

Hancock G & Smith I W M. Quenching of infrared chemiluminescence. 1.

The rates of deexcitation of CO($4 < v < 13$) by He, CO, NO, N₂, O₂, OCS, N₂O, and CO₂. *Appl. Optics* **10**:1827-42, 1971.

[Dept Physical Chemistry, Univ. Chemical Labs., Cambridge, England]

Infrared chemiluminescence was observed from CO formed in the reaction: O+CS->CO+S. By observing how the CO overtone emission was quenched, rates were determined for the deexcitation of CO($4 < v < 13$). The results were compared with theoretical predictions and the operation of CO lasers discussed. [The SCI® indicates that this paper has been cited over 130 times since 1971.]

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"In 1969, one of us (G.H.) was a nervous new graduate student and the other (I.W.M.S.) an equally nervous research director of his first graduate student. We had decided to look for infrared chemiluminescence from some simple, exothermic chemical reactions. Our main goal was to understand the factors which lead to vibrationally excited products, especially in reactions not involving hydrogen halides. But that was also an era of intense interest in chemical lasers: they were frequently reported with their day of discovery prominently recorded.

"The CO laser based on oxidation of CS₂ had recently been discovered.^{1,2} We had doubts about the proposed mechanism, believing the excited CO to be produced in the reaction. O + CS₂ → CO + S. Nevertheless, this was not the first reaction from which we tried to observe its emission. Part of our failure, which may have been a blessing,

was due to a faulty detector. Once this was changed, we soon recorded a strong CO spectrum on mixing discharged O₂ with CS₂.

"After we had observed a spectrum, experimental improvements were straightforward. Our first objectives were to establish that the excited CO was indeed formed in the O + CS reaction and to find how the CO was distributed over its vibrational states. We can both clearly recall our dismay when, just before our first paper,³ a not dissimilar paper appeared. Our fear of being scooped rapidly passed when we discovered that the spectra had been misassigned and so the chemical mechanism had been misinterpreted.

"The measurements which formed the basis for our *Applied Optics* paper evolved quite naturally from our attempts to derive the initial CO vibrational distribution. It became clear that we could reach conditions where the CO only lost energy by radiating spontaneously at known rates. Because of this 'good behaviour,' changes in the emission spectra could be interpreted in terms of *collisional* energy transfer to added species.

"Why has the paper been so frequently cited? Well, it provided the first—and still the most extensive—body of data on relaxation from a wide range of states to a variety of collision partners.⁴ Furthermore, CO is laser active, not only in chemical lasers but also in the efficient CW electrical discharge laser. Our results helped in the modelling of these devices and indicated that additives might improve laser performance. Finally, the paper showed—for an important prototype—how rates of energy transfer change as anharmonicity brings neighbouring vibrational levels closer together.

"Since this paper was published, we have both used lasers increasingly in our research. As these are rarely inexpensive, it is salutary to be reminded that this apparently successful piece of research was performed with nothing more costly than a microwave discharge unit and a simple, home-built spectrometer. In terms of rate constants per unit of expenditure we have never done so well again!"

1. Pollack M A. Laser oscillation in chemically formed CO. *Appl. Phys. Lett.* **8**:237-8, 1966.
2. Gregg D W & Thomas S J. Analysis of CS₂-O₂ chemical laser showing new lines and selective excitation. *J. Appl. Phys.* **39**:4399-404, 1968.
3. Hancock G & Smith I W M. Infrared chemiluminescence from the reaction: O + CS₂ → CO + S. *Chem. Phys. Lett.* **3**:573-80, 1969.
4. Yardley J T. *Introduction to molecular energy transfer*. New York: Academic Press, 1980. 308 p.