

NOTIZEN

A New Continuous-Wave CO Chemical Laser from the Oxidation of Acetylene

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Continuous-wave stimulated emission resulting from the oxidation of acetylene has been observed. Thirteen vibrational transitions of the first overtone band of CO have been resolved. The mechanism for laser action is proposed.

Continuous-wave (cw) laser action in both the fundamental¹ and overtone bands² of CO, resulting from the oxidation of carbon disulphide has been reported. Pulsed stimulated emissions in the fundamental band of CO from the oxidation of C_3O_2 have also been observed³. We now wish to report on a new cw CO chemical laser in the overtone band from the oxidation of acetylene.

An internal mirror system was employed. The resonator cavity was one meter in length and the mirrors, each with a 3 m radius of curvature were gold plated. The downstream mirror had a 3 mm coupling hole with a CaF_2 window.

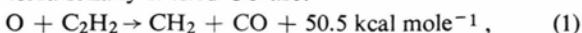
Atomic oxygen was produced either by means of a transformer discharge or a microwave discharge.

Under conditions of low partial pressures of acetylene (≈ 0.05 Torr) and of oxygen (1.0 Torr) with helium as a buffer gas at a partial pressure of 4.5 Torr, cw stimulated emission was observed in the first overtone band (2.3 – $2.8 \mu m$) of CO using an uncooled PbS detector coupled to a synchronous amplifier.

The overtone output was analysed spectroscopically with a 1 m Czerny-Turner monochromator. Lasing overtone transitions from $\nu = 14$ – 12 down to $\nu = 2$ – 0 were resolved.

Figure 1 is a comparison of the overtone spectrum obtained from the C_2H_2 – O_2 system with that obtained from the CS_2 – O_2 system⁴. There is a marked shift in the intensity distribution and it appears that in the oxidation of acetylene, CO vibrational levels up to $\nu = 14$ are populated as compared to $\nu = 16$ in the CS_2 oxidation. The spectrum is similar to that observed from the chemiluminescence of the acetylene oxidation⁵.

Mechanistic and kinetics studies of the oxidation have been reported⁶ and it appears that the major elementary reactions responsible for the production of vibrationally excited CO are:



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The elementary reaction (1) is rate determining. It has a rate constant of about $1.5 \times 10^{-13} \text{ cc molecule}^{-1} \text{ sec}^{-1}$ independent of pressure in the range 0.9 Torr to 9 Torr. Its activation energy is $< 1 \text{ kcal mole}^{-1}$. The subsequent reaction which yields stable products is much faster than the initial reaction. The heats of reaction

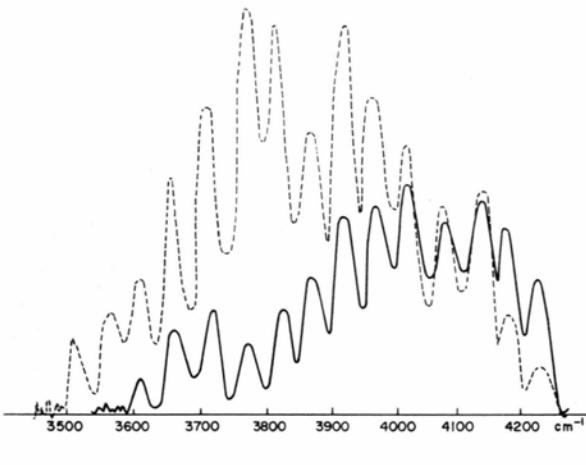


Fig. 1. Comparison of CO overtone spectra obtained from two distinct systems.

— Spectrum obtained from the system $O_2-C_2H_2$;
- - - Spectrum obtained from the system O_2-CS_2 .

were calculated from tabulated values of the thermodynamic properties of the participating species⁷.

The heat of reaction (2) is sufficient to populate vibrational levels of CO up to and including $\nu = 14$, provided all of the heat is converted to CO vibrational energy.

The exothermal energy release of the elementary reactions given above is of the same order of magnitude as in the case of the oxidation of CS_2 . The observed overtone spectrum, however, shows a very definite shift in the intensity distribution and the individual lines also have much lower intensities than in the case of the CS_2 – O_2 laser (Figure 1). This could possibly be ascribed to the following:

(a) The heats of reaction are distributed over many more reaction products and are converted to vibrations and translations of these, thus lowering the energy available for the excitation of CO.

(b) Vibrational deactivation of excited CO through collisions with other and a larger number of reaction products and intermediates.

Laser action was also observed to be more sensitive to changes in the total pressure than in the case of the

CS₂—O₂ laser. Provisional experiments seem to indicate that the maximum total pressure at which gain still exceeds collisional deactivation is much lower than with the CS₂—O₂ laser.

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