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## Vibrational Structure of the ${ }^{4} \mathbf{\Sigma}_{g}-\left(\mathbf{O}_{2}^{+}\right) \leftarrow^{3} \mathbf{\Sigma}_{g}-$ Rydberg Series of $\mathrm{O}_{2}$ <br> Y. Tanaka and T. Takamine <br> 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 ${ }^{1}$ 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 $N_{2}$ reported recently, ${ }^{2}$ except that the pressure of oxygen in the spectrograph was 0.001 mm .
Especially significant are the features we find in the region between $\lambda 740 \mathrm{~A}$ and 660 A . 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, ${ }^{3}$ 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 $\mathrm{O}_{2}{ }^{+}$electronic state which Mulliken ${ }^{4}$ tentatively called $b^{4} \Sigma_{g^{-}}$, thus constituting the ( 0,0 ) $(1,0)$ and $(2,0)$ bands of a ${ }^{4} \Sigma_{g} \leftarrow \Sigma^{-} \Sigma_{g}$ Rydberg series of $\mathrm{O}_{2}$.
If we assign the three strong bands at $\lambda 732.22 \mathrm{~A}$ (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 $\nu_{00}=146,548 \mathrm{~cm}^{-1}$ for ( 0,0 ) band, $147,705 \mathrm{~cm}^{-1}$ for ( 1,0 ), and $148,831 \mathrm{~cm}^{-1}$ for ( 2,0 ). The successive differences between the above numbers, namely $\Delta G_{\frac{1}{2}}=1157 \mathrm{~cm}^{-1}$, and $\Delta G_{1+\frac{1}{2}}=1126 \mathrm{~cm}^{-1}$ agree closely with the values $1162 \mathrm{~cm}^{-1}$, and $1127 \mathrm{~cm}^{-1}$ obtained from the known constants for the $b^{4} \Sigma^{g^{-}}$state of $\mathrm{O}_{2}{ }^{+}$.
The ionization potential corresponding to the $\mathrm{O}_{2}{ }^{+}$ $b^{4} \Sigma^{-}{ }^{-}$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 ${ }^{6}$ for the $b{ }^{4} \Sigma_{g} \rightarrow a^{4} \Pi_{u}$ bands of $\mathrm{O}_{2}{ }^{+}$with the ionization potential of the $a^{4} \Pi_{u}$ level given by Tate and

Smith and Hagstrum and Tate ${ }^{7}$ 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 $b^{4} \Sigma_{0}-$.
Since there has heretofore been no spectroscopic connection between the quartet and doublet states of $\mathrm{O}_{2}{ }^{+}$, our result would be of significance in supplying the accurate spectroscopic data for the energy of the quartet levels.

Unlike the case of $\mathrm{N}_{2}$ that we reported in these columns, the $(1,0)$ and $(2,0)$ bands in $\mathrm{O}_{2}$ 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.

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## Variations in the Relative Abundance of the Carbon Isotopes

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SEVERAL years ago it was shown ${ }^{1}$ that variations are present in the $\mathrm{C}^{12} / \mathrm{C}^{13}$ abundance ratio of carbon obtained from various natural sources. The results have now been confirmed and extended in a new investigation with the $60^{\circ}$ mass spectrometer ${ }^{2}$ of 57 specimens of widely different geological age and geographic origin.
The samples were all converted to $\mathrm{CO}_{2}$ and the $\mathrm{C}^{12} / \mathrm{C}^{13}$ ratio determined from the relative heights of the mass 44 and 45 peaks after correction had been made for $\mathrm{C}^{12} \mathrm{O}^{16} \mathrm{O}^{17}$ 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 $\mathrm{C}^{12} / \mathrm{C}^{13}$ 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

