278. *The Carbon Monoxide Flame Spectrum under High Resolution.*

By J. H. CALLOMON and A. C. GILBY.

Under high resolution the carbon monoxide–oxygen flame spectrum shows dense rotational fine structure. No evidence has been found for a separate underlying true continuum, and the difference in appearance between the flame spectrum and the afterglow spectrum from the reaction between carbon monoxide and atomic oxygen is ascribed wholly to differences of temperature. Both spectra are consistent with a transition between an excited state of carbon dioxide in which the molecule is bent and the linear ground state, as previously postulated. A triplet upper state cannot be ruled out.

CARBON MONOXIDE burns in air with a characteristic bluish flame; when it is premixed with oxygen, it gives a bluish-white flame of great brilliance. The extensive spectrum has been much studied but is still not fully understood; the subject has been recently reviewed by Gaydon.[1,2] The questions are: (1) What is the emitting species? (2) What are the spectroscopic states involved in the process of emission?

Under low resolution the spectrum of the flame resembles a long continuum extending from 3000 Å or beyond with gradually increasing intensity into the visible region and, to judge from our observations with sensitized plates, diminishes but slowly into the infrared region to at least 8500 Å. It is hard to say precisely where the maximum intensity lies, but it is probably not far from 4800 Å. Superimposed is a banded structure of low contrast and great complexity. A part of the spectrum is shown in Plate A. The extent of the spectrum, the position of the maximum, and above all the ratio of banded to apparently continuous components—the contrast—can be varied widely by changing conditions in the source. Thus, whereas Gaydon [2] estimates the banded structure to account for only 5% of the intensity of the light emitted from normal flames, contrast is improved in low-temperature flames; [3] and the same spectrum apparently free from continuum is emitted as an afterglow during reaction between carbon monoxide and atomic oxygen.[4]

The chemical evidence leaves little doubt that the emitter of the banded structure is carbon dioxide, for although the flames seem to require traces of hydrogen or moisture to maintain themselves, and almost always emit the spectra of OH, the reaction between carbon monoxide and atomic oxygen occurs in the complete absence of hydrogen.[4] There remains the question of the continuum. Two possibilities arise: that the continuum is only apparent, the result of dense, unresolved fine structure; or that it is real in the spectroscopic sense, arising from a transition to, or from, at least one unbound, unquantized continuous state. The former view was favoured by Kondratiev,[5] while Gaydon has supported the latter.[1,2,4] That the emitter is again most probably carbon dioxide was

---

[1] Gaydon, "The Spectroscopy of Flames," Chapman and Hall, London, 1957.

[2] Gaydon, "Spectra of Flames," in "Advances in Spectroscopy," ed. H. W. Thompson, Interscience Publ., Inc., New York, 1961, Vol. II, pp. 23—56.

[3] Hornbeck and Herman, Nat. Bureau Stand. Circular No. 523, 1954, p. 9.

[4] Broida and Gaydon, *Trans. Faraday Soc.*, 1953, **49**, 1190.

[5] Kondratiev, *Z. Physik*, 1930, **63**, 322.

shown by Kaskan,[6] who found that the intensity of emission of the continuum, as measured at a wavelength between two members of the banded structure, seems to follow the product [CO][O] according to the law of mass action.

To try to test these possibilities we have photographed the spectrum of the flame under high resolution.

EXPERIMENTAL

The source was a stoicheiometric flame of premixed carbon monoxide and oxygen from commercial cylinders, maintained on a slit-burner 46 cm. long and *ca.* 0·4 mm. wide. A flow-rate of 10 l./min. produced a steady flame with a uniformly luminous cross-section about 2 mm. in diameter. The flame was viewed end-on and its spectrum photographed in an Ebert grating spectrograph with a resolving power of 150,000 (0·14 cm.$^{-1}$ at 4700 Å). Source and spectrograph were matched with a two-lens condensing system [7] to make the luminous volume fill the acceptance angle of the spectrograph along the entire length of the flame. Selected parts of the spectrum were photographed between 4000 and 5800 Å on Kodak Oa-D plates with exposures of 0·5—1 hr. A reference spectrum from an iron arc was superposed. Densitometer traces were obtained with a Joyce–Loebl Mk III Microdensitometer, scanning spectra over a width of 4 mm. with effective slit width of 8 μ (against the spectral slit width of 50 μ), and recording plate-blackening directly in units of optical density.

DISCUSSION

The appearance of the spectrum under high resolution is illustrated in two selected regions in Plates B and C, the former chosen to coincide with what appears as a sharp edge under low resolution, the latter falling in a rather featureless part; but it looks much the same elsewhere. The points to note are (i) there is dense, unanalysably complex rotational fine structure throughout; (ii) the contrast in this fine structure is greater (*ca.* 15%) under high resolution than is that of the band structure seen under low resolution (5—7%); (iii) the fine structure is equally well developed in regions which, under low resolution, lie " between " bands, at density minima. Intensities at such places are therefore no specific measure of the " continuum." The high-resolution spectra do not in themselves rule out possible superimposed self-absorption,[8] but grating photographs of a xenon arc (colour temperature 6000°c, exposure 1 min.) taken through the whole length of the flame showed no signs of any.

We conclude that, in fact, the carbon monoxide flame spectrum consists probably wholly of dense, only partly resolved rotational fine structure, and that the presence of a true continuum remains to be demonstrated.

The postulate of a real continuum on the lines put forward by Gaydon, in which the upper state is repulsive, seems to us to create two difficulties. The first is that banded and continuous parts of the carbon monoxide flame spectrum must then represent two separate electronic transitions with precisely the same intensity contours and relative intensities throughout. Although not impossible, this seems highly improbable, especially in extensive systems in which, by the Franck–Condon principle, the potential curves of the combining states differ considerably. The second difficulty is theoretical. The question of emission continua has been discussed by Herzberg.[9] The point is that the effective " collision time " between two bodies along a repulsive potential curve is very much shorter than the mean radiative life-time of even a strong spectroscopic transition—the ratio is *ca.* 10^{-5}—and molecule formation through radiative deactivation of the " collision complex " is very improbable. It becomes wholly unimportant in the presence of competing radiationless processes of even only the most moderate efficiency. One such process always possible in molecular gases is deactivation in three-body collisions, the relative efficiency of which increases with pressure. Thus, as Herzberg points out, recombination continua are expected to be observable only in special circumstances, *e.g.*, from atomic gases and/or at low pressures; moreover, they are rapidly quenched by increasing the pressure, whereas the observed intensity of the alleged continuum in the carbon

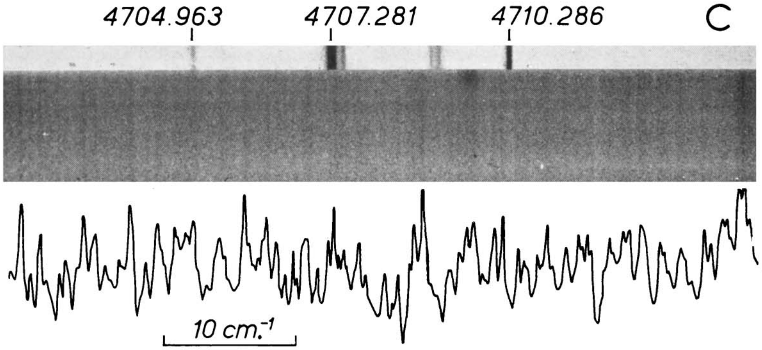
---

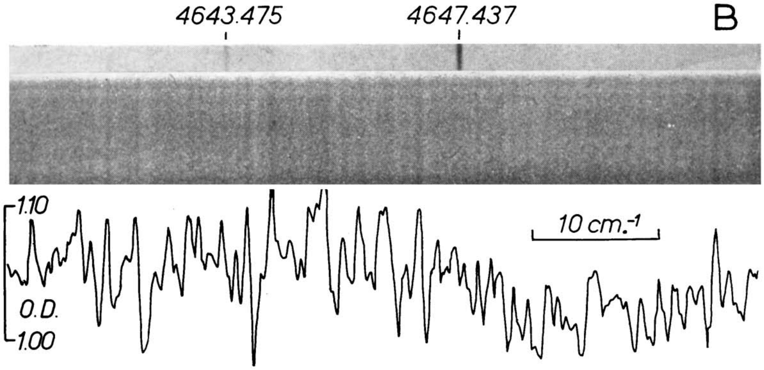
[6] Kaskan, *Combustion and Flame*, 1959, **3**, 39.

[7] Callomon, *Canad. J. Phys.*, 1956, **34**, 1046.

[8] Knipe and Gordon, *J. Chem. Phys.*, 1955, **23**, 2097.

[9] Herzberg, " Spectra of Diatomic Molecules," D. Van Nostrand, Princeton, 2nd edn., 1950, pp. 400—402.





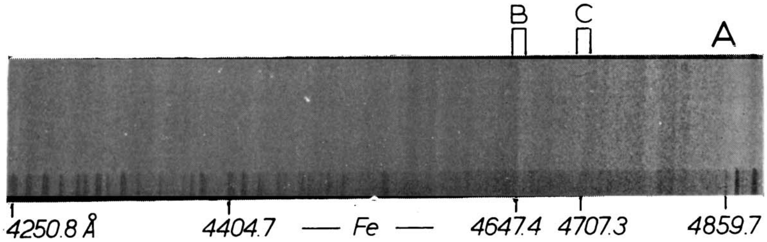


Plate A. Part of the carbon monoxide flame spectrum under low resolution, photographed on a small constant-deviation glass-prisms spectrograph. The fall in intensity at 4800 Å reflects the changing sensitivity of the photographic emulsion.

Plate B. Grating spectrogram near 4647 Å, in a region showing a sharp feature under low resolution. Densitometer-tracing with optical density scale relative to blank part of the same plate; Kodak Oa-D emulsion, $\gamma = 1{\cdot}5$.

Plate C. Grating spectrogram near 470 Å, in a region nearly featureless under low resolution.

monoxide flame spectrum increases with pressure, reaching both nearly its maximum relative intensity of 100%, and absolute intensity of *ca.* one quantum per 10^2 molecules of carbon dioxide formed,[10] at one atmosphere.

There seems no obstacle in the way of interpreting the afterglow spectrum, which is emitted during the reaction between carbon monoxide and atomic oxygen, and which is the same as the banded part of the flame spectrum, much as was done by Gaydon [11] and Walsh,[12] as a transition between two states of carbon dioxide, in one of which the molecule is linear, while in the other it is bent. Gaydon postulated the linear state as the ground state of the molecule, to which the transition occurs, thereby accounting for the extent of the spectrum and the similarity, although not coincidence, between some of the observed frequency intervals and ground-state fundamentals. This lack of coincidence led Walsh to prefer an interpretation in which the transition is between two excited states, but this may be ruled out on energetic grounds. The reaction in the afterglow is between carbon monoxide and atomic oxygen, the former being definitely in its ground state. If the oxygen atom is also in its ground state, ^3P,

$$\mathrm{CO},\ X^1\Sigma^+ + \mathrm{O},\ {}^3P + \mathrm{M} \longrightarrow \mathrm{CO_2}^* + \mathrm{M}$$

the energy of $\mathrm{CO_2}^*$ cannot lie at energies above the ground state very much in excess of the heat of dissociation ΔH_0 of this molecule, *i.e.*, 127 kcal.mole^{-1} (5·51 ev, equivalent to radiation of λ 2250 Å; and not to be confused with the dissociation-energy D_0, of 173 kcal.mole^{-1}). The emission spectrum is strong down to 3000 Å (4·1 ev), say, and if the transition terminated at an excited state this could not therefore lie much higher than 1·4 ev above the ground state. If the oxygen atoms were excited, ^1D, this limit would be raised to 3·4 ev. But 16 cm. of liquid carbon dioxide, equivalent to 160 metre-atmospheres of gas, are transparent [13] down to 2150 Å, and we find 280 metre-atmospheres to be transparent down to at least 2500 Å. It can, therefore, be said with confidence that there are no excited electronic states of carbon dioxide below 5 ev, for, from experience with other carbonyl compounds, singly or even doubly forbidden transitions should be already observable in only a few metre-atmospheres of gas.

Gaydon's original scheme is, in fact, in excellent accord with modern theory. The reaction as given in the scheme above is most likely to produce carbon dioxide in an excited state on grounds of spin-conservation, *i.e.*, one of the states of the first excited configuration [14] of $\mathrm{CO_2}$, $\cdots \pi_g{}^3.\pi_u$. In at least several of these states, including almost certainly the lowest, the molecule is expected to be bent.[12,15] Trial calculations show that in such a bent state the molecule will still approximate quite closely to a prolate symmetric top: the rotational energies will contain terms of the type $(A - \tilde{B})K^2$, where A, $\tilde{B}$ are rotational constants and $(A - B)$ will be of the order of 5 cm.$^{-1}$. Even at room temperature, levels will therefore be populated to quite high values of K. By the Franck–Condon principle, transition from such a bent state to the linear ground state will give rise to long progressions in at least the ground-state bending frequency, ν_2'', and the strongest bands, corresponding to the "vertical" transition, will terminate at quite high ν_2''. Corresponding to this quantum number there is, however, not one, but a whole manifold of vibrational levels: (i) because of vibrational degeneracy, leading to separate sublevels specified by the quantum number of vibrational angular momentum l, with energy terms $g.l^2$ (g is a small constant, 0·775 cm.$^{-1}$ for $\mathrm{CO_2}$) and $l = v_2$, $(v_2 - 2)$, $\cdots$ 1 or 0; and (ii) because of Fermi resonance between $2\nu_2$ and ν_1, their overtones and combinations. For parallel transitions, which are the ones to be expected, the selection rule is $(K' = l'') = 0$; and, for example, the transition $v_2' = 0 \longrightarrow v_2'' = 10$ could, depending on the temperature, contain up to 21 components, spread perhaps over 200—300 cm.$^{-1}$. Spectral intervals would be irregular, contain contributions of the type $[(A - \tilde{B})' - g'']K^2$, and bear little direct resemblance to ground-state fundamental frequencies. Failure to detect such frequency intervals is, therefore, no compelling reason for rejecting the ground state as the terminating state.

What is the effect of temperature expected to be on the appearance of such a spectroscopic transition? First, low-resolution plates of the afterglow spectrum show the band heads to have low contrast. This suggests that the J-structure is highly degraded so that the Q-branches

---

[10] Kondratjewa and Kondratjew, *Acta Physicochim. U.R.S.S.*, 1937, **6**, 748.

[11] Gaydon, *Proc. Roy. Soc.*, 1940, *A*, **176**, 505.

[12] Walsh, *J.*, 1953, 2260.

[13] Eiseman and Harris, *J. Amer. Chem. Soc.*, 1932, **54**, 1782.

[14] Mulligan, *J. Chem. Phys.*, 1951, **19**, 347.

[15] Mulliken, *Canad. J. Chem.*, 1958, **36**, 10.

produce no prominent features, nor do the *P*- or *R*-branches which turn in heads at low values of *J*, before reaching their maximum intensities. The effect of increasing temperature on such bands is simply to spread the bands and to reduce their contrast even further. Secondly, as mentioned above, levels of higher and higher K' become populated, rapidly increasing the number of separate bands which share the fixed total intensity. Thirdly, excited vibrational states would become populated: and the Franck–Condon distribution of transitions originating from $v_2' = 1,2 \cdots$ would be much wider than those from $v_2' = 0$. Fourthly, line widths in flames at between 1000° and 2000°K at atmospheric pressure are not negligible, the Doppler width of carbon dioxide alone being already *ca.* 0·1 cm.$^{-1}$ in the violet region. These four factors would, in our opinion, suffice to convert the relatively simple afterglow spectrum wholly into a pseudocontinuum looking just like the flame spectrum: it seems to us that all the differences can be ascribed to differences in temperature.

We have seen such a large temperature effect in another example, that of the visible emission spectrum of BO_2. The green colour of boron flames has now been shown to be due to an emission spectrum of this molecule,[16] as a transition between two states in both of which the molecule is linear, *i.e.*, a situation much simpler than the carbon monoxide flame spectrum. In absorption, at room temperature, the spectrum consists of few well-spaced bands, each with simple *P*- and *R*-branches, clearly resolved. The spectrum emitted by a relatively cool diffusion flame, such as that in air from burning coal-gas which has been bubbled through trimethyl borate, consists of a progression of sequences, each with many band-heads which are still sharp but of low contrast. The spectrum from the corona of a carbon arc with electrodes soaked in boric acid contains no sharp features, but appears as an undulating pseudocontinuum—the boric acid fluctuation bands.[17] The temperature in the corona is probably not very different from that in the carbon monoxide–oxygen flame. We have photographed the spectrum of the corona on the same grating as the carbon monoxide flame. As in the latter, fine structure is still partially resolved, but has resisted attempts to analyse it even in regions in which an analysis of the absorption spectrum in the cold was already available.

Carbon dioxide belongs to a class of small polyatomic molecules, probably not numerous, having ground states that cannot in first approximation dissociate into two ground-state fragments, and whose first excited state (or states), if stable in themselves, cannot therefore be predissociated and would be preferentially formed during recombination reactions. Internal radiationless deactivation of such an excited state by conversion to high vibrational levels of the ground state is also an improbable process for reasons analogous to the Franck–Condon principle, unless a high density of vibrational levels at the energy of conversion compensates for a very low Franck–Condon overlap. It may be additionally inhibited by spin selection rules, and hence, once populated, conditions for fluorescence from such excited states are exceptionally favourable, even if the transition probabilities are quite small. From rates of flow and the volume of the flame we can deduce a life-time of the reactant carbon monoxide in the luminous zone of *ca.* 2×10^{-3} sec., which allows us to set a lower limit on the radiative oscillator strength f of the emission of *ca.* 2×10^{-6}. The lowest excited state of carbon dioxide is expected to be a triplet state. Some idea of the f-value to be expected for a triplet–singlet transition in an oxygen-containing molecule may be obtained from the near-ultraviolet systems of formaldehyde. The first triplet–singlet transition is clearly observed in *ca.* 1 metre-atmosphere of the gas [18] (as it is also in the Cameron bands of carbon monoxide), and comparison with the adjacent singlet–singlet system [19] indicates that this corresponds to an f-value of *ca.* 1×10^{-6}. A triplet upper state in the carbon monoxide flame spectrum cannot therefore be ruled out.

The arguments relating to the dissociation of carbon dioxide apply equally to carbon disulphide. A discharge through this gives two emission spectra,[20] one of which has been unambiguously identified as due to CS_2^+. The other, however, was unanalysably complex and was only tentatively ascribed to the same emitter. Its appearance is in every way very much like that of the carbon monoxide flame spectrum, of which it might therefore well be the analogue. It is obtainable strongly at room temperature, and an attempt to correlate it with

---

[16] Johns, *Canad. J. Phys.*, 1961, **39**, 1738.

[17] Pearse and Gaydon, "The Identification of Molecular Spectra," Chapman and Hall, London, 2nd edn., 1950.

[18] Robinson and Di Giorgio, *Canad. J. Chem.*, 1958, **36**, 31.

[19] Callomon and Innes, *J. Mol. Spectroscopy*, 1963, **10**, Part 2.

[20] Callomon, *Proc. Roy. Soc.*, 1958, *A*, **244**, 220.

a specific absorption system of carbon disulphide might meet with more success than in the case of the carbon monoxide flame spectrum and the absorption spectrum of carbon dioxide.

Added in Proof. Clyne and Thrush[21] have recently described kinetic studies on the reaction between carbon monoxide and atomic oxygen at low pressures. The light emitted, *i.e.*, the carbon dioxide afterglow, depends on the concentration of the reactants in the same way as found by Kaskan[6] in the carbon monoxide–oxygen flame.

William Ramsay and Ralph Forster Laboratories,
University College,
Gower Street, London, W.C.1.

[*Received, October* 12*th*, 1962.]

---

[21] Clyne and Thrush, *Proc. Roy. Soc.*, 1962, *A*. **269**, 404.