

The InfraRed Emission and Absorption of the Carbon MonoxideOxygen Flame

S. Silverman, G. A. Hornbeck, and R. C. Herman

Citation: *The Journal of Chemical Physics* **16**, 155 (1948); doi: 10.1063/1.1746809

View online: <http://dx.doi.org/10.1063/1.1746809>

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due to the formation of the hydrogen film on iron and the continued rise of potential at lower concentrations indicates the continued but slower formation of the film.

The following observation is a significant support to our theory. An iron electrode, which had been kept unused for some years, took about 10 seconds of chemical action before gaining passivity in acid, 41.4 percent by weight, while the same iron, with its surface renewed by having it abraded with emery-cloth, took about 25 seconds. According to previous theories of passivity, this fact is due to the formation of a thin invisible film of iron oxide or of adsorbed oxygen on the old surface of iron. The potential measurement of the cell showed, however, a higher potential when the electrode of old iron surface was used than that obtained for the use of the fresh surface. In the older theories, the relative magnitudes of the potentials should have been in the opposite order. In our view, the greater potential of the cell for the older surface of iron was due to its adsorption of some hydrogen film from the atmosphere, which helped the iron to gain passivity in the dilute acid.

Many other phenomena associated with passivity are easily explained by the proposed mechanism. For example, the corroding action of halides is due to the affinity of the halogens for hydrogen, resulting in destruction of the film and so of passivity.

Details of the experimental data and application of the concept to behavior of stainless steels will be published elsewhere.

* Now at Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts.

** Now at Indian Standards Institution, New Delhi, India.

¹ For a review see Evans, *Metallic Corrosion, Passivity, and Protection* (Edward Arnold and Company, London, 1946); Uhlig and Wulff, *Am. Inst. Min. and Met. Eng.* 135, 494 (1939).

² R. Parshad, *Nature* 154, 178 (1944).

The Infra-Red Emission and Absorption of the Carbon Monoxide-Oxygen Flame*

S. SILVERMAN, G. A. HORNBECK, AND R. C. HERMAN
Applied Physics Laboratory, The Johns Hopkins University,
Silver Spring, Maryland

December 5, 1947

RECENTLY developed combustion engines, such as rockets and jet-engines of various types, have led to a renewed interest in the infra-red emission of flames, explosions, and combustion reactions in general. Numerous investigators, beginning with Julius and Paschen in the 1890's have studied the infra-red emission of different flames and hot gases.¹ The mission bands corresponding to the well-known absorption bands of the H₂O and CO₂ molecules were observed in the Bunsen flame in the region from about 1 to 12 μ . Until recently² the only observation of radiation in the longer wave-length region, from about 10 to 20 μ , was made by Rubens and Aschkinass³ in 1898, who found emission throughout that region from both the Bunsen flame and hot CO₂. Subsequently, investigators of the CO-oxygen flame⁴ reported the strong emission bands of CO₂ at 2.8 and 4.4 μ but failed to observe the fundamental at 14.95 μ .

The CO-oxygen flame has been studied to determine, if possible, the vibrational excitation of the CO₂ molecules

formed in this reaction. The flame employed in these investigations was obtained by burning a mixture of CO and O₂ in an ordinary torch. The CO was commercial grade and contained as its chief impurities about 1.5 percent each of H₂ and N₂, but no H₂O emission was observed in the infra-red. The iron carbonyl was removed from the CO in the usual manner. The instrument used was a Perkin-Elmer infra-red spectrometer with NaCl or KBr optics. It was flushed continuously with dry N₂ to minimize atmospheric absorption. The receiver was a bolometer using chopped radiation at 10 cycles/sec. with tuned amplification for drift-free recording purposes.

The emission spectrum of the CO-oxygen flame shows in addition to the peaks previously observed a number of rather weak emission bands between about 10 and 20 μ . The two strongest bands lie at 667 and 721 cm⁻¹, and agree to within about 1 cm⁻¹ with the transitions (01'0 \rightarrow 000) and (10'0 \rightarrow 01'0) of the CO₂ molecule in the ground electronic state. There are other bands in this region as shown in Fig. 1. Relative to the 4.4 μ band the intensities of the bands are quite low and it is not surprising that some earlier workers were unable to detect them. We have also repeated the study of the emission of hot CO₂ gas streaming from a furnace at about 1400°K. The emission spectrum is compared to that of the flame in Fig. 1.

To determine the absorption spectrum of the flame, radiation from a Globar was modulated and passed through it. In this way the emission from the flame itself is eliminated except for random intensity variations. Absorption bands are found at 2.8, 4.4, 14.1, and 14.95 μ of which only the two fundamentals are strong.

Further work on the CO-oxygen and other flames is being conducted and a more complete report will be made in the future. We wish to express our thanks to Dr. E. K. Plyler of the National Bureau of Standards who has shown us the results of similar studies on the Bunsen flame² and who reports finding the long wave-length bands of CO₂.

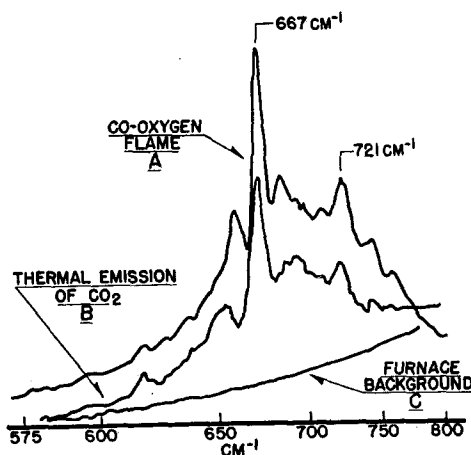


Fig. 1. Curve A: Emission from CO-oxygen flame in 15 μ region. Slit width = 0.3 mm. Curve B: Thermal emission from hot CO₂, uncorrected for background radiation from furnace, which is shown separately in curve C. Slit width = 0.5 mm. All the curves were obtained with a KBr prism and are unsmoothed for noise variations; the maximum noise is about 2 percent of the peak deflection.

We are also indebted to Mr. B. W. Bullock for valuable help in experimental matters. In conclusion we express our appreciation to Professor D. M. Dennison and Dr. E. O. Salant for their interest and many valuable discussions.

* The work described in this letter has been supported by the Bureau of Ordnance, U. S. Navy, under Contract NOrd-7386.

¹ For an extensive bibliography, see Jean Lecomte, *Le Spectre Infrarouge* (Les Presses Universitaires de France, Paris, 1928), and A. G. Gaydon, *Spectroscopy and Combustion Theory* (Chapman Hall Limited, London, 1942).

² E. K. Plyler, J. Opt. Soc. Am. **37**, 984A (1947).

³ H. Rubens and E. Aschkinass, Wied Ann. **64**, 584 (1898).

⁴ W. E. Garner and C. H. Johnson, Phil. Mag. **3**, 97 (1927); C. R. Bailey and A. H. Lih, Trans. Faraday Soc. **25**, 29 (1929).

A Cylindrical Model for the Small Soap Micelle*

WILLIAM D. HARKINS

George Herbert Jones Chemical Laboratory, University of Chicago,
Chicago 37, Illinois
December 16, 1947

THE model presented here (Fig. 1) is based on extensive papers on x-ray relations by Mattoon, Stearns, and Harkins,¹ and on a great deal of other work by Corrin, Oppenheimer, Mittelmann, Herzfeld, Roginsky, and Lind.

A quotation from a Cambridge University Symposium² (1947) is as follows:

There are different schools of thought on these matters, for example McBain postulates two types of micelle, "ionic" and "neutral," Hartley only one, the "spherical" ionic micelle. The latter view is now generally accepted, and will be followed here.

McBain's views are expressed more accurately in his 1942 review.³ His ionic micelle is spherical (adopted by Hartley) and his neutral micelle identical with Stauff's "Grossmizellen" or lamellar micelles.

Soap micelles are:

1. Small.

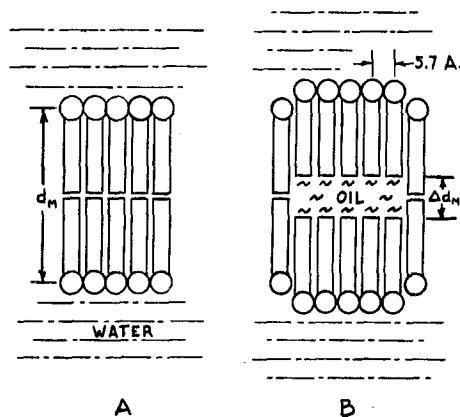


FIG. 1. Highly idealized cross section of a soap micelle. A. Without solubilized oil. B. With solubilized oil. The solubilization of an oil is found to increase the number of soap molecules in the micelle. Although a cylinder seems to represent most of the properties of the micelle as now known, it is imperfect in that it represents too large an interface at the side between hydrocarbon groups and water. Thus it seems not improbable that a model which lies between a cylinder and a cylindrical type of spheroid may be found to more perfectly represent the energy relationships. This would amount to a distortion of the side of the cylinder by means of which polar groups cover to some extent the non-polar hydrocarbon chains.

2. Not spherical and exhibit a thickness, as measured by a new x-ray *M*-band,^{4a} equal to the double length of the molecule.

3. This thickness is increased by the solubilization of a non-polar oil, but not by alcohols or amines.

4. When a salt is added the critical micelle concentration is decreased, the micelle size increased by increase in the diameter of the cylinder, and the principle of ionic strength and Debye-Hückel theory becomes invalid (Corrin and Harkins⁴).

5. The number of soap molecules per micelle is increased by solubilization of an oil and by long chain alcohols and amines.

By diffusion Hartley⁵ found the cetyl pyridinium chloride micelle to be small and to contain about 70 molecules. Our x-ray work on different detergents indicates sizes of this order, but both smaller and considerably larger.

Our earlier x-ray work appeared to favor the lamellar model of McBain and German investigators,^{3b,c} which consists of 5 or 6 large double layers of soap with interlayers of water of definite thickness (τ) as calculated from our data for potassium myristate.

After a long and intensive study, in an endeavor to find a mechanism which would control the interlayer or "bound" water in this way, the writer concluded that there is no such mechanism, and that these water layers are non-existent, but instead each double layer of molecules is a micelle and moves *freely* as a large "molecule" through the solution, until a second critical concentration (*ca.* 7 percent for potassium myristate) is reached. Above this concentration each double layer is a micelle, but the micelles now come closely enough together to restrict their motion (libration or rotation) so that above this concentration the x-ray *I*-band appears. This is related to the distance between the micelles.

Calculations of the thickness (τ) of the oil layer solubilized by the micelle, as made by the writer, proved incorrect the conception of this process as related to the lamellar model. Those who developed this model assumed (McBain's review, p. 124) that the increment (Δd_I) in the long spacing due to the oil gives the thickness of the oil layer. The mean thickness (τ) should equal the volume of oil in the micelles divided by the area of the large double soap layers, which is known, since each pair of molecules occupies 28 sq.Å. In calculations for *n*-heptane, triptane, and ethyl benzene the mean thickness (τ) was found at all

Percent soap	Water layer thickness τ in Å
8	34
10	31.7
15	26.3
20	22.5
25	19.6
30	17.2
35	15.2

concentrations of the oils to be only 0.4 as large as Δd_I . For example, for 3.5 percent *n*-heptane in 25 percent potassium laurate $\tau = 5.5\text{Å}$ but $\Delta d_I = 13.6\text{Å}$ or 2.5 times larger than it should be. It was concluded that Δd_I is not the distance