

Mass Ratio of the Carbon Isotopes from the Spectrum of CN

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With a source containing carbon enriched about ten times in C^{13} , the violet CN bands have been photographed with a dispersion of 0.63A/mm. Measurements are given of the lines of low rotational quantum number in the 0,0, 0,1 and 0,2 bands of $C^{13}N^{14}$, as well as of $C^{12}N^{14}$. The vibrational constants of the normal states of both molecules are accurately determined, and give a value of the isotope mass coefficient $\rho = \omega_e'/\omega_e$ of 0.97898 ± 0.00002 , corresponding to a mass for C^{13} of 13.0088. This is in essential agreement with the mass-spectrograph value, and it is shown that the finer corrections to the isotope effect are negligible in this case.

SOME time ago we reported¹ the preliminary results of a study of the carbon isotope effect in the violet CN bands. The bands due to $C^{13}N^{14}$ were greatly strengthened by using a source containing methane enriched about ten times in the heavier isotope of carbon by diffusion in a Hertz apparatus.² These isotope bands, as obtained from ordinary carbon, are about 1/100 as strong as the main bands due to $C^{12}N^{14}$. Therefore only a few rotational lines of the 0,0 band have heretofore been detected³ on very heavily exposed spectrograms. Our plates showed the complete $C^{13}N^{14}$ system with sufficient intensity for accurate measurement. Fig. 1 shows the enhancement of the 0,1 isotope band from the enriched sample. It is a coincidence that the head of this isotope band falls almost exactly on the null line of the corresponding main band. The head is faintly visible on the plates with ordinary carbon, giving the impression that the null line is not entirely absent.

The violet CN bands afford an excellent opportunity for the precise determination of isotope mass ratios, since they lie in a favorable region of the spectrum and have a large vibration frequency ω_e . We have therefore extended our original measurements to include the 0,0, 0,1 and 0,2 bands with a view to determining the best possible value of the mass ratio C^{13}/C^{12} . The accuracy of the final result turns out to be

comparable with that of the most accurate mass-spectrograph measurements.

EXPERIMENTAL

The source was a small end-on tube with cylindrical aluminum electrodes coaxial with the capillary, the latter being 3 cm long and 1 mm in diameter. Methane and nitrogen were first introduced, each at a pressure of about 0.5 mm, and then pure argon was added to make the total pressure 15 mm. When actuated by a 25 kv, 1 kva transformer, the tube at once showed strong CN, C_2 and CH bands, with N_2 bands very weak. After about $\frac{1}{2}$ hr. running, the bands due to carbon compounds began to fade slowly, and the N_2 bands came in more strongly. The tube was then evacuated and refilled. The spectrum of CN was photographed in the first two orders of the 21-foot grating, which has 30,000 lines per inch. The rotational lines of the 0,0 and 0,1 bands of both $C^{13}N^{14}$ and $C^{12}N^{14}$ were measured against iron arc standards in the second order, where the dispersion was 0.63A/mm. The 0,2 bands could only be measured in the first order, and here an exposure of 4 hr. was necessary, whereas 2 hr. sufficed for the other bands in the second order.

Since the primary object was to obtain accurate values of ω_e for the main and isotope bands, we confined our measurements to lines of low rotational quantum number. For the stronger bands, in which the lines of low K could be accurately measured, data were taken up to $K''=10$, while in the weaker bands it was necessary to use lines as far as $K''=16$. Table I

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¹ F. A. Jenkins and D. E. Wooldridge, *Phys. Rev.* **49**, 882 (1936).

² D. E. Wooldridge and W. R. Smythe, *Phys. Rev.* **50**, 233 (1936).

³ A. S. King and R. T. Birge, *Astrophys. J.* **72**, 19 (1930).

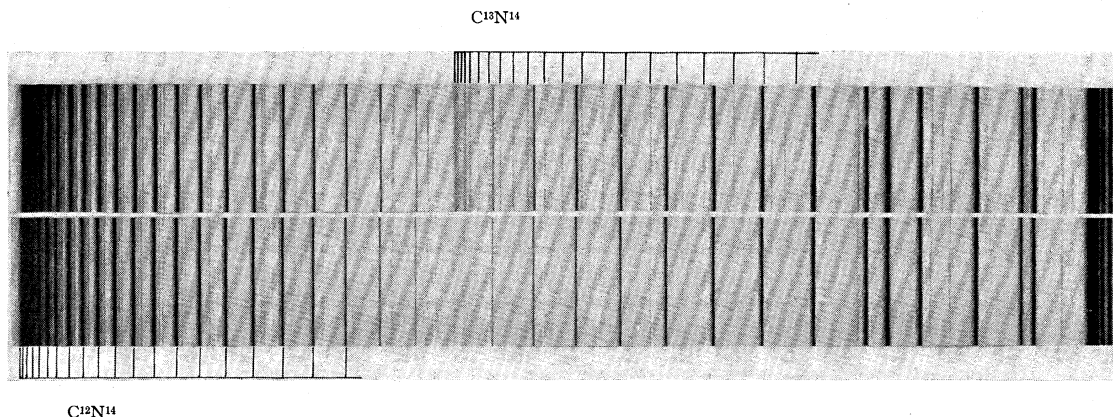


FIG. 1. Violet CN bands showing enhancement of the 0,1 isotope band from an enriched sample.

gives all of the data used in computing the mass ratio. The superscript i refers to lines of the "isotope" molecule $C^{13}N^{14}$.

The data for the 0,0 and 0,1 main bands agree excellently with those given by Uhler and Patterson⁴ and by Heurlinger,⁵ respectively. No values for the 0,2 band have been heretofore published.

RESULTS

In evaluating the molecular constants for the main and isotope bands, we have followed the procedure previously used by Jenkins and McKellar for the BO and Li_2 bands.^{6, 7} We shall therefore not describe the method in detail. Briefly, it consists in a least squares solution of the differences between corresponding lines in each pair of bands differing by unity in v'' , according to the equation

$$\Delta T = \Delta G - \alpha(K + \frac{1}{2})^2.$$

In making these solutions, values of ΔT involving lines which were unreliable because of superpositions were first discarded. The results are given in Table II. Each value is a mean for the P and R branches. The table also includes the values of the vibration frequencies ω_e and anharmonicity constants $x\omega_e$ in the equation

$$\Delta G = \omega_e - 2x\omega_e(v + \frac{1}{2}).$$

⁴ H. S. Uhler and R. A. Patterson, *Astrophys. J.* **42**, 434 (1915).

⁵ T. Heurlinger, Dissertation, Lund (1918).

⁶ F. A. Jenkins and A. McKellar, *Phys. Rev.* **42**, 464 (1932).

⁷ A. McKellar, *Phys. Rev.* **44**, 155 (1933).

We are justified in using this form, since the $\Delta G : v$ curve is known⁸ to be strictly linear up to high values of v for the normal state of CN. Incidentally, it should be noted that our value $x\omega_e = 13.144$ is appreciably lower than the figure 13.245 usually quoted.

Table II also gives the experimental values of the isotope coefficient ρ , which is found most accurately from the ratio of ω_e for the two molecules. The ratios of $x\omega_e$ and of α are consistent with this value, which gives $\rho^2 = 0.9584$ and $\rho^3 = 0.938$. Assuming our accurate ρ to represent the square root of the ratio of the reduced masses, we have, for the mass ratio

$$\frac{C^{13}}{C^{12}} = \frac{N^{14}}{\rho^2(C^{12} + N^{14}) - C^{12}}.$$

For the masses of N^{14} and C^{12} , we use the recent values of Bainbridge,⁹ 14.00750 and 12.00398. We then find, for the mass ratio, 1.08371. The corresponding mass of C^{13} is 13.0088. This is slightly greater than the mass-spectrograph result 13.0076 ± 0.0002 obtained by Bainbridge and Jordan.¹⁰ There can be no question of the correctness of the relative masses of C^{12} and C^{13} given by these authors, since they agree so well with the observed energy of the protons ejected from C^{12} under deuteron bombardment.¹¹ It

⁸ F. A. Jenkins, *Phys. Rev.* **31**, 539 (1928).

⁹ M. S. Livingston and H. A. Bethe, *Rev. Mod. Phys.* **9**, 245 (1937).

¹⁰ K. T. Bainbridge and E. B. Jordan, *Phys. Rev.* **51**, 385 (1937). The values we quote are on the slightly different mass scale of Livingston and Bethe (reference 9).

¹¹ See reference 9, p. 327.

should be noted that our first band spectrum result,¹ published simultaneously with the first mass-spectrograph data¹² on C¹³ gave independent proof that the observed gamma-ray could not be associated with this reaction.

That our result is not significantly different from the correct one is shown by calculating the value of ρ given by the most recent masses,⁹ with their stated probable errors. These give $\rho = 0.979005 \pm 0.000008$ as compared to our experimental value 0.97898 ± 0.00002 .

As a check on our experimental value of ρ , we have applied the method used by Almy and Irwin¹³ and evaluated $\rho - 1$ from the "isotope shift" of band origins in the 0,1 band. Their equation is

$$\Delta\nu_0 = \Delta\nu_e + (\rho - 1)V$$

where V is a function of the vibrational constants of upper and lower states containing ρ in its smaller terms. Assuming the ρ evaluated above, we find $V = -1972.71 \text{ cm}^{-1}$. $\Delta\nu_0$ is found experimentally by computing the origins of the main and isotope bands from several band lines. For this, the rotational constants need to be accurately known. Applying least squares to our combination differences in the usual manner, we find $B_0' = 1.9588$, $B_1'' = 1.8741$, $B_0'' = 1.8775$, $B_1'' = 1.7965$. For the origins, we then get

$$\nu_0 = 23,755.44, \quad \nu_0^i = 23,796.85, \quad \Delta\nu_0 = 41.41 \text{ cm}^{-1}.$$

Without further data it is then necessary to assume that the electronic isotope shift $\Delta\nu_e = 0$ in order to calculate ρ . If this is done, there results $\rho = 0.97901$. The fact that this agrees so well with our previous value is an indication that the electronic isotope shift is small.

POSSIBLE CORRECTIONS

Van Vleck¹⁴ lists three reasons why the observed value $\rho = \omega_e^i/\omega_e$ can differ from the true value of $(\mu/\mu^i)^{1/2}$. He states that except in the case of hydrides and deuterides these corrections are so small as to have only academic interest. To verify this in the case of CN, we have calculated their magnitudes in the cases where this

¹² K. T. Bainbridge and E. B. Jordan, Phys. Rev. **49**, 883 (1936).

¹³ G. M. Almy and G. R. Irwin, Phys. Rev. **49**, 72 (1936).

¹⁴ J. H. Van Vleck, J. Chem. Phys. **4**, 327 (1936).

TABLE I. Wave numbers of CN band lines.

0,0 bands				
K''	$R(K)$	$P(K)$	$R^i(K)$	$P^i(K)$
0	25,801.75	—	25,800.58	—
1	805.81	25,794.06	804.53	—
2	810.00	790.41	808.52	25,789.74
3	814.36	786.90	812.68	786.48
4	818.79	783.54	816.94	783.17
5	823.36	780.33	821.36	Unresolved
6	828.05	777.18	825.73	from
7	833.00	774.24	830.56	main
8	837.96	771.33	835.33	lines
9	843.10	768.71	840.04	$P(K)$
10	848.35	766.15	845.29	766.49
11	—	—	850.47	764.18
12	—	—	—	761.98
13	—	—	—	759.91
14	—	—	—	758.04
15	—	—	—	756.19
16	—	—	—	754.49

0,1 bands				
K''	$R(K)$	$P(K)$	$R^i(K)$	$P^i(K)$
0	23,759.35	—	—	—
1	763.45	23,751.69	—	—
2	767.71	748.11	23,808.62	23,789.82
3	772.14	744.70	812.86	—
4	776.72	741.46	817.25	783.45
5	781.50	738.42	821.79	780.48
6	786.38	735.51	826.50	777.71
7	791.56	732.78	831.53	775.14
8	796.82	730.17	836.46	772.63
9	802.26	727.88	841.65	770.35
10	807.85	725.65	846.99	768.22
11	—	—	852.57	766.27
12	—	—	—	764.46
13	—	—	—	762.82
14	—	—	—	761.35
15	—	—	—	760.04
16	—	—	—	758.92

0,2 bands				
K''	$R(K)$	$P(K)$	$R^i(K)$	$P^i(K)$
0	21,743.27	—	—	—
1	747.40	21,735.52	—	—
2	751.55	732.09	—	—
3	756.25	728.78	—	—
4	760.94	725.68	—	—
5	765.89	722.82	21,847.17	—
6	770.94	720.13	852.19	21,803.27
7	776.37	717.65	857.33	800.99
8	781.91	715.32	862.68	798.93
9	787.68	713.30	868.30	796.87
10	793.61	711.45	873.94	794.75
11	—	—	879.81	793.59
12	—	—	885.94	792.22
13	—	—	892.04	790.82
14	—	—	905.21	789.91
15	—	—	912.05	789.04
16	—	—	—	788.48

TABLE II. *Experimental values of the isotope coefficient.*

ν	ΔG	α	ΔG^i	α^i
$\frac{3}{2}$	2016.127	0.01723	1974.874	0.01617
$\frac{1}{2}$	2042.416	0.01738	2000.047	0.01620
$-\frac{1}{2}$	2068.705 = ω_e 13.144 = $x\omega_e$		2025.220 = ω_e^i 12.586 = $x^i\omega_e^i$	
$\rho = (\mu/\mu^i)^{\frac{1}{2}} = \omega_e^i/\omega_e = 0.97898 \pm 0.00002$ $\rho^2 = x^i\omega_e^i/x\omega_e = 0.9576$ $\rho^3 = \alpha^i/\alpha = 0.932 (\nu = \frac{1}{2})$ $= 0.938 (\nu = \frac{3}{2})$				

can be done. The anharmonicity correction¹⁵ can be found accurately, since the constants of the potential function are here well known. Using the function

$$U = 5.622 \times 10^5 \xi^2 (1 - 2.653\xi + 4.186\xi^2 - 4.607\xi^3 + 1.075\xi^4) \text{ cm}^{-1},$$

derived from the constants of the normal state,

¹⁵ In comparing the formulas for γ_a and δ_a given by Van Vleck with the original equations of Dunham (Phys. Rev. **41**, 721 (1932)), we find that the term $41a_1$ in the expression for γ_a should read $14a_1$, and that an extra term $-1155a_1^4/8$ should be included in that for δ_a .

to obtain the correction $\delta_a^i - \delta_a$ in the equation

$$\omega_e^i/\omega_e = (\mu/\mu^i)^{\frac{1}{2}}(1 + \delta_a^i - \delta_a),$$

we obtain $+4.5 \times 10^{-7}$. This is negligible compared to the probable error in ρ .

The correction for diagonal elements can also be evaluated, assuming pure precession and a value $L=1$ for the united atom. This gives $\delta_b^i - \delta_b = +7.2 \times 10^{-7}$, which is also negligible. The correction for L -uncoupling does not apply to vibrational constants ($\delta_c=0$ for both molecules). The last correction, due to interaction between states of equal Λ , cannot be found without a knowledge of the wave function, but it should be smaller than $2(B^i - B)/\nu = -6.2 \times 10^{-6}$. In this expression ν is the separation of the two $^2\Sigma$ states. This correction is again so small that it should have no influence on our experimental result. In view of these considerations, it thus appears that the accuracy of the comparison of isotope masses from band spectra of such molecules as CN is limited only by the accuracy of the wave-length measurements.

Band Spectra of PbSe, SnSe and PbTe in Absorption

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A vibrational analysis has been made of band systems in the visible region due to PbSe, to SnSe and to PbTe. These bands were observed in absorption. In each case the band heads degrade toward the red. The vibrational coefficients ω_e and $x_e\omega_e$ for the ground state and for the first excited state are compared with those of the band systems in PbO, SnO, PbS and SnS. The expected trend in these vibrational constants is observed in each case, namely a decrease in ν_h , ω_e , and $x_e\omega_e$ with increasing number of electrons in the molecule.

THE similarity of band spectra produced by diatomic molecules formed by the combination of a given element with different elements in the same group in the periodic table is generally recognized. A number of investigations have been made of band spectra produced by the diatomic molecules, PbO,¹⁻⁴ SnO,⁵⁻⁷ PbS⁸ and

SnS.⁹⁻¹¹ The band spectra due to PbSe, SnSe, PbTe and SnTe have been observed by Rochester and Howell¹² but no analyses seem to have been

⁵ Mahanti, Zeits. f. Physik **68**, 114 (1931). SnO.

⁶ Connelly, Proc. Phys. Soc. **45**, 780 (1933). SnO.

⁷ Loomis and Watson, Phys. Rev. **45**, 805 (1934). SnO.

⁸ Rochester and Howell, Proc. Roy. Soc. **A148**, 157 (1935). PbS.

⁹ Buktow and Tschassowenny, Zeits. f. Physik **90**, 815 (1934). SnS.

¹⁰ Rochester, Proc. Roy. Soc. **A150**, 608 (1935). SnS.

¹¹ Shawhan, Phys. Rev. **48**, 821 (1935). SnS.

¹² Rochester and Howell, Univ. of Durham Phil. Soc. Proc. **9**, 126 (1934).

¹ Bloomenthal, Phys. Rev. **35**, 34 (1930). PbO.

² Christy and Bloomenthal, Phys. Rev. **35**, 46 (1930). PbO.

³ Shawhan and Morgan, Phys. Rev. **47**, 377 (1935). PbO.

⁴ Howell, Proc. Roy. Soc. **A153**, 683 (1935). PbO.

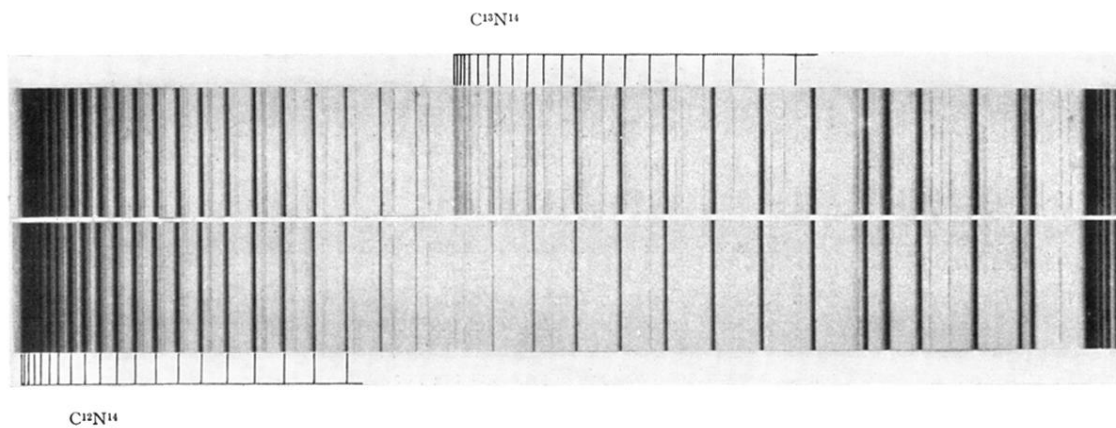


FIG. 1. Violet CN bands showing enhancement of the 0,1 isotope band from an enriched sample.