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Short Communication

The Ramansolution spectrum of tetraoxygen difluoride (O_4F_2)

D. J. GARDINER* AND J. J. TURNER
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)

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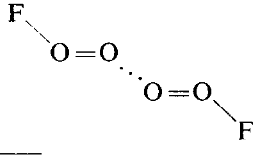
Tetraoxygen difluoride (O_4F_2), a red unstable solid m.p. 82 K, can be prepared by electrical discharge in an oxygen/fluorine gas mixture (O_2:F_2, 2:1) in a Pyrex vessel cooled to 77 K[1]. Because of its instability, information about its structure is limited. It is clear from ESR[2,3] and NMR[4] data in solution that O_4F_2 is in equilibrium with the radical O_2F. Infrared spectra[5,6] produced on allowing a low-temperature matrix (*e.g.* argon at 20 K) containing O_2F to warm slightly are consistent with $2O_2F \rightarrow O_4F_2$, the spectrum of O_4F_2 being very little different from O_2F.

We have now obtained solution Raman data for O_4F_2 by photolysing a low-temperature solution of oxygen difluoride (OF_2) in liquid oxygen at about 90 K.

The solution of OF_2 in O_2 (approx. 3:1 by volume) was prepared in a simple quartz still by methods previously described[3,7]; the Raman spectrum was obtained using a Coderg PH 1 laser instrument and showed clearly bands due to OF_2 and O_2. After photolysis with a Pyrex-filtered mercury arc (λ >320 mm) for some 15 min the solution was deep orange in colour[3] and the Raman spectrum obtained as shown in Figure 1. Compared with OF_2 the concentration of product was low. The vibrational data obtained in this and other relevant experiments are given in Table 1.

The closeness of the frequencies for ν(O–O–F) and ν(O–F) in matrix and solution suggests that the perturbing influence of the matrix or solution on the vibrational potential function is very small. Hence the position of the O–O stretching frequencies suggests that the species produced in solution is O_4F_2, not O_2F. It is striking, as has been noted before[5,6], that the degree of interaction between two O_2F radicals should only be sufficient to shift the O–O stretch by some 25 cm^{-1} and the other vibrations not at all. This is strong evidence that the O_4F_2 molecule is bonded through the oxygens in some manner:



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[*] Present address: Dept. of Chemistry, University of York, Heslington, York YO1 5DD (Great Britain).

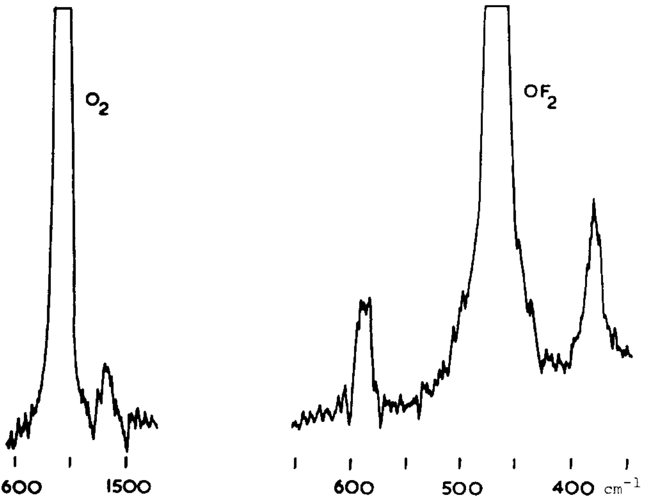

Fig. 1. Raman spectrum of photolysed OF_2/O_2 solution at approximately 90 K.

TABLE 1

VIBRATIONAL DATA FOR O_4F_2

Raman solution[a] (cm^{-1})	ρ_1[b]	IR O_4F_2 in argon 20 K[5,6] (cm^{-1})	IR O_2F in argon 20 K[5,6] (cm^{-1})	Assignment
376.8±1	0.6	376	376	δ(O–O–F)
584.6±1	0.5	586	586	ν(O–F)
1516.2±1	~0.7	1515	1590	ν(O–O)

[a] This work.

[b] $0 < \rho_1 < 0.75$ for polarized (symmetric) and $\rho_1 = 0.75$ for depolarized (asymmetric) bands.

It is interesting that there was no Raman evidence for O_2F in O_2 solution in spite of the fact that photolysed low-temperature solutions show very strong ESR signals due to the radical[3].

$$F_2 \rightarrow 2F$$
$$2O_2 + 2F \rightarrow 2O_2F$$
$$2O_2F \rightleftarrows O_4F_2 \qquad (1)$$

Presumably under the conditions of the present experiment the equilibrium (1) lies over to the right.

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