is also in the present results a marked indication of secondary maxima between the ionization potential and about 45 volts; this is most noticeable in the lines 4471 (2^3P-4^3D) and 5876 (2^3P-3^3D) (Fig. 10). A somewhat similar effect has been reported for mercury by Siebertz;[13] there is a possibility, however, that this effect in mercury is of a different order of magnitude from the effect reported here.

The sudden changes which occur in the neighborhood of the ionization potential make it rather difficult to set the currents and voltages simultaneously, consequently no attempt was made to set the current at the indicated constant value, but intensities corresponding to the indicated value could be calculated on the basis of the experimentally proved linear relation between current and intensity. Beyond about 35 volts these corrections amounted to less than the precision of the measurements.

CONCLUSIONS

From these results it may be concluded that the discharge tube used by Razek, modified so as to control the supply of electrons without changing the cathode temperature, gives excitation functions which check with those determined by other workers who used the photographic method. The hypothesis that the "hysteresis" effect noticed by Razek is associated with changes in the condition of the cathode surface is substantiated, since keeping the cathode at a constant temperature and protecting it from positive ion bombardment eliminated the effect.

The linear relation between current and intensity shows that pressures as high as those used do not lead to complications in the large, high intensity source used in this work.

In addition to checking the form of the excitation functions determined by Elenbaas, the present work indicates secondary maxima in the region between the ionization potential and forty-five volts.

The writer wishes to express his thanks to Professor C. B. Bazzoni, under whose guidance the work reported here was done; to Mr. F. R. Banks, who assisted in taking the readings, and to Dr. Joseph Razek for valuable aid and suggestions.

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[13] Siebertz, Physik. Zeits. 31, 141 (1930).

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The Infra-Red Absorption by $C^{13}O_2^{16}$ at 4.375 μ

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The fundamental vibration-rotation band ν_3 of $C^{13}O_2^{16}$ has been found with its center at a wave-length of 4.375μ or 2284.5 cm^{-1}. The individual lines in the band have been fitted by the formula $\nu_3=2284.5+0.780\ N-0.0027\ N^2$ where N takes the values -2, -4, -6, $\cdots$, etc. for the P branch and $+1$, $+3$, $+5$, $+\cdots$, etc. for the R branch. On applying the appropriate mass correction to ν_3 and to the anharmonic constant x_{33} given by Adel and Dennison, these constants take values of 2295.8 cm^{-1} and -11.4 cm^{-1}, respectively. Together these constants give the position of the center of the band as 2284.4 cm^{-1}, which is virtually in perfect agreement with observation.

I. INTRODUCTION

MEASUREMENTS in the infra-red region near 4.37μ in the atmosphere made by earlier investigators in this laboratory have shown the existence of a weak absorption maximum with resolvable rotation lines on the low frequency side of the very intense fundamental vibration ν_3 of the CO_2 molecule. Since part of this absorption region overlaps with the P branch in ν_3 of CO_2 and the lines appear to

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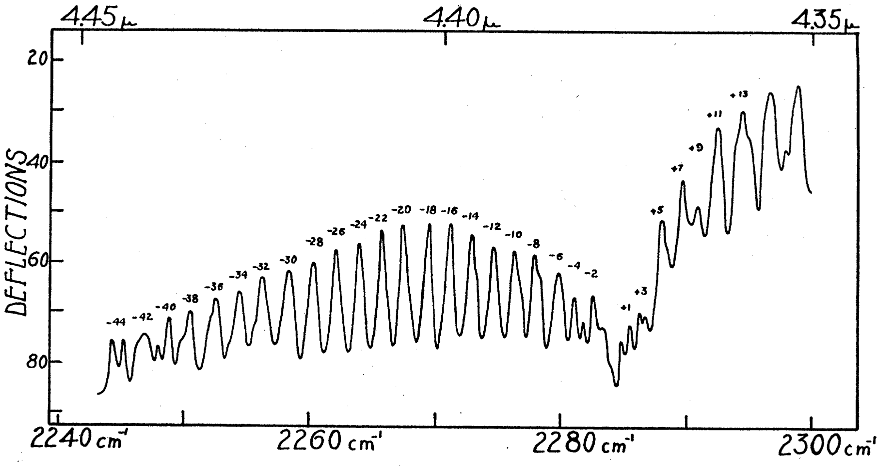

FIG. 1. The fundamental vibration-rotation band ν_3 of $C^{13}O_2^{16}$.

have the same frequency separation[1] it seemed plausible that it might be attributed to an upper stage transition in the energy of the CO_2 molecule. The existence of this band was therefore considered sufficiently interesting to warrant a thorough study of this region.

II. Experimental

The region of the infra-red near 4.37μ has been very carefully mapped with the aid of a prism-grating spectrometer equipped with an echelette grating of 3600 lines per inch ruled for this region by R. W. Wood, and described in previous reports from this laboratory. The slits were narrowed down to include a spectral interval of about 0.4 cm^{-1}, and deflections of the galvanometer were read at intervals of 0.35 cm^{-1}. Fig. 1 shows the P branch, the center, and a few lines in the R branch of the band. The number of lines in the R branch is limited because of overlapping with the P branch of the CO_2 fundamental ν_3. It may be seen that these lines are all resolved very well and the intensities in the P branch follow the usual regular envelope for such bands. The lines are numbered from the center outward. Every other line is missing because of the zero spin of the oxygen nucleus.

III. Discussion

It was possible to write a formula which would predict the frequencies of the lines in this band almost perfectly. Table I gives a list of the lines with the appropriate ordinal numbers, the observed positions in cm^{-1}, and the calculated positions in cm^{-1} as obtained from the formula

$$\nu_3 = 2284.5 + 0.780N - 0.0027N^2;$$

in which N takes the values of -2, -4, -6, -8, $-\cdots$, etc. for the P branch and $+1$, $+3$, $+5$, $+9$, $+\cdots$, etc. for the R branch. It may be seen from Table I that in only one case in the P branch is the disagreement between the observed position and calculated position more than 0.2 cm^{-1}. It may also be seen from Table I that the separation of the lines measured in cm^{-1} is the same as that in ν_3 for CO_2 which makes it almost certain that the band belongs to the CO_2 band system. Although the population of the upper energy levels is small, it was first thought possible that the band was the result of an energy transition from $V_3 = 2$ to $V_3 = 3$. The center of this band may be predicted by the use of the constants $\nu_3 = 2362.8$ cm^{-1} and $x_{33} = -12.7$ cm^{-1} derived by Adel and Dennison[2] and lies at 2299.2 cm^{-1}. Since the observed center of the band is at 2284.5 cm^{-1} the differ-

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[1] P. Martin and E. F. Barker, Phys. Rev. **41**, 291 (1932); Donald Cameron and Harald H. Nielsen, Phys. Rev. **53**, 246 (1938).

[2] A. Adel, and D. M. Dennison, Phys. Rev. **43**, 716 (1933) and Phys. Rev. **44**, 99 (1933).

ence between the observed position and this calculated position is 14.7 cm^{-1}.

It was felt that both the measurements and the theory were much more exact than this discrepancy indicates in view of the beautiful positional agreement of all the CO_2 bands following the theory of Adel and Dennison. Because of this belief the identification of the band as an upper stage transition was abandoned in favor of its assignment as ν_3 of the isotopic molecule $C^{13}O_2^{16}$. Following this assumption the individual terms in the expressions for ν_3 and x_{33} in Adel's and Dennison's paper were investigated for their dependence on the reduced mass of the molecule. On applying the appropriate mass correction for the isotopic molecule to the individual terms these expressions become:

$$\nu_3'=\omega_3\left(\frac{\mu}{\mu'}\right)^{\frac{1}{2}}+\frac{3}{2}f\frac{\mu}{\mu'}+\frac{h}{2}\left(\frac{\mu}{\mu'}\right)^{\frac{1}{2}}+i\frac{\mu}{\mu'}$$

$$-\frac{c}{4\omega_1}\left(\frac{\mu}{\mu'}\right)^{\frac{1}{2}}\left[c\left(\frac{\mu}{\mu'}\right)^{\frac{1}{2}}+6a+4b\left(\frac{\mu}{\mu'}\right)^{\frac{1}{2}}\right]$$

$$-\frac{3c^2(\mu/\mu')}{8[\omega_1+2\omega_3(\mu/\mu')^{\frac{1}{2}}]}+\frac{c^2(\mu/\mu')}{8[\omega_1-2\omega_3(\mu/\mu')^{\frac{1}{2}}]}+\frac{h\omega_3}{8\pi^2\omega_2 I};$$

and

$$x_{33}'=\frac{3}{2}f\frac{\mu}{\mu'}-\frac{c^2}{2\omega_1}\frac{\mu}{\mu'}-\frac{c^2}{4}\frac{\mu}{\mu'}\left[\frac{\omega_1}{\omega_1^2-4\omega_3^2(\mu/\mu')}\right];$$

where μ and μ' are the reduced masses with $C=12$, and $C=13$, respectively. Substitution of Adel's and Dennison's constants ω_1, ω_2, ω_3, a, b, c, $\cdots$ etc. in the above expressions gives ν_3' and x_{33}' the values 2295.8 cm^{-1} and -11.4 cm^{-1}. These together give the position of the band as 2284.4 cm^{-1} and since the observed position is 2284.5 cm^{-1} the agreement is perfect. The evidence is considered conclusive enough to permit identification of this band as the frequency ν_3 of the molecule $C^{13}O_2^{16}$. Since carbon is the central atom in CO_2, replacement by a heavier atom should not alter the moment of inertia, and this is verified by the fact that the observed spacing is the same as in the corresponding band for $C^{12}O_2^{16}$.

In conclusion the author expresses his gratitude to Professor David M. Dennison of the University of Michigan who very kindly considered this problem and suggested the identity of the band reported here. The author also acknowledges his indebtedness to Professor Alpheus W. Smith, and to Professor Harald H. Nielsen who suggested the problem and without whose cooperation these measurements could not have been made.

TABLE I. *Frequency positions of the lines in* ν_3 *of* $C^{13}O_2^{16}$.

N	OBSERVED ν	CALCULATED ν	$\Delta\nu$
−44	2245.1 cm^{-1}	2244.9 cm^{-1}	+0.2 cm^{-1}
−42	2247.1	2246.9	+0.2
−40	2249.0	2248.9	+0.1
−38	2250.8	2250.9	−0.1
−36	2252.8	2252.9	−0.1
−34	2254.8	2254.8	0.0
−32	2256.6	2256.7	−0.1
−30	2258.6	2258.6	0.0
−28	2260.6	2260.5	+0.1
−26	2262.4	2262.4	0.0
−24	2264.2	2264.2	0.0
−22	2266.0	2266.0	0.0
−20	2267.8	2267.1	+0.7
−18	2269.7	2269.5	+0.2
−16	2271.5	2271.3	+0.2
−14	2273.2	2273.0	+0.2
−12	2274.9	2274.7	+0.2
−10	2276.5	2276.4	+0.1
− 8	2278.2	2278.1	+0.1
− 6	2279.7	2279.7	0.0
− 4	2281.3	2281.3	0.0
− 2	2282.7	2282.9	−0.2
0	2284.5	2284.5	
+ 1	2285.5	2285.2	+0.3
+ 3	2286.5	2286.8	−0.3
+ 5	2288.1	2288.3	−0.2
+ 7	2289.5	2289.8	−0.3
+ 9	2290.9	2291.3	−0.4
+11	2292.4	2292.7	−0.3
+13	2294.1	2294.2	−0.1