

Note on the Theory of Ethylene

Rodolfo H. Busch

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evaluated in the usual manner by subtracting the background intensity from the line intensity as evaluated from the graph. In the special case of the 123-cm^{-1} line, the apparent background was sketched in and the intensities of the Raman line at small increments of frequency were plotted against a uniform scale. This served to show that the background had been sketched in so that the line had the correct shape and was symmetric.

Indeed, a visual estimate of the polarization seemed to indicate that the 123-cm^{-1} line was depolarized, but careful determination of the value of ρ indicated that the line was polarized. The average value from five plates was 0.63, the average deviation from this value being 0.06. The 1206-cm^{-1} line was also found to be weakly polarized. Table I below lists the values of ρ for all the lines.

These data indicate that the high energy form of *s*-dichloroethane is C_2 and not C_{2v} .

¹ W. D. Gwinn and K. S. Pitzer, *J. Chem. Phys.* **16**, 303 (1948).

² Ta-You Wu, *Vibration Spectra and Structure of Polyatomic Molecules* (Edwards Brothers, Inc., Ann Arbor, Michigan, 1946), second edition, pp. 306-312.

³ R. Ananthakrishnan, *Proc. Ind. Acad. Sci.* **5A**, 285 (1937).

⁴ G. Glockler and H. T. Baker, *J. Chem. Phys.* **11**, 446 (1943).

Note on the Theory of Ethylene

RODOLFO H. BUSCH

*Facultad de Ciencias Exactas, Físicas y Naturales, Perú 222,
Buenos Aires, Argentina
August 6, 1948*

IN a recent paper, Mulliken and Roothaan¹ use the semi-empirical linear combination of atomic orbitals, the molecular orbital method for some computations on the ethylene molecule. The purpose of this note is to direct the attention to another starting point in the double-bond problem, which is suggested by the following.

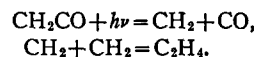
In its ground state, the carbon atom is divalent. To account for the fact that it is normally quadrivalent it must be postulated that in carbon compounds the atom is in an excited state with one *s* and three *p* electrons, all with unpaired spins.

There is no doubt of the correctness of this assumption in a great number of cases, but in the treatment of the double-bond problem there seems to exist another possibility, consisting in emphasizing the fact that the carbon atom does have the alternative of being two- or quadrivalent, and seek for the explanation of its chemical particularities by the systematic application of this argument.

The starting point may be the consideration of the problem of methylene, which is known to exist in two forms (Pearson, Purcell, and Saigh;² Burton, Davis, Gordon, and Taylor³), as the "molecule" CH_2 and as the short lived "radical" $>CH_2$. The energy required to raise the CH_2 molecule to the radical structure is about 15 kcal. (Long and Norrish⁴).

In the photolysis of ketene, investigated by Norrish, Crone, and Saltmarsh,⁵ the products obtained were

quantitatively carbon monoxide and ethylene. Ross and Kistiakowsky⁶ suggested the following mechanism:



This reaction may be the key for the theory of ethylene. We assume that the formation of ethylene is due to the interaction of the two forms of methylene:



If we label the two carbon atoms as $C(a)$ and $C(b)$, it follows that the system consisting of a "molecule" CH_2 and a "radical" $>CH_2$ at great distances is doubly degenerate:



The symmetry of this problem is in some respects similar to that of the hydrogen molecule ion; at shorter distances the interaction between the two forms may give rise to two solutions, one of which may correspond to the ethylene molecule.

The double bond might be thus interpreted as a kind of "excitation resonance." Using the data of the paper of Long and Norrish,⁴ the interaction energy results in the order of 130 kcal.

In view of the preceding discussion, we think it would be interesting to compute the interaction energy by the methods of quantum mechanics.

¹ R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.* **41**, 201 (1947).

² Pearson, Purcell, and Saigh, *J. Chem. Soc.* **1**, 459 (1938).

³ Burton, Davis, Gordon, and Taylor, *J. Am. Chem. Soc.* **63**, 1956 (1941).

⁴ Long and Norrish, *Proc. Roy. Soc. A* **187**, 337 (1946).

⁵ Norrish, Crone, and Saltmarsh, *J. Chem. Soc.* 1533 (1933).

⁶ Ross and G. B. Kistiakowsky, *J. Am. Chem. Soc.* **56**, 1112 (1934).

Addendum: Continuous Spectra and OH Absorption in Carbon Monoxide-Oxygen Explosions

G. A. HORNBECK

*Applied Physics Laboratory, The Johns Hopkins University,
Silver Spring, Maryland
August 3, 1948*

THE structural part of the CO-oxygen spectrum referred to as flame bands in a recent note¹ have been identified as belonging to the $^3\Sigma \rightarrow ^3\Sigma$ transition of the neutral oxygen molecule. The agreement of our measurements with those of Lochte-Holtgreven and Dieke² of the oxygen bands observed in a high tension arc by Runge are generally better than 0.2 cm^{-1} . Current measurements confirmed the existence of several bands of the $^3\Sigma \rightarrow ^3\Sigma$ transition in the spectra obtained from the CO-oxygen explosion. The bands found thus far are the (0-12), (0-13), (0-14), (0-15), and the (2-15). A detailed discussion of this spectrum as observed in CO-oxygen combustion will be reported in the near future.

¹ G. A. Hornbeck, *J. Chem. Phys.* **16**, 845 (1948).

² W. Lochte-Holtgreven and G. H. Dieke, *Ann. d. Physik* **3**, 937 (1929).