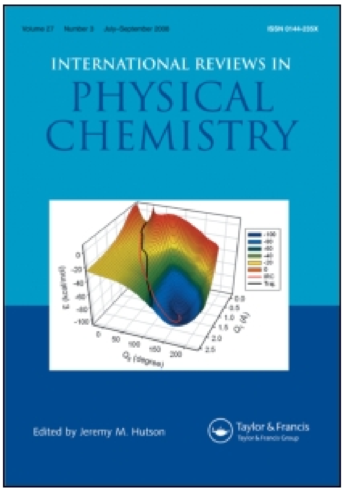

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Tricarbon monoxide. Theory and experiment

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Tricarbon monoxide. Theory and experiment

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The story of the investigation of a new small oxide of carbon—tricarbon monoxide, C_3O—presents an excellent example of the way in which theory and experiment can be interwoven. Prior to the studies of the Monash group the only appearance of tricarbon monoxide in the chemical literature appears to be a report of the probable formation of this oxide when diatomic carbon vapour is condensed in a cold carbon monoxide matrix (De Kock and Weltner 1971). An infrared band at 2241 cm^{-1} was attributed to C_3O and the attribution was supported by the appearance of bands of similar frequency when ^{13}C-enriched species and ^{18}O species were used in the matrix-isolation experiments. However, no subsequent more extensive investigation followed this short note.

The Monash interest arose from our studies of chemical processes in interstellar molecular clouds. In this galactochemistry carbon monoxide plays an important role as the most common interstellar molecule after H_2. An intriguing feature of galactochemistry is the existence of molecules containing long chains of carbon atoms in the form of cyanopolyacetylenes. Because of our laboratory studies (Brown *et al.* 1979, 1981, 1982, 1985 a) and in spite of unsuccessful interstellar searches (unpublished researches from NRAO, Kitt Peak and Onsala Space Observatories 1976) for longer-chain analogues of formaldehyde and ketene, both known interstellar molecules, we were led to the idea that there might be longer-chain versions of oxides of carbon that could arise in the interstellar medium.

Even at the elementary level of drawing out Pauling resonance structures one quickly recognizes that in close analogy with the concept of carbon sub-oxide as the 'big brother' of carbon dioxide there is a similar 'big brother' of carbon monoxide, namely C_3O (see figure 1). It is a fascinating comment on chemical history that although Linus Pauling (1960), in his textbook on valency, deliberates in detail on the electronic structures of CO_2, C_3O_2 and CO, he makes no reference to the remaining member of the quadruplet i.e. C_3O.

From these elementary considerations we were led to look in more detail at C_3O on the basis of *ab initio* molecular orbital calculations (Brown and Rice 1984). In parallel, there were continuing discussions with colleagues as to possible ways of generating this new oxide. Since some of the schemes involved a pathway via the initial formation of C_4O_2 we included this larger unknown oxide in the molecular orbital studies as a basis for judging some aspects of the feasibility of preparing C_3O in the laboratory. The results of these calculations provided, among other things, a prediction of the energy of formation of C_3O, an indication that it would not readily undergo unimolecular decomposition, and a predicted structure and dipole moment from which its microwave spectrum could be predicted with considerable accuracy (in the event the rotational constant B_0 was predicted to one part in 800). Armed with this highly

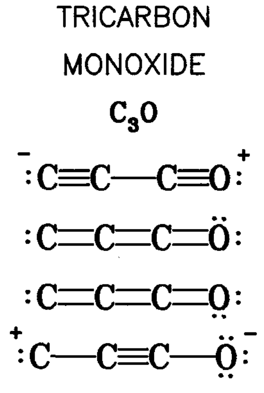

Figure 1. Resonance structures according to Pauling's prescription.

valuable insight and guidance from the side of chemical theory it made sense to focus on the experimental problem of generation and identification of this material.

The first successful generation of C_3O in the gas phase was based on the pyrolytic decomposition of a complex molecule related to Meldrum's acid (figure 2) (Brown *et al.* 1983). A number of lines of the spectrum of C_3O were identified and the dipole moment determined from the Stark effect on these lines. This spectral identification made it possible to search for alternative, rather simpler, precursors of C_3O and almost immediately it was found that fumaryoylchloride was a more convenient source of C_3O, especially for the generation of isotopically enriched versions which were needed in order to derive a precise molecular geometry from the spectroscopic constants (Brown *et al.* 1985 b). The structure so derived proved to be in close harmony with the predictions of molecular orbital calculations and confirmed the predictions that C_3O is a highly polar molecule. We might note that the direction of the moment predicted by theory is with the positive end at oxygen and the negative end at carbon, as might be inferred from the Pauling resonance structures. Of all the currently known oxides of carbon this is the only one with a dipole moment significantly different from zero!

In parallel with the laboratory studies of the spectrumof C_3O we were interested to discover whether this longer-chain oxide of carbon played a role in galactochemistry. Fortunately this could be explored theoretically by use of a computer model of galactochemistry of interstellar clouds that had been developed at Monash (Brown and Rice 1985). When the additional processes that could lead to formation and destruction of C_3O were incorporated in our model, a prediction of the time evolution of its

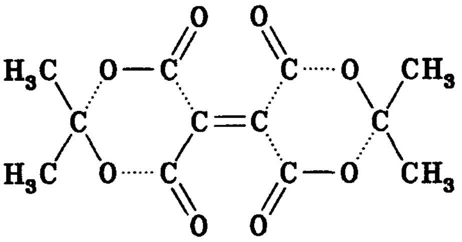

Figure 2. The pyrolytic fragmentation occurs where bonds are dotted, yielding acetone, CO_2, CO and C_3O.

concentration emerged (figure 3), implying that for cold interstellar clouds of typical age around 10^6 years it should be present in detectable amounts.

The experimental confirmation of this prediction followed very rapidly with observations of interstellar lines in the Taurus molecular cloud first at the NRAO 46 m telescope at Green Bank, West Virginia (Matthews *et al.* 1984), then at NRAO 12-m telescope at Kitt Peak, Arizona, at FCRAO at Quabbin, Mass., and on the NRO 45-m telescope at Nobeyama, Japan (Brown *et al.* 1985 c). The intensities of these different spectral lines of C_3O in the Taurus molecular cloud were fitted to an excitation model of interstellar molecules that has also been developed at Monash (see figure 4). This was consistent both with the physical conditions of the cloud that had been accepted on the basis of some previous line observations (temperature approximately 10 K, total hydrogen density about $10^4\ \mathrm{cm}^{-1}$) and also indicated a fractional abundance of C_3O in embarrassingly good agreement with the predictions of the galactochemical model. In this respect the interplay between theory and experiment was more a case of the experiments providing additional support for the reliability of the astrophysical theory of interstellar clouds, but it happens to be almost the only example of a prediction of the presence and quantity of an interstellar molecule in advance of the actual observations.

Subsequent work on C_3O has been the detailed study of its infrared spectrum by matrix isolation techniques (Brown *et al.* 1986) and the use of its microwave spectrum

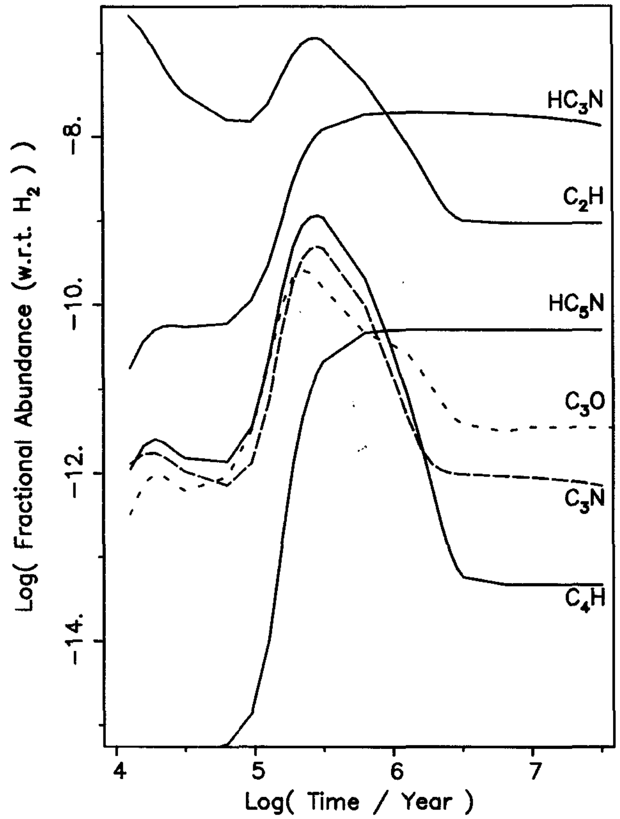

Figure 3. The time evolution of some molecular species in cold interstellar molecular clouds, according to the galactochemical model of Brown and Rice (1985).

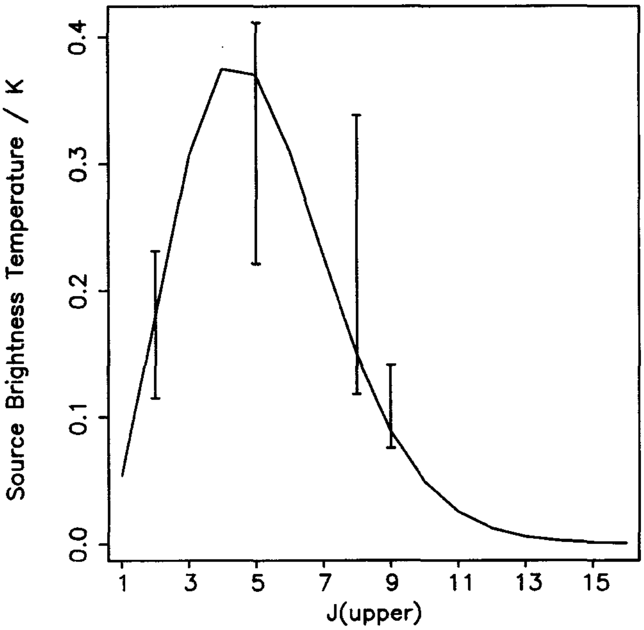

Figure 4. Intensities of observed interstellar lines of C_3O (indicated by vertical bars) in TMC1 and optimum theoretical intensity curve according to the model of Brown and Cragg, (Brown and Cragg 1985, Brown *et al.* 1985 c) for a cold cloud ($T = 10$ K) with a fractional C_3O abundance of $1{\cdot}4 \times 10^{10}$.

as a diagnostic for other methods of generation of this oxide. The infrared measurements are of interest because they have enabled us to identify with some precision three of the five fundamentals and to make use of *ab initio* molecular orbital calculations to understand the absence from our spectra of one of the stretch frequencies of the molecule. Figure 5 illustrates the infrared spectrum of C_3O and shows the presence of ν_1, ν_2 and ν_4 together with some weak bands from ^{13}C versions in natural abundance. Similar studies with isotopically enriched versions of C_3O have provided a full range of frequencies of all possible monoisotopically substituted and several disubstituted versions. A normal coordinate analysis has provided the full force field with one or two components having to be adopted from molecular orbital calculations of the force field. Perhaps the most interesting aspect of the infrared studies is that *ab initio* calculations of intensities predict that the lowest frequency stretch, ν_3, will have accidentally vanishingly small intensity—in harmony with its absence from our experimental spectra. One final point is that these infrared studies have confirmed that the original tentative identification (De Kock and Weltner 1971) of C_3O is correct. We have produced the ν_1 frequencies reported by DeKock and Weltner as part of the more complete infrared studies.

The study of this new oxide of carbon has now reached a relatively mature stage. The process has been one of very close interplay of several theoretical and matching experimental techniques. In the absence of such highly developed theories of molecular structure and of galactochemistry it is doubtful indeed whether such rapid progress could have been made in identifying and studying this interesting new small molecule.

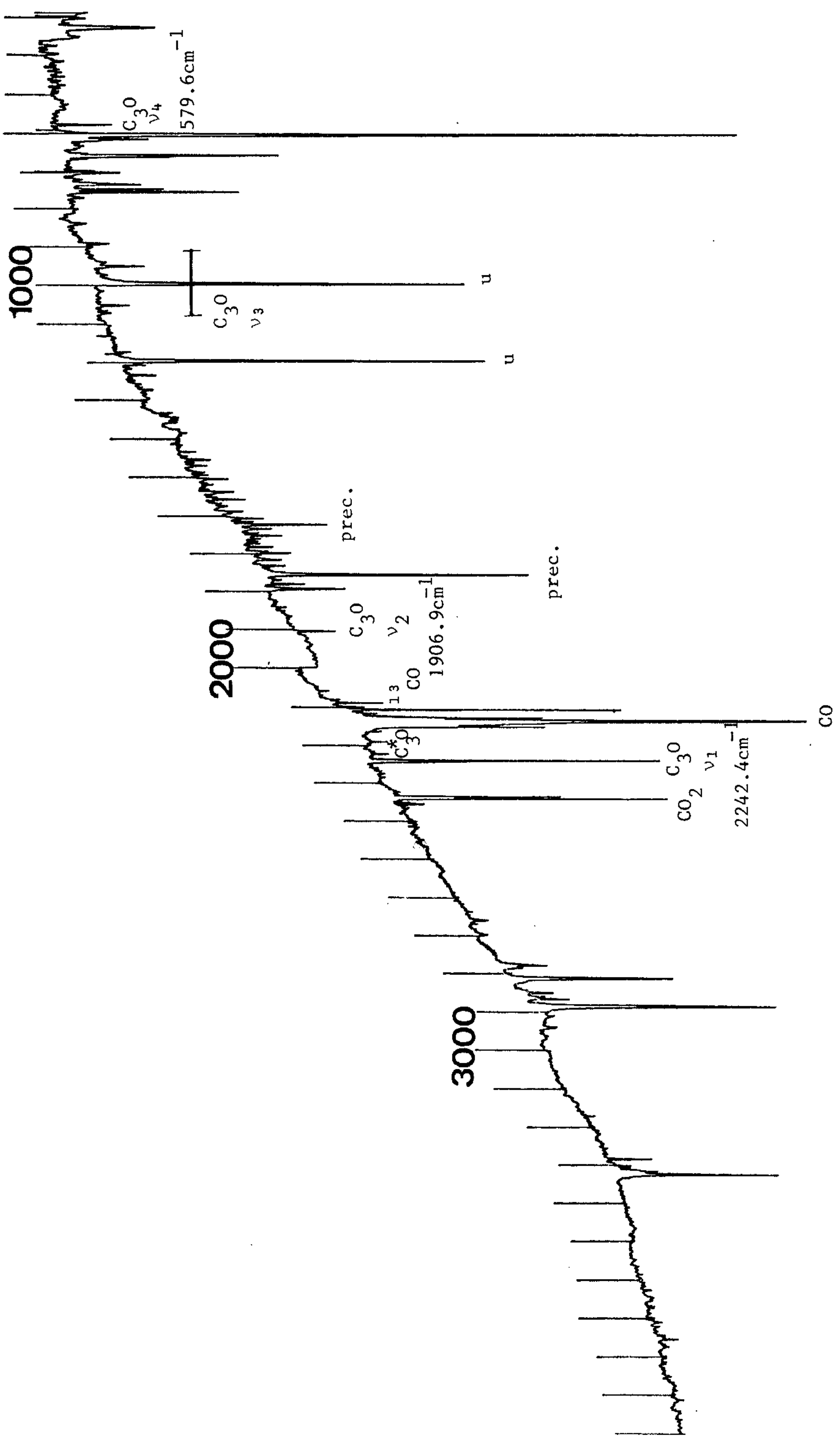

Figure 5. Infrared spectrum of C_3O deposited in an argon matrix at 15 K. Weak lines of less common isotopic forms of C_3O have been confirmed by studies with isotopic enrichment (Brown *et al.* 1986).

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