Letters to the Editor

We would like to express our appreciation to Professor Felix Bloch for his continued interest in our work. Thanks are also due Mr. William S. Gorton Jr. of the Department of Chemistry for preparing the liquid ammonia sample.

* Assisted by the Joint Program of the AEC and the ONR.
* This figure is that given by Bloch, Levingston, and Packard, Phys. Rev. 74, 1125 (1948).

The Dependence of a Nuclear Magnetic Resonance Frequency upon Chemical Compound

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January 18, 1950

In the course of measurements on NO₃⁻ mentioned in the previous letter, we made the surprising observation that its frequency of resonance, in liquid samples, depended strongly upon the chemical compound in which it was contained.² This effect is strikingly demonstrated by the appearance of two resonances, separated by 1.6 kc, in the neighborhood of 3300 kc, corresponding to a field of 10,500 gauss, using a solution of NH₄NO₃ in 2.0-molar MsO₄ as a sample. These resonances presumably arise from the NH₄⁺ and NO₃⁻ complexes, since samples of NH₄CH₂CO₂ and HNO₃ separately give rise to two different resonances whose frequencies approximate those from the above sample. The separation is four times greater than the line width measured between points of maximum slope.

We have observed, within a resolution of 0.1 kc, that the NO₃⁻ resonances from the ion NH₄⁺ from the compounds NH₄NO₃, NH₄CH₂CO₂, and NH₄Cl coincide at one frequency, while those from the ion NO₃⁻ from the compounds NH₄NO₃, HNO₃, and Ca(NO₃)₂ coincide at another frequency. Measuring the NO₃⁻ resonances from other molecules relative to that arising from the ion NO₃⁻ from HNO₃ or NH₄NO₃, we have obtained the results given in Table I. All such shift effects have been in the direction of lower frequency.

The separations of resonances from four pairs of compounds were also measured at 6700 gauss, corresponding to a frequency of 2100 kc, to determine whether or not the frequency separations were independent of the field intensity. They are apparently proportional to it, for the ratios of the separations are in agreement with the ratio 6700/10,500 = 0.64, within our experimental resolution. (See Table II.)

We further made the observation that the separation of the two resonances arising from NH₄NO₃ was dependent on the concentration of the paramagnetic salt MnCl₂ added to it. A 7.5-molar solution of this salt without MnCl₂ shows two resonances separated by 1.0 kc, as given in Table I, but with 1.0- and 2.0-molar concentrations of MnCl₂ the separations become 1.4 kc and 1.6 kc, respectively.

We shall continue to investigate this phenomenon because of its direct significance for the interpretation of nuclear magnetic resonance frequencies in terms of nuclear moments, as well as to obtain an insight into its origin. With the largest observed line shift amounting to about 5 parts in 10⁶, this effect is almost twice as large as the present value of the magnetic correction calculated for the atom. These calculations, however, do not hold for the paramagnetic molecules which we have studied and whose modification of the diamagnetism, as well as terms due to induced paramagnetism (high frequency matrix elements) can be expected, particularly in cases where three out of seven electrons may be strongly influenced by the chemical bond. The fact that the shifts are of the same order of magnitude as the diamagnetic correction and exhibit likewise proportionality to the applied field suggests a similar origin, although we have not been able to explain satisfactorily the observed magnitude of the effect. Until it is clearly understood, the accuracy of magnetic moments determined under certain conditions remains somewhat in doubt.

We should like to express our appreciation to Professor Felix Bloch for stimulating discussions about this work.

* Assisted by the Joint Program of the AEC and the ONR.
1. W. G. Proctor and E. C. Yu, Phys. Rev. 76, 1229 (1949), has observed a large frequency difference between the nuclear magnetic resonance frequency of an atom and its salt. The satisfactory explanation which he has given for this difference does not apply, however, to our case.

Spallation Products of Arsenic with 190-Mev Deuterons

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January 3, 1950

Recent investigations of the nuclei formed when arsenic is bombarded with 190-Mev deuterons in the 184-In. cyclotron have been extended.

The target material consisted of twice sublimed arsenic. Spectrographic analysis showed no impurity in sufficient quantity to account for the formation of any of the isotopes reported here. The use of improved chemical separations and counting techniques has enabled the identification of 38 nuclear species among the elements from chromium through selenium. Table I lists the isotopes identified, the observed and the "nominal" half-lives as reported in the literature, and the yields relative to that of As³² taken as 1.00.

In calculating yields, the extent of electron capture has been taken from the data collected in reference 3. For Se³⁴ and Ge³⁴, and Ga⁴⁺, crude absorption measurements indicated that approximately two-thirds of the decays are by electron capture. The yield of As³² is based on the count of beta-particles, as no x-rays were observed (< 50 percent of the disintegrations). The yields reported here should all be accurate to within a factor of two and many accurate to within 20 percent, depending on the certainty with which electron-capturing ratios and counting efficiencies of x-rays are known.

Table I contains two changes in isotope assignment differing from those previously reported.¹ The 44-mn, selenium and 53-mn.

Table I. Frequency shifts relative to the resonance from the ion NO₃⁻ at 10,500 gauss.

<table>
<thead>
<tr>
<th>Compound observed</th>
<th>Frequency shift (kc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄⁺ from NH₄NO₃, NH₄CH₂CO₂, NH₄Cl</td>
<td>1.0</td>
</tr>
<tr>
<td>Liquid NH₄NO₃ containing 0.6-molar (Cr(NO₃)₆/H₂O</td>
<td>0.7</td>
</tr>
<tr>
<td>KCN</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table II. Resonance frequency separations with different compounds and field intensities.

<table>
<thead>
<tr>
<th>Compounds compared</th>
<th>Separation (kc) at 10,500 gauss</th>
<th>Separation (kc) at 6700 gauss</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃ and NO₃⁻ from 7.5-molar NH₄NO₃</td>
<td>1.0</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>In 2.0-molar MnSO₄</td>
<td>0.7</td>
<td>0.6</td>
<td>0.9</td>
</tr>
<tr>
<td>HNO₃ and (NH₄)CO₂</td>
<td>1.0</td>
<td>0.6</td>
<td>0.9</td>
</tr>
<tr>
<td>NH₄NO₃ containing 0.6-molar (Cr(NO₃)₆/H₂O</td>
<td>1.2</td>
<td>0.7</td>
<td>0.6</td>
</tr>
</tbody>
</table>

² This figure is that given by Bloch, Levingston, and Packard, Phys. Rev. 74, 1125 (1948).