

FIG. 5. Cross sections for exciting the $3s\ ^2P_{3/2,1/2} - 3p\ ^2D_{5/2,3/2}$ ($\lambda\lambda 4415\ \text{\AA}, 4417\ \text{\AA}$) transitions in O^+ .

taking the average of the $v=0$ determinations from the (0,0) and (0,1) data. The two values were the same to within 5%. This is an indication of the accuracy of the

relative values of the calculated Franck-Condon factors. Cross sections were measured for the $O_{II}\lambda 4416\text{-}\text{\AA}$ lines ($3s\ ^2P_{3/2} - 3p\ ^2D_{5/2}$, $\lambda 4415\ \text{\AA}$ and $3s\ ^2P_{1/2} - 3p\ ^2D_{3/2}$, $\lambda 4417\ \text{\AA}$). The two components were not resolved. These measurements are shown in Fig. 5.

We took some relative measurements of other O_{II} emissions at 20 and 100 keV at reduced slit widths so that the measurements were on completely resolved lines. Relative to the $\lambda 4416\text{-}\text{\AA}$ lines, the cross sections for the $3s\ ^4P_{5/2} - 3p\ ^4D_{7/2}$ ($\lambda 4649\ \text{\AA}$), $3s\ ^4P_{3/2} - 3p\ ^4D_{1/2}$ ($\lambda 4674\ \text{\AA}$), and $3s\ ^4P_{3/2} - 3p\ ^4D_{3/2}$ ($\lambda 4662\ \text{\AA}$) transitions are 1.7, 0.26, and 0.35, respectively.

Cross-section measurements were made on the H_α and H_β emissions. We postpone the reporting of these radiations until we have developed the technique for experimentally treating the radiation from fast hydrogen atoms. However, these emissions are about the same as those reported³ for H^+ on N_2 .

³ J. L. Philpot and R. H. Hughes, *Phys. Rev.* **133**, A107 (1964).

Molecular-Beam Magnetic-Resonance Studies of the Nitrogen Molecule*

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(Received 30 June 1964)

The radio-frequency spectra corresponding to the reorientations of the N^{15} nuclear moment and the molecular rotational magnetic moment have been studied in N_2^{15} by the molecular-beam magnetic-resonance method. A magnetic-resonance molecular-beam apparatus with an electron-bombardment detector was used for the experiments. In order to study these small moments, very narrow multiple slits were employed. The intensity of the molecular beam was maintained at the normal level through the use of multiple beams. From an analysis of the N^{15} resonance, the magnitude of the spin-rotational constant for the N^{15} nucleus was determined to be 22 ± 1 kc/sec. This result can be shown to be consistent with available nitrogen chemical-shift data when the sign of the spin-rotational constant is positive. The magnitude of the rotational magnetic moment was found to be 0.2593 ± 0.0005 nuclear magnetons per rotational quantum number.

I. INTRODUCTION

CONSIDERABLE progress has been made in recent years in the field of molecular beam spectroscopy. Much of this progress is the consequence of the development and improvement of the electron bombardment detector.¹⁻⁴ Within our laboratories, a recently

constructed molecular beam magnetic resonance apparatus incorporating an improved electron-bombardment detector has greatly widened the scope of molecules to which this technique can be applied.⁴⁻⁷ In this paper, we wish to report the application of this molecular beam apparatus towards a study of the Zeeman hyperfine structure of the nitrogen molecule.

Molecular beam spectroscopy is an important tool towards the determination of certain interaction constants in the molecular hyperfine Hamiltonian. In particular, due to the collision-free conditions of a molecular beam, the method is suitable for the determination of those molecular or interaction constants, such

* Work supported by the National Science Foundation and the joint program of the U. S. Office of Naval Research and the U. S. Atomic Energy Commission.

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¹ G. Wessel and H. Lew, *Phys. Rev.* **90**, 1 (1953).

² W. E. Quinn, A. Pery, J. M. Baker, H. R. Lewis, N. F. Ramsey, and J. T. LaTourrette, *Rev. Sci. Instr.* **29**, 935 (1958).

³ W. E. Quinn, J. M. Baker, J. T. LaTourrette, and N. F. Ramsey, *Phys. Rev.* **112**, 1929 (1958).

⁴ M. R. Baker, H. M. Nelson, J. A. Leavitt, and N. F. Ramsey, *Phys. Rev.* **121**, 807 (1961).

⁵ H. M. Nelson, J. A. Leavitt, M. R. Baker, and N. F. Ramsey, *Phys. Rev.* **122**, 856 (1961).

⁶ J. A. Leavitt, M. R. Baker, H. M. Nelson, and N. F. Ramsey, *Phys. Rev.* **124**, 1482 (1961).

⁷ N. F. Ramsey, *Am. Scientist* **49**, 509 (1961).

as the spin-rotational constant and the rotational magnetic moment, which depend upon molecular rotation and which are averaged to zero in a nonmolecular beam experiment due to frequent molecular collisions. As these molecular properties are ultimately connected with the electronic distribution within the molecular system, they are of considerable fundamental importance towards the understanding of electronic structures of molecules. Thus, the use of these molecular constants as a check on the accuracy of approximate electronic wave functions is frequently invoked.⁸⁻¹² Since most of these interactions are weak, they represent only small perturbations to the unperturbed electronic Hamiltonian and calculations of these interaction constants can therefore be made using perturbation and variational methods. A comparison of the calculated results with experimental values therefore not only serves to check the accuracy of approximate wave functions, but also tests the validity of certain approximations inherent in the various perturbation and variational schemes currently employed.¹³

Approximate Hartree-Fock wave functions are presently available for the nitrogen molecule.¹⁴ However, aside from the magnetic susceptibility,¹⁵ other magnetic properties of this molecule are practically unknown. An investigation of this molecule is therefore particularly appropriate.

N₂¹⁵ was studied in lieu of the more abundant isotope N₂¹⁴ because of the strong background signal at mass 28 in the mass spectrometer adjoining the electron-bombardment detector. The N¹⁵ nucleus was also selected because N¹⁵ has an intrinsic nuclear spin of $\frac{1}{2}$ and therefore does not possess a quadrupole moment which could interact with electric field gradients within the molecule to complicate the spectrum. A large quadrupole interaction would greatly broaden the resonance, thus reducing the signal intensity below the sensitivity of the spectrometer. Also, because of the smaller magnetic moment of the N¹⁵ nucleus compared to that of H¹ and F¹⁹, narrower slits must be installed at the detector and collimator. To recover the loss of beam intensity resulting from the use of narrow slits, the technique of multiple beams, recently developed within our laboratories, has been employed. Without this new feature, the experiments described in this paper would seem to be marginal if not impossible.

⁸ M. Karplus and H. J. Kolker, *J. Chem. Phys.* **38**, 1263 (1963).

⁹ R. P. Hurst, M. Karplus, and T. P. Das, *J. Chem. Phys.* **36**, 2786 (1962).

¹⁰ T. P. Das and R. Bersohn, *Phys. Rev.* **115**, 897 (1959).

¹¹ T. P. Das and M. Karplus, *J. Chem. Phys.* **36**, 2275 (1962).

¹² C. W. Kern and W. N. Lipscomb, *J. Chem. Phys.* **37**, 260 (1962).

¹³ M. Karplus, *Rev. Mod. Phys.* **32**, 455 (1960).

¹⁴ B. J. Ransil, *Rev. Mod. Phys.* **32**, 245 (1960).

¹⁵ L. C. Hector, *Phys. Rev.* **24**, 418 (1924); F. Bitter, *ibid.* **36**, 1648 (1930); H. F. Hamerka, *J. Chem. Phys.* **34**, 366 (1961).

II. EXPERIMENTAL

A description of the molecular beam apparatus employed in this study has previously appeared in the literature.⁴ For this experiment, the mass spectrometer was tuned for mass 30, corresponding to the N₂¹⁵⁺ ion. Beam detection was achieved by means of an electron-bombardment ionizer with an over-all efficiency of 10⁻⁴ to 10⁻³. Under optimum operating conditions, the beam intensity was estimated at 10⁹ molecules/sec and the beam to background ratio was roughly $\frac{1}{3}$. The strong background is the result of the tail of a strong mass 28 peak arising from N₂¹⁴⁺ and CO⁺. The resonance was observed with a phase sensitive detector and on-off modulation of the rf current. The rf transition region was $\frac{3}{4}$ in. in length. A rf current of 4 to 5 A, which was determined to be close to optimum, was employed.

A single source slit 0.002 in. in width was used. Multiple slits were installed at both the collimator and detector. The collimator slit contained 51 slits, each 0.0005 in. wide and spaced 0.00075 in. apart (distance between nearest edges for each adjacent pair of slits). Twenty-six detector slits, each 0.001 in. wide and spaced 0.002 in. apart, were employed. For the above arrangement of slits, a "throw out power" of 1-2% was usually achieved during resonance. As mentioned above, the multiple slits were installed to compensate for loss of beam intensity resulting from the use of narrow slits necessary for the study of small moments.

The multiple collimator and detector slits were made commercially (Buckbee-Meers Inc.) and by a photo-etch process using Kodak Photo-Resist on 1 mil Be-Cu or Mo sheets. A concentrated ferric chloride solution was used for the etching. Specific details on these slits, as well as a critical evaluation of the multiple molecular beam method is presented in a thesis by Dr. Charles H. Anderson of this laboratory.¹⁶

Preliminary alignment of the multiple slits was achieved and final alignment was based on optically experimental runs with HD to obtain the best beam to background ratio as well as the best proton resonance signal. Even though the entire apparatus is mounted on a 25-ft long aluminum H beam to furnish rigidity against deflections in the manner of an optical bench, maintenance of the alignment of the multiple slits was somewhat tedious and at times difficult, as the alignment was extremely sensitive to small external mechanical pressures applied to the vacuum chambers and the collimator slit mount. After prolonged usage, the detector slits also became warped, apparently because of its close proximity to the hot tungsten filament in the electron-bombardment detector.

Nitrogen-15 gas at STP and 99.4% enrichment was purchased from the Isomet Corporation in Palisades Park, New Jersey. 90% of this gas was recovered from the source and buffer chambers and recycled by a

¹⁶ C. H. Anderson, Ph.D. thesis, Harvard University, 1961 (unpublished).

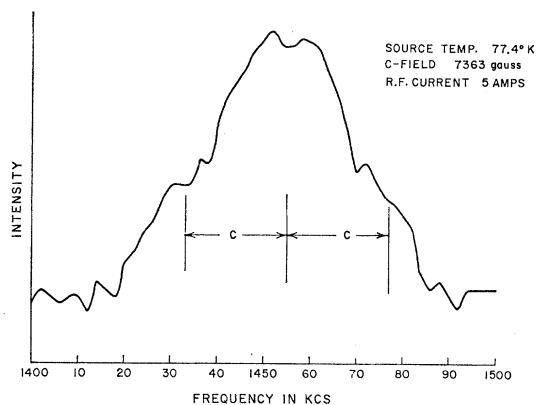


Fig. 1. The radio-frequency spectrum corresponding to the reorientation of the N^{15} nuclear moment in orthonitrogen-15.

Leybold Nachfolger mercury diffusion pump¹⁷ capable of operating into a foreline pressure of 2 mm Hg. During an experimental run, the mechanical forepump for the source and buffer chambers was bypassed and the foreline of the oil booster diffusion pump for these chambers was connected to the intake of the Leybold pump. The output of this latter pump was then connected to the gas-handling system for recycling. Condensable gases were frozen out by liquid air traps installed in the recycling system.

III. THE NUCLEAR INTERACTION

The rf spectrum corresponding to the reorientation of the N^{15} nuclear moment in *ortho*-nitrogen-15 ($I_R=1$) in a magnetic field of 6659 G is shown in Fig. 1. Partially resolved structure, originating primarily from the interaction of the N^{15} nuclear magnetic moment with the molecular rotational field, was observed in the resonance spectrum.

The effect of this spin-rotational interaction of the resonance pattern can be semiquantitatively understood in terms of the following simplified Hamiltonian:

$$\frac{\mathcal{H}}{h} = -\frac{a_N}{|\mathbf{H}|} \mathbf{I}_R \cdot \mathbf{H} - \frac{b_J}{|\mathbf{H}|} \mathbf{J} \cdot \mathbf{H} - c \mathbf{I}_R \cdot \mathbf{J}, \quad (1)$$

where a_N and b_J denote, respectively, the frequencies corresponding to the reorientations of the nuclear moment and the rotational magnetic moment in field H . c is the spin-rotational constant. The above simplifying Hamiltonian predicts the following first-order spectrum for the nuclear resonance ($\Delta m_I = \pm 1$, $\Delta m_J = 0$).

$$\nu_N = \alpha_N + cm_J \quad (2)$$

Figure 1 gives the composite spectrum from many J and m_J states. However, only the odd J states contribute due to symmetry restrictions. Since the Larmor frequencies corresponding to a given m_J (irrespective of J)

are coincident according to the above first-order theory and $|m_J| \leq J$, it follows that the composite resonances due to molecules from rotational states with $m_J=0$, and ± 1 should have the same intensity, as should resonances with $m_J=\pm 2$ and ± 3 , and resonances with $m_J=\pm 4$ and ± 5 . The resonance pattern depicted in Fig. 1 is readily understood on this basis.

An approximate value for the spin-rotational constant c can be obtained from

$$|c| = \left| \frac{\nu(m_J) - \nu(-m_J)}{2m_J} \right|, \quad (3)$$

where $\nu(m_J)$ and $\nu(-m_J)$ denote frequencies of the peak maxima corresponding to m_J and $-m_J$ in the experimental resonance pattern. From Fig. 1, a $|c|$ of 22 ± 1 kc/sec can be deduced.

A theoretical spectrum for the N^{15} resonance as determined by a computer program written by one of the authors (N.F.R.) for the Univac I computer is also shown in Fig. 1 (dashed curve). The following interaction constants were employed:

$$\alpha_N = 2.875 \text{ Mc/sec},$$

$$b_J = 1.318 \text{ Mc/sec},$$

$$c = +22 \text{ kc/sec},$$

$$g_J = 0.2593 \text{ nm}.$$

The calculations were performed for a magnetic field of 6658.7 G and for a temperature of 77.4°K. A resonance half width of 11 kc/sec was used in constructing the composite spectrum. The theoretical curve in Fig. 1 represents a composite spectrum through $J=9$. Due to limitations in the computer storage, contributions from higher J states were not included. At liquid-nitrogen temperature, errors in the intensities resulting from this truncation should not be more than 1 to 2%. Except for intensities, the agreement between experiment and theory is satisfactory with our present choice of c . We attribute the discrepancy in the intensities to an incomplete equilibration of the source oven to liquid nitrogen temperature, and to multiply successive transitions.

The sign of c was not determined in these experiments.

IV. ROTATIONAL MAGNETIC MOMENT

In Fig. 2, the resonance pattern corresponding to the reorientation of the molecular rotational magnetic moment is shown. Better signal-to-noise was possible in this experiment as the spectrum was more confined. In addition, *para*-nitrogen-15 contributes additional intensity to the resonance signal.

The observed spectrum is readily interpretable in terms of the simplified Hamiltonian given above. Here, $\Delta m_J = \pm 1$ and $\Delta m_z = 0$. Orthonitrogen-15 should give rise to a triplet of equal intensity and spaced c or 22 kc/sec apart on account of its resultant nuclear spin

¹⁷ U. S. Distributor: National Research Corporation, Cambridge, Massachusetts.

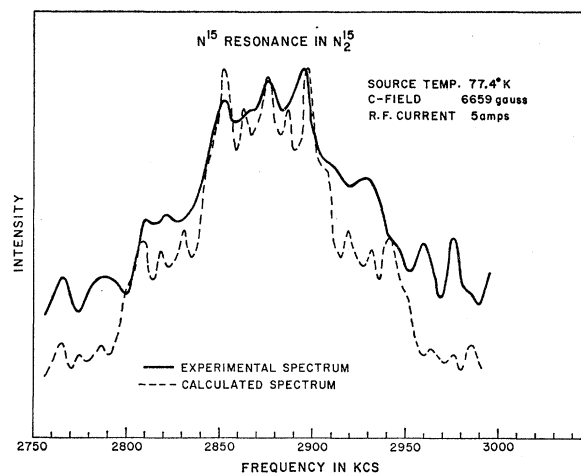


FIG. 2. The radio-frequency spectrum corresponding to the reorientation of the molecular rotational magnetic moment of nitrogen-15.

of 1. Para-nitrogen-15, having spin 0, should only contribute to the center of the resonance. Since the high-temperature limit is satisfied by the rotational partition function for nitrogen at 77.4°K, the ratio of ortho to para is 3:1. Thus the resultant resonance should be a triplet with relative intensities of 1:2:1, as observed. The triplet, however, is barely resolved.

Transitions corresponding to reorientations of the rotational moment were observed in magnetic fields of 7362.5 and 6658.7 G. In each case, the magnetic field was calibrated by the deuteron resonance in HD. At 6658.7 G, the center of the resonance was 1319 ± 1 kc/sec, and at 7362.5 G, it was 1455 ± 3 kc/sec. In this manner, the rotational g value, $g_J = \mu_J / J\mu_N$, was measured to be $\pm 0.2593 \pm 0.0005$. The sign of the rotational moment was not determined.

V. DISCUSSION

The spin-rotational constant of 22 kc/sec for the N¹⁵ nucleus in N₂¹⁵ corresponds to a large rotational magnetic field of 51 G per unit rotational quantum number at each of the N¹⁵ nuclei. The direction of this rotational field was not determined experimentally. However, it may be inferred from the following general relationship between spin-rotational interaction and nuclear magnetic shielding¹⁸:

$$\sigma = \frac{e^2}{3mc^2} \left\{ \left(\psi_0 \left| \sum_k \frac{1}{r_k} \right| \psi_0 \right) - \sum'_N \frac{z_N}{r_N} + \frac{h}{4M\mu_N^2 g_I} \sum_{\lambda} c_{\lambda\lambda} I_{\lambda\lambda} \right\}.$$

Here σ is the nuclear magnetic shielding constant for the nucleus under study and r_k , r_N denote, respectively, its distance from the k th electron and the N th nucleus in the molecule. e is the electron charge; m is the electron mass; c is the velocity of light; z_N is the charge

of the N th nucleus; M is the proton mass; h is Planck's constant; μ_N is the nuclear magneton; and g_I is the nuclear g factor. The prime in \sum'_N denotes a summation over all the nuclei in the molecule other than the one whose interactions are presently under consideration. The $I_{\lambda\lambda}$'s are the principal moments of inertia of the molecule and the $c_{\lambda\lambda}$'s are the components of the spin-rotational tensor about these principal axes. For a diatomic molecule, $c_{11}I_{11} = 0$ and $c_1 I_1 = cI$.

Ramsey and his co-workers¹⁹ have recently shown that when fluorine chemical shifts are plotted versus

$$\sum_{\lambda} c_{\lambda\lambda} I_{\lambda\lambda},$$

a straight line with slope

$$\frac{e^2}{3mc^2} \frac{h}{4M\mu_N^2 g_I}$$

is obtained. A similar linear correlation has also been found for proton chemical shifts.^{7,19} Since the sum of the first two terms in expression (4) is related to the total electrostatic potential at the nucleus under investigation, a linear correlation between σ and

$$\sum_{\lambda} c_{\lambda\lambda} I_{\lambda\lambda}$$

would imply that this potential energy is fairly insensitive to the chemical environment in which the nucleus is placed. This result is not unexpected for heavy nuclei, where there is a large number of core electrons around the nucleus.

That a major part of relative chemical shifts appears to arise from differences in the

$$\sum_{\lambda} c_{\lambda\lambda} I_{\lambda\lambda}$$

term in expression (4) is interesting within its own rights. However, for our present purposes, a useful feature of the aforementioned linear correlation is that a plot of σ versus

$$\sum_{\lambda} c_{\lambda\lambda} I_{\lambda\lambda}$$

can often unequivocally yield the signs of spin-rotational constants. As is well known, the signs of spin-rotational constants are frequently not determined in molecular beam experiments. Thus, in this manner c_F in HF, SF₆, and CF₄ have been determined to be negative.¹⁹ Even for protons, where one might expect a non-negligible contribution to the chemical shift from changes in the electrostatic potential due to different chemical environments, the signs of many spin-rotational constants have also been determined unambiguously.⁷ Thus, in HF, HCl, HBr, C₂H₂, and

¹⁸ R. Schwartz, Ph.D. thesis, Harvard University, 1953 (unpublished).

¹⁹ J. N. Pinkerton and C. H. Anderson, Bull. Am. Phys. Soc. 6, 281 (1961).

CH₄, the molecular beam spin-rotational interaction data are consistent with chemical shift data only after an appropriate choice of signs. In these cases, the c_H 's have all been determined to be positive.

The magnitudes as well as the signs of the principal components of the spin-rotational tensor are known for both N¹⁴H₃ and HCN¹⁴. A σ versus

$$\sum_{\lambda} c_{\lambda\lambda} I_{\lambda\lambda}$$

plot, employing these values plus our present result on nitrogen and available chemical shifts, indicates that the sign of c in N₂¹⁵ is positive. Since g_I is negative for the N¹⁵ nucleus, the rotational magnetic field is opposed to J .

The sum of the second and the third terms in expression (4) constitutes what is commonly referred to as the high frequency or paramagnetic part of the nuclear magnetic shielding constant.^{20,21} With our present value of $+22 \pm 1$ kc/sec for c , $\sigma^p = (-483 \pm 20) \times 10^{-6}$. An *ab initio* calculation of the paramagnetic contribution to the shielding has recently been reported by Kern and Lipscomb.¹³ Their calculated value is -23.5 ppm, which is a mere 5% of the experimental value reported here.

Kern and Lipscomb¹² have also computed the diamagnetic or Lamb term σ^d using Hartree-Fock wave functions for N₂. Their calculated value of 384.5 ppm appears to be reliable. From this value of σ^d , we obtain a value of 324.4 ppm for the quantity $-(e/3mc^2)V$, where V is the total electrostatic potential at the nitrogen nucleus. For comparison, the corresponding value for the isolated nitrogen atom as computed by Dickinson²² using Hartree-Fock atomic functions is 325.0 ppm. The above depicted constancy of the electrostatic potential at the nucleus suggests that absolute shielding constants can be obtained with accuracy from the calculated Lamb term for the isolated atom and the measured spin-rotational constant for the molecule.

Kern and Lipscomb's value for σ^d when combined with our measured σ^p of -483 ppm indicates that the nitrogen nucleus in molecular nitrogen is antishielded by about 100 ppm. Since the nuclear moment of the bare nitrogen nucleus has previously been determined

with a shielding correction of 325 ppm, a redetermination using the above antishielding correction of 100 ppm appears in order and has been reported in a separate communication.²³

The rotational magnetic moment of $\pm 0.2593 \pm 0.0005$ nm per J for N₂¹⁵ is to be compared with the corresponding value²⁴ of -0.22 for O₂¹⁶. Even though the sign of the magnetic moment was not determined, it is most probably negative.

Just as there is a close relationship between magnetic shielding and spin-rotational interaction, there is a similar relationship between the high frequency part of the magnetic susceptibility and the rotational magnetic moment.²⁵ Aside from small vibrational corrections, the paramagnetic susceptibility for a homonuclear diatomic molecule is given by

$$\chi_1^P = \frac{e^2}{4\pi mc^2} R^2 (-\mu' g_J + z_{N/2}), \quad (5)$$

where μ' is the reduced mass of the molecule in proton mass units, and R is the equilibrium internuclear distance. In Eq. (5), the origin of the magnetic vector potential has been taken at the centroid of electronic charges. Since $z_{N/2} > |\mu' g_J|$, the sign of g_J cannot be determined from the fact that χ_1^P must be positive definite.

From Eq. (5), the paramagnetic susceptibility of molecular nitrogen χ_1^P is $(4.579 \pm 0.003) \times 10^{-29}$ erg/G molecule. This experimental value is to be compared with a calculated value of 2.892×10^{-29} erg/G molecule obtained by Karplus and Kolker using a perturbed Hartree-Fock function involving four variational parameters.⁸ Karplus and Kolker's calculations were performed with the origin of the magnetic vector potential at one of the nitrogens. In order to compare their results with ours, a translation of the origin has been made in the usual manner.^{26,27}

The magnetic susceptibility of molecular nitrogen has been measured by a number of investigators.¹⁵ In view of the large uncertainties in the various experimental results, which vary from -40×10^{-6} to -44×10^{-6} erg/G mole, an experimental determination of the quantity $\langle \sum_k r_k^2 \rangle$ from the diamagnetic susceptibility will not be given.

²⁰ C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955), p. 217.

²¹ N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1956), p. 164.

²² W. C. Dickinson, *Phys. Rev.* **80**, 563 (1950).

²³ M. R. Baker, C. H. Anderson, and N. F. Ramsey, *Phys. Rev.* **133**, A1533 (1964).

²⁴ J. M. Hendrie and P. Kusch, *Phys. Rev.* **107**, 716 (1957).

²⁵ See Ref. 21, pp. 169-170.

²⁶ N. F. Ramsey, *Phys. Rev.* **86**, 243 (1952).

²⁷ S. I. Chan and T. P. Das, *J. Chem. Phys.* **37**, 1527 (1962).