Solution Raman Spectrum and Normal-co-ordinate Analysis of Dioxygen Difluoride

By **Jeremy K. Burdett,***† **Derek J. Gardiner,** and **James J. Turner,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW
Richard D. Spratley and **Peter Tchir,** Department of Chemistry, University of British Columbia, Vancouver, Canada

Raman spectra of O_2F_2 in $CClF_3$ solution are reported for the first time. A vibrational assignment is proposed based on polarisation data. A reinvestigation of the vibrational-potential function and a calculation of the barrier height to internal rotation have been made.

THE i.r. spectrum of O_2F_2 was first observed using matrix-isolation techniques by Brown,[1] by Spratley *et al.*,[2] and by Arkell,[3] the latter two groups of workers being primarily concerned with the i.r. spectrum of O_2F. None of these workers, however, observed the complete spectrum of O_2F_2. Loos *et al.*[4] have recorded the complete i.r. spectrum of solid O_2F_2 and, in an earlier paper,[5] we reported the solid-state i.r. and Raman spectra and also the i.r. spectrum of O_2F_2 trapped in various matrices at 20 K. Noble[6] has carried out a normal-co-ordinate analysis of O_2F and Loos *et al.*[4] have undertaken one for O_2F_2 using these solid-state i.r. frequencies.

This paper describes Raman polarisation studies on O_2F_2 dissolved in $CClF_3$ at about 190 K. This work was mentioned in proof in a previous publication[5] and confirms an assignment of lower-frequency modes given therein which differs slightly from that of Loos *et al.*[4] Using this assignment, and solution-phase frequencies, we have reinvestigated the vibrational-potential function of this unusual molecule.

EXPERIMENTAL

Dioxygen difluoride was prepared by electrical discharge of a 1 : 1 $O_2 : F_2$ mixture at 77 K[7] and was purified by fractionation. The $CClF_3$ was supplied by I.C.I. Ltd. The solution of O_2F_2 in $CClF_3$ was prepared in a low-temperature still, originally designed by Ogden and Turner[8] for e.s.r. and n.m.r. studies. Solutions *ca.* 4 : 1 by volume of $CClF_3 : O_2F_2$ were obtained by methods similar to those previously described.[9]

Spectra were recorded on a Coderg PH1 Raman spectrometer using a Spectra-Physics He–Ne laser emitting a vertically polarised beam at 70 mW and 6328 Å. The scattered radiation was collected at 90° to the incident beam, the polarisation of which could be rotated by means of a half-wave plate. With this geometry the depolarisation ratio ρ has the value $0 < \rho < 0.75$ for a totally symmetric vibration and $\rho = 0.75$ for a non-totally symmetric vibration. The spectrometer was calibrated with indene and CCl_4 and wavenumbers are believed accurate to ± 0.5 cm^{-1}.

RESULTS

Raman spectra obtained for O_2F_2 in solution are shown in Figure 1 using both vertically and horizontally polarised excitation. Figure 2 shows the two bands in the 600 cm^{-1} region under high resolution. Unfortunately an O_2F_2

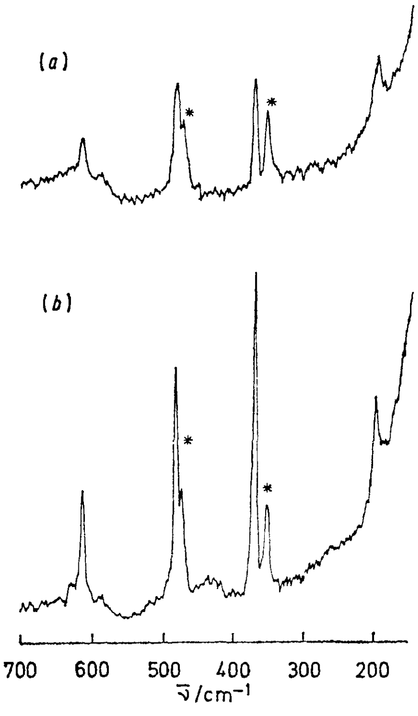

FIGURE 1 Raman spectrum with (*a*) horizontal and (*b*) vertical polarisation of O_2F_2 in $CClF_3$ solution at *ca.* 190 K (solvent bands are marked with an asterisk)

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† *Present address:* Department of Inorganic Chemistry, University of Newcastle-upon-Tyne, Newcastle-upon-Tyne NE1 7RU.

[1] H. W. Brown, personal communication quoted by Spratley, Ph.D. Thesis, Berkeley, California, U.S.A., 1965; also quoted in ref. 7.

[2] R. D. Spratley, J. J. Turner, and G. C. Pimentel, *J. Chem. Phys.*, 1966, **44**, 2063.

[3] A. Arkell, *J. Amer. Chem. Soc.*, 1965, **87**, 4057.

[4] K. R. Loos, C. T. Goetschel, and V. A. Campanile, *J. Chem. Phys.*, 1970, **52**, 4418.

[5] D. J. Gardiner, N. J. Lawrence, and J. J. Turner, *J. Chem. Soc.* (*A*), 1971, 400.

[6] P. N. Noble and G. C. Pimentel, *J. Chem. Phys.*, 1966, **44**, 3641.

[7] A. G. Streng, *Chem. Rev.*, 1963, **63**, 607.

[8] J. S. Ogden and J. J. Turner, *Chem. and Ind.*, 1966, 1295.

[9] N. J. Lawrence, J. S. Ogden, and J. J. Turner, *J. Chem. Soc.* (*A*), 1968, 3100.

band at *ca.* 460 cm^{-1} is obscured by a $CClF_3$ band in this region and all other known solvents for O_2F_2 (CCl_2F_2, O_3, OF_2, N_2F_2, and ClO_3F) [7] either have bands in this region or are unsuitable for other reasons. The region of the spectrum at *ca.* 1300 cm^{-1} was scanned with great care but no band attributable to O_2F_2 was found. A very weak band due to the solvent was observed which may have obscured any weaker O_2F_2 band. Table 1 lists the observed wavenumbers and depolarisation ratios for O_2F_2 in solution.

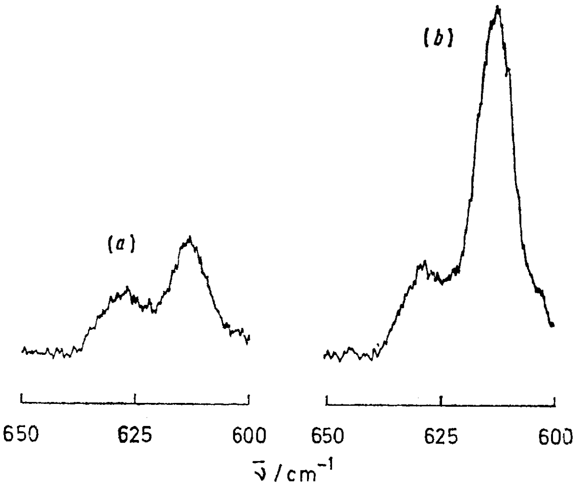

FIGURE 2 Solution Raman spectrum of O_2F_2 between 600 and 650 cm^{-1}: (*a*) horizontal; (*b*) vertical polarisation

TABLE 1

Observed Raman wavenumbers (cm^{-1}) and depolarisation ratios (ρ) of O_2F_2 in $CClF_3$ solution, compared with previous spectroscopic results on O_2F_2 (solid) and O_2F_2 matrix-isolated in argon at 20 K

I.r.		Raman				
Solid [a]	Matrix [a]	Solid [a]	Soln.[b]	ρ [b]	Symmetry species	Assignment
		173				
202			195·6	0·69	*A*	ν_4(torsion)
209						
		370				
369	366	377	366·1	0·31	*A*	ν_3 δ_{sym}(O–O–F)
		381				
		462				
457	459	468	*c*			ν_6 δ_{asym}(O–O–F)
		477				
615	611	614	610·6	0·36	*A*	ν_2 ν_{sym}(O–F)
		618				
621	624	630	624·3	0·83	*B*	ν_5 ν_{asym}(O–F)
	980	982				$\nu_2 + \nu_3$ 982
	1070	1062				$\nu_5 + \nu_6$ 1074
	1257					
1270	1274	1270				
1300	1290	1305	*d*			ν_1 ν(O–O)? + polymers [e]
1306						
1346		1339				

[a] Ref. 5. [b] This work. [c] Obscured by solvent (see text). [d] No bands in this region assignable to O_2F_2. [e] See text.

DISCUSSION

The structure of O_2F_2, determined from microwave studies by Jackson,[10] is shown in Figure 3. The molecule has C_2 symmetry and hence a vibrational representation $\Gamma_{vib} = 4A + 2B$, with all six vibrations being both i.r.- and Raman-active. The fundamental ν_1, expected to be mainly ν(O–O), was unobserved but even so the vibrational partitioning into symmetric and asymmetric blocks is unambiguous (see Table 1). The band at 624·2 cm^{-1} is assigned to the asymmetric O–F stretch ν_5, and the band at 610·6 cm^{-1} to the symmetric O–F stretch ν_2. This assignment is in conflict with Loos *et al.* who assumed it to be the other way round.[4]

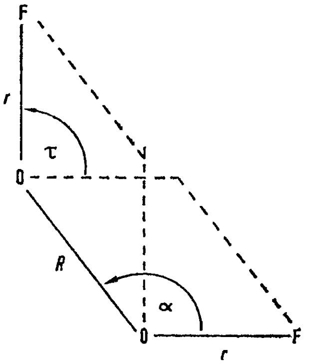

FIGURE 3 Structure of O_2F_2 (from ref. 10): $R = 1{\cdot}217$, $r = 1{\cdot}575$ Å; $\alpha = 109{\cdot}5$, $\tau = 87{\cdot}5°$

The observation of a polarised band at 366·1 cm^{-1} means that this must be due to the O–O–F symmetric bend ν_3, and thus the other bending vibration [5] at *ca.* 460 cm^{-1}, although not observed here, must be the asymmetric one ν_6. The band at 195·3 cm^{-1} is assigned to the torsional mode ν_4. (Jackson's estimate [10] from the microwave spectrum was 160 ± 20 cm^{-1}.)

[10] R. H. Jackson, *J. Chem. Soc.*, 1962, 4285.

The solution wavenumbers reported above and matrix wavenumbers from ref. 5 for O_2F_2 are in fair agreement. In addition we have observed the torsion ν_4 removed some 15 cm^{-1} from the value found by Loos *et al.*[4] for the solid. We therefore have some confidence in using the matrix wavenumbers plus the solution value of the torsional wavenumber in a normal-co-ordinate analysis. The most unusual feature about the vibrational spectrum is that, in the i.r., a band at 1257 cm^{-1} is attributed to ν_1. It is associated with other bands in this region which have been assigned to combination and overtone bands and, from matrix-annealing experiments, to polymer bands, $(O_2F_2)_n$.[5] In O_2 (bond length 1·21 Å) the O–O stretching vibration is at 1555 cm^{-1}; in O_2F, supposedly structurally related to O_2F_2, the O–O stretch is at 1500 cm^{-1}. It is thus somewhat surprising that in O_2F_2 (O–O, 1·22 Å) the O–O stretching vibration should be at 1257 cm^{-1}; this point will be taken up later.

Loos *et al.* carried out a normal-co-ordinate analysis of O_2F_2 using their solid-state frequencies.[4] * Other than interchanging the symmetry assignments for the bands at 610·6 and 624·3 cm^{-1}, and using a solid-state torsional value of 205 cm^{-1}, the general nature of the problem is the same as that above. In order to avoid the embarrassment of the low value of ν_1, Loos *et al.* fixed the O–O stretching force constant (f_R) at a high value of *ca.* 10·5 mdyn $Å^{-1}$, in keeping with the bond order of just under 2 as indicated by the bond length. Similar results to these were obtained if we used the correct symmetry assignments and the solution torsional value. The disadvantage of such a procedure is the large values of the interaction constants f_{Rr} (O–O–O–F stretch–stretch interaction constant) and $f_{R\alpha}$ (O–O–O–O–F stretch–bend interaction constant) that this high value of f_R demands. Associated with these high interaction constants is a completely ambiguous set of eigenvectors (relating normal and symmetry co-ordinates) such that none of the modes, with the exception of ν_1, are well defined. For example, the lowest mode, ν_4, expected to be clearly defined as the torsion, is a near equal mixture of torsional, O–F symmetric stretching, and O–O–F symmetric bending co-ordinates.

It is possible to obtain solutions containing smaller, and thus more reasonable, values of the interaction constants with well defined potential-energy distributions but with a much-reduced value of f_R of *ca.* 7 mdyn $Å^{-1}$. Is the latter significantly lower than the values of 11·25 and 10·5 mdyn $Å^{-1}$ observed for O_2 and O_2F respectively? If we assume the bond orders of O_2^+, O_2, and O_2^- to be 2·5, 2·0, and 1·5 respectively then a plot of O–O force constant against bond order leads to a value of *ca.* 1·6 for the O–O bond in O_2F_2 (Figure 4). If O_3 is included in the plot the O–O bond order in O_2F_2 is somewhat higher. However, in either case, it appears lower than chemical intuition would predict.

There is another possible interpretation. The matrix-isolation experiments were specifically designed to test if the O–O stretch of monomeric O_2F_2 was *ca.* 1300 cm^{-1} or if the O_2F_2 band at this wavenumber was due to solid-state interactions. Since the O_2 and F_2 dilutions in argon were low, it is possible that the monomer band is actually at *ca.* 1500 cm^{-1} and was never seen. Also, in these experiments, the 1500 cm^{-1} region is dominated by bands due to O_2F and $(O_2F)_n$ which would obscure the presence of an O_2F_2 band. It is worth adding that, in Andrews' matrix-Raman work[11] on OF dimerisation, there was no evidence for a band at *ca.* 1300 cm^{-1}. It is difficult to visualise an experiment which would unambiguously demonstrate the monomer band at 1500 cm^{-1}, but it is interesting to consider the consequences of such an assumption. The broad feature at 1280 cm^{-1} might then be due to $(O_2F_2)_n$. The i.r.-active O–O stretching frequency of $O_4F_2[(O_2F)_2]$ is observed only 30 cm^{-1} to higher frequency than that of O_2F itself. Shifting an O–O stretching frequency of (O_2F_2) to low frequency by 250 cm^{-1} $[(O_2F_2)_n]$ would be expected to lead to either extra bands or at least some broadening in the low-frequency region, which is not observed.

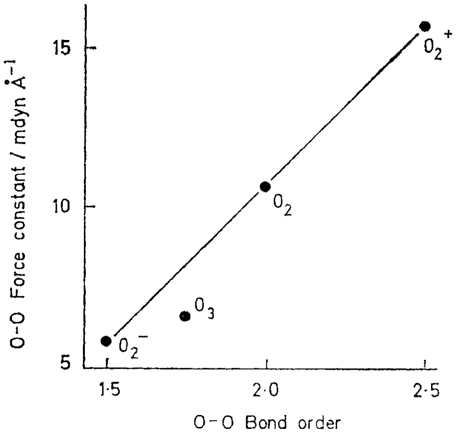

FIGURE 4 Plot of force constant against bond order for a series of diatomic O–O species

We have performed normal-co-ordinate analyses on O_2F_2 assuming ν_1 at both 1257 and 1500 cm^{-1}, using the following symmetry co-ordinates. We were unable to

Symmetry species A $S_1 = R$
$S_2 = 2^{-1/2}(r_1 + r_2)$
$S_3 = 2^{-1/2}(\alpha_1 + \alpha_2)$
$S_4 = \tau$
Symmetry species B $S_5 = 2^{-1/2}(r_1 - r_2)$
$S_6 = 2^{-1/2}(\alpha_1 - \alpha_2)$

obtain a fit to the observed wavenumbers using a simple diagonal field and further calculations were carried out

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* The units used in ref. 4 are in error. They are quoted in mdyn $Å^{-1}$ throughout whereas only the stretching force constants should be in mdyn $Å^{-1}$, the bending force constants in mdyn Å rad^{-1}, and the stretch–bend force constants in mdyn rad^{-1}.

[11] L. Andrews, *J. Chem. Phys.*, 1972, **57**, 51.

using the potential function (1), where $f_{r\alpha}$ is the interaction force constant between an O–O–F angle with the

$$2V = f_R R^2 + f_r(r_1^2 + r_2^2) + f_\alpha(\alpha_1^2 + \alpha_2^2) + f_\tau\tau^2 + f_{R\alpha}(R\alpha_1 + R\alpha_2) + f_{r\alpha}(\alpha_1 r_1 + \alpha_2 r_2) \quad (1)$$

O–F bond defining that angle. The interaction force constant between an angle with the O–F bond not contained by that angle was ignored (*i.e.* $f_{r_i\alpha_j} = f_{r\alpha}\delta_{ij}$). The *G* matrix was constructed using standard formulae (ref. 12) and contained explicit values of the bond lengths and angles shown in Figure 3. The program FPERT was used to solve the force field.[13]

The resulting force constants have units of mdyn Å^{-1} (for f_r, f_R, and f_{rR}), mdyn Å rad^{-2} (for f_α and f_τ), and mdyn rad^{-1} (for $f_{R\alpha}$ and $f_{r\alpha}$) but may be expressed in mdyn Å^{-1} by simple scaling by functions of the molecular geometry.[12] All the force constants above were allowed to vary in the iterative refinement procedure. No restraints were placed on the force constant f_R in the calculation and the resulting force constants are listed in Table 2. The calculations are extremely sensitive to the choice of off-diagonal force constants and also to their magnitude. We have generally noted ill-conditioned behaviour in all our least-squares normal equations for this molecule. Virtually identical results are found for the 1257 cm^{-1} assignment if $f_{R\alpha}$ is included in the calculation and $f_{\alpha\tau}$ left out. No significance is thus attached to some of these small interaction constants. Both the solutions suffer from the disadvantage of a high value of f_r the O–F stretching force constant (1·7 mdyn Å^{-1}), compared with the value of 1·3 mdyn Å^{-1} found by Noble and Pimentel [6] for O_2F. This may be due to the absence of the force constant f_{Rr} from our calculations but its inclusion in the O_2F calculation. The bending (O–O–F) force constant is of similar magnitude to that in O_2F however.

TABLE 2

Force constants in O_2F_2 and O_2

Force constant [a]	O_2F_2 [b]	O_2F_2 [c]	O_2F_2 [d]	O_2F [e]
f_R	10·25	7·14	10·36	10·50
f_r	1·50	1·70	1·69	1·32
f_α	1·19	1·11	1·12	1·01
f_τ	0·47	0·27	0·24	
$f_{\alpha\tau}$	[f]	0·014	[f]	
$f_{r\alpha}$	0·18	0·122 [g]	0·12	0·027
$f_{R\alpha}$	1·71	[f]	0·077	[f]
f_{Rr}	1·27	[f]	[f]	0·30

[a] Stretching force constants in mdyn Å^{-1}, bending and torsional force constants in mdyn Å rad^{-2}, and stretch–bend interactions in mdyn rad^{-1}. [b] Ref. 4. [c] Assuming ν_1 is at 1257 cm^{-1}. [d] Assuming ν_1 is at 1500 cm^{-1}. [e] Ref. 6. [f] Not included. [g] Held constant.

The observed and calculated wavenumbers and the potential-energy distributions are given in Tables 3 and 4 for the two choices of ν_1. Although Loos *et al.*[4] do not give such a description of the normal modes, but simply a table of eigenvectors, we can see that our results make better spectroscopic sense. Each mode is dominated by a large contribution from one particular force constant in our results leading to, for example, overwhelming choice of the 195 cm^{-1} mode as the torsion. Whereas, using the force field of Loos *et al.*,[4] we find that the potential-energy distribution indicates an almost equal mixture of O–F bond stretching (f_r) and O–O–F bending (f_α) in the 195 cm^{-1} vibration, with only *ca.* 1/6th of the potential energy occurring in f_τ.

TABLE 3

Force field for O_2F_2 assuming ν_1 is at 1500 cm^{-1}

	Wavenumber/ cm^{-1}		Potential-energy distribution				
	obs.	calc.	f_R	f_r	f_α	f_τ	Assignment
	1500·0	1500·0	*0·98*	0·01	0·02	0·00	ν(O–O)
	611·0	604·2	0·00	*0·75*	0·38	0·03	ν_{sym}(O–F)
	366·0	365·7	0·02	0·23	*0·72*	0·21	δ_{sym}(O–O–F)
$^{16}O_2F_2$	195·0	197·4	0·01	0·01	0·01	*0·89*	τ(F–O–O–F)
	624·0	629·0		*0·63*	0·46		ν_{asym}(O–F)
	459·0	461·3		0·37	*0·55*		δ_{asym}(O–O–F)
		1414·1	*0·98*	0·01	0·02	0·00	
	585·5	580·3	0·00	*0·78*	0·35	0·02	
	359·1	355·6	0·02	0·21	0·75	0·19	
$^{18}O_2F_2$ [a]		194·6	0·00	0·01	0·01	*0·91*	
	594·6	602·2		*0·67*	0·42		
	445·9	446·5		0·34	*0·58*		

[a] Frequencies for $^{18}O_2F_2$ from the solid-state i.r. spectrum [4] were corrected by a small frequency factor such that $\nu_i(^{18}O_2F_2)_{used} = \nu_i(^{18}O_2F_2)_{Loos}\,\nu_i(^{16}O_2F_2)_{observed}/\nu_i(^{16}O_2F_2)_{Loos}$.

TABLE 4

Force field for O_2F_2 assuming ν_1 is at 1257 cm^{-1}

	Wavenumber/ cm^{-1}		Potential-energy distribution				
	obs.	calc.	f_R	f_r	f_α	f_τ	Assignment
$^{16}O_2F_2$	1257·0	1260·9	*0·95*	0·02	0·03	0·00	ν(O–O)
	611·0	607·2	0·00	*0 74*	0·38	0·03	ν_{sym}(O–F)
	366·0	371·7	0·04	0·23	*0·62*	0·25	δ_{sym}(O–O–F)
	195·0	193·9	0·01	0·02	0·06	*0·79*	τ(F–O–O–F)
	624·0	628·2		*0·65*	0·45		ν_{asym}(O–F)
	459·0	458·1		0·36	*0·56*		δ_{asym}(O–O–F)
$^{18}O_2F_2$ [a]		1188·8	*0·95*	0·02	0·03	0·00	
	585·5	583·0	0·00	*0·77*	0·35	0·03	
	359·1	359·9	0·04	0·21	*0·66*	0·24	
		201·3	0·01	0·01	0·05	*0·82*	
	594·6	599·8		*0·69*	0·41		
	445·9	442·2		0·32	*0·60*		

[a] See Table 3.

The ' 1500 cm^{-1} ' assignment implies several points. (i) The O–O stretch of O_2F_2 monomer is at 1500 cm^{-1} but the O–O stretches of $(O_2F_2)_{2,3}$ are at 1257 cm^{-1} or thereabouts. (ii) Although the O–O stretch is sensitive to dimerisation, the other bands, with the possible exception of the torsion, are insensitive. The corresponding monomer–dimer bands of O_2F and $(O_2F)_2$ are

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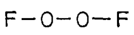
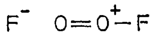
[12] E. B. Wilson, jun., J. C. Decius, and P. C. Cross, ' Molecular Vibrations,' McGraw-Hill, London, 1955.

[13] J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, 1963, **19**, 117.

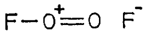
at 1490 and 1515 cm^{-1},[5,14] and the other bands are insensitive to dimerisation. It is surprisingly easy to *correlate* this behaviour with simple valence-bond models; we may write structures (I)—(III) for O_2F_2


$F-O-O-F$

(I)

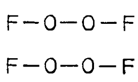

$F^- \; O{=}\overset{+}{O}-F$

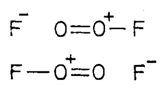
(II)

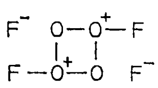

$F-\overset{+}{O}{=}O \; F^-$

(III)

monomer. Experimentally a short O–O bond in O_2F_2 is observed,[10] indicating a high contribution from (II) and (III). For a cyclic O_2F_2 dimer we may write structures (IV)—(VI) plus two other structures which


(IV)


(V)


(VI)

are simply mirror images of (V) and (VI). A *ca.* 30% contribution from (VI) is indicated based upon approximate bond-order considerations.[15] Similar considerations apply for a ' chain ' type species.

The fluorine environment thus seems to be similar in both monomeric and dimeric O_2F_2. For O_2F, dimerisation results simply from pairing of the odd electrons on the O atoms of the two O_2F groups and as such would not be expected to significantly alter the O–O bond order in each O_2F unit. The same results may be obtained using Linnett's double-quartet approach.[16] Thus, for O_2F_2 and O_2F, dimerisation should have little effect on O–F modes but considerable effect on the O–O stretch of the former. It is difficult to devise an experiment to test the hypothesis of ν_1 at 1500 cm^{-1} for O_2F_2 monomer. In the matrix experiments of ref. 5 the oxygen and fluorine dilutions in argon were very low, leading on the one hand to a reasonably fast reaction of $F\cdot$ and O_2, but on the other to the possibility of polymer formation of the O–F species, a situation prevalent in the solid. In Andrews' Raman experiments[11,17] on the OF system, and the solution study reported here where dimer formation should be small, no band between 1200 and 1500 cm^{-1} attributable to ν_1 of O_2F_2 was observed. A matrix-isolation experiment using high dilutions of reactants, to minimise dimerisation, would probably require very long photolysis times to produce a significant concentration of O_2F_2.

One other point which may shed some light on the problem of the O–O bond order is a calculation of the barrier to internal rotation. Using the observed torsional wavenumber of 195 cm^{-1} and a potential well of the form $V = 1/2V_0[1 - \cos(2\theta - \pi)]$, where θ is the dihedral angle, we arrive at a value of *ca.* 30 kcal mol^{-1}. Using the extended Hückel molecular-orbital method, we find two barriers of *ca.* 25 and 30 kcal mol^{-1}. These are both about 1·5 times higher than those calculated using the CNDO/2 method[18] of 16·6 and 20·8 kcal mol^{-1}. This barrier is considerably higher than that found for H_2O_2 and illustrates a significantly greater bond order in O_2F_2 than in the former molecule. However we feel that on the present evidence it would be presumptuous to choose between the possible force-constant calculations and hence conclude precisely how much stronger is the O–O bond in O_2F_2.

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