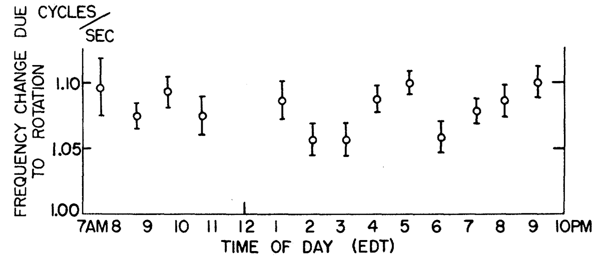

FIG. 1. Diurnal variation of the change in relative frequency due to rotating two ammonia masers through 180°.

Beams of the two masers were oppositely directed and in an east-west direction. The change of about 1.08 cps is primarily due to local magnetic fields. Maximum deviation from this value during the day is 1/50 cps. Lengths of lines indicate probable errors computed from fluctuations of 16 measurements at each point.

pendicular to the earth's axis must be less than 1/30 km/sec. Results from experiments of the Michelson-Morley type vary from an ether drift of about 8 km/sec reported by Miller[4] to an upper limit of 1.5 km/sec given by the experiments of Joos.[5] Of course a major part of the advantage of the present experiment is its first-order rather than second-order dependence on v.

Those who are already completely convinced of the correctness of special relativity, or who do not wish to consider an ether model, should note that postulates of special relativity are not necessarily inconsistent with the existence of a frequency shift in the above experiment or of an anisotropy in space. These can result from the presence of matter external to the earth which is not uniformly distributed, or which is not moving with the earth's velocity.

The preliminary results quoted here apply to September 20, 1958. It is expected that the experiment will be refined further and that additional measurements will be made at other times during the year.

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ANISOTROPY OF THE C^{13} CHEMICAL SHIFT IN CALCITE

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It has been shown by Ramsey[1] that the chemical shift of a nuclear magnetic resonance can be anisotropic. Since the shift tensor is a dyadic, the shifts will be a function of the orientation of the molecule in a magnetic field for nuclei in environments of lower than tetrahedral symmetry. An indication of the presence of such an anisotropy was first found by Bloembergen and Rowland,[2] who attributed the asymmetry of the Tl^{205} resonance in powdered Tl_2O_3 to this effect. Shift anisotropies have also been invoked by Gutowsky and Woessner[3] to explain the T_1 difference between H^1 and F^{19} in 1,3,5-trifluorobenzene, and by McConnell and Holm[4] to account for the relatively short T_1 of C^{13} in CS_2.

A direct measurement of the anisotropy of the C^{13} shift in a single crystal of calcite ($CaCO_3$) has now been made. This substance is ideal for such an experiment because all magnetic nuclei are present in such low abundance that dipolar broadening is negligible and a sharp strong line is observed. The apparatus used was a Varian 4300*B* High Resolution NMR spectrometer operating at 8.5 Mc/sec, and a Varian 12-inch electromagnet. The dispersion mode was used and the lines were measured under rapid passage conditions. The observed line widths, about 20 milligauss, were the result of H_1 broadening. The magnetic field inhomogeneity over the sample volume was about 10 milligauss, and approximate calculations by the method of Kittel and Abrahams[5] indicated a dipolar broadening of the order of 5 milligauss. T_1 was found to be about 40 minutes in the sample used, which was a cleavage rhombohedron of clear colorless "Iceland spar" about 0.3 cm^3 in volume. The crystal was aligned visually with its trigonal axis in the plane of a graduated glass ring which was set vertically in a tube filled with acetone, whose C^{13} resonances were used as secondary standards. The whole assembly was turned by a goniometer head attached to the probe. Final alignment was made by observation of the angular variation of the shift and was accurate to within about one degree.

The carbonate ion (CO_3^{--}) has a three-fold axis. The operation of the shift dyadic will, therefore, give a shift ellipsoid of revolution which can be

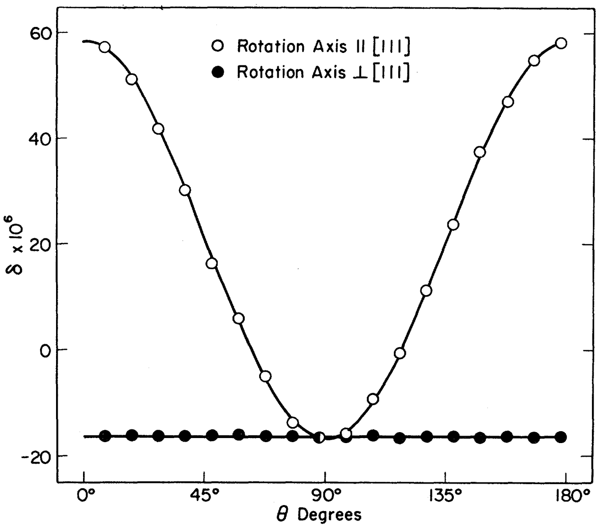

FIG. 1. The angular variation of the C^{13} chemical shift in calcite. The closed circles are for rotation about the trigonal axis, and the open circles are for rotation about an axis perpendicular to the trigonal axis.

completely specified[6] by

$$\delta = \delta_1 \cos^2\theta + \delta_2 \sin^2\theta , \qquad (1)$$

where θ is the angle between the three-fold axis and the magnetic field direction. The experimental results are shown in Fig. 1, along with a plot of Eq. (1) with the parameters $\delta_1 = 58.4\times10^{-6}$ and $\delta_2 = -16.6\times10^{-6}$. The zero of reference is the shift of the carboxyl carbon in acetic acid and the shift is defined by

$$\delta = \frac{H_{\text{sample}} - H_{\text{reference}}}{H_{\text{reference}}}. \qquad (2)$$

The average shift, $\delta_{\text{Av}} = 1/3(\delta_1 + 2\,\delta_2)$, is 8×10^{-6}, about the same as the CO_3^{--} shift in an aqueous solution of K_2CO_3 (7×10^{-6}).[7] The total anisotropy, 75.0×10^{-6}, is about one-fourth the total range of shifts observed in carbon compounds.[7, 8]

Anisotropy measurements such as those described here obviously require single crystals dilute in both the observed nuclear species and other magnetic nuclei. Carbon compounds satisfy the first criterion almost ideally, but the second is much more restrictive. The new technique of line narrowing by double resonance[9, 10] would seem to offer the possibility of extending the study of anisotropies to many other substances. The only other crystal in which we have observed an anisotropic shift to date is aragonite, the orthorhombic form of calcium carbonate.

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