# EMISSION AND ABSORPTION BANDS OF CARBON DIOXIDE IN THE INFRARED

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## ABSTRACT

The absorption spectrum produced by a 12 cm cell of $CO_2$ gas, and the Bunsen flame emission spectrum, to $3\mu$ were recorded by means of a new self-registering infrared quartz prism spectrograph of an auto-collimation type. A *new weak absorption band* was found at $2.02\mu$ which forms a linear, though not a harmonic, frequency series with known bands at $2.73\mu$ and $4.25\mu$. This was identified with a $1.99\mu$ flame emission band, which had been assigned by Paschen to water vapor. The $2.7\mu$ emission region was widely resolved into two components of practically equal intensities, with maxima at $2.58\mu$ and $2.76\mu$, corresponding to maxima identified by Paschen with water vapor and $CO_2$, respectively. When the quartz prisms were replaced by a similar rock salt pair the $4.4\mu$ emission occurred as a nearly symmetrical band, although Barker's measurements with high dispersion showed it to be double. Calculations of the *Bunsen flame temperature* from his observed separations gave 2000° K, in rough agreement with previous pyrometer determinations.

THREE regions of selective absorption due to carbon dioxide, with wave-length values for the maxima at approximately 14.7, 4.25 and $2.7\mu$, have been observed by numerous investigators.[1] Corresponding bands of emission have been found in the spectrum of the Bunsen flame by these and other investigators, and have been attributed universally to $CO_2$. Bjerrum[2] has predicted three characteristic vibrational frequencies in the near infrared for carbon dioxide on the basis of a triangular molecule. His attempt to identify the three bands mentioned above as these predicted frequencies met with some success in that the molecular heats at various temperatures calculated on the basis of these three vibrations check fairly well with observed values.

Whenever the dispersion was great enough, each of the carbon dioxide absorption bands appeared double, resembling in this respect the infrared absorption bands characteristic of diatomic gases. From its unusual behavior toward changes of temperature and pressure, Fr. Von Bahr[1] concluded that the double band at $2.7\mu$ did not constitute a regular infrared doublet. Her conclusion has recently been verified by Barker,[1]

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[1] Paschen, Ann. der Phys. und Chem. **50,** 409 (1893); Trowbridge and Wood, Phil. Mag. **20,** 898 (1910); Burmeister, Deutsch. Phys. Ges. **15,** 589 (1913); Eva von Bahr, Deutsch. Phys. Ges. **15,** 710 and 1150 (1913); Barker, Astrophys. J. **55,** 391 (1922).

[2] Bjerrum, Deutsch. Phys. Ges. **16,** 737 (1914).

who has shown with the use of especially ruled echelette gratings that both of the bands in this region are doublets with approximately equal frequency separations. Barker attempts to explain these two bands on a quantum theory basis, suggesting that each represents a fundamental of the same vibration, being caused by vibrational changes from state 0 to state 1, and from state 1 to state 2, respectively. He makes no attempt, however, to connect these with the bands at 4.25 and 14.7μ.

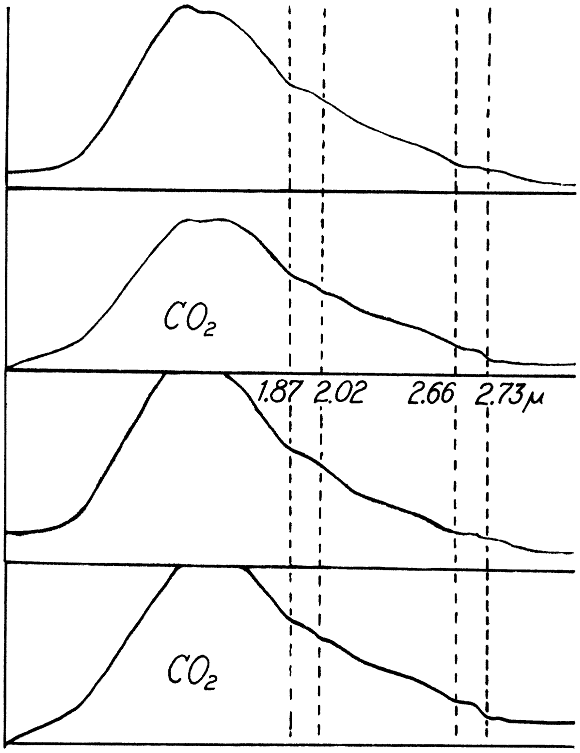

Fig. 1. Curves 1 and 3 show the distribution of energy from a tungsten lamp and the atmospheric absorption bands. Curves 2 and 4 show a deepening of the $CO_2$ bands upon introduction of a 12 cm cell.

The writer has recently put a new self-registering infrared prism spectrograph (to be described elsewhere) to the task of searching for possible new absorption bands due to $CO_2$. That such a band was found at 2.02μ is due to the accuracy with which the instrument registers details.

The dispersing system of the recording spectrograph was of an autocollimation type with a parabolic mirror of 3 cm aperture and 30.5 cm focal length and two prisms of quartz, with refracting angles of 30° and

60°, respectively. The prisms were fixed, but the spectrum to 3μ was caused to pass over the thermojunctions by a plane front surface mirror, the rotation of which was co-ordinated with the movement of the photographic plate upon which the energy distribution curves were traced.

Curves 1 and 3 of Fig. 1 show the distribution of energy from a tungsten lamp as produced by this spectrograph. In addition to the atmospheric water vapor absorption bands at 1.4, 1.87, and 2.66μ, and the $CO_2$ band at 2.73μ[3] slight indication of another band at 2.02μ appears. When a 12 cm cell of cold $CO_2$ gas was placed before the initial slit of the spectroscope this latter band was unmistakably deepened as shown in curves 2 and 4. The carbon dioxide gas, generated in a Kipp generator by running dilute hydrochloric acid over calcium carbonate, was allowed to pass continually through the absorption cell during the production of a record. That the two $CaCl_2$ drying tubes were effective in removing all water vapor, thus eliminating the possibility of attributing this 2.02μ band to that gas, is shown by the fact that the water vapor bands, cited above, were not deepened. Absorption at 2.73μ was, however, greatly increased.

The regular gradation of intensities for the 4.25, 2.73, and 2.02μ absorption bands suggests a three member series. The frequency differences between these bands are essentially the same (see Table I), but the usual harmonic relationships[4] existing among infrared vibrational bands are lacking. Because of its intensity and its wave-length values, the 14.7μ absorption maximum does not seem to belong to this group of bands.

TABLE I

*Series of carbon dioxide absorption bands*

| $\lambda$ | $\nu \times 10^{-11}$ | Diff. |
|---|---|---|
| 4.25μ | 706 | |
| | | 393 |
| 2.73 | 1099 | |
| | | 386 |
| 2.02 | 1485 | |

In the emission spectrum of the Bunsen flame we should expect to find a maximum corresponding to this 2.02μ absorption band. Fig. 2

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[3] Hettner's value Zeits. f. Phys. **1**, 351, (1920) for the 2.66μ water vapor band and Barker's value for the 2.73μ $CO_2$ band were used as calibration points in this region.

[4] Coblentz, Publication of the Carnegie Institution, **35**, (1905); Mandersloot, Dissertation, Amsterdam (1914); Brinsmade and Kemble, Proc. Nat. Acad. **3**, 420 (1917); Hettner, loc. cit.[3]; Kratzer, Zeits. f. Phys. **3**, 460 (1920); Schaefer and Thomas, Zeits. f. Phys. **12**, 330 (1924); Ellis, J. Opt. Soc. Amer. and R.S.I., **8**, 1 (1924).

shows three independent records of the Bunsen flame emission. The band at 1.99μ is doubtless this maximum. Table II shows the co-ordination of the emission bands with their corresponding absorption bands.

TABLE II

*Emission bands in spectrum of Bunsen flame*

| Emission | Absorption | Substance | Water absorption |
|---|---|---|---|
| 1.40μ | 1.40μ | water vapor | 1.48μ |
| 1.79 | 1.87 | " " | 1.98 |
| 2.58 | 2.66 | " " | 2.98 |
| 1.99 | 2.02 | $CO_2$ | |
| 2.76 | 2.73 | $CO_2$ | |

Using fluorite prisms, Paschen[5] observed three regions of characteristic emission from the Bunsen flame, and gives the following values for their maxima: 1.38, 1.83, and 2.77μ. Later, he studied these with various types of gratings and found them resolved into components as follows: 1.35 and 1.42μ; 1.803, 1.86, and 1.966μ; 2.51, 2.70, and 2.84μ. He found these to be characterized by "Knicken" and "Ecken," and suggested a possible line structure in the bands. He attributed all of the maxima, with the exception of the 2.70μ band, to water vapor, since they also occurred in the oxy-hydrogen flame. The 2.70μ band was identified with $CO_2$ gas, which also occurred with diminished intensity in the oxy-hydrogen flame.

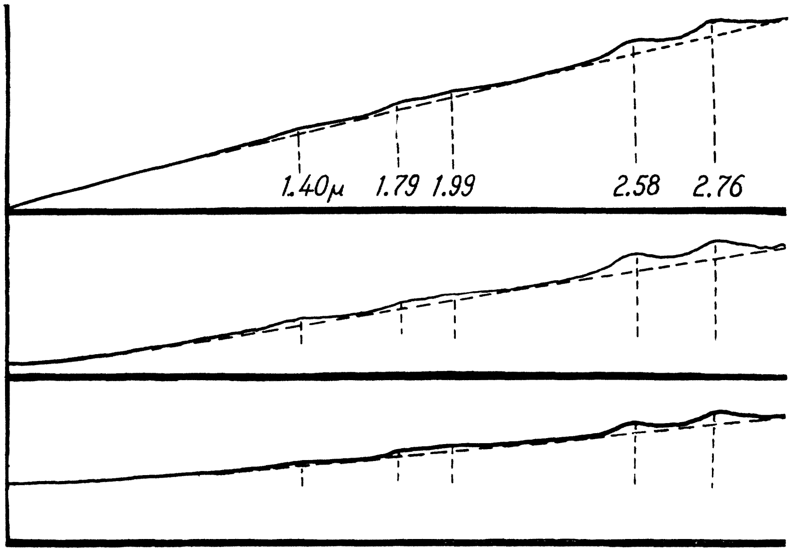

Fig. 2. Emission spectrum of the Bunsen flame obtained with quartz prisms. The slope of the records was produced by the galvanometer zero shift.

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[5] Paschen, Ann. der Phys. und Chem. **52,** 209 (1894).

The emission bands of the present investigation agree, in general, with those observed by Paschen, except that no maximum was observed corresponding to his 2.84μ value, and the 1.99 peak is identified with $CO_2$ instead of with water vapor.

Fig. 3 shows the Bunsen flame emission spectrum as obtained when two rock salt prisms were used in place of the quartz pair. Since the dispersion of rock salt in the region of 2.7μ is only one tenth of that of quartz, the 2.58μ water vapor band and the 2.76μ carbon dioxide band appear as a single unresolved maximum. It may be pointed out that when reference is made to the 2.7μ emission band of the Bunsen flame it is almost always attributed to carbon dioxide alone, whereas Fig. 2 shows that water vapor and carbon dioxide contribute almost equally to this emission. Fig. 3 shows the bands of shorter wave-lengths unresolved with a maximum at about 1.9μ.

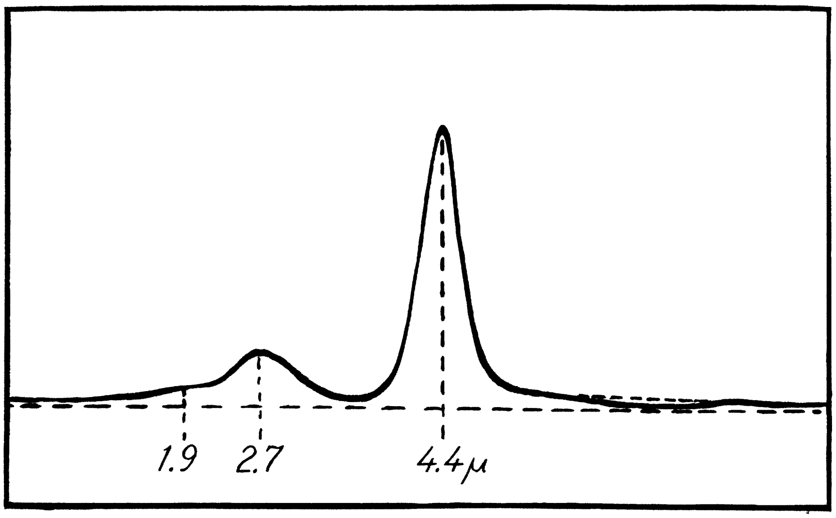

Fig. 3. Emission spectrum of the Bunsen flame obtained with rock salt prisms.

The 4.4μ region of emission occurs as a band of considerable symmetry although it is possible that absorption due to a protective varnish on the prism faces may have modified the curve to some extent. This varnish was the solution of pyroxylin in amyl acetate used by Adam Hilger, Ltd. Although the energy distribution curve is only slightly modified when the light passes through two layers of this varnish, deep absorption bands at 3.4μ and 6.7μ, characteristic of practically all organic materials,[6] do occur when the light traverses eight layers, as it does in this case.

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[6] Coblentz, loc. cit.[4]

The latter band appears in Fig. 3 as a broad minimum of transmission in the continuous black body radiation[7] of the flame.

Barker[1] has shown by taking account of the reversal due to absorption, that the $4.4\mu$ emission band is double with maxima at 4.225 and $4.38\mu$. He also found the corresponding absorption band double with maxima at $4.22\mu$ and $4.28\mu$. These two doublet separations are consistent with the formula[8]

$$\sqrt{T}\cdot\lambda_1\lambda_2/(\lambda_1-\lambda_2)=\text{a constant}$$

which connects such separations $(\lambda_1-\lambda_2)$ with the absolute temperature $T$, on the assumption that the temperature of the Bunsen flame is about 2000°K. Féry[9] has determined this temperature with an optical pyrometer and found it to be 2144°K, while Schmidt's[10] determination was somewhat lower, 1913°K.

If the primary separation of the double doublet found by Barker[1] at $2.7\mu$ were a regular infrared doublet of the Bjerrum type, the corresponding emission doublet, calculated from the above equation, would have a wave-length separation equal to the total spacing between the $2.58\mu$ water vapor and the $2.76\mu$ carbon dioxide bands.

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