cosmic-ray electrons was suggested by the present writer<sup>10</sup> prior to his more detailed development of these ideas in papers cited.<sup>2</sup> T. H. Johnson<sup>11</sup> also suggested protons as the parents of the mesotrons but invoked a primary electronic radiation in addition.

<sup>1</sup> M. Schein, W. P. Jesse, and E. O. Wollan, Phys. Rev. 59, 615

<sup>1</sup> M. Schein, W. P. Jesse, and E. O. Wonan, Frys. Act. J. (1941).
 <sup>2</sup> W. F. G. Swann, Phys. Rev. 56, 209 (1939); Rev. Mod. Phys. 11, 242 (1939). (See, in particular, pp. 251-254.) Phys. Rev. 58, 200 (1940).
 <sup>3</sup> W. F. G. Swann and G. L. Locher, Nat. Geog. Soc. Contr. Tech. Pap., Stratosphere Series No. 1, pp. 7-14 (1935).
 <sup>4</sup> W. F. G. Swann, G. L. Locher, and W. E. Danforth, Nat. Geog. Soc. Contr. Tech. Pap., Stratosphere Series No. 2, pp. 16-25 (1936).
 <sup>5</sup> W. F. G. Swann, J. Frank. Inst. 222, 1 (1936). (See, in particular, pp. 45-58.)
 <sup>6</sup> W. F. G. Swann, Phys. Rev. 56, 209 (1939).
 <sup>7</sup> And to a negligible extent by shower production, which phenomenon, however, becomes relatively more important in the lower atmosphere.

nomenon, nowever, becomes relatively more important in the lower atmosphere.
<sup>8</sup> A. H. Compton and H. Bethe, Nature 134, 734 (1934); also A. H. Compton, Rev. Sci. Inst. 7, 71 (1936).
<sup>9</sup> T. H. Johnson, Phys. Rev. 45, 569 (1934).
<sup>10</sup> W. F. G. Swann, J. Frank. Inst. 226, 757 (1938). (See, in particular, pp. 780 and 792.)
<sup>11</sup> T. H. Johnson, Rev. Mod. Phys. 11, 208 (1939).

## Vibrational Structure of the ${}^{4}\Sigma_{g}^{-}(O_{2}^{+}) \leftarrow {}^{3}\Sigma_{g}^{-}$

## Rydberg Series of O<sub>2</sub>

Y. TANAKA AND T. TAKAMINE

Department of Physics, University of California, Berkeley, California March 24, 1941

THE far ultraviolet absorption spectrum of molecular oxygen was studied by Price and Collins<sup>1</sup> in 1935. Our recent study in Berkeley, while confirming most of their observations, leads us to propose certain changes in their classification. The experimental arrangement was the same as in the case of N<sub>2</sub> reported recently,<sup>2</sup> except that the pressure of oxygen in the spectrograph was 0.001 mm.

Especially significant are the features we find in the region between  $\lambda$ 740A and 660A. Stated briefly, it appears that the bands designated as the Q progression, by Price and Collins together with some of their V and W bands,<sup>3</sup> can be arranged into three different progressions, each forming a Rydberg series and converging respectively to the normal (v=0), v=1, and v=2 vibrational states of an excited O<sub>2</sub><sup>+</sup> electronic state which Mulliken<sup>4</sup> tentatively called  $b \, 4\Sigma_{g}$ , thus constituting the (0,0) (1,0) and (2,0) bands of a  ${}^{4}\Sigma_{g} - {}^{-} {}^{3}\Sigma_{g}$  Rydberg series of O<sub>2</sub>.

If we assign the three strong bands at  $\lambda$ 732.22A (int. 4) 725.98A (4) and 720.07A (3) as the (0,0) (1,0) and (2,0) bands for n=3,5 thirteen members (n=3 to 15) were observed for each series. The frequencies of the bands in each of the three series follow a Rydberg law closely, giving as the series limit  $\nu_{00} = 146,548 \text{ cm}^{-1}$  for (0,0) band, 147,705 cm<sup>-1</sup> for (1,0), and 148,831 cm<sup>-1</sup> for (2,0). The successive differences between the above numbers, namely  $\Delta G_{\frac{1}{2}} = 1157 \text{ cm}^{-1}$ , and  $\Delta G_{1+\frac{1}{2}} = 1126 \text{ cm}^{-1}$  agree closely with the values 1162 cm<sup>-1</sup>, and 1127 cm<sup>-1</sup> obtained from the known constants for the  $b \, {}^{4}\Sigma_{g}^{-}$  state of  $O_{2}^{+}$ .

The ionization potential corresponding to the  $O_2^+$  $b \, {}^{4}\Sigma_{g}$  normal state comes out as  $18.08 \pm 0.01$  volts, which is close to the value  $18.1 \pm 0.1$  volts obtained by combining the data<sup>6</sup> for the  $b \, {}^{4}\Sigma_{g} \xrightarrow{} a^{4}\Pi_{u}$  bands of  $O_{2}^{+}$  with the ionization potential of the  $a \, {}^4\Pi_u$  level given by Tate and

Smith and Hagstrum and Tate7 from electron impact experiments.

The value obtained by Price and Collins for the  $b \, {}^{4}\Sigma_{g}$ state is  $18.2 \pm 0.1$  volts, which would seem to correspond to the mean of our values for the heights of the normal, first, and second vibrational states of  $b \, {}^{4}\Sigma_{a}$ .

Since there has heretofore been no spectroscopic connection between the quartet and doublet states of O2+, our result would be of significance in supplying the accurate spectroscopic data for the energy of the quartet levels.

Unlike the case of N<sub>2</sub> that we reported in these columns, the (1,0) and (2,0) bands in  $O_2$  are even stronger than the (0,0) band. Those bands that lie just beyond the limits of the series appear very diffuse, likely because of autoionization.

A more detailed report will appear soon in the Scientific Papers of the Institute of Physical and Chemical Research (Tokyo).

We wish to express our sincere thanks to Professor F. A. Jenkins for his continued interest.

W. C. Price and G. Collins, Phys. Rev. 48, 714 (1935). Y. Tanaka and T. Takamine, Phys. Rev. 59, 613 (1941). In these groups Price and Collins mention that their classification is uncertain

is uncertain.
<sup>4</sup> R. S. Mulliken, Rev. Mod. Phys. 4, 56 (1932).
<sup>5</sup> Our assignment is tentative.
<sup>6</sup> R. Frerichs, Zeits. f. Physik 35, 683 (1926); T. E. Nevin, Trans. Roy. Soc. 237, 471 (1938).
<sup>7</sup> J. T. Tate and P. T. Smith, Phys. Rev. 39, 270 (1932); H. D. Hagstrum and J. T. Tate, Phys. Rev. 59, 354 (1941).

## Variations in the Relative Abundance of the **Carbon Isotopes**

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 $S^{\rm EVERAL}$  years ago it was shown<sup>1</sup> that variations are present in the  $\rm C^{12}/\rm C^{13}$  abundance ratio of carbon obtained from various natural sources. The results have now been confirmed and extended in a new investigation with the 60° mass spectrometer<sup>2</sup> of 57 specimens of widely different geological age and geographic origin.

The samples were all converted to  $CO_2$  and the  $C^{12}/C^{13}$ ratio determined from the relative heights of the mass 44 and 45 peaks after correction had been made for  $\rm C^{12}O^{16}O^{17}$ molecules.3

As the measurements were made over a period of several months a control sample was included each time analyses were made. The difference between the control and the sample in question was then noted. All computed ratios are based on these differences and the assumed constancy of the control. Frequent interchecks were made. This method eliminates possible errors due to variations in the mass spectrometer.

In Table I are recorded the results obtained. Each sample was analyzed at two different times and the final number adopted was the average of the two separate determinations. In over ninety percent of the cases the two separate values found for the  $C^{12}/C^{13}$  ratio agreed within 0.4 percent. In only three cases was the agreement worse than 0.6 percent, the poorest being 0.9 percent. The differences

Source	No. of Samples	RANGE OF VALUES OF C <sup>12</sup> /C <sup>13</sup> FOR GROUP	
Limestone	10	88.8-89.4	89.2
Coal (humic origin)	10	91.3-92.0	91.8
Wood	7	91.6-92.2	91.8
Petroleum	6	92.0-92.8	92.5
Bituminous shales	7	92.1-92.7	92.5
Torbanite and kerosene shales	3	91.3-92.0	91.7
Meteoric carbon	7	89.8-92.0	91.3
Graphite	1		90.2
Zeolitic calcite	1		89.9
CO <sub>2</sub> in air Minneapolis, Minn., 3/1/41	1		91.5
Lycopodium spores	1		93.1
"Balkashite" algae	1		92.8
Marine shell	1		89.5
Sea water	1		89.3

TABLE I. C<sup>12</sup>/C<sup>13</sup> ratio for various carbon sources.

are thus significant although all of the values may be too high or too low owing to constant discrimination in the spectrometer. This constant error in the absolute numbers is probably less than 1 percent, although it may be as great as 2 percent.

A glance at the table shows that variations up to 5 percent exist in the  $C^{12}/C^{13}$  ratio. As was shown in the earlier work,  $C^{13}$  is concentrated in the limestones whereas plant forms have a preference for light carbon. There

appears to be no "age effect." The limestones varied in age from Pre-Cambrian to modern, the coal from carboniferous to Pliocene, the wood from Late Pleistocene to present. Although there are individual variations within the groups no trends with age were noted.

It is interesting to note that the values for sea water and the marine shell check closely with those for the limestones. As sea water is considered to be the regulator of atmospheric  $CO_2$ , it would have been interesting to analyze  $CO_2$  collected above the sea. The high ratio found for the sample collected in Minneapolis can, no doubt, be attributed to the  $CO_2$  produced when coal is burned.

We are indebted to Drs. H. Berman and W. C. Darrah of the Harvard University Minerological and Botanical Museums for many of the samples. The meteor samples were kindly given to us by Professor G. P. Baxter of the Harvard Chemistry Department. The bituminous shales, plant spores and algae were supplied by Dr. Taisia Stadnichenko of the U. S. Geological Survey. Mr. R. O. Belkengren of the Botany Department kindly permitted the use of his Van Slykes apparatus for converting samples to  $CO_2$ . Through his efforts the old wood samples were obtained.

<sup>1</sup> A. O. Nier and E. A. Gulbransen, J. Am. Chem. Soc. **61**, 697 (1939)
 <sup>2</sup> A. O. Nier, Rev. Sci. Inst. **11**, 212 (1940).
 <sup>3</sup> B. F. Murphey, Phys. Rev. **59**, 320 (1941).

## Proceedings of the Metropolitan Section of the American Physical Society

MEETING OF MARCH 28, 1941

THE second meeting of the Metropolitan Section of the American Physical Society for the season 1940–1941 was held at 3:00 P.M. on Friday, March 28, 1941, in the Pupin Physics Laboratories of Columbia University. The following papers were presented:

The Structure of Black Carbon. A. H. WHITE.

Microphonic Contacts and the Properties of Pyrolitic Carbon. R. O. GRISDALE.

Quantum Relationships in Vision. Selig Hecht, Simon Shlaer, and Maurice H. Pirenne.

The following officers were elected for the season 1941–1942:

Chairman, BERNHARD KURRELMEYER Vice Chairman, RICHARD T. COX Secretary-Treasurer, W. S. GORTON Members of the Executive Committee, J. M. B. KELLOGG DAVID B. LANGMUIR W. S. GORTON

Secretary-Treasurer