

The Negative Bands of N14 – N15

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Citation: *The Journal of Chemical Physics* **6**, 734 (1938); doi: 10.1063/1.1750159

View online: <http://dx.doi.org/10.1063/1.1750159>

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this by 0.002 ev to allow for the effect of the outer electron we obtain, as in the ground state, the same correction as at complete separation. We have, therefore, taken this correction as 0.009 ev at all values of R .

The empirical results are taken from a paper⁷ in which we have discussed methods of obtaining empirical potential curves of high accuracy, using as illustrative material computations on this state. The relation of our theoretical results to our best empirical determination is precisely what

⁷ A. S. Coolidge, H. M. James, and E. L. Vernon, *Phys. Rev.* **54**, 726 (1938).

our experience with the theoretical computations has led us to expect. It will be noted, however, that these theoretical results are definitely incompatible with some of the empirical curves set up by less accurate and more usual methods, lying below rather than above the presumptive "observed" curve.

From the varying energy errors of the several functions it will be clear that there is also a considerable variation in the root-mean-square error of these functions. An estimate of 1 percent for this quantity for the best functions, 3 percent for the worst, should not be far from the mark.

The Negative Bands of $N^{14}-N^{15}$

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(Received August 8, 1938)

The negative bands of nitrogen were photographed with a mixture which contained about 15 percent of N^{15} . The $0 \rightarrow 0$, $1 \rightarrow 0$ and $0 \rightarrow 1$ bands of the $N^{14}-N^{15}$ molecule were analyzed. Their position is within the limits of experimental errors where the elementary theory of the isotopic shifts predicts them. The bands do not show any intensity alternations and there are no perturbations at the places where the corresponding bands of ordinary nitrogen have them.

INTRODUCTION

THE availability of mixtures with a considerable percentage of the heavy nitrogen isotope N^{15} now makes possible a study of the molecules which contain one or more atoms of N^{15} . The most interesting of these molecules would be $N^{15}-N^{15}$ because with its help the spin of the N^{15} atom can be determined. With the determination of the spin as chief aim we have begun the investigation of some bands of the nitrogen molecule. This research was made possible through the courtesy of Professor H. C. Urey, who supplied us with a small amount of ammonium nitrate prepared in his laboratory which yielded nitrogen with a concentration of about 15 percent of the heavy isotope.

The present communication gives some of the preliminary results. Although we have photographed several $N^{15}-N^{15}$ bands, they are, with the available sample, relatively weak compared to the $N^{14}-N^{15}$ and the $N^{14}-N^{14}$ bands, so that

reliable intensity measurements necessary for the determination of the spin would be difficult. The $N^{14}-N^{14}$ bands are naturally by far the strongest bands. Therefore we hope to repeat the experiments with more concentrated samples in order to obtain the spin. In this paper we report on some bands of $N^{14}-N^{15}$.

The nitrogen molecule has many band systems in the ultraviolet and visible. Most of these, e.g., the first and second positive groups, are of a rather complicated structure, and can be completely resolved only with difficulties. It is obvious that weak bands of $N^{14}-N^{15}$ or $N^{15}-N^{15}$ partly overlapped by the much stronger $N^{14}-N^{14}$ bands would represent rather unfavorable objects for analysis. However, the so-called negative bands due to the N_2^+ ion have a relatively simple structure and therefore we have chosen them for a first study. The present paper contains the three bands $0 \rightarrow 0$, $1 \rightarrow 0$ and $0 \rightarrow 1$ of the positive $N^{14}-N^{15}$ ion.

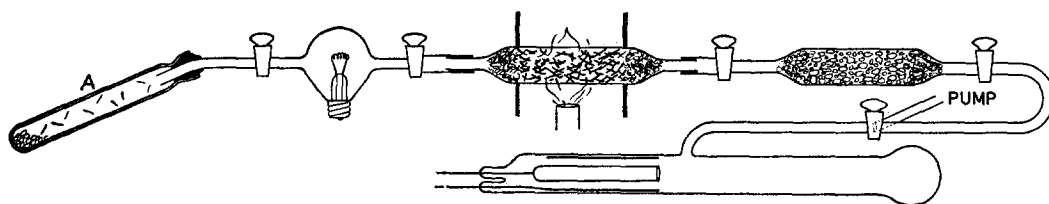


FIG. 1.

EXPERIMENTAL PROCEDURE

Owing to the limited amount of material available, it seemed best to construct a generator for the preparation and purification of the gas, with as small a capacity as possible.

The salt was decomposed by heating in contact with sodium hydroxide, the liberated ammonia broken down by the incandescent filament of a 6-volt automobile lamp, the hydrogen removed by hot copper oxide, and the water vapor and any residual ammonia absorbed by granulated barium perchlorate. The purified nitrogen was then admitted to the discharge tube, which was furnished with a hollow cathode and a coaxial anode of sheet nickel. It is well known that this type of tube emits the negative bands with great intensity and suppresses the otherwise very strong second positive bands. Fig. 1 shows the gas generator and discharge tube on a scale of about one-third natural size.

In charging the generator tube *A*, a short stick of caustic soda was first fused and boiled in the tube until the liberation of steam had almost subsided. It was then corked and rotated in a nearly horizontal position until cool, thus coating the inner wall with a thin layer of the anhydrous salt, which served as a drying agent for any water vapor liberated from the mixture of ammonium nitrate and sodium hydroxide, subsequently introduced. The cracks which form in the vitreous layer of sodium hydroxide should not be mistaken for cracks in the glass. The tube *A* was then cemented to the rest of the system with sealing wax, and the whole exhausted with an oil pump, after which the stopcocks were closed and the mixed salts heated with a small flame, the effervescence being watched carefully to avoid too high a pressure; the proper amount of heating was soon learned from experience. After the tube had cooled, the lamp filament was brought to a dull red heat and

the first stopcock opened, the diminution of the light furnishing a rough measure of the pressure of the gas. The stopcock was then closed and the filament raised to incandescence for about five minutes.

The copper oxide, in a tube of fused quartz (the wax seals screened from radiation by asbestos disks) was then heated to a dull red by a Bunsen flame and the second stopcock opened and closed. After about ten minutes, the third cock was opened and closed, admitting some of the gas into the barium perchlorate desiccating tube. After half an hour the three-way stopcock was turned into such a position that the highly exhausted discharge tube was cut off from the pump and put in communication with the desiccating tube. The fourth stopcock was now turned very slowly until the pressure, indicated by the appearance of the discharge, amounted to a few millimeters. If no luminosity appeared in the interior of the hollow cathode, the pump was operated until the blue glow filled its interior at maximum brilliancy.

Ordinary nitrogen was prepared by substituting a tube containing a small amount of sodium azide for the tube *A*.

The discharge tube was excited by a small 5000-volt transformer in connection with a mercury rectifier, and the spectra photographed in the second order of a six-inch, 21-foot radius, concave grating ruled with 30,000 lines to the inch on aluminized Pyrex glass. The dispersion is about 0.6Å per mm. Exposure times varied from one to four hours, according to the intensity of the bands, an absorbing filter for suppressing ultraviolet of higher order being used when necessary. After long operation with heavy nitrogen, it was found that the electrodes had absorbed a great deal of the gas. Repeated fillings with pure N_2 obtained from ordinary sodium azide and long operation of the tube with this

TABLE I

<i>K</i>	<i>P</i> BRANCH ν	<i>I</i>	<i>K</i>	<i>R</i> BRANCH ν	<i>I</i>	<i>K</i>	<i>P</i> BRANCH ν	<i>I</i>	<i>K</i>	<i>R</i> BRANCH ν	<i>I</i>
1 \rightarrow 0 band						0 \rightarrow 0 band					
0	—	—		27,900.87	0	0				25,568.34	1
1	27,893.20	1		05.10	1	1	25,560.61	1		72.67	2
2	89.71	1		09.81	2†	2	57.15	2		77.23	2
3	86.57	1		14.35	1 <i>c</i>	3	54.04	2		82.14	3
4	83.54	2		19.29	0 <i>c</i>	4				87.32	3
5	80.84	2 <i>b</i>		24.32	1 <i>c</i>	5	<i>P</i> ₄ to <i>P</i> ₂₂			92.79	3
5				24.57	2†	6	Confused with the			98.58	3
6	78.30	1 <i>c</i>		29.93	6 <i>b</i>	7	head of the N ¹⁴ —N ¹⁴			25,604.64	3
6	78.47	1 <i>c</i>		35.53	3†	8	band			11.01	3
7	76.11	1		35.85	3	9				17.69	3
7	76.29	1		41.46	4†	10				24.64	3 <i>b</i>
8	74.11	1		41.86	3	11				31.86	3 <i>b</i>
8	74.32	1				12				39.42	3 <i>b</i>
				<i>P</i> BRANCH		13				47.18	2
9	72.39	1	21	71.39	0	13				47.32	2
9	62.65	1	21	72.05	0	14				55.27	2
10	70.87	1 <i>c</i>	22	73.03	0	14				55.44	2
10	71.30	1 <i>c</i>	22	73.58	0	15				63.64	2
11	69.66	2*	23	74.87	0	15				63.84	2
11	70.11	2*	23	75.42	0	16				72.38	2
12	68.79	2*	24	76.87	0	16				72.57	2
12	69.14	2*	24	77.46	0	17				81.34	2
13	67.96	4 <i>d</i> *	25	79.25	0	17				81.66	2
13	68.35	1*	25	79.75	0	18				90.50	2
14	67.96	4 <i>d</i> *	26	81.77	0	18				90.83	2
14			26	82.33	0	19				25,700.17	2
15	67.45	2*	27	84.59	0	19				00.50	2
15	67.96	4 <i>d</i> *	27	85.14	0	20				10.04	2
16	67.45	2*	28	87.66	0	20				10.26	2
16	67.96	4 <i>d</i> *	28	88.30	0	21				20.15	2
17	67.96	4 <i>d</i> *	29	91.01	0	21				20.42	2
17	68.35	1*	29	91.56	0	22				30.60	2
18	68.35	1*	30	94.52	0	22				30.83	2
18	68.79	2*	30	95.17	0 <i>c</i>						
19	69.14	2*	31	98.32	0						
19	69.66	2*	31	98.86	0						
20	70.11	2*	32	02.39	00						
20	70.69	0	32	03.04	[5]Ni						

gas did not remove from the spectrum traces of the bands of the heavy isotope.

ANALYSIS

On the second-order plates which we obtained, the principal N¹⁴—N¹⁵ bands are well developed

and we have measured and analyzed the 0 \rightarrow 0, 1 \rightarrow 0 and 0 \rightarrow 1 bands. Other bands are also present, but we want to postpone their analysis until we can obtain more favorable plates. The head of the 1 \rightarrow 0 band of N¹⁵—N¹⁵ was also present, but the band was too weak for obtaining

TABLE I—Continued

K	P BRANCH ν	I	K	R BRANCH ν	I	K	P BRANCH ν	I	K	R BRANCH ν	I
0→0 band						0→0 band					
23	53.33	1d		41.27	2	27	67.37	1		86.93	0
23	53.57	1		41.55	1	27	67.62	1		87.17	0
24	56.45	1		52.27	2	28	71.67	1		98.82	0
24	56.66	1		52.53	2	28	71.86	1		99.25	0
25	59.75	1		63.60	1	29	76.07	0		10.50	1?
25	60.02	1		63.82	1	29	76.33	0		11.56	0
26	63.41	1		75.13	1	30	80.68	0			
26	63.65	1		75.39	1	30	81.07	0			
0→1 band						0→1 band					
0	—	—									
1				23,434.01	[6b]†	14	04.04	1c*†		20.22	1
2	23,418.57	1b		38.58	1	14	04.24	1c*		20.39	1
3	15.39	[5b]†		43.54	1r	15 unresolved part 15 between 04.75 and 05.35				29.12	1
4	12.77	1		48.88	2					29.34	1
5	10.42	2		54.54	2	16	06.27	1		38.45	1
6	08.41	2		60.53	2	16	06.49	1		38.71	1
7	06.71	2		66.84	2	17	07.87	1		48.02	1
8	05.35	1c		73.49	2	17	08.10	1		48.23	1
9	04.24	1c		80.40	[5]†	18	09.90	[4b]†		57.95	1
10	03.64	1c*†		87.81	2b	18				58.16	1
11	03.17	1c*		95.37	1c	19	12.12	1		68.19	1
11	03.35	1c*		95.50	1c	19	12.31	1		68.40	1
12	03.17	1c*		23,503.33	1c	20	14.65	2b†		78.76	1
12	03.35	1c*		03.46	1c	20	14.94	0		78.98	1
13	03.35	1c*		11.62	1c	21	17.65	0		89.64	0
13	03.64	1c*†		11.76	1c	21	17.88	0		89.86	0
						22		†			
						22		†			
						23	24.54	0			
						23	24.73	0			

* means that the line is a blend with another $N^{14}-N^{15}$ line; † means that the line is a blend with a $N^{14}-N^{14}$ line.

a satisfactory analysis. In addition, the strongest bands of the second positive nitrogen group are found on the plates with the corresponding $N^{14}-N^{15}$ and $N^{15}-N^{15}$ bands. On some plates a few nickel lines appear.

As could be expected, the position of the $N^{14}-N^{15}$ bands with respect to the corresponding bands of ordinary nitrogen is different for the three bands under investigation. The origins of the 0→0 bands lie less than 2 wave numbers apart, and the head of the $N^{14}-N^{15}$ band is just 0.14A inside the head of the $N^{14}-N^{14}$ band. As

the lines of the P branch which form the head are so crowded together that their resolution is incomplete in the vicinity of the head, the lines P_4 to P_{22} of $N^{14}-N^{15}$ are lost among the much stronger $N^{14}-N^{14}$ lines. The other lines of this band appear near the corresponding lines of the ordinary band but well separated from them and there are practically no superpositions.

The head of the 1→0 band lies near 3587.4A. The part of the band between its head and 3582.3A, the head of the corresponding ordinary

band,* is quite free from superposition with any lines of ordinary nitrogen.

The lines R_2 to R_8 , however, lie on the short wave-length side of this last head and are very much interfered with by the strong lines of the ordinary band. The lines beyond R_8 are covered by the dense band 3577 of the second positive group and no attempt was made to locate them.

The 0→1 band lies entirely within the ordinary 0→1 band. The position of the heads is at 4271.7Å and 4278.1Å, respectively. Owing to the high dispersion of the plates there is, however, relatively little disturbance of the $N^{14}-N^{15}$ band by the much stronger $N^{14}-N^{14}$ band.

Table I gives the frequencies and intensities of the three bands. The plates were measured in the usual way under the comparator against iron standards. As we were chiefly interested in a comparison with the corresponding bands for ordinary nitrogen, we applied a small correction to our wave-lengths so as to make those of ordinary nitrogen agree with the measurements of Coster and Brons. We are unable to say whether this means that there was a slight shift between the nitrogen lines and the iron comparison on our plates, or whether that shift was on the plates of Coster and Brons, who also admit the possibility of such a shift on their plates.

The negative bands of ordinary nitrogen have been the subject of considerable study. The most accurate data of the bands in question are probably those by Coster and Brons.¹ There are older measurements as well as the first analysis of the principal bands by Fassbender² and the measurements by Childs³ of the bands 0→0 and 0→1 obtained from an arc discharge in nitrogen, which go up to very high values of the rotational quantum number.

The best procedure would be to obtain the rotational and vibrational constants from the $N^{14}-N^{15}$ bands and compare them with those

* This 1→0 band of ordinary N_2 apparently has never been analyzed, undoubtedly due to the fact that a considerable part of it is hidden under the head (at 3577Å) of the very strong 0→1 band of the second positive group. We measured and analyzed it and shall include the results in a future paper.

¹ D. Coster and H. H. Brons, Zeits. f. Physik **73**, 747 (1932).

² M. Fassbender, Zeits. f. Physik **30**, 73 (1924).

³ W. H. J. Childs, Proc. Roy. Soc. **A137**, 641 (1932).

TABLE II.

		$N^{14}-N^{14}$		$N^{14}-N^{15}$	
		INITIAL	FINAL	INITIAL	FINAL
Y_{10}	ω_e	2419.84	2207.19	2379.28	2170.20
Y_{20}	$-x$	-23.189	-16.136	-22.418	-15.600
Y_{30}	y	-0.5375	-0.0400	-0.5109	-0.0380
Y_{40}	z	-0.04949	—	-0.04626	—
Y_{01}	B_e	2.085	1.930	2.016	1.866
Y_{02}	D_e	$4.3 \cdot 10^{-6}$	$2.9 \cdot 10^{-6}$	$4.02 \cdot 10^{-6}$	$2.71 \cdot 10^{-6}$
Y_{11}	α	0.0242	0.020	0.0230	0.019

for the $N^{14}-N^{14}$ molecule. However, the new bands are not known yet with the same completeness as those of ordinary nitrogen, and therefore the constants cannot be obtained with as high degree of reliability. Therefore we have taken the constants for $N^{14}-N^{14}$ and calculated from them those for $N^{14}-N^{15}$ and then tested whether they account with sufficient accuracy for the observed new bands. The outcome is that they do.

In order to calculate the constants of $N^{14}-N^{15}$ from those of $N^{14}-N^{14}$ it is necessary to multiply each of the constants of the latter molecule by a certain power of the isotopic factor $\rho = \sqrt{(\mu_1/\mu_2)}$ in which μ_1 and μ_2 are the reduced masses of the two molecules. From the masses⁴

$$N^{14} = 14.0076, \quad N^{15} = 15.0050$$

for the two nitrogen atoms we find

$$\rho = 0.983242.$$

In Table II the rotational and vibrational constants of the ordinary N_2^+ molecule are given, obtained from the data of Coster and Brons together with those of $N^{14}-N^{15}$ calculated from them. The constants are defined by the formula

$$E = \sum_{n,m} Y_{nm} (V + \frac{1}{2})^n K^m (K+1)^m$$

for the rotational and vibrational energy. The second column gives the more conventional symbols for these constants.

With the constants in Table II the rotational energies for final and initial state can be calculated and it is found that the frequencies of the individual lines of the bands can be represented with good accuracy by means of these calculated values. For low values of K the agreement is

⁴ K. T. Bainbridge and E. B. Jordan, Phys. Rev. **51**, 384 (1937).

within the limits of the errors of measurement. But for the higher K values there are small systematic deviations. They are of the same kind as those found in the $N^{14}-N^{14}$ bands and result from the imperfection of the formula used.

The origins of the three bands are found to be

$1 \rightarrow 0$	27,896.90
$0 \rightarrow 0$	25,564.33
$0 \rightarrow 1$	23,425.46

The difference between the first two of these numbers is the first vibrational difference of the initial state and the difference of the last two numbers yields the same quantity for the final state.

The values are:

	Initial	Final
Obs.	2332.57	2138.87
Calc.	2332.56	2138.86

The values of the second row are those calculated with the constants of Table II. The agreement between calculated and observed values is perfect.

Finally we find as the origin of the whole band system

$$25,461.56 \text{ for } N^{14}-N^{15}$$

$$25,461.48 \text{ for } N^{14}-N^{15}$$

These two values agree also within the limits of experimental errors.

We have found so far that the relation between the negative bands of $N^{14}-N^{14}$ and of $N^{14}-N^{15}$ is exactly that postulated by the elementary theory of band spectra. The good agreement shows that there are no exceptional interactions which would behave in an anomalous way. Such anomalous behavior is often found e.g., in the H_2 bands.

There are, however, some points in which the bands of the light and the heavy molecule differ. In the first place, the characteristic intensity alternations found in the $N^{14}-N^{14}$ bands have disappeared, as they should, as $N^{14}-N^{15}$ is not a symmetric molecule. Furthermore, for both molecules the lines are all narrow doublets except those with the lowest K values which are not resolved. This doublet separation is due to the interaction of rotation and electron spin, but is influenced greatly by the interaction of the initial state with a neighboring Π state. If this interaction becomes considerable, perturbations are observed. As the character of the perturbation is chiefly determined by the close approach of rotational levels with the same J value, and as this occurs more or less accidentally, the state of affairs will be different for the two isotopic molecules, and perturbations will occur at different places.

This is borne out by the facts. There is a very pronounced perturbation for $V'=1$ in $N^{14}-N^{14}$ of which there is no trace in $N^{14}-N^{15}$. It is true that the lines which should show the maximum perturbation are those in the unresolved part of the head. But in such a perturbation a large number of lines are affected and it could not have escaped notice if it existed. We hope to come back to the interesting problem of doublet separation and perturbations, when we have accumulated more material.

We wish to express our great indebtedness to Professor H. C. Urey for the heavy ammonium nitrate without which this investigation could not have been accomplished. We wish to thank also Dr. N. Ginsburg for his help with taking the plates.