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Isotope Shifts in Some Lines of Nitrogen

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The line spectrum of a mixture of approximately 70 atomic percent N^{15} to 30 atomic percent N^{14} was photographed with a Fabry-Perot interferometer. The source used was a liquid-air cooled quartz tube with external electrodes excited by a 12-meter oscillator. The tube was charged with helium at a few mm pressure containing about 0.03 mm of the before-mentioned nitrogen isotope mixture. The lines from this discharge were so sharp that it was possible to resolve the two components due to N^{14} and N^{15} in nine infra-red lines. No nitrogen lines were found in this type of discharge in the visible or ultraviolet. The oscillator excitation produced a remarkably high intensity in the lines observed. The lines arising from $^4P\rightarrow{}^4P$ and $^4S\rightarrow{}^4P$ transitions showed a negative isotope shift of the order of $0.06\ \mathrm{cm}^{-1}$. Those from $^2P\rightarrow{}^2P$ transitions showed a positive shift of the order of $0.07\ \mathrm{cm}^{-1}$. The variations in the isotope shifts within the $^2P\rightarrow{}^2P$ multiplets indicate some deviation from Russell-Saunders coupling. No hyperfine structure in either component was observed in any of the lines. The directions of the shifts were checked by obtaining the abundance ratio of the isotopes in the discharge from the intensities of the isotopic heads in the second positive N_2 bands.

INTRODUCTION

HUGHES and Eckart have formulated a theory to account for the isotope shifts in the spectra of light elements and have applied it successfully to the cases of Li I and Li II.[1] The same theory has been applied by Opechowski and De Vries[2] and by Vinti[3] to the isotope shift in boron with close agreement with the measured shift.[4] This theory also accounts fairly well for the isotope shift in Ne I but breaks down in the case of Ne II.[5] Thus it was felt worth while to measure the isotope shift in some lines of nitrogen.

EXPERIMENTAL

The present measurement was made possible through the generosity of Professor H. C. Urey, who kindly furnished a sample of NH_4Cl in which the nitrogen had been enriched to 70 atomic percent N^{15} by the exchange reaction technique developed in his laboratory.[6] The nitrogen was extracted from the NH_4Cl by means of a reaction with a eutectic mixture of NaOH and KOH.[7]

The experimental difficulties in exciting the atomic lines of nitrogen without a background of the molecular bands are quite great, but fairly good results have been obtained in the past by mixing a trace of nitrogen with one of the rare gases and exciting the mixture with a high current-density discharge.[8] The theory of this excitation is that the atomic nitrogen spectrum is produced by collisions of the second kind; first the nitrogen molecule is dissociated by collision with a metastable atom of the rare gas, after which the nitrogen atoms thus formed collide with other metastable atoms of the rare gas and are excited by them.[9]

The foregoing process is carried on most efficiently with a high current density; in fact, in previous attempts to excite these lines it has been found that without an extremely high current density the atomic lines fail completely to appear and only the bands of nitrogen are emitted. In any attempt to measure isotope structure, however, it is impossible to use a high current density since this increases the width of the lines to such an extent that the isotope structure is likely to be obscured.

It is impractical in a problem of this sort to use a conventional discharge tube such as a Schuler tube since there is too rapid an electrical clean-up on the metal electrodes for the small amount of N^{15} available. The tube which was finally used

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[1] D. S. Hughes and C. Eckart, Phys. Rev. **36**, 694 (1930).
[2] W. Opechowski and D. A. De Vries, Physica **9**, 913 (1939).
[3] J. P. Vinti, Phys. Rev. **56**, 1120 (1939).
[4] S. Mrozowski, Zeits. f. Physik **112**, 223 (1939).
[5] J. H. Bartlett and J. J. Gibbons, Phys. Rev. **44**, 538 (1933).
[6] H. C. Urey, J. Chem. Phys. **5**, 856 (1937).
[7] R. W. Wood, J. Chem. Phys. **6**, 734 (1938).
[8] M. Kamiyama and T. Sugiura, Sci. Pap. Inst. Phys. Chem. Res. Tokyo **37**, 479 (1940).
[9] K. T. More and O. E. Anderson, Phys. Rev. **38**, 1995 (1931).

was remarkably successful in all respects. It consisted simply of a quartz tube in which the gas mixture was excited by means of external electrodes connected to a twelve-meter oscillator. The electrical clean-up was inconsiderable and only very small amounts of nitrogen were necessary. Quite sharp lines could be obtained and the intensity was very great.

The discharge tube was about 22 cm in length and consisted of a narrower portion 15 cm long and 11 mm in diameter and a thicker portion which was about 3 cm in diameter, and terminated in a plane window. The tube was mounted vertically so that the narrow part could be immersed in liquid air and the discharge was photographed end-on through the top window. With a pressure of a few mm of helium and a trace of nitrogen in the tube the discharge is concentrated in the narrow portion and can thereby be kept below the level of the liquid air.

Very strong nitrogen lines appear when a mixture of about 10 mm of helium and 0.06 mm of nitrogen are excited at high current density in this discharge. As soon as the current density is lowered for the purpose of investigating the isotope structure of the lines not only do the nitrogen lines decrease in intensity, but several nitrogen bands of the first positive system appear, and these increase in intensity as one goes toward the visible. The lowered intensity makes it difficult to obtain exposures in a reasonable length of time in the infra-red, and the presence of band heads in the background naturally makes the analysis of the lines very difficult.

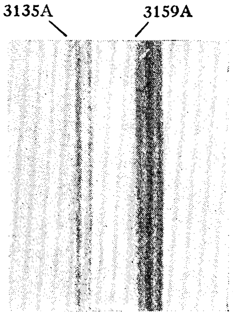

FIG. 1. Triple heads on second positive bands of isotope mixture.

It was found that the nitrogen bands could be attenuated, without seriously diminishing the intensity of the line spectrum, by decreasing the amount of nitrogen in the discharge. Consequently, for each group of lines and each current density, there is an optimum gas mixture, which just produces those lines without any appreciable band intensity. The final plates were taken with a total pressure of about three mm to reduce pressure broadening of the lines, and at nitrogen pressures ranging from 0.01 mm for the lines closest to the visible to 0.03 for those of longer wave-length. During a long exposure there is some clean-up of the nitrogen so that the concentration decreases during the exposure. This can be minimized by running a discharge of the nitrogen isotopes alone in the tube before the exposure is started so that the walls of the tube become impregnated with the isotope mixture.

The ratio of N^{15}/N^{14} in the discharge was checked by photographing the spectrum of the second positive bands of nitrogen in the ultraviolet, which are triple-headed in the case of this mixture of two isotopes.[10] The intensity ratios of these heads will be in the ratio $r^2 : 2r : 1$, where r is the ratio N^{15}/N^{14} in the discharge. Figure 1 is an enlargement of the bands given by an approximately 40 : 60 mixture of N^{14} and N^{15}. If the discharge tube has not been thoroughly outgassed before the N^{14-15} mixture is admitted, sufficient N^{14} may be given off from the walls during the discharge to reverse the abundance ratio and lead to a false conclusion as to the direction of the isotope shift unless this ratio is checked.

The spectrograph used was a Fabry-Perot interferometer in series with a three-prism glass spectrograph, the interferometer being mounted between the collimator lens and the prisms. The spectra were taken on plates especially developed for this experiment by the Eastman Company and designated by them "Experimental Infra-Red Plates" Emulsion No. 193684. These plates are very fast and have a remarkably good contrast and clear background. Before exposure the plates were hypersensitized by a two-minute immersion in a four percent ammonia solution in forty percent alcohol.[11]

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[10] G. Herzberg, Zeits. f. physik. Chemie **B9**, 43 (1930).

[11] F. A. Jenkins and S. Mrozowski, Phys. Rev. **60**, 225 (1941).

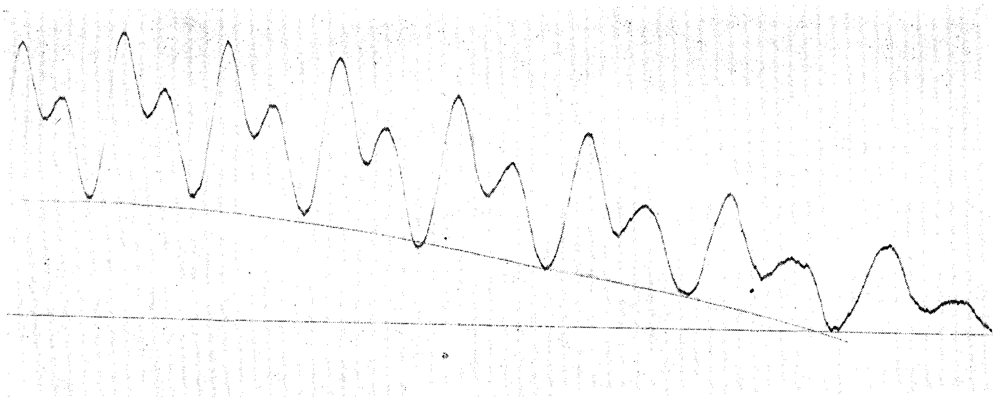

FIG. 2. Microphotometer trace of λ8629.2.

To measure the isotope shifts, each line was microphotometered on a Zeiss microphotometer. A microphotometer trace of one of the lines is shown in Fig. 2. By means of a second degree equation the isotope shifts were calculated from measurements on the traces.

RESULTS

The final measurements were made on plates taken with the etalon separation 2.8001 cm. In most cases the lines were microphotometered several times and a mean value taken from measurements on the various traces. As can be seen from the figures, the components of none of the lines were so completely resolved as to be entirely free from overlapping. If one is to measure the isotope shifts by measuring the peak separation it is first necessary to check the amount of overlapping. If a tail of one component overlaps the maximum of another to any appreciable extent, the two peaks may be shifted toward each other because of this superposition, and thus give a spuriously small value to the isotope shift.

In order to estimate the amount of overlapping, the contour of one of the lines was plotted on coordinate paper in such a way that the abscissa scale is linear in wave numbers, and the ordinate values give true relative intensities. It appeared from the resultant contour (Fig. 3) that overlapping would have a negligible effect on the peak separation in this case. Since the effect of the overlapping seemed so small, no attempt was made to correct for it in any of the lines measured. It is of some interest to note that the half-width of the lines, if it is assumed to be due entirely to Doppler broadening, corresponds to a temperature of about 164°C, a value not far different from that found in liquid-air cooled Schuler tubes.[4]

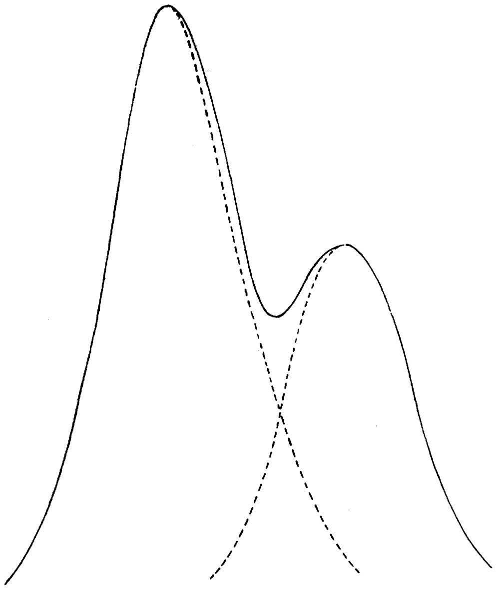

FIG. 3. Contour of λ8595.1.

The nitrogen lines for which the isotope shifts were finally measured are listed in Table I, which contains the average shifts measured and their probable errors. The signs assigned to the isotope shift follow the usual convention that a shift to higher frequencies in going from N^{14} to N^{15} is called positive.

There are other strong lines on the infra-red side of the 8656.3 line, but they are too closely grouped to be investigated on this instrument. What appeared to be an extremely strong line at 8683A revealed itself in the etalon pattern (Fig. 4) to be two strong lines completely overlapping each other. Similarly there are three weaker lines at 8703A which might be investigated by the use of a higher dispersion spectrograph, but which overlapped each other on all of my plates.

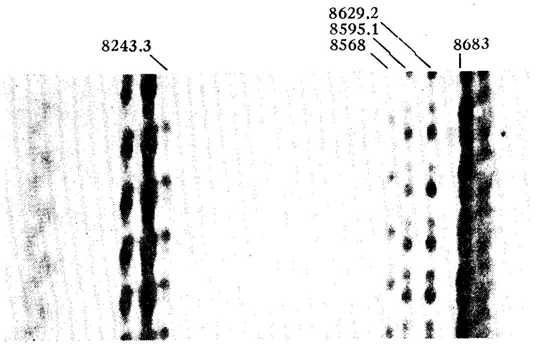

FIG. 4. Interferometer pattern of two groups of nitrogen lines, showing the strong component due to N^{15} and the weaker component due to N^{14}.

Kamiyama and Sugiura[8] observed many nitrogen lines in this region which did not appear on my plates. Also in many cases the relative intensities and wave-lengths of the lines observed here did not agree with the values assigned by them. Usually the wave-lengths obtained agreed more closely with the results of Duffendack and Wolfe[12] than with those of Kamiyama and Sugiura. Perhaps these differences may be ascribed to the different methods of excitation used.

It is seen in Table I that the strong nitrogen lines tend to appear in rather closely spaced groups which actually constitute multiplets. In the $^4P \rightarrow {}^4P$ group at about 8200A the spacing was so small that it was impossible to microphotometer the line λ8223.9 because of the presence of a very close neighboring line, the pattern of which overlapped that of λ8223.9 between orders. It was possible, however, to estimate the shift in this line by visual comparison with the line λ8243.3. As closely as could be seen with an eyepiece the shift was the same in the two lines. Hence it was decided to assign a value for λ8223.9 roughly equal to that of λ8243.3 but with a probable error ten times as great.

Three lines appeared in the $^4S \rightarrow {}^4P$ group at about 7400A, but the weakest of them, λ7423.9, was too faint to produce a measureable etalon pattern in a reasonable exposure time. The presence of band heads in this region made the investigation of such a weak line even more difficult.

It will be noticed that the magnitude of the shift is greatest in the four lines in which the shift is positive. This result might be expected because of the fact that the normal mass effect is always positive and would therefore increase the magnitude of a positive shift and decrease that of a negative one, the normal mass effect for these lines being about 0.03 cm^{-1}. If one calls the difference between the observed isotope shift and the normal mass effect the specific shift, one finds the magnitude of the specific shift to be much greater for the lines which stem from $^4P \rightarrow {}^4P$ and $^4S \rightarrow {}^4P$ transitions than for those from $^2P \rightarrow {}^2P$ transitions.

In all of the microphotometer traces it can be clearly seen that both components of the lines are completely symmetrical. Thus no trace of hyperfine structure is detected in either the N^{14} or N^{15} lines. As can be seen in Table I the isotope shifts are of the order of magnitude of 0.05 cm^{-1}; inasmuch as these shifts were so cleanly resolved it seems likely that any hyperfine structure as great as 0.03 cm^{-1} would at least reveal itself as an asymmetry in the components. It seems safe to say that there is no hyperfine structure in these lines with an over-all spread as great as 0.03 cm^{-1}.

TABLE I. Isotope shifts in N.

Wave-length	Transition	Intensity	Isotope shift cm^{-1}
8656.3 IA	$3p\ {}^2P_{1/2} \rightarrow 3s\ {}^2P_{3/2}$	4	0.0785 ±0.0014
8629.2	$3p\ {}^2P_{3/2} \rightarrow 3s\ {}^2P_{3/2}$	10	0.0694 ±0.0008
8595.1	$3p\ {}^2P_{1/2} \rightarrow 3s\ {}^2P_{1/2}$	6	0.0751 ±0.0006
8568.0	$3p\ {}^2P_{3/2} \rightarrow 3s\ {}^2P_{1/2}$	4	0.0678 ±0.0009
8243.3	$3p\ {}^4P_{3/2} \rightarrow 3s\ {}^4P_{5/2}$	4	−0.0596 ±0.0006
8223.9	$3p\ {}^4P_{1/2} \rightarrow 3s\ {}^4P_{3/2}$	4	−0.06 ±0.006
8216.6	$3p\ {}^4P_{5/2} \rightarrow 3s\ {}^4P_{5/2}$	6	−0.0579 ±0.0005
7468.7	$3p\ {}^4S_{3/2} \rightarrow 3s\ {}^4P_{5/2}$	10	−0.0565 ±0.0011
7442.6	$3p\ {}^4S_{3/2} \rightarrow 3s\ {}^4P_{3/2}$	6	−0.0485 ±0.00117

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[12] D. S. Duffendack and R. A. Wolfe, Phys. Rev. **34**, 409 (1929).

DISCUSSION OF RESULTS

The measured isotope shift of a line in the spectrum of an element does not give the isotope shift in the energy levels of the atom, but simply the difference in the isotope shifts of the two levels involved in the transition. The primary theoretical interest, however, is in the absolute shift in the levels themselves.

In general it is possible to obtain the shifts in the energy levels if one has made experimental measurements on enough lines. The usual procedure is to assume that the isotope shift in a level of high principal quantum number is zero.[13] This assumption can be verified by studying transitions between this level and other levels of higher principal quantum number; the observed shifts in such lines should be zero if the above assumption is true. Then if a shift is observed in a transition from the level of high principal quantum number it will be equal to the shift in the lower level. Knowing the shift in this level we can find transitions to other levels and thereby obtain the isotope shift in a great many levels of the atom. Also if there are many transitions that show the same isotope shift and have one energy level in common, the shifts of all the other levels must be the same or zero. If they are unrelated levels it is reasonable to assume that the shifts are probably all zero and that the total shift is due to the common level.

TABLE II. Differences in the isotope shifts of levels of a multiplet.

$\Delta\nu(\lambda 8629.2) - \Delta\nu(\lambda 8656.3) = \Delta(3p\ ^2P_{3/2}) - \Delta(3p\ ^2P_{1/2}) = -0.0091$

$\Delta\nu(\lambda 8568.0) - \Delta\nu(\lambda 8595.1) = \Delta(3p\ ^2P_{3/2}) - \Delta(3p\ ^2P_{1/2}) = -0.0073$

Mean $\Delta(3p\ ^2P_{3/2}) - \Delta(3p\ ^2P_{1/2}) = -0.0082$

$\Delta\nu(\lambda 8568.0) - \Delta\nu(\lambda 8629.2) = \Delta(3s\ ^2P_{3/2}) - \Delta(3s\ ^2P_{1/2}) = -0.0016$

$\Delta\nu(\lambda 8595.1) - \Delta\nu(\lambda 8656.3) = \Delta(3s\ ^2P_{3/2}) - \Delta(3s\ ^2P_{1/2}) = -0.0034$

Mean $\Delta(3s\ ^2P_{3/2}) - \Delta(3s\ ^2P_{1/2}) = -0.0025$

$\Delta\nu(\lambda 8216.6) - \Delta\nu(\lambda 8243.3) = \Delta(3p\ ^4P_{5/2}) - \Delta(3p\ ^4P_{3/2}) = 0.0017$

$\Delta\nu(\lambda 7442.6) - \Delta\nu(\lambda 7468.7) = \Delta(3s\ ^4P_{5/2}) - \Delta(3s\ ^4P_{3/2}) = 0.008$

As can be seen from Fig. 5, which shows the levels and transitions for the lines here studied, either of the above procedures is impossible with the limited data at hand. From the measurements it can be seen, however, that within a multiplet the difference in the level shift is very small, never much more than 10 percent of the measured shift in the lines. For instance the difference between the observed shifts in the lines $3s\ ^2P_{3/2} - 3p\ ^2P_{1/2}$ and $3s\ ^2P_{3/2} - 3p\ ^2P_{3/2}$ gives the difference in the shifts of the levels $3p\ ^2P_{1/2}$ and $3p\ ^2P_{3/2}$.

Let us call the shift in the $3p\ ^2P_{3/2}$ level $\Delta(3p\ ^2P_{3/2})$, and designate the other shifts similarly. It is then possible to apply the combination principle to the observed differences from Table I to obtain Table II which shows the differences of isotope shift of the levels of a multiplet.

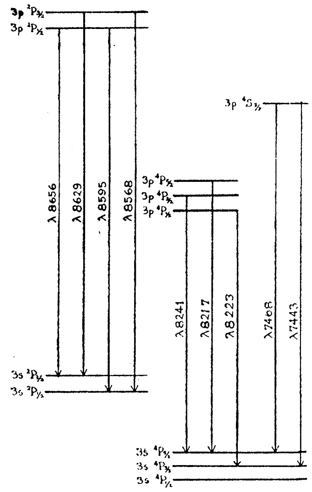

FIG. 5. Energy levels of the lines in which isotope shift has been measured.

If the nitrogen atom were a case of pure Russell-Saunders coupling one would expect the shift in the energy levels to be independent of the J value and therefore the lines of a multiplet should exhibit the same isotope shift. As is shown in Table II this is not true, indicating that there is some deviation from pure Russell-Saunders coupling in the case of nitrogen.

It appears from these figures that in the ^2P states the shift within a multiplet is greater in the state with the smallest J value. On the other hand, in the ^4P states, in any particular multiplet, the shift seems to be greater for the levels of higher J value. The differences, however, are not much greater than the probable error, and accordingly no great weight should be given to these conclusions.

It appears to be impossible to assign an upper limit to the magnetic moment of the N^{15} nucleus on the basis of the absence of hyperfine structure in the lines observed, as was done for N^{14} by

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[13] H. Kallman and H. Schuler, Ergeb. d. exakt. Naturwiss. 11, 162 (1932).

Bacher.[14] It seems that the lines observed by Bacher did not appear in this discharge and none of those that did appear were favorable for such a calculation. Any estimate based upon these lines would be too large to be significant.

In conclusion I wish to acknowledge the kindness of Professor H. C. Urey in supplying me with the sample of enriched nitrogen; furthermore, I wish to acknowledge my indebtedness to Professor F. A. Jenkins for his stimulating direction of my work.

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[14] R. F. Bacher, Phys. Rev. **43**, 1001 (1933).

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Dispersion of Elastic Waves in Solid Circular Cylinders[*]

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The theory of elastic vibrations in solid circular cylindrical rods of homogeneous isotropic materials is redeveloped from the general equations of elasticity with the following general results: 1. For any mode of vibration the ratio of the velocity of any elastic wave traveling along the rod to the velocity c_0 of shear waves is the same for any two rods whose Poisson ratios are equal and whose ratios of circumference to shear wave-length are equal; 2. If the velocity of propagation for any particular mode remains less than c_0 as the frequency or radius is increased indefinitely, this velocity approaches that of Rayleigh surface-waves; 3. If the velocity of propagation for any particular mode remains greater than c_0 as the frequency or radius is increased indefinitely, this velocity approaches c_0 in the limit; and 4. A considerable simplification is introduced into the method of computing dispersion curves for any mode. This investigation not only generalizes and extends the work of D. Bancroft on elongational waves but further includes the computation of an exact table of dispersion curves for the flexural mode of vibration. The dispersion curves for magnesium are compared with the experimental results of Shear and Focke. Excellent agreement between theory and experiment is obtained for the first elongational and flexural branches.

INTRODUCTION

THE last few years have seen much progress, from both experimental[1] and theoretical[2–4] viewpoints, in the study of the phenomena associated with the vibrations of rods, particularly dispersion at high frequencies. Without exception, the exact theoretical treatments take as their starting points the solutions of the general dynamical equations of elasticity obtained originally by L. Pochhammer[5] for infinitely long rods. The most complete of these discussions is that of D. Bancroft,[2] who has calculated a table of velocities of elongational waves as a function of the ratio of the diameter of the rod to the wave-length for a wide range of values of Poisson's ratio.

An examination of experimental data reveals the existence of several types of rod vibrations often occurring either in conjunction with or to the exclusion of the elongational mode. This suggests the extension of the theoretical treatment to higher modes of vibration, to obtain dispersion curves for the associated elastic waves. Such calculations will be extremely useful in the future study of the stability and interaction of various modes of vibration and the study of the vibrations of a bar of finite length. The present article gives a general treatment of the problem of the propagation of longitudinally-traveling waves along a solid circular cylinder of infinite length, and presents a simplified method for the exact calculation of dispersion curves.

With a few important exceptions the quantities used in the analysis are similar to those

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[*] Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Brown University, Providence, Rhode Island.

[†] Now at the David Taylor Model Basin, Navy Department, Washington, D. C.

[1] S. K. Shear and A. B. Focke, Phys. Rev. **57**, 532 (1940).

[2] D. Bancroft, Phys. Rev. **59**, 588–593 (1941).

[3] E. Giebe and E. Blechschmidt, Ann. d. Physik **11**, 905 (1931); **18**, 417–485 (1933).

[4] G. S. Field, Can. J. Research **5**, 619–624 (1931); **8**, 563–574 (1933); **11**, 254–263 (1934).

[5] L. Pochhammer, J. f. d. reine u. angew. Math. (Crelle) **81**, 33–80 (1875).

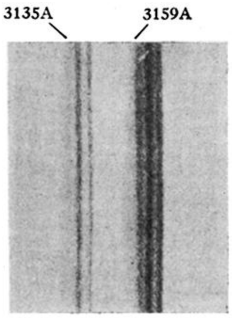

FIG. 1. Triple heads on second positive bands of isotope mixture.

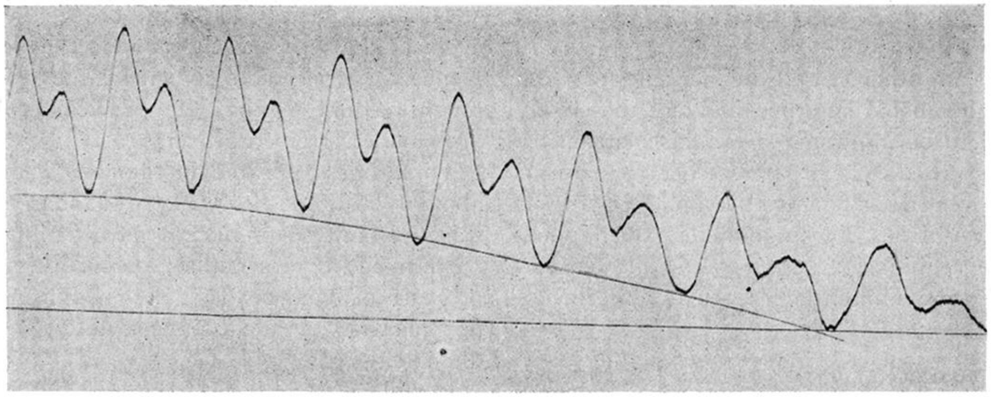

FIG. 2. Microphotometer trace of λ8629.2.

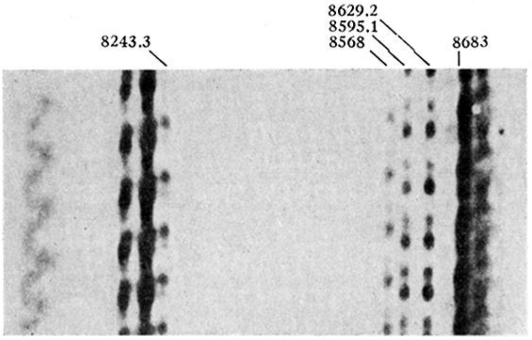

FIG. 4. Interferometer pattern of two groups of nitrogen lines, showing the strong component due to N^{15} and the weaker component due to N^{14}.