would also expect to observe two lines from the methylene carbons split by the adjacent ^{14}N nuclei and indeed we have found this to be the case. However, in the spectrum of Fig. 1, the methylene lines are degenerate and we observe three instead of six lines due to dipolar coupling to the ^{14}N . It should be mentioned that the carboxyl carbon linewidths are orientation dependent and in fact one can discern small splittings of these lines in Fig. 1. This coupling most probably arises from ^{14}N nuclei on an adjacent molecule in the unit cell.

From an orientation dependent study of the ^{13}C - ^{14}N dipolar couplings one can determine the C-N distance in the glycine molecule and its direction in the unit cell;

we will present these data in a future publication. The principal values of the ^{13}C carboxyl chemical shift tensor (relative to external benzene) in glycine are given below and the orientation of the tensor is similar to that found for other carboxyl groups.^{8,9} That is, σ_{11}

$$\sigma_{11} = -122.6 \text{ ppm}$$

$$\sigma_{22} = -54.0 \text{ ppm}$$

$$\sigma_{33} = 22.0 \text{ ppm}$$

is approximately along the C-C bond, σ_{22} is in the COO plane perpendicular to the C-C bond, and σ_{33} is perpendicular to the COO plane.

We believe that ^{13}C - ^{14}N dipolar splittings such as we report here, together with shift anisotropy data, could be an important source of structural information, particularly for amino acids and peptides as well as for other molecules. If one assumes that the length of a carbon-carbon bond is known, and is primarily interested in the conformation of a molecule, then such information could be obtained from shift anisotropies and dipolar splittings. Moreover, if accurate values for ^{14}N quadrupole couplings and asymmetry parameters are available,^{6b} then one could employ selective ^{13}C enrichment to examine the conformation of part of a relatively large molecular species such as a protein with spatial resolution of $\sim 0.01 \text{ \AA}$. Such resolution is not commonly available from x-ray diffraction studies of large molecules. Finally, it should be clear that dipolar couplings

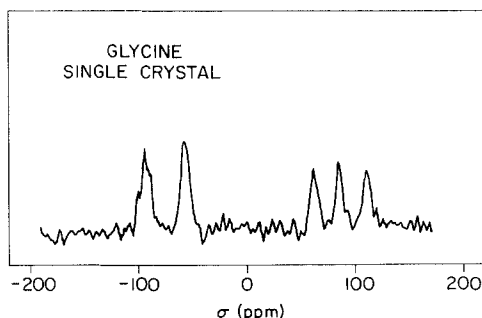


FIG. 1. 24.4 MHz ^{13}C spectrum of a single crystal of glycine. The lines on the left are due to the carboxyl carbons and those on the right to the methylene carbons dipolar split by adjacent ^{14}N nuclei.

in ^{13}C spectra should be observable from nuclei other than ^{14}N so long as they are magnetically dilute.

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⁶(a) ^{13}C - ^{14}N dipolar splittings have also been observed in powdered samples of acetonitrile [S. Kaplan, A. Pines, R. G. Griffin, and J. S. Waugh, *Chem. Phys. Lett.* **25**, 78 (1974)]; and (b) in single crystals of $\text{K}_2\text{Pt}(\text{CN})_4 \cdot \text{Br}_{0.3} \cdot 3\text{H}_2\text{O}$ enriched to 60% in ^{13}C [M. E. Stoll, R. W. Vaughn, R. B. Saillant, and T. Cole, *J. Chem. Phys.* **61**, 2896 (1974)].

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Low energy dynamics for reactive collisions of C^+ with D_2

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The reaction $\text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+ + \text{H}$ has been of great interest to both experimentalists¹ and theoreticians.² The most complete experimental study to date has been that of Mahan and Sloane³ who investigated the reaction at relative energies between 2.86–7.06 eV. At relative energies below 4 eV, these authors found:

(a) a high but not perfect degree of symmetry for the CH^+ product angular distribution in the center of mass system,

(b) similar product angular distributions for CH^+ and CD^+ formed from the reactants $\text{C}^+ + \text{HD}$, and

(c) a high degree of product internal excitation.

On the basis of orbital correlation diagrams, Mahan and Sloane³ inferred that ground state $\text{C}^+ + \text{H}_2$ reactants could correlate with ground state CH_2^+ , which is bound by ~ 4.0 eV. Their conclusion was that the $\text{C}^+ + \text{H}_2$ system at relative energies below 4 eV fit the "osculating" complex model,⁴ in which a complex lasting approximately one rotational period is formed. This conclusion was in reasonable accord with RRKM estimates of the complex lifetime.^{3,5}

To test the "osculating" complex model, we have studied the dynamics of the system $\text{C}^+ + \text{D}_2 \rightarrow \text{CD}^+ + \text{D}$ at relative energies between 0.64–1.58 eV. At such low energies, complex formation should become more prominent.⁵ The experiments were performed with an ion-beam, gas-target scattering apparatus, described elsewhere.⁶ The C^+ beam was produced in a commercial plasma source (Colutron) from a CO-He mixture. Ion beam laboratory energy spreads were typically ~ 0.2 eV (FWHM) and angular spreads ~ 1 – 2° (FWHM). Since the first metastable state of C^+ lies > 5 eV above the ground state, it is unlikely that a significant portion of the beam

was in an excited state.⁷ The reaction of ground state C^+ and ground vibrational state D_2 is ~ 0.4 eV endothermic.⁸ Hence our lowest energy results are barely above threshold.

Figure 1 depicts product intensity data collected at a laboratory angle of 0° at three relative energies: 1.45, 1.13, and 0.89 eV. The CD^+ relative intensity is plotted as a function of v/v_0 , the ratio of product to projectile laboratory velocity. The velocity of the center of mass is also shown. All products with velocity less than the

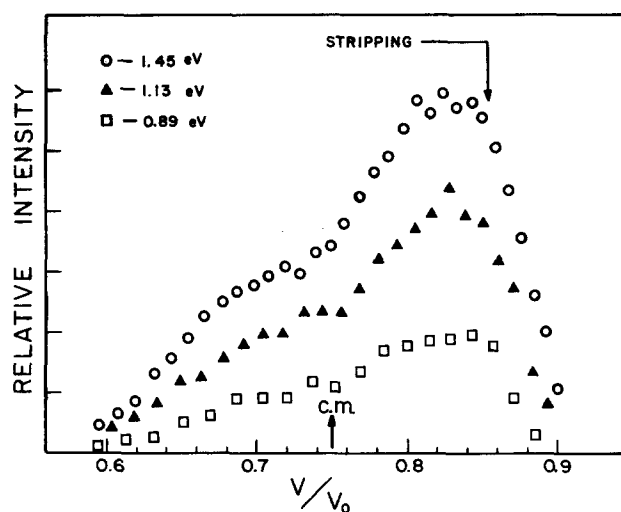


FIG. 1. Relative intensity of CD^+ is plotted against v/v_0 , the ratio of product to projectile velocity, at a laboratory angle of 0° . The center of mass velocity occurs at $v/v_0 = 0.75$, whereas the velocity expected for pure spectator stripping occurs at $v/v_0 = 0.856$. The relative magnitude of the three curves is not indicative of their absolute cross sections.