The Infrared Emission Spectra of CO_2 and H_2O Molecules

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Nearly all the energy radiated from the Bunsen flame arises from transitions between the energy levels of the molecules of water vapor and carbon dioxide. In order to check the validity of various theories of combustion, it is highly desirable to know the relative amount of energy which is radiated during the various transitions. In Gaydon's book, *Spectroscopy and combustion theory*, the suggestion is advanced that the energy radiated by the flame may arise from chemical rather than thermal processes. This suggestion is based, in part, on the uncertainty of the existence of certain emission bands in the 15-μ region of the infrared spectrum which should be produced by allowed energy transitions of the CO_2 molecule. Many investigators have not been able to detect radiation in this region. Actually, energy was observed in the infrared region of 15 μ by Rubens and Aschkinass (*1*) in 1898. They observed the energy from the Bunsen flame and also from heated carbon dioxide gas. Their studies on the emission of water vapor and CO_2 were of high quality, but because other workers failed to find sufficient energy for measurement in the 15-μ region, their experimental data have not been fully accepted.

During the past two years the Radiometry Unit of the National Bureau of Standards has been engaged in a study of the emission of infrared radiation from flames. This study is being conducted by the writer and other members of the staff. In the work at the Bureau the CO_2 radiation at 15 μ has been detected in the Bunsen flame, confirming the observations of Rubens and Aschkinass. The radiation consists of two emission bands occurring at 14 and 15 μ. These bands have been observed in the Bunsen flame while burning either manufactured or natural gas.

In addition to the two emission bands of CO_2, there are a number of emission lines of water vapor. It would not have been possible to identify the CO_2 bands from the array of bands in the 15-μ region if the emission of CO_2 had not been previously measured from the flame of burning CO in air. During the war the writer made the measurements of CO_2 radiation at the University of Michigan in connection with some confidential industrial work. In Fig. 1 these results are given for the first time. A grating with 1,200 lines/inch was used in the spectrometer and a KBr foreprism was used for separating the various orders. The graph indicates the amount of energy emitted by CO_2 produced by burning CO in the air. Two regions of the spectrum were found, 14 and 15 μ, where the energy was relatively intense. The 15-μ maximum has a side band on the short wave length side. These three regions of emitted energy, $(10^{\circ}0)$ to $(01^{1}0)$, $(02^{2}0)$ to $(01^{1}0)$, and $(01^{1}0)$ to $(00^{\circ}0)$, correspond to the transitions between known energy levels of the CO_2 molecule. These transitions produce bands with frequencies of 721 cm^{-1}, 668 cm^{-1}, and 667 cm^{-1}. The transition $(10^{\circ}0)$ to $(01^{1}0)$ shows that one of the energy levels of the inactive frequency of CO_2 changes at the same time as an active frequency, and radiation occurs. This inactive frequency may also lose energy by other transitions and collisions of the molecule with others. Some energy was observed in the entire region from 13 to 17 μ. However, as stated above, the two strongest regions of radiation were observed at 14 and 15 μ. There are other allowed transitions between energy levels which produce bands in this region. Also, it may be possible to find a band at 647 cm^{-1} for the $C^{13}O_2^{16}$ molecule.

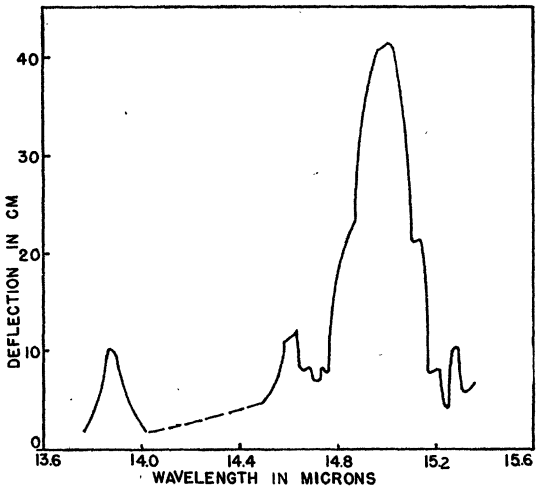

FIG. 1. The infrared emission of the CO_2 molecule in the regions of 13.9 and 15.0 μ.

Why were Rubens and Aschkinass able to observe this radiation of the CO_2 molecule at 15 μ, and, up to the present time, other observers have not been able to do so? The answer is that Rubens and Aschkinass used a KCl prism, which does not absorb in the 15-μ region. The absorption of a NaCl prism reduces the energy so much that it is difficult to detect the small amount of transmitted energy. Others could easily have observed the CO_2 radiation had they used a KCl or KBr prism. This was discussed in a paper by the writer, read before the Optical Society of America meeting in Cincinnati, October 23–25, 1947, and slides were shown comparing the energy in the 15-μ region as measured with NaCl and KBr prisms.

Considerable additional experimental data have been obtained which will be reported in a paper scheduled to appear in the February issue of the *Journal of Research of the National Bureau of Standards.* These include certain bands which are attributed to hydrocarbons. In the region between 2.8 and 3.1 μ, 15 rotational lines, which were equally spaced and separated by 22 cm^{-1}, were observed. Many lines which are a part of the rotational spectrum of the H_2O molecule were observed in the region between 12 and 24 μ.

Reference

1. RUBENS, H., and ASCHKINASS, E. *Ann. Phys. Chem.*, 1898, **64**, 584.