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Temperature Dependence of Hyperfine Pressure Shifts. II. Nitrogen in Helium, Neon, and Molecular Nitrogen†*

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Spin-exchange optical pumping has been used to measure the hyperfine pressure shift of atomic nitrogen in helium, neon, and molecular nitrogen as a function of temperature. In the range 70–500 °C, the change in pressure shift was linear with temperature, and the values were for helium, $-(0.1\pm0.1)\times10^{-4}$; for neon, $(0.6\pm0.1)\times10^{-4}$; and for molecular nitrogen, $(1.4\pm0.3)\times10^{-4}$ in units of Hz/Torr °C. The measurements also give $A=10\,450\,929.4\pm1.8$ Hz for the free atom. The quadrupole interaction constant was also measured and found to be independent of temperature and pressure. The value was $B=1.3\pm0.5$ Hz.

When the hyperfine structure of an atom is measured in the presence of a buffer gas, small frequency shifts are detected which depend essentially linearly[1] on the buffer-gas pressure. Theoretical attempts to understand these shifts indicate an expected dependence on the temperature of the buffer gas as well as on the density. With the recently discovered ability to optically pump over an extended temperature range,[2] it is now possible to investigate this aspect of the theory.

Recently we reported measurements of the temperature dependence of the hyperfine pressure shift of deuterium in helium.[3] The present paper describes similar measurements made on atomic nitrogen in helium, neon, and molecular nitrogen. Pressure shifts of atomic hydrogen (the isotopic mass dependence of these shifts is negligible[4]) and atomic nitrogen are of particular interest because of the recent extensive theoretical calculations made for them.[5,6]

The experiment consisted of the measurement of the hyperfine intervals of N^{14} at a variety of buffer-gas pressures and temperatures. By extrapolating to zero pressure, at fixed temperature, one is able to infer the free-atom magnetic dipole (A) and electric quadrupole (B) interaction constants. Although nitrogen would not be expected to have any ground-state hyperfine structure to first order if LS coupling were rigorously applicable,[7] Heald and Beringer[8] measured A to be 10.45 ± 0.02 MHz. Numerous measurements since then have confirmed and extended this value.[9–14]

The most recent theoretical[15] attempt to understand the dipole constant A, utilizing a many-body technique, predicts 10.49 ± 0.15 MHz. Core polarization accounts for 5.7 MHz of this, and correlation effects the remaining 4.8 MHz. The reported measurements using the maser[14] also reported a value of 1.3 ± 0.3 Hz for the quadrupole interaction constant B. Prior to this measurement, Holloway, Luscher, and Novick[12] attempted to predict B. Their calculation utilized only the ^2P and the ^2D levels in addition to the ^4S ground state which can be constructed from the $(1s)^2\,(2s)^2\,(2p)^3$ configuration. These levels are used in second-order perturbation theory with the magnetic dipole perturbation to get an apparent quadrupole constant for N^{14} of + 2.0 Hz. They also consider the admixture of the ^4S ground state with the ^2P and ^2D levels caused by spin-orbit and spin-spin interactions. The latter effect gives a true quadrupole interaction of -3.4 ± 1.6 Hz, and their final predicted observable value for B is -1.4 Hz. Owing to the absence of an error assignment to the apparent B, it is impossible to know whether there is a significant disagreement between theory and experiment.

The principal motivation for this work was the determination of the temperature dependence of the hfs pressure shift of nitrogen in helium. We have also measured the same quantity in molecular nitrogen and neon in order to get some idea of the effect of different buffer gases. There has been no previous experimental work on this subject. In the process of these experiments we have also remeasured A, B, and the nitrogen hfs pressure shifts in helium, neon, and molecular nitrogen.

After describing the experimental technique and the apparatus used, we give the results and finally, a comparison between theory and experiment.

METHOD AND APPARATUS

The spin-exchange optical pumping technique was used to measure the hfs of atomic nitrogen as a function of temperature and pressure. Rubidium resonance radiation from an electrodeless discharge was filtered to select the $5\,^2P_{1/2} \leftrightarrow 5\,^2S_{1/2}$ line and then circularly polarized. This light was passed through a flask containing rubidium vapor, a buffer gas, and atomic nitrogen. The transmitted light was focused on a gas phototube. The atomic nitrogen was produced by a radio-frequency discharge. The angular momentum of the incident circularly polarized light is absorbed by the rubidium vapor and, as a result of spin-exchange collisions, transferred to the atomic nitrogen. When the nitrogen polarization is changed by the application of a radio-frequency magnetic field at the nitrogen hyperfine frequency, the change is transmitted by collision to the rubidium vapor and thence to the transmitted resonance radiation, which provides the signal.

The resonance radiation was produced by a lamp especially designed to minimize noise. In our previous lamps the Rb metal was in a flask inside the exciting coil, and the slight motion of the metallic droplets caused substantial fluctuations in the light output. In order to eliminate this effect, a short side arm (6 mm o.d., 25 mm long) was added to a 25-cm^3 spherical Pyrex flask. A quarter of a gram of rubidium was distilled into this side arm, and 2.5 Torr of argon was added. The side arm was outside the exciting coil and kept at about 100 °C by a heater. Excitation was provided by a 100-W 27-MHz crystal-controlled oscillator. The lamp was essentially at the shot noise limit, and was run continuously for periods as long as six months with no discoloration of the glass.

The resonance radiation was filtered of the D_2 component ($5\,^2P_{3/2} \leftrightarrow 5\,^2S_{1/2}$) at 7800 Å by a Spectrolab interference filter. The transmitted light was monitored with a 6953 gas phototube, and the ac variation in the transmitted light was amplified by a Tektronix 122 preamplifier and fed both to an EMC model RJB phase-sensitive detector and an oscilliscope.

The measurements were made for the most part in the component of the earth's magnetic field along the light beam (~0.1 G). The other field components were cancelled by Helmholtz coils. Static inhomogeneities in the field were reduced with bar magnets.[16] The ac fields along the light axis principally at 60 and 120 Hz were reduced by more than two orders of magnitude by a feedback system.[17]

The rf was generated with a GR 1164 frequency synthesizer which was phase locked to a GR 1160-P3 standard frequency oscillator. The frequency was measured with a HP 5245L frequency counter which was maintained accurate to parts in 10^9 with a HP 117A VLF comparator tuned to WWVB. The rf was square wave modulated at 10 Hz with a James C2099 chopper and fed into a rf Helmholtz coil whose axis was perpendicular to the light beam.

Atomic nitrogen was produced in the absorption flask by dissociating molecular nitrogen with a 48-MHz rf discharge. The oscillator produced pulses of a few milliseconds duration during both the on and off period of the resonant rf in order to minimize discharge effects on the phase-sensitive detector. The amplitude of the discharge was reduced until it had no effect on the linewidth of the nitrogen signals.

The oven for the absorption flasks was constructed with Johns Manville JM 2300 clay bricks. This type of brick was chosen because of low iron content; the addition of the oven had no effect on the linewidth. Heating coils were made of No. 20 Chromel A wire and were covered with Fiberfrax.[18] Two 4-in.-diam circular Pyrex plates were used for each window. The oven temperature was maintained at better than ± 25 °C at each measurement temperature.[17] Gradients in the oven were of the order of 10 °C between the top and bottom of the absorption flasks.

The Pyrex flasks used below 500 °C have been described previously.[2] Above 500 °C flasks were made with GE fused-quartz spheres of approximately 250 cm^3. Because of the difficulty of fusing electrodes to quartz, the flasks were made with two thin quartz tubes into which tungsten electrodes could be inserted from the outside. A typical quartz flask is shown in Fig. 1. The rubidium in the flask was placed in the side arm, which was air cooled in order to maintain a suitably low density while the body of the flask was held at temperatures ranging between room temperature and 700 °C. The prepara-

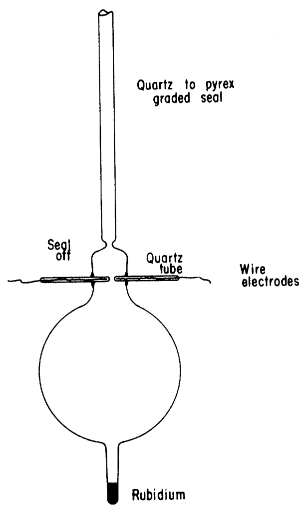

FIG. 1. Quartz flask used for optical pumping above 500 °C.

tion of the flasks has been described.[2] The buffer-gas pressures were measured with oil and mercury manometers.

MEASUREMENTS AND RESULTS

The Hamiltonian which describes the ground state of the nitrogen atom in a weak external magnetic field can be written in the form

$$H=A\vec{I}\cdot\vec{J}+|g_J|\mu_0\vec{J}\cdot\vec{H}-g_I\mu_0\vec{I}\cdot\vec{H}$$

$$+\frac{B}{2I(2I-1)J(2J-1)}[3(\vec{I}\cdot\vec{J})^2+\tfrac{3}{2}(\vec{I}\cdot\vec{J})-\vec{I}^2\vec{J}^2]\ .$$

Here A is the magnetic dipole hyperfine interaction constant, B the quadrupole hyperfine interaction constant, and g_I and g_J are the nuclear and electronic gyromagnetic ratios, measured in terms of the Bohr magneton. For N^{14} the total electronic angular momentum J is $\frac{3}{2}$ and the nuclear spin I is 1. Figure 2 shows the ground-state energy levels in a weak magnetic field. Since no $\Delta M_F=0$ transitions were observable,[10] the $\Delta M_F=\pm 1$ pairs having the smallest magnetic field dependence $[(F=\frac{5}{2},\ M_F=\pm\frac{5}{2})\leftrightarrow(F=\frac{3}{2},\ M_F=\pm\frac{3}{2})]$ and the $[(F=\frac{3}{2},\ M_F=\pm\frac{3}{2})\leftrightarrow(F=\frac{1}{2},\ M_F=\pm\frac{1}{2})]$ were used. By using the sums and differences of these pairs it is possible to remove the magnetic field dependence. It was necessary to expand the energy levels to fourth order in the field dependence to get sufficient accuracy. For reducing the data, the g_J values of Heald and Beringer[8] and the g_I values of Anderson, Pipkin, and Baird[10] were used.

Measurements were made on the Pyrex cells at room temperature before heating to 500 °C. To do this, it was necessary to empty the rubidium out of the side arm into the flask in order to obtain sufficient rubidium vapor. After measuring the Rb^{85} linewidth (typically 40 Hz) at low rf, the discharge was turned on and adjusted for minimum nitrogen hyperfine transition linewidth. These linewidths

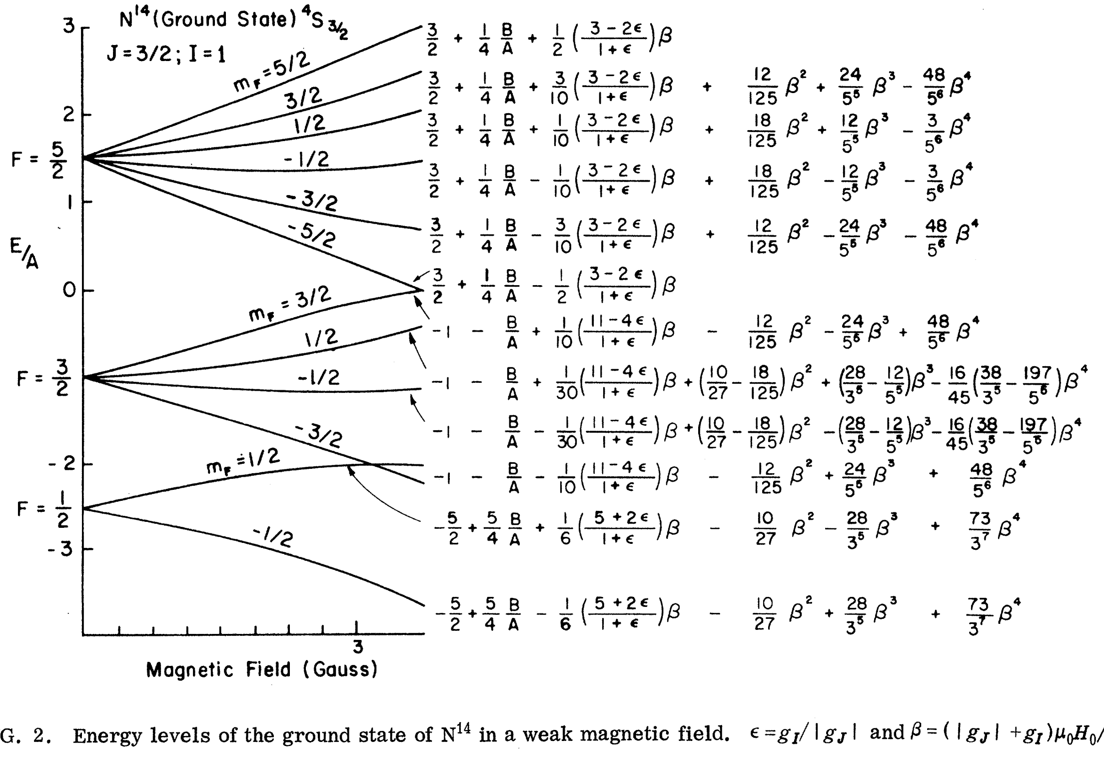

FIG. 2. Energy levels of the ground state of N^{14} in a weak magnetic field. $\epsilon=g_I/|g_J|$ and $\beta=(|g_J|+g_I)\mu_0H_0/A$.

TABLE I. Summary of the nitrogen data for the individual flasks.

Buffer	Buffer-gas pressure at 300 °K(Torr)	Temperature (°C)	Number of measurements	Average dipole constant $A - 10\,450\,900$ Hz	Average quadrupole const B(Hz)
Nitrogen	16.44	65	30	60.5 ± 0.2	1.55 ± 0.2
	35.84	85	20	97.9 ± 0.3	0.83 ± 0.3
	35.84	300	10	98.2 ± 0.7	0.58 ± 0.6
	35.84	500	20	99.7 ± 0.4	1.26 ± 0.4
Helium	47.6	70	30	40.5 ± 0.5	1.63 ± 0.5
	47.6	300	20	41.2 ± 0.6	1.82 ± 0.5
	47.6	480	20	40.3 ± 0.7	1.47 ± 0.6
	63.8	70	30	43.3 ± 0.3	1.09 ± 0.4
	126.1	70	40	57.5 ± 0.3	1.37 ± 0.3
	126.1	300	20	57.2 ± 0.3	1.46 ± 0.3
	126.1	480	20	57.0 ± 0.4	1.66 ± 0.5
	180	70	10	68.9 ± 0.6	2.74 ± 0.7
	190.7	70	40	70.0 ± 0.3	1.44 ± 0.3
	190.7	300	20	69.1 ± 0.4	0.83 ± 0.4
	190.7	480	40	69.0 ± 0.4	1.11 ± 0.5
Neon	220.1	85	20	140.1 ± 0.4	0.99 ± 0.3
	220.1	300	20	142.4 ± 0.3	0.99 ± 0.3
	220.1	500	20	145.5 ± 0.4	1.18 ± 0.6
	408.7	80	10	235.9 ± 0.2	1.59 ± 0.2
	408.7	125	10	235.9 ± 0.4	0.84 ± 0.4
	408.7	205	10	237.5 ± 0.7	0.73 ± 0.5
	408.7	300	10	240.7 ± 0.3	2.04 ± 0.3
	408.7	400	20	242.7 ± 0.4	1.16 ± 0.4
	408.7	480	10	245.2 ± 0.8	1.86 ± 0.7
	408.7	500	10	245.8 ± 0.4	1.42 ± 0.5

were typically between 50 and 100 Hz, depending on buffer-gas pressure and discharge setting. The $\Delta F = 1$, $\Delta M = \pm 1$ pairs of transitions were measured as quickly as possible in order to minimize the effects of field drift. One determination of the hyperfine splitting consisted of two measurements of each of the pair. Data were taken with external magnetic field both parallel and antiparallel to the light beam. Measurements were taken, for each of the above cases, with both right- and left-circular-polarized light. We could detect no frequency shifts caused by these variations. Efforts to discover a long-term decrease in the nitrogen pressure caused by the formation of Rb_3N and RbN_3[19] were unsuccessful. Since the amplitudes of the $\Delta M = +1$ and $\Delta M = -1$ signals for fixed sense of circular polarization differed by a factor of 4 or so, measurements were made with the polarization sense set for maximum signals. Measurements were taken in sets of 10 for each interval.

The sample was then slowly heated to 500 °C (requiring approximately $1\frac{1}{2}$ h) while blowing a stream of cold air into the cooling tube. After coming to thermal equilibrium at 500 °C, the Rb vapor pressure could be maintained at any desired value. The measurements at high temperature were made in the same manner as at low temperature, and each bulb was cycled at least twice between 500 °C and room temperature.

The quartz cells were measured in the same way as the Pyrex cells except that once the Rb was driven into the main flask the walls became saturated

TABLE II. Results of this investigation. Errors listed here (with the exception of the 700 °C data) are the standard deviation in the mean multiplied by 2. The criterion chosen for this estimate of the error was that it should be no smaller than $\frac{1}{40}$ of the experimental linewidth. It was felt that asymmetries in the line shape might introduce nonstatistical errors of this order of magnitude.

Buffer gas	Zero-pressure dipole constant (Hz)	Pressure shift (Hz/Torr) 70 °C	399 °C	480 °C	700 °C	Temperature shift (10^{-4} Hz/°C mm)
Helium	10 450 930.3 ± 2	0.21 ± 0.01	0.20 ± 0.02	0.20 ± 0.01	0.21 ± 0.02	−0.1 ± 0.1
Neon	10 450 928.7 ± 2	0.50 ± 0.01	0.52 ± 0.01	0.53 ± 0.01	...	0.6 ± 0.1
Nitrogen	10 450 929.3 ± 1	1.9 ± 0.1	1.9 ± 0.1	2.0 ± 0.1	...	1.4 ± 0.5

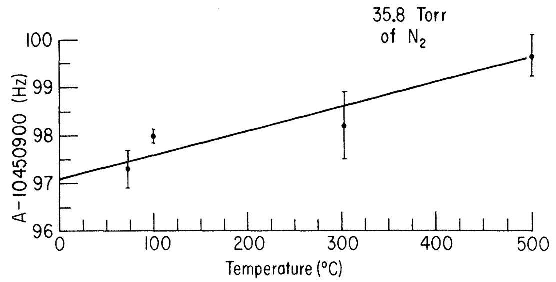

FIG. 3. Variation of the nitrogen hyperfine splitting with temperature for the highest-pressure sample using N_2 as buffer gas.

and control at high temperature could not be obtained. Because of this, all quartz samples were first measured between 300 and 700 °C. After these measurements were completed, the Rb was poured out into the flask, and room temperature measurements were made.

RESULTS

It was assumed the magnetic dipole interaction constant could be represented as

$$A_{\text{meas}} = A + \left(\frac{\partial A}{\partial P}\right)_B P_B + \left(\frac{\partial A}{\partial P}\right)_{N_2} P_{N_2} ,$$

where A is the free-atom value and $(\partial A/\partial P)_B$ and $(\partial A/\partial P)_{N_2}$ are the pressure shifts caused by the buffer gas and the inevitable molecular nitrogen, respectively. The pressures of the buffer gas and the molecular nitrogen were measured close to and corrected to 25 °C. The pressures were corrected for the expansion of the glass. In order to measure the pressure shifts caused by helium and neon, it was first necessary to measure the pressure shift caused by the molecular nitrogen (between 1 and 2 Torr) in the helium and neon flasks. Two flasks containing pure nitrogen were measured at several temperatures, and the data are given in Table I. It was found that the temperature dependence of the pressure shifts for all of the buffer gases used could be fitted satisfactorily to straight lines. Table II gives the resulting A, B, and temperature shift in cycles/deg Torr. The temperature dependence of A for the highest-pressure nitrogen flask is shown in Fig. 3.

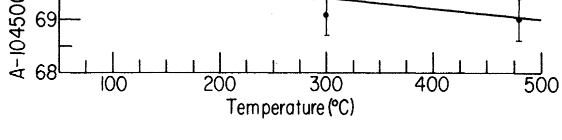

FIG. 4. Variation of the nitrogen hyperfine splitting with temperature for the highest-pressure sample using He as buffer gas.

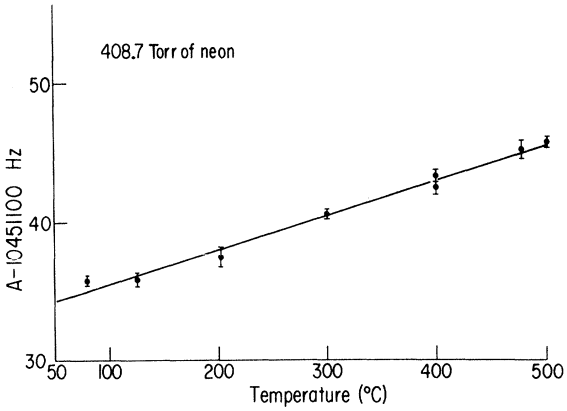

FIG. 5. Variation of the nitrogen hyperfine splitting with temperature for the highest-pressure sample using neon as buffer gas.

A number of flasks containing helium were measured in a similar manner; the results are also shown in Tables I and II. Figure 4 shows the results for the highest-pressure helium flask. Measurements of helium in quartz at 1000 °K were also attempted, and a very sensitive method for determining the rate at which helium leaks through quartz was discovered. Although no precise value for the temperature dependence could be determined, our data indicate that extrapolation of the lower temperature data "agrees" with the estimated 1000 °K results and that therefore there is essentially no change in $\partial A/\partial P$ with temperature up to that point.

Finally, measurements were made on two neon flasks. In this case, as with the molecular nitrogen, there is a clear temperature dependence as shown in Fig. 5. The data are summarized in Tables I and II.

An additional result of these experiments is a value for A. Table III contains this result and also a comparison with previous work done on nitrogen. Our result was derived from a weighted average (inversely by the statistical errors) of the results for neon, helium, and nitrogen. The error of ± 1.6 Hz is based on the spread in the zero-pressure intercepts.

Each set of measurements also produced a value for B. These were plotted as a function of type and pressure of buffer gas and temperature. We were unable to find any statistically significant dependence of B on any of these variables. Figure 6 is a histogram of all the measured values of B. The average of all the data gives $B = 1.3 \pm 0.5$ Hz. The quoted error is the experimental standard deviation. This

TABLE III. Summary of the recent measurements of the nitrogen hyperfine interaction constants and their pressure shifts. All measurements, except two, were done with optical pumping methods. The first (Ref. 8) was done by the paramagnetic-resonance technique and the second (Ref. 14) with a hydrogen maser.

$A(N^{14})$ (10^6 Hz)	Error in A (Hz)	$B(N^{14})$ (Hz)	$N-N_2$	N-He	N-Ne	Ref.
10.45	±20 000.	...	...	...	...	8
10.451 12	±170.	−200±200	...	...	...	9
10.450 91	±70.	−50±80	...	...	<10	10
10.450 928	±45.	5±35	<60	...	...	11
10.450 925	±20.	−7±20	1.9±0.4	...	...	12
10.450 930	± 8.	1±5	1.65±0.21	0.27±0.07	0.57±0.07	13
10.450 929 06	± 0.19	1.32±0.20	...	...	...	14
10.450 929 4	± 1.8	1.3±0.5	1.9±0.1	0.21±0.01	0.50±0.01	This work

value, rather than the standard deviation of the mean, was chosen because it represents approximately one-fortieth of the experimental linewidth (note B is one-fifth of the high-frequency transition minus one-third of the low-frequency transition), and we could not determine the symmetry of the line to much better than this. The standard deviation of the mean was an order of magnitude smaller.

COMPARISON WITH THEORY

There have been two calculations of the N-He pressure shifts.[5,6,20] The older calculations of Adrian[20] utilized only the long-range part of the interaction. He derived the shift in the dipole constant due to a buffer-gas atom a distance R away to be of the form $\Delta A = C_m/R^6$, where C_m is proportional to the polarizability of the buffer gas, and also the average energies required in order to use closure. The ensemble average was performed using a LJ 6-12 potential. From Adrian's Table III and his Fig. 1 it is possible to calculate the change in the pressure shift in going from 70 to 480 °C. The variation is sufficiently smooth to be replaced by a straight line. The results are shown in Table IV. It is seen that even if the theoretical data are corrected to agree with experiment at room temperature, they still predict a considerably greater temperature dependence than is actually found. His prediction for helium is also shown in Fig. 7.

A considerably more extensive set of calculations have been made for the He-N system recently by Das *et al.*[5,6] Their calculations include both a more elaborate treatment of the long-range interaction as well as a treatment of short-range effects caused by the exclusion principle. The predicted long-range and total effects are also shown in Fig. 7. It can be seen that his short-range contribution produces a significant, and unobserved, temperature dependence. It should be noted that the curves in Fig. 7 differ from those shown in the last reference of Ref. 5. This is because his curves are computed for constant pressure, whereas the experiment was performed at essentially constant density. We have therefore multiplied his curve by $\frac{1}{300}T$ to produce Fig. 7. To give an idea of the magnitudes involved, we consider a flask containing 200 Torr of He. The experiment gives a shift of −1±1 Hz in going from 80 to 480 °C. Adrian predicts an increase of 30 Hz and Das an increase of 36 Hz. This is a significant disagreement between theory and experiment.

We note our values of A and B agree with the somewhat more accurate values produced by the maser.[14]

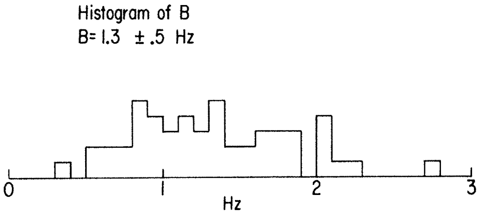

FIG. 6. Histogram of all the nitrogen quadrupole data.

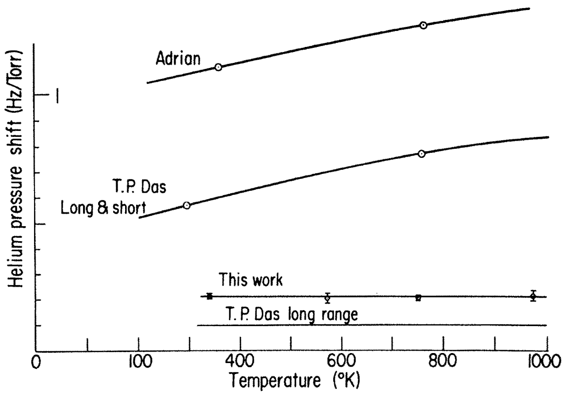

FIG. 7. Pressure shift of nitrogen in helium as predicted by Adrian (Ref. 20) and Das *et al.* (Refs. 5 and 6). The experimental results are also shown.

TABLE IV. Comparison of theoretical pressure shifts ($\partial A/\partial p$) and their temperature dependence ($\partial^2 A/\partial p\,\partial T$) with experiment.

Buffer gas	$\frac{\partial A}{\partial p}$ (Hz/Torr)			$\frac{\partial^2 A}{\partial T \partial p}$ (Hz/Torr °C)		
	Adrian (Ref. 20)	Das *et al.* (Refs. 5, 6)	Expt	Adrian (Ref. 20)	Das *et al.* (Refs. 5, 6)	Expt
Helium	1.1	0.57	0.21 ± 0.01	3.7×10^{-4}	4.5×10^{-4}	$0.1 \pm 0.1 \times 10^{-4}$
Neon	1.8		0.50 ± 0.01	5.6×10^{-4}		$0.6 \pm 0.1 \times 10^{-4}$
N_2	4.8		1.9 ± 0.1	7.3×10^{-4}		$1.4 \pm 0.3 \times 10^{-4}$

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