Measurements of C_2 Radicals in Flames with a Tunable Dye-Laser

K. H. Becker, D. Haaks, and T. Tatarczyk
Institut für Physikalische Chemie der Universität Bonn

(Z. Naturforsch. **29 a**, 829–830 [1974];
received March 19, 1974)

By laser excited fluorescence using extra-cavity techniques the $C_2(a^3\pi_u)$ radical concentration in an acetylene oxygen atom flame was measured in comparison to the emission intensity from $C_2(d^3\pi_g)$ radicals which are produced by chemiluminescent reactions.

It is known since many years that hydrocarbon oxygen flames produce a variety of diatomic and polyatomic radicals in their electronic ground states as well as in electronically excited states [1].

Experimental results of previous work indicate close links between some ground state radicals and chemiluminescence as well as chemi-ionisation processes in atom flames [2]. Ground state diatomics such as OH, CH, or C_2 have been measured by absorption spectroscopy in the flame zone [3]. The excited states of these radicals were analysed by their characteristic emission bands [1]. The optical absorption technique is somewhat difficult for determining radical concentrations under a wide range of flame conditions. It has been tried to overcome these difficulties by using mass-spectrometric techniques [4], but again without real success in the case of highly reactive diatomic radicals at low concentrations in diluted atom flames.

In studying some of the radical steps in flames one problem arrises from the lack of knowledge of the concentration ratio $(X^*)/(X)$ in different parts of the reaction zone where (X) and (X^*) mean the concentrations of a particular radical in its electronic ground state and in its excited state, respectively.

Recently is has been shown that resonance fluorescence excitation by a tunable dye-laser in extra-cavity operation is an excellent tool for measuring low concentrations of radicals such as OH [5, 6], CN [7], SH [8], or CH [9]. Work on Raman scattering in flames has also been reported [10]; in the case of C_2 radicals a resonance Raman effect or an incidental resonance excitation of C_2 by the argon ion laser line at 5145 Å was observed. Intra-cavity techniques for fluorescence excitation [11–13] as well as absorption measurements [14–16] have also been tested; both methods yield a high detection sensitivity for atoms and radicals but give no simple relation between the signal and the concentration of the optically active species.

In continuing our work on flame studies using the extra-cavity laser technique we have measured C_2 radicals in the acetylene oxygen atom flame. Figure 1 shows schematically the reaction chamber in which acetylene was mixed with atomic oxygen generated by a flow of molecular oxygen through a microwave discharge. Through an additional inlet hydrogen atoms could be added to the reaction system $C_2H_2 + O$. The reactants at concentrations in the mtorr region were diluted by argon up to a pressure of 1 torr. The pumping speed through the reaction chamber was about $10\,l\,s^{-1}$. The flashlamp pumped dye laser used for the fluorescence excitation was essentially the same as previously described [6]. With a 80 mg/l solution of coumarin-30-dye (Kodac) in ethanol, a tuning range from 4800 to 5250 Å was obtained. This range of laser output was appropriate for excitation of the $\Delta v = 0$ bands of the Swan system, $C_2(d^3\pi_g \longleftrightarrow a^3\pi_u)$. The fluorescence was focussed onto the cathode of a photomultiplier, RCA 1P28. To suppress the scattered laser light from the detection system, the region of the $\Delta v = -1$ bands was selected by interference filters. Table 1 gives the wavelengths of the band heads, λ_e, where the C_2 excitation was achieved, and the wavelength of the band heads, λ_f, where the fluorescence was measured.

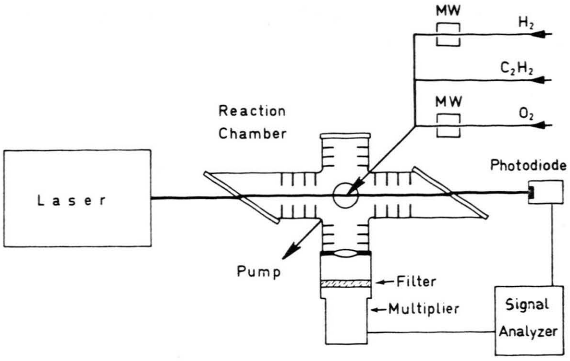

Fig. 1. The reaction chamber for laser excited fluorescence studies in atom flames.

Table 1.

(v', v'')	λ_e	λ_f
(0, 0)	5165	–
(0, 1)	–	5635
(1, 1)	5129	–
(1, 2)	–	5585
(2, 2)	5097	–
(2, 3)	–	5540

The signal-to-noise ratio of the fluorescence signal was sufficiently high for monitoring the exponential fluorescence decay after the laser pulse on an oscilloscope over a considerable length of time.

In our preliminary studies the intensity of the emission from the $C_2(d^3\pi_g, v=0)$ radicals formed by chemiluminescent reactions in the C_2H_2+O+H flame was compared with the laser excited fluorescence intensity which is a measure of the $C_2(a^3\pi_u, v=0)$ radical concentration. Figure 2 shows the relative concentration of the excited $C_2(d^3\pi_g, v=0)$ radicals formed in the flame plotted against the relative concentration of $C_2(a^3\pi_u, v=0)$. These measurements were made by changing the input rate of atomic hydrogen.

Similar dependences were found by the variation of other flame parameters. A detailed discussion of the dependence of the $(C_2^*)/(C_2)$ ratio on different flame conditions will be given elsewhere after more measurements have been completed. Preliminary results on the CH analysis in flames by laser excited fluorescence have also been obtained and will be used for further flame studies.

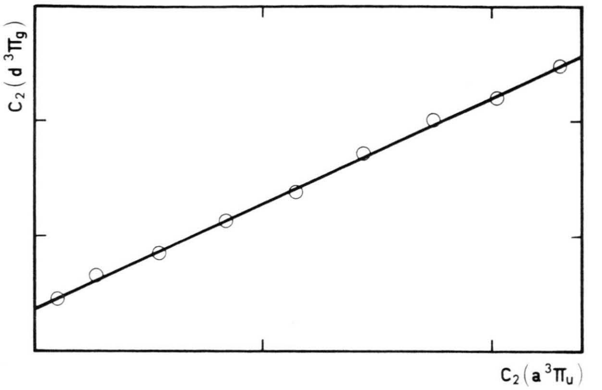

Fig. 2. A plot of the $C_2(d^3\pi_g, v=0)$ emission intensity formed by chemiluminescent reactions against the concentration of $C_2(a^3\pi_u, v=0)$ radicals in relative units.

This work was financially supported by the "Deutsche Forschungsgemeinschaft".

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[1] A. G. Gaydon, The Spectroscopy of Flames, Chapman & Hall, London 1957.

[2] K. H. Becker, D. Kley, and R. J. Norstrom, Twelfth Symposium (International) on Combustion, p. 405, The Combustion Institute, Pittsburgh 1969; K. H. Becker and D. Kley, Chem. Phys. Lett. **4**, 62 [1969].

[3] R. Bleekrode and W. C. Nieupoort, J. Chem. Phys. **43**, 3680 [1965].

[4] K. H. Homann, W. Lange u. H. Gg. Wagner, Ber. d. Bunsenges. **75**, 121 [1971].

[5] E. L. Baardsen and R. W. Terhune, Appl. Phys. Lett. **21**, 209 [1972].

[6] K. H. Becker, D. Haaks, and T. Tatarczyk, Z. Naturforsch. **27 a**, 1521 [1972]; K. H. Becker, D. Haaks, and T. Tatarczyk, Chem. Phys. Lett., in press.

[7] W. M. Jackson, XI. International Symposium on Free Radicals, paper no. 32, Berchtesgaden-Königssee, Sept. 1973.

[8] K. H. Becker, G. Capelle, D. Haaks, and T. Tatarczyk, to be publ.

[9] R. H. Barnes, C. E. Moeller, J. F. Kircher, and C. M. Verber, Appl. Optics **12**, 2531 [1973].

[10] C. J. Vear and P. J. Hendra, J. Chem. Soc. Comm., 381 [1972].

[11] L. M. Fraser and J. D. Winefordner, Anal. Chem. **43**, 1693 [1971].

[12] M. B. Denton and H. V. Malmstadt, Appl. Phys. Lett. **18**, 485 [1971].

[13] J. Kuhl and H. Spitschan, Opt. Comm. **7**, 256 [1973].

[14] N. C. Peterson, M. J. Kurylo, W. Braun, A. M. Bass, and R. A. Keller, J. O. S. A. **61**, 746 [1971].

[15] R. J. Thrush, H. v. Weyssenhoff, and J. S. Shirk, J. Chem. Phys. **55**, 4659 [1971].

[16] G. H. Atkinson, A. H. Laufer, and M. J. Kurylo, J. Chem. Phys. **59**, 350 [1973].