NIST-JANAF Thermochemical Tables for the Oxygen Fluorides

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The thermodynamic and spectroscopic properties of the oxygen fluoride species have been reviewed. Recommended thermochemical tables are given for five gaseous oxygen fluorides: OF, OFO, FOO, FOF, and O_2F_2. Sufficient information is not available to generate thermochemical tables for any condensed phase species. Annotated bibliographies (over 600 references) are provided for all neutral oxygen fluorides which have been reported in the literature. There are needs for additional experimental and theoretical data to reduce the uncertainties in the recommended values for these five species. Of all the species mentioned in the literature, many have not been isolated and characterized. In fact, some do not exist. Throughout this paper, uncertainties attached to recommended values correspond to the uncertainty interval, equal to twice the standard deviation of the mean.

Key words: evaluated/recommended data; literature survey; oxygen fluorides; spectroscopic properties; thermodynamic properties.

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1. Introduction

This study of the neutral oxygen fluorides is the first of four critical reviews on the thermodynamic and spectroscopic properties of the halogen oxides. An earlier partial study on

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the chlorine oxides[1] has already been reported. Subsequent articles will deal with bromine oxides and iodine oxides. We will not discuss the astatine oxides, as there appears to be only an estimated D_0° value reported in the literature for AtO(g). Specifically, this study examines the thermodynamic properties of the neutral oxides, not the gaseous ionic or aqueous ionic species. The main purpose of this article is to generate thermochemical tables for oxygen fluoride species. In general, there is scant data available for the description of the spectroscopic and thermodynamic data for any of the oxygen fluorides, except for OF, FOO, FOF, and O_2F_2. Although the prime emphasis was on the diatomic and triatomic species, a thorough search of all oxygen fluorides was conducted to decide which species had sufficient data.

For the time period 1907 to 1994, there are 882 citations in Chemical Abstract Services (CAS) dealing with the oxygen fluorides of which there are 15 fluorides and 9 isotopomers. 484 citations deal with OF_2, 133 deal with O_2F_2, 78 deal with FOO, and 69 with OF. The remaining 118 references deal with 11 fluorides and 9 isotopomers. Of the 24 fluorides mentioned, however, there is not conclusive evidence as to the existence of all of them.

The present interest in the numerous oxygen fluorides is due to the important role these compounds play in stratospheric chemistry and as strong fluorinating agents. For this reason, the spectroscopic characterization of these species is mandatory in order to explain possible reactions thermodynamically and kinetically. In addition, numerous researchers are examining bonding trends within all halogen oxide species. There appears to be no commercial uses of the oxygen fluorides mentioned in the literature. In the past, the dominant use of oxygen fluorides was in rocket industry as propellants, due to the fact that they are strong oxidizers. There is also mention of the use of the oxygen fluorides in flash bulbs.

The current study is aimed at providing a complete and thorough coverage of the literature for spectroscopic and thermodynamic information. Although it is not the purpose of this article to summarize and critique the chemistry of the oxygen fluorides, all such references are provided here. The references were obtained primarily by use of commercial abstracting services and all NIST Data Centers.[a] Since the literature survey revealed so few references in total for all neutral oxygen fluorides (except OF_2) all citations are listed in Sec. 9 (References-Annotated Bibliography). Since there are well over 400 references for OF_2, we only include those which are important from a spectroscopic and thermodynamic point of view. We have not included articles which seemingly deal with the formation, preparation, reaction, NMR, and patents of OF_2. It should be noted that the reading of the individual articles yielded additional references, many of which are included in the attached bibliography. Not included are all articles or books (textbooks and handbooks) which simply present a summary of properties with no critical evaluation. Note that although there was brief mention of oxygen fluorides in 1910, in depth studies began in the late 1920s. Even though many citations are not relevant to this study, future investigators will not have to search the past literature, but simply concentrate on the publications since 1994.

The current version (1985) of the JANAF Thermochemical Tables[2] includes three oxygen fluorides (OF, FOO, FOF), whereas the 1989 version of the Thermochemical Properties of Individual Substances (TPIS)[3] only contains information on OF and FOF. For the JANAF Thermochemical Tables, the data evaluations were actually performed in 1966 for OF and O_2F and in 1969 for OF_2. For TPIS, the analysis for OF is based on data up to 1973, however a footnote referring to a 1979 reference was included. The most recent reference for FOF was 1966. There is sufficient new data available to warrant revisions to these tabulations, although the numeric changes are not large. The NBS Tables of Chemical Thermodynamic Properties[4] and its Russian counterpart by Glushko and Medvedev[5] listed values (C_p°, H°, S°, and $\Delta_f H^\circ$) at 298.15 K for OF(g) and OF_2(g), but only $\Delta_f H(298\ \mathrm{K})$ for O_2F_2(g) and O_3F_2(g). In addition, Glushko and Medvedev include an enthalpy of formation value for O_5F_2(g). [Neither of these latter two publications provide any data on aqueous ions.] It should be noted that the NBS study was performed prior to 1964, while the Russian study, prior to 1965.

There are many NASA-JPL publications on chemical kinetics in which enthalpy of formation tables are given. Of all the oxygen fluorides, only OF, OF_2, O_2F, and O_2F_2 were listed by NASA-JPL.[6] These data were presented without citation or reference to the original source. Most of the recommendations were based upon data in the IUPAC evaluations (Atkinson *et al.* 1989[7], 1992[8]). Some of the values were different from the current IUPAC recommendations, reflecting more recent studies that have not yet been accepted and incorporated into those publications. IUPAC cited the origin of their values. All citations given by IUPAC are included in this article.

There are numerous reviews dealing with the oxygen fluorides. Hahn[9], in 1959, gave a thorough review of the preparation properties of OF_2 and O_2F_2 and discussed the existence of OF and O_3F_2. In 1986, as an update to the review of the oxygen fluorides for this Gmelin series, Jager *et al.*[10] summarized the properties of OF, OFO, FOO, O_3F, O_4F, OF_2, O_2F_2, O_3F_2, O_4F_2, O_5F_2, O_6F_2, OF_3, OF_4.

In 1963, Schmeisser and Brandle[11] summarized the status of four compounds (OF_2, O_2F_2, O_3F_2, O_4F_2). At the time of this review, the structure was known only for OF_2. The melting points and enthalpies of formation were available for OF_2, O_2F_2, and O_3F_2.

In a review of advanced inorganic oxidizers, Lawless and Rowatt[12] discussed eight oxygen fluorides, of which three were stated to be well characterized (O_2F, OF_2, O_2F_2). Additional reviews are provided by Allamagny[13] and Nikitin and Rosolovskii.[14]

[After this article was written and reviewed, this author became aware of the existence of another review article by Wayne *et al.*[20] This article provides discussion on the thermodynamic and spectroscopic data on many oxygen fluorides. Although not of importance for our purposes, the article also discusses many other topics, including photochemistry and kinetics.]

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[a] Chemical Kinetics Data Center; Chemical Thermodynamics Data Center; Ion Kinetics and Energetics Data Center; Molecular Spectra Data Center; Vibrational and Electronic Energy Levels of Small Polyatomic Transient Molecules; Crystal and Electron Diffraction Data Center.

In reading Sec. 5, the reader will soon learn that the existence of many of the oxygen fluoride compounds is questionable. The thermal instability of the oxygen fluorides has led to numerous difficulties in characterizing specific oxygen fluorides. The syntheses are not always reproducible. The following table summarizes our interpretations of the probable existence of the compounds mentioned:

Exist and have been observed: OF (^{18}OF); FOO (O^{17}OF, ^{17}OOF, ^{17}O$_2$F); FOF; O_2F_2 (^{17}O$_2$F$_2$, ^{18}O$_2$F$_2$)

Compounds that may exist (have not been isolated but some characterization available): OFO; O_3F; O_4F_2; OF_3

No conclusive confirmation as to existence: O_4F; FFO; O_3F_2; O_5F_2; FOOOOOF;O_6F_2; FOOOOOOF; O_7F_2; O_8F_2

In the following discussions, analyses and calculations, the 1993 atomic weights of the elements[15] are used: $A_r(F) = 18.9984032 \pm 0.0000009$; $A_r(O) = 15.9994 \pm 0.0003$. Since the mid-1950s, the relative atomic weight of oxygen has changed by 0.0006 to 15.9994. Similarly for fluorine, the relative atomic weight has changed by 0.0000032 to 18.9984032. Relatively speaking, these changes are sufficiently small that we will not consider any conversions due to relative atomic weights.

In addition, the 1986 fundamental constants[16] are used. The key constant of interest in this work is the molar gas constant: $R = 8.314510 \pm 0.000070$ J·mol^{-1} K^{-1}. In comparison to the 1973 fundamental constants[17], R has changed by +0.0001 J·mol^{-1} K^{-1}. Using the 1986 fundamental constants (instead of the 1973 fundamental constants), the S(298.15 K) values are increased by approximately 0.004 J·mol^{-1} K^{-1} for the four polyatomic oxygen fluorides.

SI units are used for the final recommendations. Since we are dealing only with spectroscopic information, the resulting calculated thermodynamic tables refer to thermodynamic temperatures. Thus, no temperature scale conversions are necessary.

In the following discussions, the numeric values (and their uncertainties if given) presented are those reported in the original publication in addition to the SI value. This is to ensure quick confirmation of the extracted results and their uncertainties. These uncertainties (not always based on experimental and mathematical analyses) are the values quoted by the original authors and are often not fully described as to their origins. Our reported uncertainties for $S°$ and $\Delta_f H°$ are calculated using a propagation of errors approach.

The recommended data presented in the NIST-JANAF Thermnochemical Tables are a result of a combined appraisal of results from experimental studies, calculations (e.g. quantum-mechanical treatments) and estimations. All tables are calculated using the full significance of all numeric values. Rounding occurs at the end of the calculations. The uncertainty given represents our best attempt for twice the standard deviation.

The NIST-JANAF Thermochemical Tables (Sec. 6) are calculated using the current atomic weights and fundamental constants, as well as the thermochemical tables for monatomic and diatomic fluorine and oxygen. These latter reference state thermochemical tables, as originally calculated, were based on on the 1973 fundamental constants[17] and the 1981 relative atomic weights.[18] This will cause a slight offset in the formation properties of the order 0.01 kJ·mol^{-1} at most; such an offset is well within the uncertainty range of the enthalpy of formation of the oxygen fluorides. Neumann[19] has presented an identical thermochemical table for FO(g); this table was prepared jointly with this author.

1.1. References for the Introduction

[1] S. Abramowitz and M. W. Chase, Thermodynamic properties of gas phase species of importance to ozone depletion, J. Pure. Appl. Chem. 63(10), 1449–54 (1991).

[2] M. W. Chase, Jr, C. A. Davies, J. R. Downey, Jr., D. A. Frurip, R. A. McDonald, and A. N. Syverud, JANAF Thermochemical Tables, 3rd Edition, J. Phys. Chem. Ref. Data 14, Supplement No. 1, 1856 pp (1985).

[3] L. V. Gurvich, I. V. Veyts, and C. B. Alcock, Thermodynamic Properties of Individual Substances, 4th Edition, two parts (551 pp and 340 pp), Hemisphere Publishing Corporation, New York (1989).

[4] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, The NBS Tables of Chemical Thermodynamic Properties. Selected Values for Inorganic and C_1 and C_2 organic substances in SI units, J. Phys. Chem. Ref. Data 11, Supplement No. 2, 393 pp (1982).

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[6] W. B. De More, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb and M. J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling, NASA-JPL Publication 92–20 (1992); this is one of a series of similar publications.

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[8] R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampsom Jr., J. A. Kerr and J. Troe, Evaluated kinetic and photochemical for atmospheric chemistry: supplement IV, J. Phys. Chem. Ref. Data 21(6), 1125–1568 (1992).

[9] O. Hahn, Fluorine, Gmelins Handbuch der Anorganischen Chemie, Verlag Chemie GMBH, Weinheim, 258 (1959).

[10] S. Jager, J. von Jouanne, H. Keller-Rudek, D. Koschel, P. Kuhn, P. Merlet, S. Rupecht, H. Vanecek, and J. Wagner, Fluorine, System No. 5, Suppl. 4, Gmelin Handbook of Inorganic Chemistry, Springer-Verlag, Berlin, 408 (1986).

[11] M. Schmeisser and K. Brandle, Oxides and oxyfluorides of the halogens, Adv. Inorg. Radiochem. 5, 41–89 (1963).

[12] E. W. Lawless and R. J. Rowatt, Review of advanced inorganic oxidizers, Amer. Chem. Soc., Div. Fuel Chem., Prepr. 12(2), 108–19 (1968); CA 71R 119057e.

[13] P. Allamagny, The fluorides of oxygen, Gauthier-Villars: Paris, 66 pp. (1969); CA 72B 27946m.

[14] I. V. Nikitin and V. Ya. Rosolovskii, Oxygen fluorides and dioxygenyl compounds, Usp. Khim. 40(11), 1913–34 (1971); Engl. transl., Russ. Chem. Rev. 40(11), 889–900 (1971).

[15] IUPAC Commission on Atomic Weights and Isotopic Abundances, Atomic weights of the elements 1993, J. Phys. Chem. Ref. Data 24(4), 1561 (1995); Pure & Appl. Chem. 66(12), 2423 (1994).

[16] E. R. Cohen and B. N. Taylor, The 1986 CODATA recommended values of the fundamental physical constants, J. Phys. Chem. Ref. Data 17(4), 1795 (1988).

[17] E. R. Cohen and B. N. Taylor, The 1973 least-squares adjustment of the fundamental constants, J. Phys Chem. Ref. Data 2(4), 663 (1973).

[18] N. E. Holden and R. L. Martin, Atomic weights of elements — 1981, Pure Appl. Chem 55, 1101 (1983).

[19] D. B. Neumann, NIST-JANAF Thermochemical Tables, Supplement 1995, J. Chem. Phys. Ref. Data, submitted for publication (1995).

[20] R. P. Wayne, H. Poulet, P. Briggs, J. P. Burrows, R. A. Cox, P. J. Crutzen, G. D. Hayman, M. E. Jenkin, G. Le bras, G. K. Moortgat, U. Platt and R. N. Schindler, Halogen oxides: radicals, sources, and reservoirs in the laboratory and in the atmosphere, Atmos. Env. 29(20), 2675–2884 (1995).

2. Chemical Species Coverage

The following is a list of all oxygen fluoride species cited in the Chemical Abstract Services (CAS) Indices (formula and substance). Aqueous ions and gaseous ions are not included in this study. The chemical name, formula, and Chemical Abstracts Services Registry Number (when available) are given. This list is complete through Volume 121 of Chemical Abstracts Services (December 1994). It is important to note that this listing gives species whose existence is now questioned. Deleted CA Registry Numbers are given to assure the reader that all past citations were retrieved. It is important to note that there is limited information on the existence of the asymmetric isomer FFO and the symmetric isomer, OFO. The analogous chlorine species, ClClO and OClO, however, do exist.

TABLE 2.1. Oxygen fluoride species

		Chemical Abstracts Registry Numbers	
Formula[a]	Name	Deleted #	Current #[b]
	Oxygen fluoride	—	1116–01–1
OF(FO)	Oxygen fluoride	14986–71–1 77318–95–7 54974–53–7	12061–70–0
FO(^{18}OF)	Oxygen fluoride	—	38536–87–7
O_2F(FOO)	Oxygen fluoride	99873–96–8 92340–10–8 12507–32–3 12020–93–8 61825–17–0 12061–71–1	15499–23–7
$O^{17}OF$	Oxygen fluoride	—	15891–85–7
^{17}OOF	Oxygen fluoride	—	?
$^{17}O_2F$	Oxygen fluoride	—	15844–91–4
$^{18}O_2F$	Oxygen fluoride	—	59139–28–3
$O^{18}OF$	Oxygen fluoride	—	52139–29–4
O_2F(OFO)	Oxygen fluoride		(?)
O_3F	Oxygen fluoride	—	12191–80–9
O_4F	Oxygen fluoride	—	?
OF_2(FOF)	Oxygen fluoride	86100–45–0	7783–41–7
$O^{18}F_2$(FOF)	Oxygen fluoride	—	149228–80–8
$^{17}OF_2$	Oxygen fluoride	—	—
$^{18}OF_2$	Oxygen fluoride	—	—
OF_2(FFO)	Fluorosyl fluoride	—	86825–57–2
O_2F_2(FOOF)	Oxygen fluoride	—	7783–44–0
$^{17}O_2F_2$	Oxygen fluoride	—	12178–94–8
$^{18}O_2F_2$	Oxygen fluoride	—	22303–73–7
O_3F_2(FOOOF)	Oxygen fluoride	12020–92–7	16829–28–0
O_4F_2(FOOOOF)	Oxygen fluoride	12020–93–8	107782–11–6
O_5F_2	Oxygen fluoride	—	12191–79–6
O_5F_2(FOOOOOF)	Fluorine oxide	—	13847–63–7
O_6F_2(FOOOOOOF)	Fluorine oxide	—	13847–64–8
O_6F_2	Hexaoxygen difluoride	—	12191–80–9
O_7F_2(O_3F—O—FO_3)	Fluorine oxide	—	106996–21–8
O_8F_2	Difluorooxide	—	153851–83–3
OF_3	Oxygen trifluoride	—	12434–38–7
OF_4	Oxygen tetrafluoride	—	—
OF_6	—	—	152574–75–9

[a] A secondary formula is intended to suggest the assigned structure.If there isno secondary formula given, this means that no structure has been determined for this species, but the atomic ratio is known.

[b] If no CA Registry Number appears in this column, then the species is assumed NOT to exist.

3. Historical Perspective of Oxygen Fluoride Studies

It is informative to briefly summarize the types of studies which have been conducted through the years on the oxygen fluorides. Specific references are given in Sec. 9. This section is intended to simply highlight developments through the years.

Using the Chemical Abstracts Services Collective Indices as a backdrop for these historical comments, the period 1907 to 1926 (the 1st and 2nd Collective Indices) revealed only two citations for the oxygen fluoride species, both of which were for unspecified oxygen fluoride compounds.[1,2] The references referred to a reaction of F_2 and O_2 in an ozonizing apparatus. Although no temperature is specified in the abstract, unstable compounds were formed which caused an explosion.

In the time period 1927 to 1946 (the 3rd and 4th Collective Indices), Chemical Abstracts mentioned a total of forty citations dealing with oxygen fluorides. In the 3rd Index these compounds were referred to as fluorine oxides but starting with the 4th Index, they were called oxygen fluorides. At this time four fluorides had been identified: OF, OF_2, O_2F_2, and O_3F_2.

For the time period 1947 to 1961 (the 5th and 6th Collective Indices), 48 additional articles were indexed in Chemical Abstracts Services. The dominant species under study was OF_2. Numerous physical, spectroscopic, and thermodynamic properties were studied extensively. This was undoubtedly due to applications in the rocket industry. The formation and decomposition of OF, O_2F_2, and O_2F_3 were studied.

For the time period 1962 to 1971 (the 7th and 8th Collective Indices), 348 references were cited. Not including isotopomers, nine oxygen fluorides are discussed. The main emphasis of the studies appeared to revolve around the use of these oxides in the propellant industry. The bulk of the references dealt with preparation, formation and reactions.

In the time period of the 9th and 10th Collective Indices (1972–1981), there were six oxygen fluoride species (and three isotopomers) mentioned. In all cases, the dominant studies involved spectroscopic and bond energy investigations. There were however, numerous studies involving the formation, the reaction and kinetics of these fluorides. There were a few references to oxidizers for propellant systems. There seemingly were no commercial applications and very few patents. The patents typically refer to compounds or adducts involving the oxygen fluorides.

For the 11th and 12th Collective Indices (1982–1991), there was one reference dealing with the formation of O_4F_2, but many dealing with OF, OF_2, O_2F, and O_2F_2. The emphasis appeared to be on the formation, preparation, reaction, fluorination and determination of spectroscopic properties of the oxygen fluoride species.

In summary, the recent studies concentrated on four species (OF, FOF, FOO, and O_2F_2). While these species are now well characterized spectroscopically, the enthalpy of formation values need confirmatory studies (by direct measurement if at all possible). Also, recent studies lend credence to the fact that these are the only fluorides which do exist. In the 1960s, when many additional fluorides were mentioned, it appeared that separation and identification problems existed.

3.1. References for Historical Perspective

[1] G. Gallo, 'Oxygen compounds of fluorine. III,' Atti accad. Lincei, 19, I, 753–5 (1910); Chem. Zentr, 1910, II, 544.

[2] G. Gallo, 'Attempt to prepare oxygen compounds of fluorine,' Atti accad. Lincei, 19, I, 295–9 (1910); Chem. Zentr., 1910, I, 1952.

4. Summary of the Data for the Oxygen Fluoride Species

4.1. Spectroscopic Information

The construction of thermodynamic tables for polyatomic gas phase species requires a knowledge of the spectroscopic constants of the molecule including electronic energy levels and quantum weights, vibrational frequencies and structure. This information is necessary for any low-lying excited electronic states, as well as the ground state. These data are obtained either from direct spectroscopic measurements, from theory, or by analogy with other similar chemical compounds. In some cases, theoretical quantum mechanical calculations are used. There is complete spectral information available for gaseous FOO, FOF and O_2F_2. The other species have not been experimentally characterized. Quantum mechanical information was used for OFO.

For diatomic molecules, spectroscopic information on the electronic energy levels and vibrational-rotation structure is necessary. Experimental data of this type is available for OF(g).

4.2. Thermodynamic Information

The literature survey revealed little or no information on the thermodynamic properties of any of the oxygen fluorides, except for FOF and O_2F_2.

For the gas phase species, OF(g), dissociation energy values are available so that an enthalpy of formation may be calculated. Experimental formation information has been reported in the literature for the gaseous oxygen fluorides (OF_2, O_2F_2, O_3F_2).

There is insufficient data available to permit the calculation of thermodynamic functions for the condensed phase of any of the oxygen fluorides. The literature does not reveal heat capacity or enthalpy of formation data for any of these oxides. There are some data for the melting, density and vapor pressure of the various condensed phase. This information is summarized in the reviews listed in Sec. 1.

5. Discussion of the Literature Data

The information is discussed in terms of the individual oxygen fluoride species. All species cited in Chemical Abstracts formula and substance indices are discussed as well as those additional species which are mentioned in the individual articles. This is not to imply that all those species exist, that is, have been isolated and characterized.

The reaction of fluorine with oxygen under varying conditions seemingly yields a mixture of oxygen fluorides. The discussion of any particular species is then difficult due to the fact that a pure compound has not always been under consideration.

5.1. OF

There are many references for OF(g). Unfortunately, there are few experimental studies which truly define the spectroscopic properties of OF(g), including the dissociation energy. In searching the literature, many references were found which reported dissociation energy values. The same values are repeated numerous times. We have listed many sources, but have NOT included all data collections which simply repeated values already given by others. The goal here is to provide information on experimental studies and theoretical investigations. Unfortunately, there is no thermochemical data to help fix the properties of OF(g).

For many years, the experimental detection and characterization of OF(g) was futile. Burkholder *et al.* [86BUR/HAM] stated that "the failure to detect OF was due to two factors, (a) its very small permanent dipole moment which renders it difficult to observe by microwave or gas-phase EPR spectroscopy and (b) its highly predissociated electronic spectrum."

All references dealing with OF are listed in the following eight categories. For the purpose of this article, the primary interest is in the spectroscopic and dissociation energy information.

1. Spectroscopy —
   - Experimental — [58DUR/RAM], [65ARK/REI2], [69ARK], [71AND/RAY], [72AND], [72YAN], [74SMA/FOX], [79MCK], [80AND], [80DYK/JON], [83MCK/YAM], [86BUR/HAM], [88HAM/SIN]
   - Theoretical — [63TAN], [74LAT/CUR], [89SUN], [90FRA/GOL], [91HAA], [92KOS/SCH], [93FRA/SU2], [94CHO], [94FRA]
2. EPR —
   [65NEU/VAN], [72LEV]
3. Dipole moment —
   [83LAN/BAU], [83MCK]
4. Formation/preparation/decomposition —
   [33RUF], [33RUF/MEN], [34RUF/MEN], [36FRI/SCH], [36FRI/SCH2], [61VIS], [62STA/SIC], [63HAM/IVE], [63WAL], [65KIR], [65MAG], [65NEU/VAN], [68SOL/KAC], [74SMA/FOX], [74SMA/FOX2]
5. Kinetics —
   [60GRE/LIN], [69LIN/BAU], [70HOM/SOL], [71CLY/WAT], [71WAG/WAR], [72HOU/ASM], [72LIE], [72WAG/ZET], [73CHE/TUP], [73POL/POL], [74CLY/WAT], [74WIG/BRI], [76ALE/NIK], [78APP/CLY], [79GAR/TUR], [80BAU/COX], [81RAY/WAT], [82ANT], [82BAU/COX], [82LER/PEE], [86DOS/CAS], [86PAT/SHA], [86SWE], [86THA/SHA], [88FRA/GOL], [88RAH/BEC], [88SYM/ROS], [92BED/MAR], [92BED/MAR2], [92FRA], [93BED/MAR], [93BED/MAR2], [93BED/MAR3], [93FRA/SU2]
6. Dissociation energy —
   - Experimental — [34KOB/SCH], [57DIB/REE], [59HIL], [65ARK/REI2], [67MAL/MCG], [67OGD/TUR], [69ARK], [71CLY/WAT], [72CZA/SCH], [72LEV], [73BER/DEH], [94ZHA/KUO]
   - Calculations — [48GLO], [49GLO], [50SCH], [62PRI/HAR], [63PRI/PAS], [65MOR], [69ION/ION], [70OHA/WAH], [70OHA/WAH2], [70OHA/WAH3], [72LIE], [77GLI], [78DEW/RZE], [78DEW/RZE2], [80GLI], [80JUG/NAN], [80NAN/JUG], [86MEL], [90ZHA/FRA], [91BRA/WRI], [93FRA], [93FRA/SU], [94CHO]
   - Review — [50SCH2], [53GAY], [58BRE], [62VED/GUR], [63SCH], [66VED/GUR], [68GAY], [69BRE/ROS], [69FRA/DIL], [70DAR], [76BEN], [79HUB/HER], [82WAG/EVA]
7. Review —
   [60GEO], [68TUR], [72BRI], [80SOL]
8. Miscellaneous —
   [62SVE], [65ARK/REI], [73ROZ/GUT], [80HAR/BLI], [81LEN/JAF], [83ALE/FED], [84ALE/VOL], [84DMI/MYR], [84SAU/TAT], [85CHA/CAN], [86JAF/AKE], [87HER], [87KAR], [88MAL/PER], [89THA/PED], [90CHI/KRA], [91THO/CAR], [91XIE/XIA], [92MCI/AND], [92XIE/LIU], [93XIE/XIA]

There is currently sufficient experimental spectroscopic information to reliably describe the electronic ground state of OF, $X^2\Pi_{3/2}$ (inverted doublet). The calculational results for OF were done primarily to provide information on many fluorine containing compounds. OF(g) was often included as a benchmark species, concentrating on r_e and ω_e values. The vibrational and rotational structure of OF was first fully described by [86BUR/HAM]. Earlier work determined in part the vibrational (only ω_e) structure or rotational structure. The value of A, the splitting of the ground state, has been determined experimentally in five studies [79MCK, 80DYK/JON, 83MCK/YAM, 86BUR/HAM, 88HAM/SIN]. All values are summarized in Table 5.1.1.

The two EPR studies do not provide any thermodynamic or spectroscopic information for this review.

[65NEU/VAN]: Possible formation/identification of OF in the irradiation of pure liquid OF_2 at −196 °C and OF_2 in $CFCl_3$ matrix; observed an isotopic doublet.

[72LEV]: Observed reaction ($H + OF_2 \rightarrow HF + + OF$) in the microwave cavity of an EPR spectrometer; did not detect OF radicals.

The reported dissociation energy information (experimental, theoretical and reviews) is summarized in Table 5.1.2. The early values were based on the assumption that the dissociation energy of OF was approximately equal to 1/2 of the enthalpy of atomization of OF_2. More recently, there are results derived from quantum mechanical calculations as well as photoionization studies.

The citations under miscellaneous are:

[62SVE]:	Viscosity and thermal conductivity (calculated values)
[65ARK/REI]:	Manufacture
[73ROZ/GUT]:	Thermal functions (estimated)
[80HAR/BLI]:	Electronegativity
[81LEN/JAF]:	Valence calculations on several states of OF(g)
[83ALE/FED]:	Electron affinity
[84ALE/VOL]:	Ionization potential; electron affinity
[84DMI/MYR]:	Isotope effects
[84SAU/TAT]:	Partition functions
[85CHA/CAN]:	Vibrational linewidths
[86JAF/AKE]:	Low lying electronic states
[87HER]:	Review of thermochemical data for S/F/O/H species
[87KAR]:	Electron affinity
[88MAL/PER]:	Calculations in coal processing gases
[89THA/PED]:	Electron momentum
[90CHI/KRA]:	Vibrational relaxation
[91THO/CAR]:	Vibrational lifetimes
[91XIE/XIA]:	Laser emission (article not obtained)
[92MCI/AND]:	IR spectra of OF complexes
[92XIE/LIU]:	Calculation of oscillator strength
[93XIE/XIA]:	Six electronic states at MRSDCI level

TABLE 5.1.1. Vibrational/rotational structure, cm^{-1}

Source	State	A	ω_e	$\omega_e x_e$	B_e	α_e	r_e(Å)	Comments
Experimental Values								
58DUR/RAM								Did not observe any OF bands
65ARK/REI2			1028					Photolysis of OF_2 in a N_2 or Ar matrix at 4K; fundamental IR absorption of $O^{16}F$ and $O^{18}F$; ω_e=1050 cm^{-1} is a value presumably corrected for matrix effects by 70OHA/WAH
69ARK	$O^{16}F$ $O^{18}F$		1028.6±0.3 997.7±0.3					IR matrix study
71AND/RAY			1028.6				1.36±0.03	Matrix infrared spectrum
72AND	$O^{16}F$ $O^{18}F$		1028.9±0.5 998.4±0.5					Argon matrix Raman study
72YAN			916					Review of trends in ω_e for many diatomic molecules
74SMA/FOX								FO discussed but no data presented
79MCK	$X^2\Pi$	−177.3	1044		1.05955±0.00019	0.013475±0.000035	1.35789±0.00025	CO_2 laser magnetic resonance; first detection of rotational constant B_e; B_0 = 1.05282±0.00019 cm^{-1}; first observation of OF in the gas phase; ω_e can be estimated from this data
80AND								Laser Raman matrix isolation spectra; restates information obtained in 72AND
80DYK/JON		−160±30	1044				1.35789	He(I) photoelectron spectrum ionization of OF($X^2\Pi$); estimated splitting of ground state; r_e and ω_e values were taken from 79MCK
83MCK/YAM	$^2\Pi_{3/2}$	−177.3	*1033.4829		**1.05285±0.00009			IR diode laser spectroscopy; *ω_o value; **B_o value
86BUR/HAM	$^2\Pi_{3/2}$	−198.3	1053.42	10.23	1.052869	0.01325	1.35412	High resolution Fourier transform spectroscopy
88HAM/SIN		−193.80	1052.99	9.9003 *−0.068456 *−0.0010881 *−0.00005945	1.05870547			High resolution IR chemiluminescence (emission); *$\omega_e y_e$, $\omega_e z_e$ and $\omega_e a_e$ values
Calculated Values								
63TAN								Molecular orbital theory (3 electron bond discussion)
74LAT/CUR							1.337	Ab initio calculations

TABLE 5.1.1. Vibrational/rotational structure, cm^{-1} — Continued

Source	State	A	ω_e	$\omega_e x_e$	B_e	α_e	r_e(Å)	Comments
89SUN								Article not available at this time
90FRA/GOL							1.344	Ab initio molecular orbital theory
91HAA			1017	12.21			1.38	QCISD(T) calculation; ω_e and $\omega_e x_e$ values given at 4 different levels of calculation
92KOS/SCH		−187.90					2.5058	Ab initio molecular orbital method
93FRA/SU2			1542				1.344 1.328	Ab initio calculations; r_e values derived from UMP2/6–31G(d) and UMP2/6–311G(d,p)
94CHO			1156	8.29		0.01070		Calculations based on deMon density functional program
94FRA			1542				1.323	Ab initio method; UMP2/6–31G(d)

TABLE 5.1.2. Dissociation energy/enthalpy of formation, $kJ \cdot mol^{-1}$

Source	D_0°(FO)	$\Delta_f H$	Temperature	Comments (as reported values)
Experimental Values				
34KOB/SCH	240.58			Kinetic study of thermal decomposition of OF_2 between 250–270 °C; dissociation energy based on average bond energy of OF_2; 57.5 $kcal \cdot mol^{-1}$
57DIB/REE	106.3			Electron impact study; direct calculation not feasible from ion data; D(F−O) calculated from known $\Delta_f H(OF_2,g)$ and AP(F−); experiment suggested $D(OF)+D(FO-F)=3.9\pm0.1$ eV with $D(FOF-F)=2.8$, $D(OF)=1.1$ eV
59HIL		135.6±42	298 K	Value derived from $\Delta_f H$ of OF_2; 32.4±10 $kcal \cdot mol^{-1}$
65ARK/REI2	~236.4			Matrix IR (photolysis of OF_2 in a N_2 or Ar matrix at 4 K) study; location of OF absorption indicated (qualitatively) that D(O−F) may be higher than the average energy in OF_2; similar results for the chlorine molecules; suggested 48GLO reasonable; ~2.45 eV
67MAL/MCG		126		Mass spectrometric investigation of O_3F_2; no specific $\Delta_f H$ value given; however $\Delta_r H$ values are given for four reactions from which $\Delta_f H$(OF,g) ~30 $kcal \cdot mol^{-1}$
67OGD/TUR	>167.4			Based on kinetic description of the photolysis of fluorine with N_2O; study suggested lower limit for the dissociation energy, $D^\circ(OF)>40$ $kcal \cdot mol^{-1}$; 69ARK suggested presence of SiF_4 in fluorine sample might have caused a problem in the absorption spectra
69ARK	>167.4			Photolysis of OF_2-N_2O or OF_2-CO_2 mixtures; observations supported a lower limit estimate, $D^\circ>40$ $kcal \cdot mol^{-1}$
71CLY/WAT	215±17			Molecular beam study; measurement of appearance potential of OF^+ from OF and OF_2; D° dependent on enthalpy of atomization for OF_2; 2.25±0.15 eV
72CZA/SCH	212.5±8.4			Thermal decomposition of OF_2 using a method; D(O−F) calculated from known $\Delta_f H(F_2)$ and the activation of an observed reaction

TABLE 5.1.2. Dissociation energy/enthalpy of formation, kJ·mol — Continued

Source	D_0°(FO)	$\Delta_f H$	Temperature	Comments (as reported values)
72LEV	243.2±17.4			EPR study; $2.34 < D^\circ < 2.70$ eV; 2.52±0.18 eV is the recommended dissociation value
73BER/DEH		109.3±20.9	0 K	Enthalpy of formation obtained from photoionization study; 26.11±2.3 kcal·mol^{-1}
94ZHA/KUO		109.5±8.0		Calculated from photoionization efficiency spectra and a previous appearance energy measurement
Calculated Values				
48GLO	236.4			Estimated based on assumption that D(OF)~1/2D(OF_2); supported by data for ClO and Cl_2O and trends in CO, NO, O_2 and OF; [2.45 eV]
49GLO	265.3			As in 48GLO, estimated from OF_2; no indication to source of value for OF_2 or reason for different value for OF; [2.75 eV]
50SCH	169.5±12.6			Calculation; assumes D(F−O)=1/2D(OF_2); 40.5±5 kcal·mol^{-1}
62PRI/HAR	212.3			Value was estimated by a method of isoelectronic similarity; [2.2 eV]
63PRI/PAS	217.1			Value was estimated in part by a method of ioelectronic similarity and because it fits in with the total bond energy of OF_2 and in comparisons with the chlorine and fluorine systems; [2.25] eV
65MOR	209.6			Calculated value, 50.1 kcal·mol^{-1}; refers to an experimental value of 53 kcal·mol^{-1} but no indication as to the origin of this value
69ION/ION				Analysis of Mulliken's overlap energies; although dissociation energy for OF was discussed, no value was given
70OHA/WAH	290±30/−80			Hartree-Fock wave functions; calculation dependent on auxilary information for OF_2, O and F; 3.0±0.3, −0.8 eV
70OHA/WAH2				Hartree-Fock wave functions; OF mentioned only in comparison to SeF and SF
70OHA/WAH3				Hartree-Fock wave functions; −174.19502 Hartree
72LIE				Comments on the results of 70OHA/WAH
77GLI		113.4		Source of this experimental value not identified
78DEW/RZE		109.2		Observed and calculated enthalpy of formation values respectively, 26.1 kcal·mol^{-1}, 32.5 kcal·mol^{-1}; observed value taken from 73BER/DEH
78DEW/RZE2		90.8		MNDO semiempirical SCF−MO method; 21.7 kcal·mol^{-1}
80GLI		106	0 K	Study directed at use of MINDO approximation for other oxygen fluorides
80JUG/NAN		135.9 115.1	298 K	Enthalpy of formation calculation using SINDO and MNDO techniques; value reported is the difference between the experimental and calculated values; refers to an experimental enthalpy of formation value of 26.1 kcal·mol^{-1} and states that it was taken from Dewer's earlier papers (1978); 6.4 kcal·mol^{-1} (MNDO, $\Delta_f H$) and 1.4 kcal·mol^{-1} (SINDO1; E_B)
80NAN/JUG				No value given

TABLE 5.1.2. Dissociation energy/enthalpy of formation, kJ·mol — Continued

Source	D_0°(FO)	$\Delta_f H$	Temperature	Comments (as reported values)
86MEL		102.1	0 K	BAC/MP4 calculation of enthalpy of formation; 24.4 kcal·mol^{-1}
90ZHA/FRA		116.3±4.2		Ab initio studies using MP theory up to the fourth order; enthalpy of formation calculated using an isodesmic reaction scheme; 27.8±1 kcal·mol^{-1}
91BRA/WRI	225.8			7 different calculations using MRD-CI potential surfaces; refers to the experimental value of 71CLY/WAT; 1.607 – 3.11 eV, 2.29 eV, 2.34 eV; the last value is designated as the best value
93FRA		116.3		Ab initio calculations to investigate stability of HOOF in the reaction of HO with OF; refers to an enthalpy of formation value of 90ZHA/FRA; 27.8 kcal·mol^{-1}
93FRA/SU		*116.3±4.2*		*Enthalpy of formation; value taken from* 90ZHA/FRA; 27.8±1 kcal·mol^{-1}
94CHO	403.7±188.5			Local density calculation; 4.184±1.954 eV
Review				
50SCH2				Review; no value given
53GAY	144.7±48.2			Value based on results of 48GLO; using (DF_2)=1.6 eV this gives 1.5 eV for OF; 1.5±0.5 eV, (35 kcal·mol^{-1})
58BRE	167.36			Review; recommended a value of 40 kcal·mol^{-1}
62VED/GUR	184±42			Assumed $D^\circ(OF)=1/2D^\circ(OF_2)$
63SCH		106.1		Based on results of 57DIB/REE; 1.1 eV
66VED/GUR	184.1±41.8		0 K	The recommended dissociation value was based on the assumption $D^\circ(OF)=1/2D^\circ(OF_2)$; 44±10 kcal·mol^{-1}; refers to electron impact data of 57DIB/REE
68GAY	231.6±38.6			Review; refers to 5 studies with values ranging from 1.1 to 2.45 eV; 2.4±0.4 eV (55 kcal·mol^{-1})
69BRE/ROS	230±40		0 K	Dissociation energy values; refer to numerous studies, preferred results of 65ARK/REI and 48GLO; 55 kcal·mol^{-1}
69FRA/DIL		171.5	298 K	Value taken from Wagman *et al.* (1968); 41 kcal·mol^{-1}; reprinted value in 1982 is different
70DAR		115±13		Based on three studies, 57DIB/REE, 62VED/GUR, and 68WAG/EVA (reprinted as 82WAG/EVA); 37±3 kcal·mol^{-1}
76BEN		108.8±4.2	300 K	Review; 26±1 kcal·mol^{-1}
79HUB/HER	215.2			Based on results of 71CLY/WAT; indirectly obtained from the difference between electron potentials of OF and OF_2 and the known enthalpy of formation of OF_2; considered results of 70OHA/WAH and 72LEV; 2.23 eV
82WAG/EVA		108.78	0 K	Reprint of 1968 edition; based on consideration of four studies by 66MAL/MCG, 71CLY/WAT, 72LEV and 73BER/DEH

5.2. ^{18}OF

Through the photolysis of OF_2 at 4 K, Arkell *et al.* [65ARK/REI] observed a fundamental infrared frequency which they attributed to OF. Assignments were made in argon and nitrogen matrices for ^{16}OF and ^{18}OF. The calculated isotopic shift agreed with observations.

An infrared absorption spectrum, assigned to OF, was observed by Andrews and Raymond [71AND/RAY] in the reaction of metals with OF_2. OF (and ^{18}OF) were produced by the reaction of metals with OF_2 (or $^{18}OF_2$). Andrews [72AND] observed the Raman spectra of OF, ^{18}OF and ^{16}OF free radicals.

5.3. O_2F (FOO)

All references dealing with O_2F are listed in the following eight categories. Of prime interest are the spectroscopic studies.

1. Rotational constants/structure —
   [65ARK], [66SPR/PIM], [66SPR/TUR], [67ADR], [67ATH/HIN], [68GOR/POP], [69GOL/HAY], [70HAR], [73CAR/MAC], [74SIN/NAG], [75BIS/VAL], [75MCC/PAL], [79PAN/CHA], [80GLI], [80HIN], [80THY/SUB], [84YAM/HIR], [85GOS/RAG], [86MEL], [87MCK/BUR], [89BOG/DAV], [90FRA/GOL], [91BLE/DAV], [92FRA/ZHA]
2. Vibrational frequency/spectroscopy —
   [65ARK], [66NOB/PIM], [66SPR/PIM], [66SPR/TUR], [71GAR/LAW], [74SIN/NAG], [80JAC], [84JAC], [84YAM/HIR], [85KIM/CAM], [87MCK/BUR], [88CAM], [88JAC], [89LYM], [94JAC]
3. EPR —
   [65KAS/KIR], [65NEU/VAN], [66FES/SCH], [66KIR/STR], [66LAW/OGD], [66MET/WEL], [66WEL/MET], [67ADR], [68LAW/OGD], [70VED/GER], [73CHE/TUP], [75MCC/PAL], [76CHR/WIL], [76MAT/TUP], [76TUP/MAT], [84GLI]
4. Enthalpy of formation/dissociation —
   [58BRE], [61ARM/KRI], [61BRE/ROS], [65LEV/COP], [66MAL/MCG], [66SPR/TUR], [67ADR], [67MAL/MCG], [68LEV/COP], [68TUR], [69FRA/DIL], [76MAT/TUP], [77GLI], [78DEW/RZE], [79SHA/KOT], [80GLI], [80THY/SUB], [84FRE], [85GOS/RAG], [86MEL], [87PAG/RAT], [88CAM], [88LYM/HOL], [89LYM], [90FRA/GOL], [92FRA/ZHA], [94ELL/SEH], [95CAM/CRO]
5. Kinetics —
   [37SCH/FRI], [68SOL/KEI], [73CHE/TUP], [73ZET], [76MAT/TUP], [78CHE/TUP], [79COO/HOR], [79SHA/KOT], [80BAU/COX], [82BAU/COX], [82DAV/TEM], [84CHR], [85KIM/CAM], [87PAG/RAT], [88CAM], [90CAM], [94ELL/SEH], [95CAM/CRO]
6. Formation/decomposition/detection —
   [65KIR], [65MAG], [66MCG/MAL], [68SOL], [69GOE/CAM], [73NIK/DUD], [73ROZ/GUT], [75ALE/NIK], [76ALE/NIK], [78COO/PIL], [78LEG/MAK], [80GRI/DIS], [80SMI/WRI], [80SOL], [81SLI/SOL], [81SMI/WRI], [83BAS/VAG], [83TEM/WAG], [86YU], [87FIT/DUN], [88MAL/PER], [89TIM/PRU], [90FRA/GOL], [92CHR], [92LIU/DAV]
7. Reactions —
   [68SOL], [69GOE/CAM], [77COO/PRI], [79COO/HOR2], [80COO/HOR], [82COO/HOR], [88SYM/ROS], [89APP/DOW], [91LUT/SMA], [92ALM/HOL], [92MAR/SZE], [94SEH/SEH]
8. Review —
   [61MCG], [68TUR], [70DAR], [72BRI], [84BUR/LAW], [88JAC], [89LYM], [90JAC], [94JAC]

Since this asymmetric molecule is bent, the point group is C_s. The three vibrational frequencies are IR and Raman active. There are numerous studies that report the geometry of FOO, either derived from rotational constants or quantum theory calculations. These studies are summarized in Table 5.3.2. We recommend and adopt the values measured by 84YAM/HIR based on gas phase IR diode laser spectrometry. Subsequent studies by [87MCK/BUR] and [91BLE/DAV] are in excellent agreement.

Numerous experimental studies have measured the vibrational frequencies of FOO, both in the gas phase and matrices. In addition, many of the experimental studies have involved the observation of spectra due to four isotopic species $^{16}O_2F$, $^{18}O_2F$, $^{16}O^{18}OF$, and $^{18}O^{16}OF$. The results are summarized in Table 5.3.3. There is some confusion in the literature due to the assignments of ν_2 and ν_3 as to which one is the bending frequency. ν_1 consistently represents the O−O stretch. All reported values are in good agreement. We recommend and adopt the gas phase vibrational frequencies as suggested by [94JAC] in her review. The adopted frequencies are based on the results of 66SPR/TUR, 84YAM/HIR, 85KIM/CAM and 87MCK/BUR.

Gosavi *et al.* [85GOS/RAG] assigned $^2A''$ as the ground state of FOO and $^2A'$ as an excited state at approximately 1.07 eV (24.7 kcal·mol^{-1}, 103.2 kJ·mol^{-1}, 8630 cm^{-1}). Total energies were computed by CI calculation at the SCF level optimized geometry. Numerous authors stated that the ground state of this free radical has doublet character including [66SPR/TUR, 89BOG/DAV].

There are numerous EPR studies on the oxygen fluorides, including FOO. In most of these studies, a spectra was associated with the radical FOO which was formed under a number of decomposition conditions (photolysis). In all cases the radical was assumed to be a nonlinear molecule with a doublet ground state. Refer to the discussion for O_3F for a possible reinterpretation of this EPR data. The EPR articles are listed in the following summary table. Unfortunately, no specific structural information was provided in these studies.

There are no direct measurements for the enthalpy of formation or dissociation energy (of either bond) for this FOO radical. However, there are numerous kinetic studies from which bond dissociation energy was derived based on the 89LYM discussion, 87PAG/RAT and 88CAM. These values are listed in Table 5.3.4. The results discussed in the mass spectral studies [65MAL/MCG, 66MAL/MCG, 67MAL/MCG] are not reasonable in comparison to the more recent kinetic studies. We recommend and adopt an enthalpy of formation value $\Delta_f H°(\text{FOO, g, 298.15 K}) = 23\ \text{kJ·mol}^{-1}$.

TABLE 5.3.1. EPR spectra assigned to FOO

Source	Technique
65KAS/KIR	EPR spectra of F_2O_2 and F_2O_3
65NEU/VAN	EPR spectra of the decomposition of FSO_2OOF
66FES/SCH	EPR spectra during electron irradiation of liquid CF_4-O_2
66KIR/STR	EPR spectra of O_4F_2, O_2F_2 and OF_2
66LAW/OGD	EPR NMR spectra of O_2F_2 in CF_3Cl
66MET/WEL	EPR study of liquid OF_2; with photolysis, observed a radical classified O_xF
66WEL/MET	EPR spectra of O_2F_2; isotopic species (^{17}OOF, $O^{17}OF$, $^{17}O_2F$) contributed to the paramagnetism
67ADR	IR and EPR spectra of O_2F
68LAW/OGD	EPR-NMR spectra of O_2F_2
70VED/GUR	EPR study of F–O system
73CHE/TUP	IR spectroscopy and EPR spectra of OF, O_2F and O_2F_2
75MCC/PAL	SCF-MO calculations, EPR spectra of FOO
76CHR/WIL	EPR study of dioxygenyl salts; spectra in excellent agreement with other FOO studies
76MAT/TUP	Electronic absorption spectra and EPR of O_2F and O_2F_2
76TUP/MAT	EPR spectrum of FOO
84GLI	Calculated spin density and hyperfine coupling constants; refers to 67ADR

TABLE 5.3.2. Rotational constants/structure

Source	Rotational constants, cm^{-1}			Bond distance, r(Å)		Bond angle	Comments
	A	B	C	(F–O)	(O–O)		
65ARK				1.63	1.22	100	IR spectra in matrix (Ar, O_2, N_2) isolated FO_2 at 4 K
66SPR/PIM							Discusses bending in oxygen fluorides and related compounds; does not give a quantitative structure for O_2F
66SPR/TUR				1.575	1.217	109.5	IR spectra of N_2, Ar, and O_2 matrix isolated FOO at 77 K; molecular parameters are analogous to those of O_2F_2
67ADR				1.575	1.22	90.5	Assumed bond angle; bond distances are taken from O_2F_2
67ATH/HIN						bent	Unrestricted Hartree-Fock method with CNDO/2 approximation; authors assumed molecule was bent; no quantitative geometry given
68GOR/POP				1.19	1.19	110.6	Calculated geometry via INDO self-consistent theory; no experimental data available for comparison
69GOL/HAY				1.63	1.23	128°22'	Nonempirical LCAO-MO-SCF calculations to determine the relative stability of FOO and OFO; estimated geometry; the bond distances are taken from 65ARK

TABLE 5.3.2. Rotational constants/structure — Continued

Source	Rotational constants, cm^{-1}			Bond distance, r(Å)		Bond angle	Comments
	A	B	C	(F−O)	(O−O)		
70HAR						bent	Discusses bond orders in FOO and O_2F_2; assumed a bent molecule but no quantitative data given; refers to 68TUR review for bond lengths and force constants
73CAR/MAC				1.195	1.220	112	CNDO/2 method
74SIN/NAG				1.575	1.217	109°30"	These values were taken from the data of O_2F_2; incorrectly stated that no experimental structural data available
75BIS/VAL				1.19	1.195	109.9	SCF-INDO method used to calculate the O−O bond length and the angle; assumed an F−O distance
75MCC/PAL				*1.575	*1.217	*109.5	SCF calculations of the g-tensor; ESR; *adopted values from 66SPR/TUR
79PAN/CHA							Isotropic hyperfine coupling constants estimated by SCF-MO-LCAO-UHF-MINDO/3; no quantitative information on structure was given
80GLI				1.496	1.211	117.1	Calculated using MINDO approximation
80HIN				1.43	1.32	109	SCF-MO calculations
80THY/SUB							Assumed force constants and structure from 66SPR/TUR
84YAM/HIR	2.619±0.017	0.334008	0.295365	1.649± 0.013	1.200± 0.013	111.19 ±0.36	Gas phase IR diode laser spectrometry: molecular constants for the ν_2=0
85GOS/RAG				1.4402 1.4280 1.3810	1.3328 1.4586 1.2547	106.7 100.92 107.73	Ab initio molecular geometry optimization at the RHF-SCF level with 6–31G and 6–31G* basis set for $^2A''$; confirms the $^2A''$ state for the ground state as suggested by 66FES/SCH and 67ADR;
				1.3606	1.3792	101.18	$^2A'$ is suggested as the excited state
86MEL				1.35	1.254		BAC/MP4 calculations
87MCK/BUR	2.613396	0.333987	0.295403				Fourier transform infrared spectra; rotational constants for the ν_0 band
89BOG/DAV	2.616116	0.33402482	0.2953756				Microwave spectrum; original units in GHz, presented here in cm^{-1}
90FRA/GOL				1.380 1.383	1.437 1.250	107.6 109.6	Theoretical geometries were calculated at the RHF/6–31G* level and the UMP2/6–31G* level
91BLE/DAV	2.6161477	1/2(B+C)=0.314704075 1/2(B−C)=0.019324842					Infrared LMR spectra at wavelengths near 920μm; original units in GHz presented here in cm^{-1}
92FRA/ZHA				1.709	1.198	111.8	Structure calculated using MP-CASSCF-QCI; geometries for 11 different levels of calculation presented; values given here refer to QCISD(T)–6–31G(D)

TABLE 5.3.3. Vibrational frequencies, cm^{-1}

Source		ν_1	ν_2	ν_3	Comments
65ARK		1494	584		IR spectra of matrix (Ar, O_2, N_2) isolated FOO at 4 K
66NOB/PIM	$F(^{16}O_2)$	1495.0	584.5	376.0	IR spectra of N_2 matrix isolated FOO are based on the measurements of 4 isotopic species; ν_3 is the bending frequency
	$^{18}O^{16}OF$	1453.9	581.2		
	$F(^{18}O_2)$	1453.9	563.4		
	$^{16}O^{18}OF$	1411.7	560.1	366.6	
66SPR/PIM					Discussed possible bonding in FOO but relies on earlier data
66SPR/TUR	$F(^{16}O_2)$	1499.7	586.4	376.0	IR spectra of the N_2, Ar, and O_2 matrix isolated FOO at 77 K is based on measurements of 4 isotopic species; electronic ground state is a doublet and ν_3 is the bending frequency
	$^{18}O^{16}OF$	1459.7	586.4	366.6	
	$F(^{18}O_2)$	1416.4	562.5	366.6	
	$^{16}O^{18}OF$	1459.7	562.5	376.0	
71GAR/LAW		1490	586		Prime measurement was the IR and Raman spectra of solid and matrix isolated O_2F_2; observed the decomposition to O_2F
74SIN/NAG					Used values of 66SPR/TUR and 66NOB/PIM
80JAC		1490	583.5		Ar matrix spectrosopy; agree well with results of 65ARK and 66SPR/TUR
84JAC		1490	376	579.32	Review; ν_1 and ν_2 values are based on IR spectra of matrix isolated (Ar or N_2) studies of 65ARK, 80JAC and 66SPR/TUR respectively; ν_3 is based on the diode laser gas phase study of 84YAM/HIR
84YAM/HIR				579.32	Gas phase IR diode laser spectroscopy
85KIM/CAM		1489			Laser flash photolysis of the gas phase O_2F radical
87MCK/BUR		1487		579.32	Fourier transform IR spectra of O_2F; $\nu_2+\nu_3=940$ cm^{-1}, $2\nu_3=1142$ cm^{-1}, $\nu_2+2\nu_3=1496$ cm^{-1}, $2\nu_1=2948$ cm^{-1}
88CAM		1490			FTIR study of equilibrium between O_2F and O_2F_2 and O_2
88JAC		1486.96	376	579.32	ν_1 and ν_3 are based on the gas phase IR studies of 85KIM/CAM, 87MCK/BUR and 84YAM/HIR; ν_2 is based on the N_2 matrix isolated study of 66SPR/TUR
89LYM		1490.0	376.0	579.3	Based on the laser flash photolysis results of 85KIM/CAM, the IR diode laser values of 84YAM/HIR, the IR results of 66NOB/PIM and the argon matrix study of 80JAC
94JAC		1486.93		579.32	Review; ν_2 is the bending frequency; reported values are from 66SPR/TUR, 84YAM/HIR, 85KIM/CAM and 87MCK/BUR; 1st line is gas phase, 2nd line is N_2 matrix, and 3rd line is Ar matrix studies
		1500	376	586	
		1490		584	

TABLE 5.3.4. Enthalpy of formation, kJ·mol^{-1}

Source	$\Delta_f H°$(FOO,g, 0 K)	Reaction	Comments (as reported values)
61ARM/KRI	>154.3	$FO_2(g)=F(g)+2O(g)$	Review; estimate taken from 61BRE/ROS
61BRE/ROS	>154.3	$MO_2(g)\rightarrow M(g)+2O(g)$	Estimated enthalpy of formation based on trends in atomization energies; this value may refer to OFO (rather than FOO); $\Delta_f H°(298\ K) = <100$ kcal·mol^{-1}
65LEV/COP	14.5	$FOO\rightarrow F+O_2$	Calculated $\Delta_f H=3.5$ kcal·mol^{-1} from an estimated $\Delta_r H=17.3$ kcal·mol^{-1} for O_2F_2=FOO+F; assumed enthalpy of formation of O_2F_2 was 4.73 kcal·mol^{-1} from 59KIR/GRO; this led to $D°(F-O_2)=15$ kcal·mol^{-1}
65MAL/MCG	0.1 −105.1	$FOO\rightarrow F+O_2$ $FOO\rightarrow O+OF$	Mass spectrometry; enthalpy of formation was derived from dissociation energy values; assumed $D(F-O_2)$= 0.8 eV, =18.45 kcal·mol^{-1}; D(O−OF)= 4.8 eV, =110 kcal·mol^{-1} [these two values are not at all consistent with the currently adopted D(FO)]

TABLE 5.3.4. Enthalpy of formation, kJ·mol^{-1} — Continued

Source	$\Delta_f H°$(FOO,g, 0 K)	Reaction	Comments (as reported values)
66MAL/MCG	0.1 −105.1	FOO→F+O_2 FOO→O+OF	Mass spectrometry; enthalpy of formation was derived from dissociation energy values; assumed D(F−O_2)= 0.8 eV, =18.45 kcal·mol^{-1}; D(O−OF)= 4.8 eV, =110 kcal·mol^{-1} [these two values are not at all consistent with the currently adopted D(FO)]; claimed these results supported earlier study 65MAL/MCG
66SPR/TUR			Thermal functions calculated but no enthalpy of formation given; normal coordinate analysis suggested O−O double bond as in O_2 and FOOF and a much weaker F−O bond
67ADR	−73.34	FOO→F+O_2	Derived bond order from EPR results, estimated D(F−O_2) ~36 kcal·mol^{-1}
67MAL/MCG			Mass spectrometry; reaction scheme and enthalpies given for the decomposition of O_3F_2; described in terms of FOO radical; no enthalpy of formation given
68LEV/COP	14.5	FOO→F+O_2	Discussed stability; suggests the F−O_2 bond is approximately 15 kcal·mol^{-1} as in 65LEV/COP
68TUR	2.0 −105.06	O_2F→O_2+F O_2F→O+OF	Review; gives two modes of decomposition; reported 18 and 110 kcal·mol^{-1} respectively (from 65MAL/MCG); these two values are not at all consistent with the currently adopted D(FO)
69FRA/DIL	14.401		Review; value taken from JANAF (1967); $\Delta_f H°$(298 K)= 3.0 kcal·mol^{-1}
76MAT/TUP			Could calculate a limiting value based on the photochemical decomposition O_2F→O_2+F; discussion mentions dissociation values from 65MAL/MCG
77GLI	14.401		Value extracted from JANAF (1967); $\Delta_f H°$(298 K)= 3.0 kcal·mol^{-1}
78DEW/RZE	102.6		$\Delta_f H°$(298 K)= 24.1 kcal·mol^{-1}; calculated enthalpy of formation by the half-electron method; refers to a value of 3.0 kcal·mol^{-1} from the JANAF Tables 2nd Edition
79SHA/KOT	23.44		EPR measurement of rate constants
80GLI			MINDO approximation; total energy is −1095.4976 eV
80THY/SUB	−1.9	FOO(g)→F(g)+2O(g)	Calculated the enthalpy of atomization (136.9 kcal·mol^{-1}) based on force constants data; refers to 66SPR/TUR value of 135.0±5 kcal·mol^{-1}
84FRE	52.14	O_2+F_2→O_2F+F	Reactions in O_2 matrix by visible and UV radiation of Hg arc; laser irradiation; spectral range of F_2+O_2 reaction is 14500−16600 cm^{-1}; enthalpy of reaction value given in introduction (31 kcal·mol^{-1}); no source given for data;
85GOS/RAG			Molecular geometry optimization at the RHF-SCF level with 6–31G and 6–31G* basis sets; total energies computed by CI calculations at SCF level optimized geometry
86MEL	99.6		BAC-MP4 theory; 23.2 and 23.8 kcal·mol^{-1} given for 298 and 0 K respectively
87PAG/RAT	27.94±2	F+O_2=FO_2	Spectrokinetic study (295–359 K) = −12.62±0.5 kcal·mol^{-1}; gas phase equilibrium; led to D(F−O_2)=11.68±0.5 kcal·mol^{-1}
88CAM	18.9	2O_2F=O_2F_2+O_2	Gas equilibrium; FTIR study; yielded K=22 at 286 K
88LYM/HOL	24.81±1.7		Derived from a kinetic study of reactions of fluorine atoms with oxygen; derived $\Delta_f H$(298 K) = 5.49 ± 0.40 kcal·mol^{-1}
89LYM	24.73±1.7 24.81±1.7 25.98 25.77		5.47±0.4 kcal·mol^{-1}, recommended value based on mean of three studies; 5.49±0.4 kcal·mol^{-1} based on interpretation of 88LYM/HOL; +5.77 kcal·mol^{-1} based on preliminary analysis of unpublished results; value calculated by Lyman based on data of 85KIM/CAM and 79SHA/KOT (5.16 kcal·mol^{-1}); both of these works are kinetic studies; results of 65LEV/COP also discussed
90FRA/GOL			Enthalpy of formation was underestimated by two different levels of ab initio MO calculations; refers to 4 experimental values: 87PAG/RAT, 89LYM, JANAF (3rd Edition), 76BEN

TABLE 5.3.4. Enthalpy of formation, kJ·mol^{-1} — Continued

Source	$\Delta_f H°$(FOO,g, 0 K)	Reaction	Comments (as reported values)
92FRA/ZHA	37.24±12.6		Enthalpy of formation (T/K=0)=8.9±3 kcal·mol^{-1}; calculated by MP perturbation, CASSCF, and QCI ab initio MO methods
94ELL/SEH	27.94±2	FOO→F+O$_2$	Refers to F−O$_2$ bond strength = 13 kcal·mol^{-1} from 87PAG/RAT
95CA/CRO	49.8±1	FOO→F+O$_2$	F + O$_2$ reaction system studies under high pressure and low temperature conditions; K determined below 315 and 420 K

5.4. O^{17}OF

Welsh *et al.* [66WEL/MET] studied the EPR spectra of the three O$_2$F isotopic species (O^{17}OF,^{17}OOF,^{17}O$_2$F). This article is discussed with the other EPR-related studies in the FOO section (Sec. 5.3) as is the related study by Fessenden and Schuler [66FES/SCH].

5.5. ^{17}OOF

Welsh *et al.* [66WEL/MET] studied the EPR spectra of the three O$_2$F isotopic species (O^{17}OF,^{17}OOF,^{17}O$_2$F). This article is discussed with the other EPR-related studies in the FOO section (Sec. 5.3) as is the related study by Fessenden and Schuler [66FES/SCH].

5.6. ^{17}O$_2$F

Welsh *et al.* [66WEL/MET] studied the EPR spectra of the three O$_2$F isotopic species (O^{17}OF,^{17}OOF,^{17}O$_2$F). This article is discussed with the other EPR-related studies in the FOO section (Sec. 5.3) as is the related study by Fessenden and Schuler [66FES/SCH].

5.7. O^{18}OF

Singh and Nagarajan [74SIN/NAG] surveyed the vibrational spectra studies on four isotopic species (^{16}O^{18}O^{19}F,^{18}O^{18}O^{19}F,^{18}O^{16}O^{19}F,^{16}O^{18}O^{19}F). The authors calculated root mean square amplitudes, molecular polarizability and thermal functions for these four species. The fundamental vibrational frequencies were taken from the work of [66NOB/PIM] and [66SPR/TUR]. The molecular structure was assumed to be similar to that derived from FOOF [66SPR/TUR]; r(O−F) = 1.575Å, r(O−O) = 1.217Å, ∠(OOF) = 109°30''. The structure data is included in Table 5.3.2, whereas the vibrational frequency information is noted in Table 5.3.3.

5.8. ^{18}O$_2$F

Singh and Nagarajan [74SIN/NAG] surveyed the vibrational spectra studies on four isotopic species (^{16}O^{18}O^{19}F,^{18}O^{18}O^{19}F,^{18}O^{16}O^{19}F,^{16}O^{18}O^{19}F). The authors calculated root mean square amplitudes, molecular polarizability and thermal functions for these four species. The fundamental vibrational frequencies were taken from the work of [66NOB/PIM] and [66SPR/TUR]. The molecular structure was assumed to be similar to that derived from FOOF [66SPR/TUR]; r(O−F) = 1.575Å, r(O−O) = 1.217Å, ∠(OOF) = 109°30''. The structure data is included in Table 5.3.2, whereas the vibrational frequency information is noted in Table 5.3.3.

5.9. OFO

The calculations by Gole and Hayes [69GOL/HAY], based on double-zeta sp basis set SCF total energy calculations as a function of OFO bond angle (assumed O−F bond distance of 1.19Å), predicted the ground state to be^2 B$_1$ with a bond angle of 128.22°. Using the authors results for ClO$_2$ one would estimate the uncertainty of this bond angle is of the order ± 4°. The non-empirical LCAO-MO-SCF calculations on O$_2$F indicated that OFO was thermodynamically unstable relative to FOO by over 100 kcal·mol^{-1}. However, the possible existence of a kinetically stable OFO species was not ruled out. No vibrational frequency information was provided.

Molecular geometry optimization of the ^{2}B$_1$, ^{2}B$_2$, $^2A_1$, and ^{2}A$_2$ states of OFO and the ^{2}A'' and ^{2}A' states of FOO was carried out at the RHF-SCF level with 6–31G and 6–31G* basis sets [85GOS/RAG]. These calculations predicted the ^{2}B$_1$ and ^{2}B$_2$ states of OFO to lie close in energy, with the ^{2}B$_2$ state lying approximately 3 kcal·mol^{-1} lower and designated as the ground state. These calculations yielded the result that FOO was more stable than OFO by 85 kcal·mol^{-1}. This order could change with complete optimization at the full CI level. The corresponding calculations for FOO were stated to be in agreement with experimental observations. These calculations (OFO) assigned a bond distance of 1.5591Å and a bond angle of 76.75°. No information is given on the vibrational frequencies.

5.10. O$_3$F

The photochemical reaction between fluorine and ozone was stated to produce O$_3$F as an intermediate [62STA/SIC]. No information was provided as to its vibrational frequencies or enthalpy of formation.

In examining the irradiation of a mixture of F$_2$ and O$_2$ using a water filter, Arkell [65ARK] tentatively assigned a band at 1503 cm^{-1} to O$_3$F. No other information was given on this radical.

The EPR spectra obtained by Kasai and Kirshenbaum [65KAS/KIR] on O$_2$F$_2$ and O$_3$F$_2$ were identical. Although the spectra was attributed to FOO, a later reference [72MCC/PAL] suggested that the radical was really O_3F.

McCain and Palke [72MCC/PAL], in their study of the hyperfine coupling constants, stated that the data for FOO shows very poor agreement. A comparison of experimental data with calculations suggested that the radical was actually O_3F.

Glidewell [80GLI], using MINDO approximation, calculated the geometry and enthalpy of formation ($+107.69$ $kJ \cdot mol^{-1}$), and predicted an asymmetric molecular structure of $F-O_1-O_2-O_3$ for O_3F: $r(F-O_1)=1.489$Å, $r(O_1-O_2)=1.314$Å, $r(O_2-O_3)=1.257$Å; $\angle(F-O_1-O_2)=116.2°$, $\angle(O_1-O_2-O_3)=124.2°$, $\angle(F-O_1-O_2-O_3)=53.1°$. It is important to note that this compound does not have a pyramidal structure, in contrast to the other halogen oxides (XO_3) which are thought to have a pyramidal structure. No vibrational frequencies were provided.

5.11. O_4F

In examining the irradiation of a mixture of F_2 and O_2 using a water filter, Arkell [65ARK] tentatively assigned a band at $1512\ cm^{-1}$ to O_4F. The author proposed the formation of O_3F from the decomposition of O_4F. No other data as to the structure or vibrational frequencies were provided.

Spratley and Pimentel [66SPR/PIM] discussed the bonding in fluorine oxygen compounds. Although the O_4F radical was not specifically discussed, it was presented in a table with the structure $F-O-O-O-O$. No other information was provided.

Goetschel *et al.* [69GOE/CAM], in their radiolysis of O_2-F_2 mixtures, briefly mentioned that the existence of O_4F would be consistent with some of their observations. No data was provided.

Christe *et al.* [76CHR/WIL], in their study of dioxygenyl salts, briefly referred to the possible formation of O_4F. No spectroscopic or thermodynamic information was provided.

Glidewell [80GLI], using MINDO approximation, calculated the geometry and enthalpy of formation ($+134.01$ $kJ \cdot mol^{-1}$), and predicted the structure $F-O_1-O_2-O_3-O_4$ for O_4F: $r(F-O_1)=1.488$Å, $r(O_1-O_2)=1.312$Å, $r(O_2-O_3)=1.439$Å, $r(O_3-O_4)=1.253$Å; $\angle(F-O_1-O_2)=110.1°$, $\angle(O_1-O_2-O_3)=122.0°$, $\angle(O_2-O_3-O_4)=123.3°$, $\angle(F-O_1-O_2-O_3)=80.4°$, $\angle(O_2-O_3-O_4=47.8°)$. It is important to note that this compound is not of a tetrahedral structure, in contrast to the presumed structure of the other (XO_4) halogen oxides. No vibrational frequencies were provided.

5.12. OF_2

As mentioned in the introduction, the following does not represent a complete coverage of all references dealing with OF_2. As a result, coverage in the areas dealing with preparation, reation, kinetics and patents is not complete. Note that many of the enthalpy of formation and dissociation studies refer back to the same experimental studies. Thus, there is not much firm experimental data for the enthalpy of formation. The remaining references dealing with OF_2 are listed in the following ten categories:

1. Preparation/formation/decomposition — [27BRA], [27LEB/DAM], [29LEB/DAM], [33RUF], [34KOB/SCH], [39YOS], [59RIC], [62GAT/STA], [64GAT/STA], [65KIR], [65NEU/VAN], [66HEN/RHO], [67OGD/TUR], [68SOL/KAC], [69DAU/SAL], [71AND/RAY], [72HOU/ASM], [73NIK/DUD], [79NIE], [92BED/MAR]
2. Physical properties — [30RUF/CLU], [30RUF/MEN], [31RUF/MEN], [31RUF/MEN2], [32RUF/EBE], [51TOO], [51TOO2], [52AND/SCH], [52SCH/SHE], [52THO], [57GAL], [59KIR/GRO], [62SVE], [63OSH], [63WAL], [65BIS/HAM2], [66FEI], [66LIP/NAG], [66THI], [69RIP/ZER], [72LIE], [73ROZ/GUT], [74MIK], [76ALE/NIK], [81PAL/HIO], [82CRU/AVR], [83AYM/PAR], [85EPI/LAR], [90SAA/KAU], [93OHW]
3. Enthalpy of formation — [30RUF/MEN], [30WAR/KLI], [31RUF/MEN2], [31WAR], [33YOS/HAT], [36BIC/ROS], [50BRE/BRO], [50LUF], [50SCH2], [52ROS/WAG], [54COU], [55EVA/MUN], [61ARM/KRI], [65BIS/HAM], [65BIS/HAM2], [66BIS/HAM], [66VED/GUR], [67MAL/MCG], [67TRO/WAG], [68KIN/ARM], [69FRA/DIL], [71CLY/WAT], [72HOU/ASM], [75BIN/DEW], [76KOE/JOL], [77GLI], [78DEW/RZE], [80GLI], [83DEK/JAS], [86MEL], [87HER], [88TYK], [89LIV/TAK], [90VAN/KEL]
4. Reactions — [33ISH/MUR], [34ISH/MUR], [35ISH/SAT], [35ISH/TAK], [41AOY/SAK], [45DAU/HAI], [62WIE/MAR], [63RHE], [69LIN/BAU], [72LEV], [92BED/MAR], [93BED/MAR], [93JAC/KRA], [93OHW]
5. Spectroscopy/vibrational frequencies:
   Experimental — [35HET/POH2], [36POH/SCH], [36SUT/PEN], [42BAR], [50BER/POW], [51JON/KIR], [51NIE], [62AGA/GRA], [65ARK/REI2], [66NEB/MET], [66SPR/TUR], [67MOR/YAM], [67OGD/TUR], [71AND/RAY], [71GAR/TUR], [71TRE/SAV], [72AND], [79KOL/KON], [83TAU/JON], [86TAU/JON], [87TAU]
   Theoretical — [81POP/SCH], [82MAR/RAO], [87BUR/SCH], [88THI/SCU], [90AND/PAL], [90SAA/KAU]
   Force constants — [36PEN/SUT], [51DUC/BUR], [52LIN/HEA], [56GOU/BUE], [59VEN/THI], [61PIE/JAC], [62NAG], [62OKA/MOR], [62VEN/THA], [63NAG], [63PIE/DIC], [63VEN/THA], [64RAJ], [65KUC/MOR], [66KUC/MOR], [66MOR/SAI], [66POP/SEG], [67OGD/TUR], [68CYV/CYV], [69BRU/RAF], [70NAR], [70THA/RAI], [70RED], [71TIM/GOD], [72KIR], [72MOH/MUE], [72NAT/RAM], [72SRI/JEY], [73SIC], [74SIM/CHO],

    [74SIM/NOV], [75DIA/SIM], [75SPE/SPI], [76ALI/RAI], [76GIR/SAS], [77VIZ/SEB], [80VIZ/SEB], [83DWI], [84CYV/CYV], [84WAS/MOO], [87KEE], [90AND/PAL], [93ALL/CSA]
  - Electronic spectra — [34GLI/SCH], [35HET/POH], [83BUS/SIB],
  - Miscellaneous — [46GOR], [53ARO], [57DIC/LIN], [60WUL], [61DUR/BAT], [61PIE/JAC], [63PIE/DIC2], [65STR/STR], [67NEB/MET], [68PET/SCR], [69BON/PET], [69POC/STO], [70BRO/BUR], [71HOL], [71RAD/HEH], [72ROB/KUE], [74MIN/MIT], [79NIE], [79SUG/KAU], [80MAY], [81ZHI/KOL], [83SCH/KAT], [84MAG], [84TAK/HOS], [90MAG], [92MCI/AND], [93MAG], [93WAT], [94LI/HON]

6. Dissociation energy/ionization potential —
   [32PAU], [34GLI/SCH], [45SKI], [46WIC], [48GLO], [49GLO], [49POT], [50SCH], [55AOK], [57DIB/REE], [63PRI/PAS], [63SCH], [65MOR], [66VED/GUR], [67TRO/WAG], [70DAR], [71CLY/WAT], [71COR/FRO], [72BRU/ROB], [72CZA/SCH], [73BER/DEH], [73ROT/SCH], [77GLI], [78CHO/HER], [78LEO/MED], [80VAL/VAS], [81LAN/CHO], [84ALE/VOL], [92CHO]
7. Geometry/structure:
   - Experimental — [35BOE], [35BOE2], [35HET/POH], [35HET/POH2], [35SUT/BRO], [36POH/SCH], [50BER/POW], [53IBE/SCH], [61HIL/JAC], [61PIE/JAC], [63PIE/DIC], [66MOR/SAI], [71TRE/SAV], [83TAU/JON],
   - Theoretical — [51DUC/BUR], [63SCH2], [66BUE/PEY], [66POP/SEG], [66SPR/PIM], [67ALL/RUS], [68GOR/POP], [70NEW/LAT], [73SIC], [74MIN/MIT], [75BIN/DEW], [76PLE/KOC], [79SCH/CRU], [80GLI], [80LAW/VAS], [80VAL/VAS], [82AHL/TAY], [82MAR/RAO], [82ZHU/MUR], [83DEK/JAS], [83DWI], [83MAR/DIX], [86DWI], [86MEL], [87REE/SCH], [88THI/SCU], [89BAI], [90SAA/KAU], [92GIL/ROB], [94GIM/ZHA]
   - Review — [36BRO], [37STU], [40MAX], [76CAL/HIR], [79HAR/LAU]
8. Review —
   [33YOS/HAT], [36BIC/ROS], [36BRO], [40SID/POW], [41SCH/STE], [46WIC], [50BRE/BRO], [52ROS/WAG], [54COU], [55EVA/MUN], [60GEO], [61ARM/KRI], [63STR], [66FOX/JAC], [66VED/GUR], [68TUR], [69FRA/DIL], [70DAR], [72BRI], [78LEO/MED], [84BUR/LAW]
9. Dipole moment —
   [60BRA/KUN], [60DOD/LIT], [61PIE/JAC], [66POP/SEG], [67POP/BEV], [68BON/PET], [68PET/SCR], [73ROT/SCH], [74BRO/WIL], [74BRU], [75PEI], [85DEL/PRI], [85KOL/SHC], [89LIV/TAK]
10. EPR —
    [65FLY], [65NEU/VAN], [66LAW/OGD], [66MET/WEL], [72LEV]

The geometry and vibrational frequencies of OF_2 were well established by the early 1950s. As a result, there are numerous studies involving the use of this information in force constants, vibrational amplitude and inertial defect studies. In these types of studies there is normally no new spectroscopic information available. As a result, these articles will not be discussed. Similarly, articles listed under miscellaneous include studies which do not provide any new experimental or theoretical information of interest for this review. The vibrational frequencies are summarized in Table 5.12.1, while the geoemtry and structure data is summarized in Table 5.12.2.

Since this symmetric molecule is bent, the point group is C_{2v}. There are three vibrational frequencies, all of which are IR and Raman active.

The enthalpy of formation has been established experimentally by King and Armstrong [68KIN/ARM]. These authors provided an excellent discussion of previous experimental studies [30RUF/MEN, 30WAR/KLI, 65BIS/HAM, 65BIS/HAM2]. The current adopted value is based on the flame calorimetry study of [68KIN/ARM]. All reported enthalpy of formation studies are summarized in Table 5.12.4.

There are numerous articles which refer to dissociation energy results. It is not always clear what the definition of the dissociation energy is. Most are used to derive the enthalpy of formation for FO. These studies have all been summarized in Table 5.1.2, earlier in this paper. Dissociation energy studies are listed in Table 5.12.3; however, they do not provide definitive enthalpy of formation values for either FO or FOF.

TABLE 5.12.1. Spectroscopy/vibrational frequencies, cm^{-1}

Source		ν_1	ν_2	ν_3	Comments
35HET/POH					IR spectra between 1 and 27μ
35HET/POH2					IR spectra; vibrational frequencies observed but assignments for the 3 specific frequencies not made
36POH/SCH		870	1280	1740	IR absorption spectra
36SUT/PEN		833	492	1110	Reinterpretation of the absorption spectra
42BAR					IR spectra; no assignments made
50BER/POW		929	461	828	IR spectra of $OF_2(g)$
51JON/KIR		928	461	831	IR spectra; comparisons made with 35HET/POH2; ν_2 not directly observed
51NIE					Explanation of history of some previous studies; no data given
62AGA/GRA					IR spectra; no assignments made
65ARK/REI2		929	461	826	Matrix IR studies; values from another unnamed source
66NEB/MET		945.1	470.4	858.8	IR spectrum; reinvestigation of Fermi resonance; harmonic frequencies and harmonicity constants also given
66SPR/TUR					IR spectra of products of photolysis of F and O in a matrix; 3 observed frequencies assigned to OF_2; ν_2 not observed; no assignments made
67MOR/YAM					IR spectra; attempt to examine the Fermi resonance between ν_1 and $2\nu_2$ states; rotational constants given
67OGD/TUR	$^{16}OF_2$ $^{18}OF_2$	925, 915 898, 889	461 457	821 794	IR matrix spectra of $^{16}OF_2$ and $^{18}OF_2$ in argon; the 2 values for ν_1 refer to the Fermi doublet
71AND/RAY					Matrix IR spectra of OF_2 or $^{18}OF_2$ in Ar; main emphasis is on the formation of LiOF rather than the examination of OF_2
71GAR/TUR		925.2	461.1	821.1	Raman spectra of liquid OF_2; polarization studies confirm earlier IR assignments and support existence of Fermi resonance
71TRE/SAV		412–416	456–462	812–845	Raman and IR spectra of OF_2 (cr)
72AND	 $^{18}OF_2$	920 892	465 461	825 799	Ar matrix Raman spectra
79KOL/KON		918.0±0.8 922.2±0.8	459.8±0.8	823.0±0.5	Absorption spectra in liquid N_2 at 80 K; Fermi resonance; also presents harmonic frequencies and anharmonicity constants
81POP/SCH		1167	480	1227	Ab initio calculations HF/3–21G; harmonic frequencies given
82MAR/RAO		1053.1	493.5	1081.4	Ab intio SCF calculations at the 4–31G level; harmonic frequencies given (source of frequencies not given)
83TAU/JON		924.15			Fermi diad at 928 cm^{-1} studied by IR-MW double resonance
86TAU/JON					Fermi resonance; diode laser spectra to resolve the true vibrational center for ν_1 and $2\nu_2$
87BUR/SCH		460.56			A, B, C and ground state calculated
87TAU					IR diode laser spectroscopy; ν_3 frequency range examined; Coriolis coupling
88THI/SCU		976	475	923	Ab initio prediction at the SCF, CISD and CCSD levels, using DZP and TZP basis sets; results listed for TZP CCSD/SCF
90AND/PAL		885	489	832	Simple spring model in terms of Cartesian coordinates
90SAA/KAU		944.93	469.22	843.86	Curvilinear internal coordinate Hamiltonian; harmonic frequencies calculated

TABLE 5.12.2. Geometry and structure

Source	Bond length(Å)	Bond angle(°)	Comments
35BOE		100±3	Electron interference technique; 35BOE2 assumed to be the same article
35HET/POH			IR spectra supports bent structure
35HET/POH2		100.6	IR spectra
35SUT/BRO	1.4±0.1	105±5	Electron diffraction study
36BRO	1.41±0.05	100±3	Review based on 3 studies [35SUT/BRO, 35BOE, 35BOE2]
36POH/SCH		100.6	Absorption spectra; refers to 35HET/POH2
37STU	1.4	105±5	Recalculated values based on data of 35BOE
40MAX	1.41±0.5	100±3	Review of electron diffraction data based on three studies: 35BOE, 35BOE2, 35SUT/BRO
50BER/POW	1.38±0.3	101.5±1.5	IR spectra of $OF_2(g)$
51DUC/BUR		101°30′	No mention as to the source of this value
53IBE/SCH	1.413±0.019 *1.418	103.8±1.5 *103.2	Electron diffraction study; *recommended values based on present work and 3 other studies
61HIL/JAC	1.3896	104.16	Microwave spectroscopy; derived 3 average rotational constants; also derived centrifical distortion constants
61PIE/JAC	1.409	103°18′	Microwave spectrum; dipole moment and inertial defect determined
63PIE/DIC	1.4124	103°10′	Microwave spectroscopy; derived average structure
63SCH2			Use of Walsh rules; a simple MO-LCAO calculation with Slater functions
66BUE/PEY			LCAO-MO-SCF calculations; correlate the internuclear angle with orbital energies
66MOR/SAI	1.4053±0.0004	103°4′±3′	Microwave spectra; determined equilibrium structure
66POP/SEG	1.410	99.2	SCF-MO-CNDO, SCF-MO-CNDO/2 calculations; refers to 53IBE/SCH
66SPR/PIM			Prediction of structures of molecules; only data for OF_2 implies a bent structure
67ALL/RUS		102	Ab initio SCF-MO calculations
68GOR/POP	1.18	106.6	SCF-MO calculation
70NEW/LAT	1.358 1.18	102.4 106.6	STO-3G approximation for STO basis functions; STO-3G and INDO value respectively; compared calculations to r_e structure of 66MOR/SAI
71TRE/SAV			Raman and IR spectra of crystalline OF_2; solid is not centrosymmetric; contains at least 2 molecules per primitive cell; site symmetry is C_s or C_1
73SIC	1.176	106.8	CNDO/2-MO study
74MIN/MIT		99.2	CNDO/2 study
75BIN/DEW	1.439	55.2	MINDO/3 calculations
76CAL/HIR	1.4053±0.0004	103.067±0.50	Review; based on four studies
76PLE/KOC	1.3585	102.91	Ab initio MO theory (STO-2G, STO-4G)
79HAR/LAU	1.409 1.412 1.405	103.3 103.2 103.1	Review; values based on 63PIE/DIC and 66MOR/SAI; 3 sets of values, refer to effective geometry, average geometry, and equilibrium geometry respectively
79SCH/CRU	1.407	102.0	Ab initio calculations VSEPR model; refers to 66MOR/SAI
80GLI	1.447	103.3(fixed)	MINDO calculation
80LAW/VAS	1.40 1.36 1.36	103.0 103.0 103.3	Orbital exponents were optimized for bond functions (Gaussian s and p orbitals located between nuclei); 3 different levels of calculation: DZ, DZD and DZB
80VAL/VAS	1.40 1.36 1.41	103 103 103	SCF-CI studies (DZ-SCF, DZP-SCF, DZP-CI)
82AHL/TAY	1.339 1.440 1.40	103.7 102.9 103.5	High quality correlated wave functions (SCF, CEPA 3 different types of frozen orbitals)
82MAR/RAO	1.422±0.08	102.5±8	Ab intio SCF calculations at the 4-31G level
82ZHU/MUR	1.339 1.335	103.35 103.01	SCF calculations 6–311G and 6–311G**; refers to data of 66MOR/SAI and 79SCH/CRU

TABLE 5.12.2. Geometry and structure — Continued

Source	Bond length(Å)	Bond angle(°)	Comments
83DEK/JAS	1.281	109.1	MO calculations using the MNDO method
83DWI	1.160	180	*SINDO calculations*
83MAR/DIX	1.356 1.422 1.396	102.4 102.5 102.7	Ab initio SCF calcualtions (3G, 4–31G, STO1); refers to 66MOR/SAI
83TAU/JON			Fermi resonance; IR-MW double resonance
86DWI	1.271	104	SINDO calculations
86MEL measured at 0 K	1.3484		Critical review; BAC/MP4 method using geometries optimized at HF–6–3G*; value
87REE/SCH	1.348 1.408	103.3 97.1	Ab initio 6–31G* calculations; optimized geometries with respect to E(Lewis)
88THI/SCU	1.3416 1.3428 1.3390 1.3861 1.3814 1.4141 1.4085	103.43 103.40 103.47 103.03 103.13 102.87 102.98	Ab initio prediction at the SCF, CISD and CCSD levels
89BAI	~1.4	102	Ab initio MO calculations (STO-3G); values extracted from a graph
90SAA/KAU	1.4052	103.07	Equilibrium geometry calculated from 66MOR/SAI, 86TAU/JON, 87BUR/SCH
92GIL/ROB			Only provides bond distance; relies on other sources for numeric values
94GIM/ZHA	1.3483 1.4229	103.22 102.61	Ab initio SCF-MO calculations at the RHF and MP2 levels using the 6–31G** basis set

TABLE 5.12.3. Dissociation energy

Source	Comments (as reported values)
34GLI/SCH	Absorption maximum attributed to OF_2 dissociation to 2F+O; <2100–
45SKI	Review; bond energy values from $\Delta_f H$ from 36BIC/ROS; 117.0 $kcal\cdot mol^{-1}$
46WIC	Review; $D_0(OF)=1/2D_0(OF_2)=115$ $kcal\cdot mol^{-1}$; no reference as to the origin of the value
49POT	No value recommended; refers to 3 earlier experimental enthalpy of formation studies
55AOK	Used Mulliken's magic formula (calculation); 5.62 eV
65MOR	Three-dimension Huckel calculations; refers to an observed value of 95 $kcal\cdot mol^{-1}$ (no source of value given); 94.9 kcal/cal
67TRO/WAG	Source of value not clear but presumably derived from kinetic study; $D_0^\circ(FO-F)=37\pm1$ $kcal\cdot mol^{-1}$
70DAR	Review; recommended value taken from 68WAG/EVA; 268±13 (T/K=0) kJ·mol (64±3,T/K=0, $kcal\cdot mol^{-1}$)
71COR/FRO	Photoionization of OF_2; no dissociation energy value given
72BRU/ROB	Comparison of ionization potentials and MO calculations; no dissociation energy value given
73ROT/SCH	*SCF calculations for the electronic ground state;* a contracted Gaussian basis set *of double zeta plus polarization quality;* -1.52 eV
77GLI	Calculation of dissociation energies from an experimentally reported $\Delta_f H$ value
78CHO/HER	Refers to earlier work on OF_2 by Chong; no dissociation energy given
78LEO/MED	Critical review; values based on analysis (with current 1978 auxilary data) of 30RUF/MEN, 30WAR/KLI, 66BIS/HAM and 68KIN/ARM; $D_0^\circ(OF-F)=38\pm5$ $kcal\cdot mol^{-1}$; $D_0^\circ(O-F)=52\pm4$ $kcal\cdot mol^{-1}$
80VAL/VAS	FCS-CI-DZ studies; ionization potentials; no dissociation energy value given
81LAN/CHO	Ionization potentials; no dissociation energy value given
84ALE/VOL	Ionization potentials; no dissociation energy value given
92CHO	Ionization *potentials;* no *dissociation energy value given*

TABLE 5.12.4. Enthalpy of formation

Source	$\Delta_f H$(298.15 K) (kJ·mol^{-1})	Comments (as reported values)
30RUF/MEN	10.9±8	Calorimetric study; 4.6±2 kcal·mol^{-1}
30WAR/KLI	46.0±8	Estimated from experimental data on 3 different reactions; 11±2 kcal·mol^{-1}
31RUF/MEN2	38.5	Calorimetric study; 9.2 kcal·mol^{-1}
31WAR	37.7 *19.2±21	Reanalysis of 3 earlier measurements [30RUF/MEN, 30WAR/KLI, 31RUF/MEN2] 9 kcal·mol^{-1}; *reanalysis of 30RUF/MEN, 4.6±5 kcal·mol^{-1}
33YOS/HAT	37.9	Origin of value not given; 9 kcal·mol^{-1}
36BIC/ROS	23.0	Critical review based on 30WAR/KLI; 5.5 kcal·mol^{-1}
50BRE/BRO	29±8	Review; value taken from 36BIC/ROS; 7±2 kcal·mol^{-1}
50LUF		Did not obtain article
50SCH2	29±8	Review of numerous properties; value based on work of 30RUF/MEN and 30WAR/KLI; 7±2 kcal·mol^{-1}
52ROS/WAG	23.0	Critical review; value based on 30WAR/KLI, 31RUF/MEN2, and 31WAR; 5.5 kcal·mol^{-1}
54COU	23.0±21	Critical review; value based on 52ROS/WAG and 36BIC/ROS; 5.5±5 kcal·mol^{-1}
55EVA/MUN	31.8±8	Based on 30WAR/KLI data; 7.6±2 kcal·mol^{-1}
61ARM/KRI	31.8±8	Review; adopted value of 55EVA/MUN; 7.6±2 kcal·mol^{-1}
66BIS/HAM	16.99	Calorimetric study; 4.06 kcal·mol^{-1}
66BIS/HAM2	16.99±9.2	Calorimetric study; 4.06±2.2 kcal·mol^{-1}
66VED/GUR	33.5±13	Critical review; 8.0±3 kcal·mol^{-1}
67MAL/MCG		Appearance potential; no enthalpy of formation data
67TRO/WAG	25.1	Private communication from W. C. Solomon in 1967; 6 kcal·mol^{-1}
68KIN/ARM	24.52±1.59	Calorimetric study in flame; 5.86±0.38 kcal·mol^{-1}
69FRA/DIL	21.72	Ionization potential review; value taken from 68WAG/EVA; 5.2 kcal·mol^{-1}
71CLY/WAT	24.5±1.6	Derived from 68KIN/ARM
72HOU/ASM	25.1	Quotes value of 68KIN/ARM; 6 kcal·mol^{-1}
76BIN/DEW	18.5	At 25 °C; MINDO calculation; refers to a value taken from 69FRA/DIL
76KOE/JOL	18.4	Value extracted from a summary of oxidizer properties; 4.4 kcal·mol^{-1}
77GLI	18.4	Source unknown
78DEW/RZE	76.1	MNDO method; 18.2 kcal·mol^{-1}
80GLI	21.31	MINDO approximation
83DEK/JAS	76.1	MNDO method; value taken from 78DEW/RZE; value reported by [83DEK/JAS] gives 18.2 kcal·mol^{-1}
86MEL	27.2	Critical review; BAC/MP4 method using geometries optimized at HF/6−31G*; value calculated at 0 K; 6.5 kcal·mol^{-1}
87HER	24.52±1.59	Value taken from 71STU/PRO and JANAF
88TYK		Estimated properties; no specific value given
89LIV/TAK		Semi-empirical method HAM/3 method (did not obtain article)
90VAN/KEL		Ab initio reaction energy computations; comparisons made to earlier recommendations of Wagman and JANAF

5.13. $^{17}OF_2$

Reinhard and Arkell [65REI/ARK] modified the method for the preparation of ordinary OF_2 (refer to [59ENG/NAC] in OF_2) to produce samples containing $O^{18}F_2$ and $O^{17}F_2$.

5.14. $^{18}OF_2$

Reinhard and Arkell [65REI/ARK] modified the method for the preparation of ordinary OF_2 (refer to [59ENG/NAC] in OF_2) to produce samples containing $O^{18}F_2$ and $O^{17}F_2$.

5.15. FFO

83DEK/JAS, using the MNDO method, calculated an enthalpy of formation of FFO, and reported a value of 526.3 $kJ \cdot mol^{-1}$. Similar calculations on FOF sugggested that FFO was less stable by 509 $kJ \cdot mol^{-1}$. However, the absolute values presented may be too high by 51 $kJ \cdot mol^{-1}$ (in comparison to experimental data for FOF). No references to previous work on this species were cited.

5.16. O_2F_2

All references dealing with O_2F_2 are listed in the following nine categories. Of prime interest are the spectroscopic, geometry and enthalpy of formation studies.

1. Vibrational frequencies/spectroscopy —
   [37BRO/FRI], [65ARK], [65BRO], [66SPR/TUR], [67LAW], [67SPR], [68LOO/GOE], [69GOE/CAM], [70LOO/GOE], [71GAR/LAW], [72MEL/AND], [73BUR/GAR], [76MAT/TUP], [78GRI/EDW], [80JAC], [85KIM/CAM], [85KIM/CAM2], [87WOO/LAR], [88CAM], [89RAG/TRU], [90MCG/CLE], [93AMO/MUR], [94JAC]
2. Geometry/structure —
   [62JAC], [62WIL], [63LIN], [67TUR/HAR], [68GOR/POP], [69GOR], [70GIM], [70LOO/GOE], [70NEW/LAT], [73LEI], [73MIN/MIN], [76CAL/HIR], [76PLE/KOC], [78LUC/SCH], [78OLS], [79HAR/LAU], [80GLI], [82AHL/TAY], [84BUR/LAW], [86MEL], [87ROH/HAY], [88HED/HED], [88MAC/OBE], [89LEE/RIC], [89MAC/OBE], [89RAG/TRU], [90MCG/CLE], [93AMO/MUR], [94GIM/ZHA]
3. EPR/NMR —
   [65KAS/KIR], [65NEU/VAN], [66LAW/OGD], [66WEL/MET], [67NEB/MET], [68LAW/OGD], [68SOL/KEI], [67SOL/RAN], [79SUG/KAW]
4. Enthalpy of formation/dissociation/heat of atomization —
   [58KIR/AST], [59KIR/GRO], [59KIR/GRO2], [61ARM/KRI], [61KIR/AST], [65MOR], [65MAL/MCG], [66MAL/MCG], [66VED/GUR], [68TUR], [69FRA/DIL], [70DAR], [86MEL]
5. Formation/decomposition/preparation/characterization —
   [33RUF/MEN], [34RUF/MEN], [36FRI/SCH], [36FRI/SCH2], [37FRI/SCH], [37FRI/SCH2], [37SCH], [37SCH/FRI], [38AOY/SAK], [41AOY/SAK], [58BAL/MAN], [59KIR/GRO], [59KIR/GRO2], [61KIR/STR], [64YOU/HIR], [65ARK], [65KIR], [65MAL/MCG], [65STR/STR], [66NAG], [66NOB/PIM], [66SPR/PIM], [66STR/STR], [67MAL/MCG], [68GOE/CAM], [68NIK/ROS], [69GOE/CAM], [69RIP/ZER], [70HAR], [72MEL/AND], [73GAR], [74MIN/MIN], [81SLI/SOL], [83TEM/WAG], [84FRE], [84TAK/HOS], [84YAM/HIR], [85BEA], [87CLA/SCH], [88KIS/POP], [88KIS/POP2], [88LYL/LOI], [88MAL/PER], [91AOM/SOD], [91DIX/AND], [91RAS/COC], [92RAS/BAG], [94SAM/MAS]
6. Density/vapor pressure —
   [58KIR/AST], [59KIR/GRO]
7. Review —
   [33RUF], [50SCH], [60GEO], [61ARM/KRI], [61MCG], [63STR], [66FOX/JAC], [66VED/GUR], [68TUR], [70DAR], [72BRI], [76CAL/HIR], [79HAR/LAU], [84BUR/LAW], [89LYM], [94JAC]
8. Kinetics/reaction —
   [36FRI/SCH], [37SCH/FRI], [62HOL/COH], [62STR/GRO], [62STR/GRO2], [62STR/GRO3], [63STR], [63STR/KIR], [63STR/KIR2], [64SOL], [65MOR/YOU], [66SOL], [66SOL2], [67JOL], [67SOL], [68BAN/SUK], [68LAW/TUR], [68SOL], [SOL/KAC], [68SOL/KAC2], [68SOL/KAC3], [69LIN/BAU], [69PED], [69SOL/KEI], [70SOL], [71STR], [73CHE/TUP], [73CHE/TUP2], [73NIK/DUD], [74SOL/KEI], [75LEU], [75SMA/LUT], [78SRT/BEZ], [78CHE/TUP], [79JAC], [80SOL], [82DAV/TEM], [82DAV/TEM2], [82DAV/TEM3], [84ASP/ELL], [84ELL/MAL], [84MAL/ELL], [84PAR/MOR], [85EPI/LAR], [85KIM/CAM3], [85KIN/ASP], [86ASP/KIN], [87BAI/BAS], [87BAI/BAS2], [87ELL/PEN], [87HER], [88LYM/HOL], [90CAM], [90CAM/FOR], [90LEE/REN], [90NIE/KIN], [91EBE], [91LUT/SMA], [91MIL], [91SCU], [92ALM/HOL]
9. Referenced articles in [63STR] —
   [59STR/GRO], [60MAG], [62MAG], [62STR], [62STR/GRO], [62STR/GRO2]

The vibrational and structural information are summarized in Tables 5.16.1 and 5.16.2. There are two citations to dissertations [67LAW, 67SPR]. Although these dissertations are listed in our bibliography we have not had access to them and cannot discuss in detail the data contained therein. It appears that each of these authors have written subsequent articles which we do discuss.

There are also included in the literature citations a number of personal communications to which data has been assigned [57GLO/DAV, 62MAG, 65BRO, 86MEL]. This information is included for completeness whenever possible, but it is not considered in the final analysis unless a subsequent publication has been made.

Brodsersen *et al.* [37BRO/FRI] measured the absorption spectra and extinction coefficients between 2000 and 10000Å. [76MAT/TUP] obtained the electronic absorption spectra and the extinction coefficients in the 190–600nm region.

Goetschel *et al.* [69GOE/CAM] described the preparation of O_2F_2 but presented no definitive structural or vibrational information. The observed IR spectra was compared with previously reported spectra of fluorine oxides. The authors stated that pure O_2F_2 is yellow, melts sharply at 119 K and is diamagnetic.

Jacox [94JAC] provided recommended data for FOOF as follows: a C_2 structure was adopted based on the microwave data of [62JAC]; the rotational constants and resulting geometry were derived from the same microwave study; the tabulated vibrational frequencies were taken from five infrared studies [65ARK, 66SPR/TUR, 71GAR/LAW, 80JAC, 85KIM/CAM]. We adopt the gas phase values for ν_1 through ν_5.

TABLE 5.16.1. Vibrational frequencies, cm^{-1}

Source		ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	Comments
Observed and Experimental Values								
65ARK								Matrix infrared study; observed ν(OF asymmetric stretch) of 624 cm^{-1}; assignment was made by 65BRO
66SPR/TUR								Absorption spectra; observed 4 frequencies (624.4, 612.0, 461.9, 368.1) from the photolysis of fluorine-oxygen mixtures
68LOO/GOE		*1300	615	367	209	621	547	*Values quoted by other authors, refer to the natural abundance molecule; IR spectra of solid; preliminary announcement of data reported in 70LOO/GOE
	$^{16}O_2F_2$	1306	621	369	205	615	457	
	$^{18}O_2F_2$	1239	595	362	195	586	444	
70LOO/GOE	$^{16}O_2F_2$	1306	621	369	205	615	457	IR spectra of solid isotopic species
	$^{18}O_2F_2$	1239	595	362	–	586	444	
71GAR/LAW		1270	618	364	–	612	468	IR and Raman spectra of solid at 77 K; partial IR of matrix isolated at 20 K; assignment of vibrational frequencies refers to results by 65BRO, 66SPR/TUR, 65ARK, 68LOO/GOE, 67LAW, 67SPR
72MEL/AND		~1300						Studied the O–O stretching frequency in fluoro-peroxides; refers to 70LOO/GOO and 71GAR/LAW
73BUR/GAR		1290	611	366	195.6	624	459	Raman spectra in $CClF_3$ solution; detailed discussion as to the assignment of vibrational frequencies
78GRI/EDW								Raman study of solid
80JAC	$^{16}O_2F_2$	1250	612	366	195	627	466	IR spectra of Ar matrix; observed and calculated values given respectively
		1250	608.5	367.1	194.7	627.5	466.9	
	$^{16}O^{18}OF_2$	–	595	–	–	618	459	
		1214.9	592.2	361.4	193.3	620.1	458.7	
	$^{18}O_2F_2$	–	584	–	–	601	452	
		1178.6	585.8	355.9	192.0	602.9	450.4	
85KIM/CAM		1210	630	360	202	614	471	FT-IR (± 3 cm^{-1}); ν_2 and ν_5 are different from those presented in 80JAC; no numerical structure information; observed all six vibrational frequencies
85KIM/CAM2								Laser flash photolysis; examined the equilibrium existence between O_2F and O_2F_2; compared O–F stretch and O–O stretching in both molecules

TABLE 5.16.1. Vibrational frequencies, cm^{-1} — Continued

Observed and Experimental Values — Continued

Source	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	Comments
87WOO/LAR	1281	607	373	197	623	461	Condensed phase Raman spectra
88CAM							IR intensity study of equilibrium between O_2F_2, O_2F and O_2

Calculated Values

Source	Calculational methods
89RAG/TRU	Quantum-mechanical calculations; results compared to 85KIM/CAM; HF/6-31G*, HF/DZP, QCISD(T)/6-31G*
90MCG/CLE	HF/6-31G* and MP2/6-31G* calculations
93AMO/MUR	Calculated values based on 6 different calculational techniques: TZ2P/SCF, TZ2P/LDA, TZ2P/BLYP, TZ2Pf/LDA, TZ2Pf/BLYP, TZ2Pf/CCSD(T)
94JAC	Review

TABLE 5.16.2 Geometry and structure

Experimental Values

Source	Bond distance (Å)<° F–O	O–O	dihedral<°	Comments	
62JAC	1.575 ±0.003	1.217 ±0.03	109.50 ±0.5	87.5 ±0.5	Microwave spectroscopy of 3 isomers, $^{16}O_2F_2$, $^{18}O_2F_2$, and $^{16}O^{18}OF_2$; r_0 structure
73MIN/MIN				87.5	Refers to a dihedral angle; extended Huckel calculation; the experimental value is the same and refers to 68WIN/WIN
88HED/HED	1.586	1.216	109.2	88.1	Electron diffraction study at −42°C; r_g structure

Calculated Values

Source	Calculational methods
62WIL	Quotes calculations of 62JAC
63LIN	Refers to geometry given by 62JAC; discussed bonding
67TUR/HAR	MO treatment of bonding; structure assumed to be FOOF; 4 calculations assuming different bond distances; VESCF
68GOR/POP	INDO calculation of geometry
69GOR	Refers to 62JAC values; CNDO/2 calculations; barriers to internal rotations
70GIM	Reported a C_2 symmetry; extended Huckel calculations
70LOO/GOE	Structure adopted from 62JAC microwave work
70NEW/LAT	Refers to 62JAC values; STO-3G, INDO
73LEI	Results in part based on 62JAC; CNDO/2
76CAL/HIR	Data taken from 62JAC
76PLE/KOC	Refers to the results of 62JAC; ab initio calculations; STO-2G, STO-4G
78LUC/SCH	Comparison with the experimental data of 62JAC; quantum-mechanical calculations RHF/4-31G, RHF/DZ, RHF/DZP(O), RHF/DZP(OF), CI/DZ, CI/DZP(O); a C_{2h} symmetry constraint (RHF/4-31G); a C_{2v} symmetry constraint (RHF/4-31G)
78OLS	Ab initio calculations; rigid-rotor calculations on O_2F_2; 4-31G
79HAR/LAU	Results taken from the work of 62JAC; authors cite values in reference to effective structure except for the (O−O) value being a substitution value
80GLI	MINDO calculations
82AHL/TAY	Quantum-mechanical calculation; calculated results compared with those of 62JAC performed; SCF, ODC, CEPA, CI(SD), MR CI(SD)
84BUR/LAW	Selected from 62JAC, 73BUR/GAR, 80JAC; no bond angle is given
86MEL	BAC/MP4 calculation
87ROH/HAY	Quantum-mechanical calculation; comparison with 62JAC; DZP: RHF, CI, CEPA; 6-31G*: RHF, MP2, 92-CAS/CCI, 92-CAS/CCI+Dav., 600-CAS/CCI, 600-CAS/CCI+Dav.; Diffuse: RHF/6-31G*, MP2/6-31G*, MP3/6-31G*, MP4SDQ/6-31G*, RHF/D95*, MP2/D95*, MP4SDQ/D95*

TABLE 5.16.2 Geometry and structure — Continued

Source	Calculational Methods
88MAC/OBE	Ab initio calculations; comparisons with 8 other calculational techniques; RHF/6-31G*, MP2/6-31G*, MP3/6-31G*, MP4SDQ/6-31G*, RHF/D95*, MP2/D95*, MP4SDQ/D95*
89LEE/RIC	Comparison to 62JAC; quantum-mechanical; MP2, CISD, CPF, CCSD
89MAC/OBE	Article not available
89RAG/TRU	Quantum-mechanical calculations; 6-31G*: HF, MP2, CAS+CI+D, QCISD(T); 6-31G(sp): HF, MP2, CAS+CI+D, QCISD(T)
90MCG/CLE	Quantum-mechanical calculation; HF/6-31G*, MP2/6-31G*
93AMO/MUR	Quantum-mechanical calculation; comparison with 62JAC and 85KIM/CAM; TZ2P/SCF, TZ2P/LDA, TZ2P/BLYP, TZ2Pf/LDA, TZ2Pf/BLYP, TZ2Pf/CCSD(T)
94GIM/ZHA	Ab initio SCF-MO calculations; a C_2 symmetry is proposed; RHF/6-31G**, MP2/6-31G**

There are numerous references to the enthalpy of formation of $O_2F_2(g)$. The reported values are summarized in Table 5.16.3. In fact, there are two articles referring to the calorimetric determination of the enthalpy of formation. Ten of other eleven citations essentially refer to this result. The [86MEL] citation is a quantomechanical calculation.

TABLE 5.16.3 Enthalpy of formation, kJ·mol

Source	$\Delta_f H$(298.15 K)	Comments (as reported values)
58KIR/AST	20.9±1.7	Measured the enthalpy of decomposition at 100K calorimetrically; 5.00±0.40 kcal·mol^{-1}
59KIR/GRO2	19.8±1.3	4.73±0.30 kcal·mol^{-1}
61ARM/KRI	19.8±1.3	From 59KIR/GRO (4.73±0.3 kcal·mol^{-1}, although referenced as the source of this value, the quoted value really comes from 59KIR/GRO2);
	19.5	from 61WAG (4.65 kcal·mol^{-1}, estimated $\Delta_{vap}H$ and calculated $\Delta_f H$);
	–	from 50SIM and 54SIM; discussed dissociation energy;
	66.9	from 57GLO/DAW, 16.0 kcal·mol^{-1}
65MAL/MCG		Estimated value [0.8 eV], assuming $D(F-O_2F)=D(O_2F)$; the second value, $D(FO-OF)=4.5\pm0.2$ eV, is based on appearance potential measures; this latter value was compared with a similar value derived from 59KIR/GRO2 and differed by 0.15 eV
65MOR		Three-dimensional Huckel MO calculations; $E_{atom}=156.5$ kcal·mol^{-1} (obs.), =151.6 kcal·mol^{-1} (calc.); no reference as to the observed value
66MAL/MCG		Refers to a mass spectrometrically derived value, presumably in 65MAL/MCG; quotes a value $D(F-O_2F)=0.8$ eV
66VED/GUR	19.8±1.3	Review; from 59KIR/GRO2; 4.73±0.30 kcal·mol^{-1}
68TUR		Review; refers to mass spectral study of 65MAL/MCG; FOOF→FO+OF, 103 kcal·mol^{-1}; FOOF→F+OOF. ~18 kcal·mol^{-1}
69FRA/DIL	18	From 270–3; 4.3 kcal·mol^{-1}
70DAR		From 66MAL/MCG; FOOF→FO_2+F; $\Delta_f H°(0K)=18.4$ kcal·mol^{-1}
86MEL	61.5	BAC/MP4 calculation; 14.7 kcal·mol^{-1}
89LYM	19.2±0.8	Review; corrected 59KIR/GRO; 4.58±0.20 kcal·mol^{-1}

Kirshenbaum *et al.* [59KIR/GRO, 59KIR/GRO2] studied the decomposition of O_2F_2 and O_3F_2 calorimetrically at 90 and 121 K respectively. From these values, the $\Delta_fH(298\text{ K})$ for the two gases were calculated: $O_2F_2 = +4.73 \pm 0.30$ kcal·mol^{-1} and $O_3F_2 = 6.24 \pm 0.75$ kcal·mol^{-1}. Auxilary information was required to convert the measured data at low temperatures to 298.15 K. The authors estimated ΔC_v for O_2, F_2 and O_2F_2 in order to convert the results at low temperature to 298 K. Lyman [89LYM] recalculated this correction using known data for the three species and arrived at $\Delta_fH = 4.58 \pm 0.2$ kcal·mol^{-1}. A correction of -0.15 kcal·mol^{-1} from results originally reported by [59KIR/GRO] was given.

5.17. $^{17}O_2F_2$

Welsh *et al.* [66WEL/MET] studied the EPR spectrum of liquid O_2F_2. The authors suggested that the paramagnetism is due to the O_2F radicals. The EPR spectrum was measured using solid O_2F_2 and solid enriched$^{17}O_2F_2$.

5.18. $^{18}O_2F_2$

Jackson [62JAC] examined the rotational spectra of three isotopically substituted O_2F_2 compounds:$^{16}O_2F_2$,$^{16}O^{18}OF_2$, and$^{18}O_2F_2$. From this microwave data, the author calculated the moments of inertia and the resulting structure of O_2F_2 (see Table 5.16.2).

Loos *et al.* [68LOO/GOE] observed and analysed the IR spectra of solid$^{16}O_2F_2$ and$^{18}O_2F_2$. The authors reported the fundamental frequencies for both isotopic species (See Table 5.16.1). A subsequent study [70LOO/GOE] involving the same two isotopes and$^{16}O^{18}OF_2$ provided additional infrared data. This was coupled with a normal coordinate calculation and a Huckel-MO calculation to confirm the vibrational assignments and the nature of the bonds.

5.19. O_3F_2

The more recent articles suggest that O_3F_2 does not exist. Instead, the compound observed is a mixture of O_2F_2 and O_4F_2. Since 1976, there are only two citatioms dealing with this presumed compound — both are calculations involving the molecular structure.

Summary comments in numerous reviews have shifted from O_3F_2 being a well-characterized compound [60GEO, 66FOX/JAC] to a presumed compound which has an oxygen to fluorine ratio of 3 to 2 [68TUR]. Finally, in 1972 [72BRI], it was clear that O_3F_2 does not exist as a distinct molecular entity. Thus, discussions of the following articles must be interpreted in the light of O_3F_2 not existing as a separate entity.

All references dealing with O_3F_2 are listed in the following eight categories. Of prime interest are the spectroscopic, geometry and enthalpy of formation studies.

1. Formation/decomposition —
   [38AOY/SAK], [41AOY/SAK], [59KIR/GRO], [59RIC], [61GRO/STR], [63MCG], [65MAL/MCG], [65STR/STR], [66STR/STR], [67JOL], [67MAL/MCG], [70MEI/GEN]
2. Enthalpy of formation/vaporization/dissociation —
   [58KIR/AST], [59KIR/GRO2], [61KIR/AST], [63PRI/PAS], [65MOR], [66VED/GUR], [69RIP/ZER], [76PLE/KOC], [80GLI]
3. Structure —
   [65MAG], [67NEB/MET], [67SOL/RAN], [68SOL/KEI], [76PLE/KOC], [80GLI], [94GIM/ZHA]
4. Properties —
   [61KIR/AST], [61KIR/STR], [62RIE/PER], [64AMS/CAP], [64SOL], [65MAG] [65STR/STR], [66STR]
5. EPR —
   [65KAS/KIR], [65NEU/VAN]
6. Review —
   [60GEO], [61ARM/KRI], [61MCG], [63STR], [66FOX/JAC], [68TUR], [72BRI]
7. Patent —
   [64HEM], [69HEM/TAY]
8. Reactions —
   [64SOL], [65BOY/BER], [65KIR/STO], [66AMS/NEF], [66SIM], [66SOL], [66SOL2], [68DIC/AMS], [75LEL]

The articles classed as formation/decomposition present modes of preparation of the so called O_3F_2 and some of its properties, in particular melting point. The more recent articles in this group dismissed purification and improved identification procedures.

There are numerous studies related to the experimental and theoretical determination of the enthalpy of formation.

— Kirshenbaum *et al.* [59KIR/GRO, 59KIR/GRO2] studied the decomposition of O_2F_2 and O_3F_2 calorimetrically at 90 and 121 K respectively. From these values, the $\Delta_fH(298\text{ K})$ for the two gases were calculated: $O_2F_2 = +4.73 \pm 0.30$ kcal·mol^{-1} and $O_3F_2 = 6.24 \pm 0.75$ kcal·mol^{-1}. Auxilary information was required to convert the measured data at low temperatures to 298.15 K.

— Mortimer [65MOR] reported an energy of atomization of 204.1 kcal·mol^{-1} compared to an observed value of 219 kcal·mol^{-1}. This corresponds to an enthalpy of formation, $\Delta_fH(0\text{K}) = 9.8$ kcal·mol^{-1}. There is no indication as to where the latter value came from.

— Vedeney *et al.* [66VED/GUR] quoted a value for the enthalpy of formation at 298 K of 6.24 ± 0.75 kcal·mol^{-1} based on the enthalpy od dissociation study by [59KIR/GRO2].

— Rips *et al.* [69RIP/ZER], using the method of correlating increments, calculated the enthalpy of vaporization of O_3F_2 as well as critical properties.

— Plesnicar *et al.* [76PLE/KOC], using *ab initio* molecular orbital theory (STO-2G and STO-4G), calculated the total energy and the decomposition energies to OF_2 and O_2F_2.

— Glidewell [80GLI], using MINDO approximation, calculated the heat of formation of O_3F_2 to be -11.23 kcal·mol^{-1}.

Although O_3F_2 has not been definitively characterized as a distinct species, there are numerous calculational studies specifying the presumed compound's geometry.

Plesnicar *et al.* [76PLE/KOC], using *ab initio* molecular orbital theory (STO-2G and STO-4G), studied the equilibrium geometry of O_3F_2. Their calculated values were: $r(F-O) = 1.3564Å$, $r(O-O) = 1.4069Å$, $\angle(FOO) = 103.77°$, $\angle(OOO) = 102.76°$, $\angle(OOF) = 103.77°$, and the dihedral $\angle = 88.37°$. There was no experimental data available at the time with which to compare these calculations. No information on the vibrational frequencies was provided.

Glidewell [80GLI], using MINDO approximation, calculated the energy and structure of O_3F_2. The geometry was given as: $r(F-O) = 1.481Å$, $r(O-O) = 1.331Å$, $\angle(FOO) = 112.7°$, $\angle(OOO) = 120.2°$, and the dihedral $\angle = 71.1°$. No vibrational frequency information was provided.

Gimarc and Zhao [94GIM/ZHA] calculated the geometry optimized total energies of O_3F_2 from *ab initio* SCF-MO calculations at the RHF and MP2 levels using 6–31G** basis set. A C_2 symmetry was proposed. The total energy and all bond angles and bond distances have been calculated and are presented in the paper as:

	RHF	MP2
(O−O)	1.3399	1.3974
(O−F)	1.3640	1.4525
∠OOO	108.12	107.25
∠FOO	105.28	104.63
∠OOOF	81.47	80.28

No vibrational frequency information was provided.

There are several studies which relate to the determination of various properties, such as melting point, vapor pressure, density, extinction coefficients, surface tension, etc. There are no studies involving the measurement of heat capacity or enthalpy of the solid or liquid.

The EPR studies [65KAS/KIR, 65NEU/VAN] of O_2F_2 and O_3F_2 showed identical EPR spectra which was attributed to FOO. These results may be more indicative of the decomposition of these materials.

Maguire [65MAG] measured many properties in an attempt to determine the structure of O_3F_2. However, the structure, by these studies, was not clearly defined.

Malone and McGee [67MAL/MCG] attempted to correlate mass spectrometric, EPR, infrared and NMR data and concluded that O_3F_2 had the features of an O_2F and OF radicals loosely bonded together. No quantitative data was given.

Nebgen *et al.* [67NEB/MET] were not able to make an unequivocal interpretation of ^{19}F NMR signal from O_3F_2. The authors postulated a model which consisted of O_2F_2 and interstitial O_2.

The NMR study of Solomon *et al.* [67SOL/RAN, 68SOL/KEI] was interpreted in terms of O_3F_2 being a mixture of O_2F_2 and O_4F_2. [68SOL/KEI] provided NMR data which supported the conclusion that O_3F_2 is a mixture of O_2F_2 and $(OOF)_n$.

5.20. O_4F_2

There are numerous reviews which cover the preparation and properties of this fluoride. However, there is not sufficient data available on the structure and vibrational frequencies to calculate the thermal functions. Enthalpy of formation data has been estimated via quantum mechanical means. The structure and vibrational frequencies of O_4F_2 have not been completely and definitively determined. The structure was assumed to be FOOOOF. There are two calculational studies which propose the structure. There are spectroscopic studies which have proposed a tentative assignment for three vibrational frequencies (there are 12 vibrations to be assigned in O_4F_2). It is interesting to note that the most recent experimental study intended to characterize the properties of O_4F_2 was the Raman solution experiments of Gardiner and Turner in 1971. Since that time there have been three calculational studies (structure and enthalpy of formation) and three experimental studies (formation and reactions). The calculational studies all imply a chain structure. The three experimental studies do not explicitly confirm the existence of the molecule, in that F/O is determined, but the molecule itself was not isolated and characterized.

All references dealing with O_4F_2 are listed in the following six categories. Of prime interest are the spectroscopic and geometry studies.

1. Decomposition/formation —
   [58KIR/AST], [61GRO/STR], [65ARK], [65STR/STR], [66SOL], [66STR/STR], [67JOL], [67MAL/MCG], [68GOE/CAM], [69GOE/CAM], [73NIK/DUD], [91LUT/SMA]
2. Properties —
   [61GRO/STR], [61KIR/AST], [64SOL], [66STR], [69RIP/ZER]
3. EPR/NMR —
   [66FES/SCH], [66KIR/STR], [67SOL/RAN], [68LAW/OGD], [68SOL/KEI]
4. Spectroscopy/structure —
   [63BRO/HAR], [65ARK], [65STR/STR], [66SOL], [66SPR/TUR], [69GOE/CAM], [71GAR/LAW], [71GAR/TUR], [76PLE/KOC], [80GLI], [94GIM/ZHA]
5. Review —
   [61ARM/KRI], [61MCG], [63STR], [66FOX/JAC], [68TUR], [72BRI]
6. Reaction —
   [68KEI/SOL], [71SOL/KAC]

The preparation of O_4F_2 has been described by numerous authors. All preparations involved the reaction of molecular fluorine with molecular oxygen. There are a variety of fluorine oxides formed during the reaction.

The five property references [61GRO/STR, 61KIS/AST, 64SOL, 66STR, 69RIP/ZER] presented limited vapor pressure data, thermal stability, some solubility information, and values for melting and boiling points of O_4F_2.

Kirshenbaum and Streng [66KIR/STR] measured the EPR spectrum of O_4F_2. The results revealed doublets which most likely were the isotopic EPR spectrum of the FOO radical. This work and a reevaluation of the O_2F_2 spectrum and of UV-irradiated OF_2 suggested that the same free radical was observed in all three cases. The authors also referenced unpublished work by Reinhard which confirmed the doublet obtained with O_4F_2.

Solomon *et al.* [67SOL/RAN] studied the ^{17}O and ^{19}F NMR spectra of O_2F_2 and the presumed O_3F_2. The NMR results showed conclusively that what was once called O_3F_2 was truly a mixture of O_2F_2 and O_4F_2. It was suggested that the latter is $(O_2F)_n$ which probably existed as O_2F and O_4F_2. Although not conclusive, the structure was assumed to be FOOOOF.

Three additional studies refer to O_4F_2 and the attempted resolution of the EPR/NMR results [66FES/SCH, 68LAW/OGD, 68SOL/KEI].

Through matrix infrared studies, Arkell [65ARK] observed two fundamental absorption bands at 588 and 1519 cm^{-1}. For calculational purposes, the molecule was treated as two equivalent triatomics. A bending mode vibrational frequency was assigned at 290 cm^{-1}. The authors assumed $r(O-F) = 1.63Å$, $r(O-O) = 1.22Å$, and the $\angle(OOF) = 100°$. Force constants were calculated for two of the bonds. No prior structural data was available.

Streng and Streng [65STR/STR] measured molar extinction coefficients from 350 to 750μ.

Spratley *et al.* [66SPR/TUR] proposed a tentative assignment of O_4F_2 in analogy to the formation suggested by [61GRO/STR]. Spratley *et al.* stated that the bending mode frequency value of 290 cm^{-1} given by [65ARK] was incorrect. These authors suggest a value of 376 cm^{-1} for the bending mode vibrational frequency of O_4F_2. Additional bands were observed at 586 and 1510 cm^{-1}.

Goetschel *et al.* [69GOE/CAM] stated that the strong bands observed in the radiolysis of liquid mixtures of O_2 and F_2 can all be attributed to O_4F_2. The authors assumed the molecule is diamagnetic and that at 80–90°, the dissociation energy of $O_4F_2 \rightarrow 2O_2F$ is 3 kcal·mol^{-1}. They estimated the entropy change to be 15 cal K^{-1} mol^{-1}. The spectra is compatible with that of [65ARK −584, 1519 cm^{-1}] and [66SPR/TUR −376, 586, 1510 cm^{-1}].

Using Raman spectra coupled with earlier EPR/NMR data, [71GAR/LAW, 71GAR/TUR] suggested that O_4F_2 is a red unstable solid with a melting point at 82 K, and its spectrum being very little different from O_2F. There was strong evidence that the O_4F_2 molecule is bonded through the oxygen as follows: $F-O=O---O=O-F$. Raman solution data observed $\nu(O-O) = 1516.2 \pm 1$ cm^{-1}, $\nu(O-F) = 584.6 \pm 1$ cm^{-1}, and $\delta(O-O-F)$ of 376.8 ± 1 cm^{-1}.

Plesnicar *et al.* [76PLE/KOC], using *ab initio* molecular orbital theory, calculated the geometry, the total energy and the decomposition enthalpy of O_4F_2 to O_2F_2 and O_2. Their calculated values were: $r(F-O) = 1.3564Å$ (taken from H_2O_3 and O_3F_2) and $r(O-O) = 1.406Å$.

Glidewell [80GLI], using MINDO approximation, calculated the energy and geometry of O_4F_2. The geometry was given as: $r(F-O) = 1.48Å$, $r(O_1-O_2) = 1.51Å$, $r(O_2-O_3) = 1.42Å$, $\angle(FOO) = 112°$, $\angle(OOO) = 121.0°$, dihedral $\angle(FOOO) = 79.6°$, and dihedral $\angle(OOOO) = 53.3°$. The enthalpy of formation of O_4F_2 was calculated to be $\Delta_fH° = +36.2$ kcal·mol^{-1}.

Gimarc and Zhao [94GIM/ZHA] calculated the geometry optimized total energies of O_4F_2 from *ab initio* SCF-MO calculations at the RHF and MP2 leveles using 6–31G** basis set. A C_2 symmetry was proposed. The total energy and all bond angles and bond distances were calculated and were presented in the paper as:

	RHF calculations	
$r(O_1-O_2)$	1.3346	$\angle(OOO) = 107.81°$
$r(O_2-O_3)$	1.3669	$\angle(OOF) = 105.42°$
$r(O-F)$	1.3650	dihedral$\angle(OOOF) = 81.58°$
		dihedral$\angle(OOOO) = 79.49°$

No vibrational frequency information was available.

5.21. O_5F_2

Schumacher [50SCH] in 1950 questioned the existence of O_5F_2.

[61ARM/KRI, 62ARM/KRI], in their review of the inorganic fluorine compounds, list an estimated enthalpy of formation of $O_5F_2(g)$, $\Delta_fH(298.15K) = -53.6$ kcal·mol^{-1}. This estimation was stated to have been taken from a private communication (June 1957) by Glocker and Dawson.

Streng and Grosse [66STR/GRO] prepared O_5F_2 by mixing O_2 and F_2 in an electrical discharge apparatus and found it to be stable at 60 K. On warming, O_5F_2 decomposed to form lower oxygen fluorides and ozone. No other characterization was provided. [67JOL] presented a summary of electric discharge reactions used to produce thermodynamically unstable products which are difficult to prepare by other methods. Turner [68TUR], in a subsequent review, did not feel the evidence was conclusive as to the existence of O_5F_2.

Goetschel *et al.* [69GOE/CAM], aware of the early work by [66STR/GRO], examined the radiolysis of liquid mixtures of O_2 and F_2 at 77 K. Although there was some evidence of higher oxygen fluorides being produced, there was no conclusive evidence that O_5F_2 was formed.

Brisdon [72BRI], in a 1972 review, stated that sufficient data was not available to reach any definite conclusion as to the existence of O_5F_2 or its structure.

5.22. FOOOOOF

Gimarc and Zhao [94GIM/ZHA] calculated the geometry optimized total energies of O_5F_2 from *ab initio* SCF-MO calculations at the RHF and MP2 levels using 6–31G** basis set. The total energy and all bond angles and bond distances have been calculated and are presented in the paper. No vibrational frequency information was presented. In this study O_5F_2 was assumed to have a chain structure.

5.23. O_6F_2

Streng and Grosse [66STR/GRO] prepared O_6F_2 by mixing O_2 and F_2 in an electrical discharge apparatus and found it to be stable at 60 K. On warming, O_6F_2 decomposes to form lower oxygen fluorides and ozone. No other characterization was provided. [67JOL] presented a summary of electric discharge reactions used to produce thermodynamically unstable products which are difficult to prepare by other methods. Turner [68TUR], in a subsequent review, did not feel the evidence was conclusive as to the existence of O_6F_2.

Goetschel *et al.* [68GOE/CAM, 69GOE/CAM], aware of the early work by [66STR/GRO], examined the radiolysis of liquid mixtures of O_2 and F_2 at 77 K. Although there was some evidence of higher oxygen fluorides being produced, there was no conclusive evidence that O_6F_2 was formed.

Brisdon [72BRI], in a 1972 review, stated that sufficient data was not available to reach any definite conclusion as to the existence of O_6F_2 or its unknown structure.

5.24. FOOOOOOF

Gimarc and Zhao [94GIM/ZHA] examined oxygen ring strain energies obtained from *ab initio* SCF MO calcualtions at two levels: MP2/6–31G** and RHF/6–31G**. They calculated strain energies for cyclic $O_nF_2 (n = 2 - 8)$, converting cyclic $O_nF_2 (n = 2 - 8)$ to chain-like O_nF_2.

5.25. O_7F_2

[85WEI/WEI], using quantum mechanical calculations compared the results of O_7F_2 and Cl_2O_7. CNDO-2 MNDO geometry optimizations were conducted, where the structures were assumed to be $O_3X-O-XO_3$. The results indicated that O_7F_2 was unstable.

Gimarc and Zhao [94GIM/ZHA] examined oxygen ring strain energies obtained from *ab initio* SCF MO calculations at two levels: MP2/6–31G** and RHF/6–31G**. They calculated strain energies for cyclic $O_nF_2 (n = 2 - 8)$, converting cyclic $O_nF_2 (n = 2 - 8)$ to chain-like O_nF_2. Note: This study deals with a possible ring structure as opposed to the structure discussed by [85WEI/WEI].

5.26. O_8F_2

Gimarc and Zhao [94GIM/ZHA] examined oxygen ring strain energies obtained from *ab initio* SCF MO calcualtions at two levels: MP2/6–31G** and RHF/6–31G**. They calculated strain energies for cyclic $O_nF_2 (n = 2 - 8)$, converting cyclic $O_nF_2 (n = 2 - 8)$ to chain-like O_nF_2.

5.27. OF_3

Price *et al.* [63PRI/PAS] have estimated the dissociation energy of OF_3 through a comparison of all dissociation energies of the fluorides of all the first row elements and their ions, $D(F_2O-F) = 0.7$ eV. Although not specifically stated, the structure would appear to be planar (D_{3h}), not pyramidal (C_{3v}).

6. NIST-JANAF Thermochemical Tables

NIST-JANAF Thermochemical Tables for OF(g) (Sec. 6.1), FOO(g) (Sec. 6.2), OFO(g) (Sec. 6.3), FOF(g) (Sec. 6.4), and O_2F_2 (g) (Sec. 6.5) are presented on the following pages.

Oxygen Fluoride (OF) Ideal Gas $M_r = 34.9978032$ Oxygen Fluoride (OF) $F_1O_1(g)$

$D_0^\circ = 18030 \pm 850\ \mathrm{cm^{-1}}$
$S^\circ(298.15\ \mathrm{K}) = 216.40 \pm 0.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$

$\Delta_f H^\circ(0\ \mathrm{K}) = 108 \pm 10\ \mathrm{kJ\ mol^{-1}}$
$\Delta_f H^\circ(298.15\ \mathrm{K}) = 109 \pm 10\ \mathrm{kJ\ mol^{-1}}$

Electronic Levels and Molecular Constants ($^{16}O^{19}F$), $\mathrm{cm^{-1}}$

State	T_e	g_i	ω_e	$\omega_e x_e$*	B_e	α_e**	$D_e\ 10^6$**	r_e/Å
$X^2\Pi_{3/2}$	0	2	1052.99376	9.90030	1.05870547	−0.0138015	4.28739	1.35412
$X^2\Pi_{1/2}$	193.80	2	1052.99376	9.90030	1.05870547	−0.0138015	4.28739	1.35412

* $\omega_e y_e = -0.068456$, $\omega_e z_e = -0.0010881$, $\omega_e a_e \times 10^{-5} = -5.945$
** 3 additional higher order terms are also available

$\sigma = 1$

Enthalpy of Formation

The dissociation energy has been calculated by many different techniques. The derived values range from 106.3 to 403.7 kJ·mol^{-1}. The values may be grouped into two types: (1) derived from a molecular orbital calculation and (2) extracted from reaction studies involving F_2O. We adopt $D_0^\circ(\mathrm{OF}) = 18030 \pm 850\ \mathrm{cm^{-1}}$ (215.687 ± 10 kJ·mol^{-1}) based on the experimental studies of Clyne and Watson[1], Czarnowski and Schumacher[2], Berkowitz *et al.*[3], and Zhang *et al.*[4] These four studies are all dependent on the enthalpy of formation of $OF_2(g)$ and are mass spectrometric studies except for the thermal decomposition of OF_2 by Czarnowski and Schumacher[2]. From the adopted value, we calculate $\Delta_f H^\circ(\mathrm{OF,g,\ 298K}) = 109 \pm 10$ kJ·mol^{-1}. Additional data needed for the calculations presented here, e.g. thermal functions for the F(g) and F_2(ref), O(g) and O_2(ref), are taken from the JANAF Thermochemical Tables.[5]

Heat Capacity and Entropy

The spectroscopic results tabulated above are for the $^{16}O^{19}F$ isotopomer. Isotopic relationships[6] are used to convert the above constants to those for the normally occurring, i.e. natural abundance, species. The latter values are then used in the calculation of the thermal functions. Only the X state is included in the calculation of the thermal functions; a sum–over–states technique is used.

The ground state, $X^2\Pi_{3/2}$, has been characterized by Burkholder *et al.*[7] The observations were made using a high resolution Fourier transform spectrometer and a multiple reflection absorption cell equipped to study short–lived molecules under fast flow conditions. Hammer *et al.*[8] used a high resolution Fourier transform spectrometer to study the OF infrared chemiluminescence. This latter study, the results of which we have adopted, provided values which were slightly different from the Burkholder *et al.*[7] work.

The value of A, the splitting of the ground state, has been determined experimentally by five authors: McKellar[9] (177.3 ± 5.6 cm^{-1}), Dyke *et al.*[10] (160 ± 30 cm^{-1}), McKellar *et al.*[11] (177.3 cm^{-1}), Burkholder *et al.*[7] (198.3 ± 6.7 cm^{-1}), and Hammer *et al.*[8] (193.80 ± 0.97 cm^{-1}). We adopt the value of Hammer *et al.* as determined by high resolution Fourier transform spectroscopy.

An $A^2\Pi$ state is assumed to exist at approximately 35,000 cm^{-1} but has not been observed. This state would not contribute significantly to the thermal functions below 6000 K.

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = p° = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.000	0.000	INFINITE	−9.388	108.392	108.392	INFINITE
50	30.058	159.390	318.327	−7.947	108.382	107.996	−112.819
100	32.600	181.178	244.853	−6.367	108.506	107.572	−56.188
150	32.472	194.419	225.985	−4.735	108.682	107.066	−37.283
200	31.935	203.681	219.310	−3.126	108.828	106.505	−27.816
250	31.788	210.783	216.922	−1.535	108.939	105.911	−22.128
298.15	31.995	216.396	216.396	0.000	109.025	105.320	−18.451
300	32.007	216.594	216.397	0.059	109.028	105.297	−18.333
400	32.917	225.920	217.662	3.303	109.177	104.030	−13.585
500	33.860	233.369	220.083	6.643	109.304	102.728	−10.732
600	34.620	239.612	222.831	10.069	109.414	101.402	−8.828
700	35.193	244.994	225.622	13.561	109.502	100.059	−7.466
800	35.621	249.723	228.345	17.102	109.571	98.705	−6.445
900	35.941	253.938	230.959	20.681	109.620	97.344	−5.650
1000	36.183	257.738	233.450	24.288	109.651	95.978	−5.013
1100	36.367	261.195	235.817	27.916	109.664	94.610	−4.493
1200	36.509	264.366	238.066	31.560	109.661	93.241	−4.059
1300	36.619	267.293	240.203	35.217	109.641	91.874	−3.691
1400	36.704	270.010	242.236	38.883	109.606	90.509	−3.377
1500	36.770	272.544	244.173	42.557	109.553	89.146	−3.104
1600	36.821	274.919	246.021	46.236	109.485	87.788	−2.866
1700	36.859	277.153	247.788	49.921	109.401	86.434	−2.656
1800	36.886	279.260	249.478	53.608	109.300	85.086	−2.469
1900	36.903	281.255	251.099	57.297	109.184	83.744	−2.302
2000	36.910	283.148	252.654	60.988	109.053	82.408	−2.152
2100	36.906	284.949	254.149	64.679	108.908	81.079	−2.017
2200	36.891	286.666	255.589	68.369	108.749	79.758	−1.894
2300	36.865	288.305	256.976	72.057	108.577	78.445	−1.781
2400	36.826	289.873	258.314	75.742	108.394	77.138	−1.679
2500	36.774	291.375	259.607	79.422	108.199	75.838	−1.585
2600	36.707	292.816	260.856	83.096	107.994	74.549	−1.498
2700	36.626	294.200	262.066	86.763	107.779	73.266	−1.417
2800	36.530	295.531	263.238	90.420	107.554	71.992	−1.343
2900	36.418	296.811	264.373	94.068	107.321	70.725	−1.274
3000	36.292	298.043	265.475	97.704	107.077	69.469	−1.210
3100	36.151	299.231	266.545	101.326	106.824	68.220	−1.149
3200	35.996	300.376	267.584	104.933	106.561	66.977	−1.093
3300	35.828	301.481	268.595	108.525	106.289	65.745	−1.041
3400	35.647	302.548	269.578	112.098	106.007	64.521	−0.991
3500	35.454	303.579	270.535	115.654	105.715	63.305	−0.945
3600	35.251	304.575	271.467	119.189	105.411	62.098	−0.901
3700	35.038	305.538	272.375	122.703	105.096	60.897	−0.860
3800	34.818	306.469	273.260	126.196	104.769	59.710	−0.821
3900	34.589	307.371	274.123	129.667	104.431	58.529	−0.784
4000	34.355	308.243	274.965	133.114	104.079	57.353	−0.749
4100	34.116	309.089	275.787	136.538	103.714	56.193	−0.716
4200	33.873	309.908	276.590	139.937	103.336	55.036	−0.684
4300	33.627	310.702	277.374	143.312	102.943	53.891	−0.655
4400	33.379	311.472	278.140	146.662	102.536	52.755	−0.626
4500	33.129	312.220	278.889	149.988	102.114	51.629	−0.599
4600	32.879	312.945	279.622	153.288	101.677	50.510	−0.574
4700	32.630	313.650	280.338	156.564	101.224	49.403	−0.549
4800	32.381	314.334	281.039	159.814	100.755	48.306	−0.526
4900	32.134	314.999	281.726	163.040	100.270	47.221	−0.503
5000	31.889	315.646	282.398	166.241	99.767	46.142	−0.482
5100	31.646	316.275	283.056	169.418	99.247	45.075	−0.462
5200	31.407	316.887	283.700	172.571	98.711	44.015	−0.442
5300	31.170	317.483	284.332	175.699	98.155	42.970	−0.423
5400	30.937	318.064	284.952	178.805	97.582	41.935	−0.406
5500	30.708	318.629	285.559	181.887	96.990	40.909	−0.389
5600	30.483	319.180	286.154	184.947	96.379	39.895	−0.372
5700	30.263	319.718	286.738	187.984	95.748	38.890	−0.356
5800	30.046	320.242	287.312	190.999	95.097	37.900	−0.341
5900	29.834	320.754	287.874	193.993	94.426	36.918	−0.327
6000	29.627	321.254	288.426	196.966	93.734	35.950	−0.313

PREVIOUS: September 1966 (1 bar)   CURRENT: September 1995 (1 bar)

Oxygen Fluoride (FOO) Ideal Gas $M_r = 50.9972032$ Oxygen Fluoride (FOO) $F_1O_2(g)$

$S°(298.15\ K) = 259.5 \pm 0.2\ J\ K^{-1}\ mol^{-1}$

$\Delta_f H°(0\ K) = 27.2 \pm 2\ kJ\ mol^{-1}$
$\Delta_f H°(298.15\ K) = 25.4 \pm 2\ kJ\ mol^{-1}$

Electronic Level and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
X^2A''	0.0	2
2A'	8630	2

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1486.93(1)
376(1)
579.32(1)

Point Group: C_s $\sigma = 1$
Bond Distances: F–O = 1.649Å ; O–O = 1.200Å
Bond Angle: F–O–O = 111.2°
Product of the Moments of Inertia: $I_A I_B I_C = 84.3487 \times 10^{-117}\ g^3cm^6$

Enthalpy of Formation

The enthalpy of formation of $O_2F(g)$ at 298.15 K, 25.4 ± 2 kJ·mol^{-1}, is based on six experimental results.[1–6] Two earlier studies[7,8] are not included in this analysis. The review by Lyman[4] recommended an enthalpy of formation value based on three experimental studies.[1,7,8]

These six experimental studies and their recommended values are:

Author	$\Delta_f H°(298\ K)$, kJ·mol^{-1}	T/K of study	Technique
Lyman and Holland[1]	23.0 ± 1.7	298 K	Kinetic study of reaction $F+O_2$
Holland *et al.*[2]	24.1		Unpublished; kinetic study of reaction $F+O_2$
Shamonima and Kotov[3]	21.6	223–293 K	EPR measurement of rate constants
Lyman[4]	22.9		Review
Pagsberg *et al.*[5]	26.1 ± 2.1	295–359 K	Spectrokinetic study
Campuzano–Jost *et al.*[6]	24.7 ± 4	100–420 K	Spectrokinetic study

Heat Capacity and Entropy

The structure of this molecule is bent with a F–O–O angle of 111.2° based on the diode–laser spectrum as obtained by Yamada and Hirota.[9] The bond length is F–O = 1.649Å and O–O = 1.200 ÅSupporting structural information is available from the infrared study of McKellar *et al.*[10], a microwave study by Bogey *et al.*[11], and a laser magnetic resonance study by Bley *et al.*[12] The principle moments of inertia (in g cm^2) are: $I_A = 1.0714\times10^{-39}$, $I_B = 8.3532\times10^{-39}$, and $I_C = 9.4246\times10^{-39}$.

There are numerous studies from which vibrational frequencies are derived: Yamada and Hirota[9], Mckellar *et al.*[10], Arkell[13], Noble and Pimentel[14], Spratley *et al.*[15], Jacox[16], and Kim and Campbell.[17] We adopt the recommendations of Jacox[18], using gas phase values for ν_1 and ν_3 and the nitrogen matrix *X* value for ν_2.[15] Similar vibrational frequencies were recommended by Lyman[4] in an earlier review.

Lyman stated that the published absorption spectra of O_2F Glissman and Schumacher[19] and Matchuk *et al.*[20] indicated no electronic states at energies below the dissociation energy of the molecule. Jacox[18] in her review, discussed four absorption studies in which a maximum has been observed at 205nm by Chegodaev and Tupikov[21], 420nm by Fessenden and Schuler[22], and 445nm Matchuk *et al.*[20] Jacox[16] observed the onset of dissociation near 490nm. Only the *X* and *A* states are used in the calculation.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−11.256	27.240	27.240	INFINITE
50	33.278	193.625	385.481	−9.593	26.728	28.458	−29.730
100	34.495	216.933	296.015	−7.908	26.230	30.385	−15.872
150	37.360	231.437	272.202	−6.115	25.839	32.554	−11.336
200	40.260	242.593	263.455	−4.172	25.590	34.833	−9.098
250	42.627	251.841	260.233	−2.098	25.455	37.162	−7.765
298.15	44.453	259.511	259.511	.000	25.400	39.422	−6.907
300	44.516	259.786	259.511	.082	25.399	39.509	−6.879
400	47.417	273.011	261.295	4.687	25.422	44.213	−5.774
500	49.606	283.838	264.753	9.542	25.537	48.899	−5.108
600	51.295	293.038	268.720	14.591	25.689	53.557	−4.663
700	52.594	301.047	272.778	19.788	25.856	58.189	−4.342
800	53.595	308.138	276.763	25.100	26.026	62.796	−4.100
900	54.372	314.498	280.609	30.500	26.193	67.382	−3.911
1000	54.983	320.259	284.290	35.969	26.355	71.950	−3.758
1100	55.472	325.523	287.803	41.492	26.510	76.502	−3.633
1200	55.872	330.368	291.151	47.060	26.656	81.040	−3.528
1300	56.210	334.854	294.342	52.665	26.793	85.567	−3.438
1400	56.504	339.030	297.387	58.301	26.920	90.083	−3.361
1500	56.769	342.938	300.295	63.965	27.037	94.590	−3.294
1600	57.015	346.609	303.076	69.654	27.145	99.090	−3.235
1700	57.250	350.073	305.739	75.367	27.244	103.584	−3.183
1800	57.478	353.352	308.294	81.104	27.334	108.072	−3.136
1900	57.702	356.466	310.748	86.863	27.418	112.555	−3.094
2000	57.925	359.431	313.109	92.644	27.496	117.034	−3.057
2100	58.146	362.262	315.383	98.448	27.571	121.509	−3.022
2200	58.366	364.972	317.575	104.273	27.644	125.981	−2.991
2300	58.585	367.572	319.693	110.121	27.716	130.449	−2.963
2400	58.800	370.070	321.740	115.990	27.791	134.913	−2.936
2500	59.012	372.474	323.722	121.881	27.870	139.375	−2.912
2600	59.220	374.793	325.642	127.793	27.954	143.834	−2.890
2700	59.421	377.032	327.504	133.725	28.046	148.289	−2.869
2800	59.616	379.196	329.312	139.677	28.146	152.741	−2.849
2900	59.803	381.292	331.068	145.648	28.257	157.189	−2.831
3000	59.982	383.322	332.776	151.637	28.378	161.633	−2.814
3100	60.152	385.292	334.439	157.644	28.512	166.073	−2.798
3200	60.313	387.204	336.058	163.667	28.659	170.507	−2.783
3300	60.465	389.062	337.636	169.706	28.819	174.937	−2.769
3400	60.606	390.869	339.175	175.760	28.992	179.363	−2.756
3500	60.738	392.628	340.678	181.827	29.180	183.783	−2.743
3600	60.861	394.341	342.145	187.907	29.382	188.197	−2.731
3700	60.973	396.010	343.578	193.999	29.597	192.606	−2.719
3800	61.077	397.637	344.979	200.101	29.826	197.009	−2.708
3900	61.171	399.225	346.350	206.214	30.068	201.406	−2.698
4000	61.256	400.775	347.691	212.335	30.323	205.795	−2.687
4100	61.332	402.289	349.004	218.465	30.589	210.179	−2.678
4200	61.400	403.767	350.291	224.601	30.867	214.556	−2.668
4300	61.461	405.213	351.551	230.744	31.156	218.926	−2.659
4400	61.513	406.626	352.787	236.893	31.455	223.289	−2.651
4500	61.559	408.009	353.999	243.047	31.762	227.645	−2.642
4600	61.598	409.363	355.188	249.205	32.077	231.994	−2.634
4700	61.631	410.688	356.355	255.366	32.399	236.337	−2.627
4800	61.657	411.986	357.500	261.531	32.726	240.673	−2.619
4900	61.678	413.257	358.625	267.698	33.058	245.002	−2.612
5000	61.694	414.503	359.730	273.866	33.393	249.324	−2.605
5100	61.705	415.725	360.816	280.036	33.729	253.640	−2.598
5200	61.712	416.924	361.884	286.207	34.066	257.948	−2.591
5300	61.714	418.099	362.933	292.379	34.402	262.251	−2.585
5400	61.713	419.253	363.966	298.550	34.736	266.546	−2.578
5500	61.708	420.385	364.981	304.721	35.065	270.835	−2.572
5600	61.700	421.497	365.980	310.891	35.389	275.120	−2.566
5700	61.688	422.589	366.964	317.061	35.706	279.398	−2.560
5800	61.674	423.661	367.932	323.229	36.014	283.671	−2.555
5900	61.658	424.716	368.886	329.396	36.312	287.937	−2.549
6000	61.639	425.752	369.825	335.560	36.598	292.200	−2.544

PREVIOUS: September 1966 (1 bar) CURRENT: September 1995 (1 bar)

Oxygen Fluoride (OFO) Ideal Gas $M_r = 50.9972032$ Oxygen Fluoride (OFO) $F_1O_2(g)$

$\Delta_{at}H°(0\ K) = [790 \pm 20]\ kJ\ mol^{-1}$
$S°(298.15\ K) = [251 \pm 1]\ J\ K^{-1}\ mol^{-1}$

$\Delta_fH°(0\ K) = [381.2 \pm 20]\ kJ\ mol^{-1}$
$\Delta_fH°(298.15\ K) = [378.6 \pm 20]\ kJ\ mol^{-1}$

Electronic Levels and Quantum Weights

State	cm^{-1}	g_i
[$^2B_2$]	0	[2]
[$^2B_1$]	[1049.3]	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[1050](1)
[600](1)
[1200](1)

Point Group: [C_{2v}] $\sigma = 2$
Bond Distance: F–O = [1.5591]Å
Bond Angle: O–F–O = [76.75]°
Product of the Moments of Inertia: $I_AI_BI_C = [116.8132 \times 10^{117}]\ g^3cm^6$

Enthalpy of Formation

The enthalpy of formation was calculated based on the molecular geometry optimization of Gosavi *et al.*[1] This calculation yielded the result $\Delta_fH(OFO) - \Delta_fH(FOO) = 356\ kJ{\cdot}mol^{-1}$. It is assumed that this calculated difference referred to 0 K. In contrast, Gole and Hayes[2] earlier calculated difference of >418 kJ·mol^{-1}.

Heat Capacity and Entropy

The molecular geometry adopted here is that used by Gosavi *et al.*[1] in their quantum mechanical calculations (6–31G basis sets). The structure was calculated to be bent with a O–F–O angle of [76.75°]. The bond length was calculated to be [1.5591]Å. The principle moments of inertia (in g cm^2) are: $I_A = 2.9573 \times 10^{-19}$, $I_B = 4.9779 \times 10^{-39}$, and $I_C = 7.9351 \times 10^{-39}$.

Gosavi *et al.*[1] examined the molecular geometry optimization of four electronic states of OFO at the RHF–SCF level with 6–31G and 6–31G* basis sets. In contrast, earlier calculations by Gole and Hayes[2] were based on a double–zeta sp basis set SCF total energy calculations as a function of the OFO bond angle. This latter study suggested a $^2B_1$ ground state with a bond angle of 128.22° (assuming a O–F bond distance of 1.19 Å).

The vibrational frequencies are estimated from the corresponding vibrational frequencies which describe the other OXO(g) molecules, where X = Cl and Br.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	.000	.000	INFINITE	−10.538	381.180	381.180	INFINITE
50	33.258	189.213	366.723	−8.875	380.667	382.618	−399.719
100	33.370	212.280	284.393	−7.211	380.149	384.770	−200.983
150	34.218	225.938	262.776	−5.526	379.650	387.190	−134.832
200	35.991	236.005	254.874	−3.774	379.210	389.772	−101.798
250	38.446	244.290	251.951	−1.915	378.860	392.454	−81.999
298.15	41.126	251.289	251.289	.000	378.622	395.096	−69.219
300	41.230	251.544	251.290	.076	378.615	395.198	−68.810
400	46.544	264.155	252.973	4.473	378.431	400.764	−52.334
500	50.581	275.001	256.319	9.341	378.557	406.338	−42.450
600	53.294	284.481	260.240	14.544	378.864	411.867	−35.856
700	55.036	292.837	264.312	19.967	379.257	417.337	−31.142
800	56.142	300.264	268.351	25.530	379.678	422.748	−27.603
900	56.849	306.920	272.273	31.183	380.098	428.107	−24.847
1000	57.306	312.935	276.043	36.892	380.501	433.419	−22.640
1100	57.606	318.412	279.650	42.639	380.878	438.693	−20.832
1200	57.806	323.434	283.092	48.410	381.228	443.933	−19.324
1300	57.942	328.066	286.376	54.198	381.548	449.146	−18.047
1400	58.034	332.364	289.509	59.997	381.838	454.334	−16.951
1500	58.098	336.370	292.501	65.804	382.098	459.503	−16.001
1600	58.143	340.121	295.361	71.616	382.329	464.656	−15.169
1700	58.174	343.647	298.099	77.432	382.531	469.795	−14.435
1800	58.196	346.973	300.723	83.250	382.703	474.923	−13.782
1900	58.211	350.120	303.240	89.071	382.848	480.042	−13.197
2000	58.222	353.106	305.660	94.892	382.967	485.154	−12.671
2100	58.230	355.947	307.987	100.715	383.061	490.261	−12.195
2200	58.235	358.656	310.229	106.538	383.131	495.365	−11.761
2300	58.238	361.244	312.391	112.362	383.180	500.465	−11.366
2400	58.240	363.723	314.479	118.186	383.209	505.563	−11.003
2500	58.241	366.101	316.497	124.010	383.221	510.661	−10.670
2600	58.242	368.385	318.449	129.834	383.218	515.759	−10.362
2700	58.242	370.583	320.339	135.658	383.201	520.857	−10.077
2800	58.241	372.701	322.172	141.482	383.174	525.956	−9.812
2900	58.240	374.745	323.949	147.307	383.138	531.055	−9.565
3000	58.240	376.719	325.676	153.131	383.094	536.157	−9.335
3100	58.239	378.629	327.353	158.954	383.045	541.260	−9.120
3200	58.238	380.478	328.985	164.778	382.992	546.364	−8.918
3300	58.237	382.270	330.572	170.602	382.937	551.470	−8.729
3400	58.235	384.008	332.119	176.426	382.881	556.579	−8.551
3500	58.234	385.697	333.625	182.249	382.824	561.688	−8.383
3600	58.233	387.337	335.095	188.072	382.769	566.799	−8.224
3700	58.232	388.933	336.528	193.896	382.716	571.911	−8.074
3800	58.231	390.485	337.928	199.719	382.665	577.026	−7.932
3900	58.230	391.998	339.295	205.542	382.618	582.142	−7.797
4000	58.229	393.472	340.631	211.365	382.574	587.258	−7.669
4100	58.228	394.910	341.937	217.188	382.535	592.376	−7.547
4200	58.227	396.313	343.216	223.011	382.499	597.494	−7.431
4300	58.226	397.683	344.466	228.833	382.467	602.614	−7.320
4400	58.226	399.022	345.691	234.656	382.439	607.733	−7.215
4500	58.225	400.330	346.891	240.478	382.416	612.854	−7.114
4600	58.224	401.610	348.066	246.301	382.395	617.974	−7.017
4700	58.223	402.862	349.219	252.123	382.378	623.096	−6.925
4800	58.222	404.088	350.349	257.945	382.363	628.218	−6.836
4900	58.222	405.289	351.458	263.768	382.350	633.341	−6.751
5000	58.221	406.465	352.547	269.590	382.339	638.463	−6.670
5100	58.220	407.618	353.615	275.412	382.327	643.586	−6.592
5200	58.220	408.748	354.665	281.234	382.315	648.708	−6.516
5300	58.219	409.857	355.696	287.056	382.302	653.832	−6.444
5400	58.219	410.945	356.709	292.878	382.286	658.955	−6.374
5500	58.218	412.014	357.705	298.700	382.266	664.078	−6.307
5600	58.218	413.063	358.684	304.521	382.241	669.203	−6.242
5700	58.217	414.093	359.647	310.343	382.210	674.327	−6.180
5800	58.217	415.106	360.594	316.165	382.172	679.453	−6.119
5900	58.216	416.101	361.527	321.986	382.125	684.577	−6.061
6000	58.216	417.079	362.445	327.808	382.068	689.705	−6.004

PREVIOUS: CURRENT: September 1995 (1 bar)

Oxygen Fluoride (OFO) $F_1O_2(g)$

Oxygen Fluoride (FOF) **Ideal Gas** **M_r = 53.9962064** **Oxygen Fluoride (FOF)** **$F_2O_1(g)$**

$\Delta_{at}H^\circ(0\ K) = 375 \pm 2\ kJ\ mol^{-1}$
$S^\circ(298.15\ K) = 247.46 \pm 0.4\ J\ K^{-1}\ mol^{-1}$

$\Delta_fH^\circ(0\ K) = 26.8 \pm 2\ kJ\ mol^{-1}$
$\Delta_fH^\circ(298.15\ K) = 24.5 \pm 2\ kJ\ mol^{-1}$

Electronic Level and Quantum Weight

State	ϵ_i, cm^{-1}	g_i
[X^1A]	0.0	1

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
928(1)
461(1)
831(1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: F–O = 1.412 Å
Bond Angle: F–O–F = 103° 10'
Product of the Moments of Inertia: $I_AI_BI_C = 101.8236 \times 10^{-117}\ g^3cm^6$

Enthalpy of Formation

King and Armstrong[1] have established the enthalpy of formation with a series of reactions in a flame calorimeter. They burned OF_2 in hydrogen to give HF aqueous; in addition they burned F_2 in hydrogen and O_2 in hydrogen so that the enthalpy of formation, 24.52 kJ mol^{-1}, was directly obtainable. This value was in good agreement with the recalculated values of Wartenberg and Klinkott[2], 23.85 ± 12.6 kJ mol^{-1}, and of Ruff and Menzel[3], 19.66 ± 8.45 kJ mol^{-1} but differed from that of Bisbee *et al.*[4], − 16.99 ± 8.4 kJ mol^{-1}. There are several factors in the experiments of Bisbee *et al.* that might cause the enthalpy of formation to be too negative. We adopt the value of 24.52 kJ mol^{-1}, reported by King and Armstrong.[1]

Heat Capacity and Entropy

The structural parameters are those reported by Pierce *et al.*[5] for the average ground state molecule from the microwave spectrum. Earlier measurements of Hilton *et al.*[6] disagree but according to Pierce *et al.*[7], the line assignments used by Hilton *et al.* are incorrect. The microwave study of Morino and Saito[8] yielded $r_e = 1.4053$ Å and an angle of 103°4' which is in agreement with our adopted values. The principle moments of inertia (in g cm^2) are: $I_A = 1.4392 \times 10^{-39}$, $I_B = 7.7225 \times 10^{-39}$ and $I_C = 9.1617 \times 10^{-39}$.

We adopt the vibrational frequencies reported by Jones *et al.*[9], several other investigators reported similar values.[10-12] Nebgen *et al.*[13] obtained the harmonic frequencies and the anharmonic constants for the three vibrations.

There are numerous more recent studies focusing on Fermi resonance and Coriolis coupling but the results support our adopted values.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K_f
0	.000	.000	INFINITE	−10.895	26.791	26.791	INFINITE
50	33.261	183.592	368.242	−9.232	26.278	28.436	−29.707
100	33.751	206.729	282.351	−7.562	25.765	30.795	−16.085
150	35.531	220.714	259.612	−5.835	25.307	33.412	−11.635
200	38.056	231.271	251.255	−3.997	24.946	36.171	−9.447
250	40.796	240.057	248.159	−2.026	24.686	39.009	−8.150
298.15	43.302	247.460	247.460	.000	24.520	41.784	−7.320
300	43.393	247.728	247.461	.080	24.515	41.891	−7.294
400	47.586	260.820	249.217	4.641	24.371	47.711	−6.230
500	50.463	271.769	252.663	9.553	24.388	53.546	−5.594
600	52.400	281.152	256.648	14.702	24.484	59.369	−5.169
700	53.728	289.336	260.746	20.013	24.616	65.173	−4.863
800	54.664	296.574	264.781	25.435	24.760	70.957	−4.633
900	55.343	303.054	268.680	30.937	24.905	76.723	−4.453
1000	55.847	308.912	272.415	36.498	25.045	82.473	−4.308
1100	56.232	314.254	275.979	42.103	25.175	88.210	−4.189
1200	56.531	319.160	279.376	47.741	25.294	93.935	−4.089
1300	56.768	323.695	282.613	53.407	25.398	99.651	−4.004
1400	56.958	327.909	285.699	59.093	25.487	105.359	−3.931
1500	57.113	331.844	288.646	64.797	25.560	111.061	−3.867
1600	57.241	335.534	291.462	70.515	25.616	116.759	−3.812
1700	57.348	339.008	294.158	76.245	25.654	122.455	−3.763
1800	57.438	342.288	296.742	81.984	25.676	128.148	−3.719
1900	57.515	345.396	299.221	87.732	25.682	133.841	−3.680
2000	57.580	348.348	301.605	93.487	25.674	139.534	−3.644
2100	57.637	351.159	303.898	99.248	25.656	145.227	−3.612
2200	57.687	353.841	306.108	105.014	25.628	150.922	−3.583
2300	57.730	356.406	308.239	110.785	25.595	156.617	−3.557
2400	57.768	358.864	310.298	116.560	25.561	162.314	−3.533
2500	57.801	361.223	312.288	122.338	25.527	168.013	−3.510
2600	57.831	363.491	314.214	128.120	25.498	173.713	−3.490
2700	57.858	365.674	316.080	133.904	25.478	179.414	−3.471
2800	57.882	367.778	317.889	139.691	25.468	185.116	−3.453
2900	57.903	369.810	319.644	145.481	25.473	190.817	−3.437
3000	57.923	371.773	321.349	151.272	25.495	196.519	−3.422
3100	57.940	373.673	323.007	157.065	25.535	202.219	−3.407
3200	57.956	375.513	324.619	162.860	25.597	207.917	−3.394
3300	57.971	377.296	326.188	168.656	25.682	213.614	−3.381
3400	57.984	379.027	327.717	174.454	25.792	219.307	−3.369
3500	57.996	380.708	329.207	180.253	25.927	224.997	−3.358
3600	58.007	382.342	330.660	186.053	26.090	230.682	−3.347
3700	58.018	383.931	332.079	191.855	26.279	236.363	−3.337
3800	58.027	385.479	333.464	197.657	26.496	242.038	−3.327
3900	58.036	386.986	334.817	203.460	26.742	247.707	−3.318
4000	58.044	388.456	336.140	209.264	27.016	253.369	−3.309
4100	58.052	389.889	337.433	215.069	27.318	259.024	−3.300
4200	58.059	391.288	338.699	220.874	27.649	264.672	−3.292
4300	58.065	392.654	339.938	226.681	28.006	270.311	−3.284
4400	58.071	393.989	341.151	232.487	28.392	275.942	−3.276
4500	58.077	395.294	342.340	238.295	28.803	281.563	−3.268
4600	58.082	396.571	343.505	244.103	29.241	287.175	−3.261
4700	58.087	397.820	344.647	249.911	29.704	292.778	−3.254
4800	58.092	399.043	345.768	255.720	30.192	298.370	−3.247
4900	58.097	400.241	346.867	261.530	30.702	303.952	−3.240
5000	58.101	401.415	347.947	267.339	31.236	309.523	−3.234
5100	58.105	402.565	349.006	273.150	31.790	315.083	−3.227
5200	58.108	403.694	350.047	278.960	32.366	320.632	−3.221
5300	58.112	404.800	351.070	284.771	32.961	326.171	−3.215
5400	58.115	405.887	352.075	290.583	33.573	331.697	−3.209
5500	58.118	406.953	353.063	296.394	34.203	337.211	−3.203
5600	58.121	408.000	354.035	302.206	34.849	342.716	−3.197
5700	58.124	409.029	354.991	308.019	35.510	348.207	−3.191
5800	58.127	410.040	355.931	313.831	36.184	353.687	−3.185
5900	58.129	411.034	356.857	319.644	36.871	359.155	−3.180
6000	58.131	412.011	357.768	325.457	37.568	364.612	−3.174

PREVIOUS: December 1969 (1 bar) CURRENT: September 1995 (1 bar)

Oxygen Fluoride (FOF) **$F_2O_1(g)$**

Oxygen Fluoride (FOOF) Ideal Gas M_r = 69.9956064 Oxygen Fluoride (FOOF) $F_2O_2(g)$

$\Delta_f H°(0\ K) = 22.9 \pm 2.0$ kJ mol^{-1}

$S°(298.15\ K) = 277.2 \pm 0.2$ J K^{-1} mol^{-1} $\Delta_f H°(298.15\ K) = 19.2 \pm 2.0$ kJ mol^{-1}

Electronic Level and Quantum Weight

State	ϵ_i, cm^{-1}	g_i
	0.0	1

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν,cm^{-1}
1210(1)	202(1)
630(1)	614(1)
360(1)	466(1)

Point Group: C_s $\sigma = 1$

Bond Distances: F–O = 1.575 Å; O–O = 1.217 Å

Bond Angles: O–O–F = 109°30'; dihedral angle = 87°30'

Product of the Moments of Inertia: $I_A I_B I_C = 1.3348 \times 10^{-114}$ g^{3}cm^6

Enthalpy of Formation

A critical measurement for the calculation of the thermodynamic functions for both O_2F and O_2F_2 is the standard enthalpy of formation of O_2F_2 by Kirshenbaum *et al.*[1] These authors made a calorimetric measurement at 190 K for decomposition of O_2F_2 into O_2 and F_2. Conversion of that measurement from 190 K to the standard enthalpy of formation at 298 K required knowledge of the difference in constant–volume heat capacity between the reactant (O_2F_2) and the products (O_2 and F_2). The authors assumed that difference to be zero over the entire range. With the published heat capacities for fluorine and oxygen, plus that for O_2F_2 reported here, we find that the average heat capacity difference over the 190 to 298 K temperature range to be 1.41 cal K^{-1} mol^{-1}. The standard enthalpy of formation that Kirshenbaum *et al.* reported was $\Delta_f H°(O_2F_2$, 298.15 K) = 19.8 ± 1.3 kJ·mol^{-1}. With the heat capacity correction suggested by Lyman[2], it became $\Delta_f H°(O_2F_2$, 298.15 K) = 19.2 ± 0.84 kJ·mol^{-1} as suggested by Lyman.[2]

The value adopted is that recommended by the evaluation of Lyman[2], with an increased uncertainty.

Heat Capacity and Entropy

The structure of this molecule is estimated to be a nonlinear chain with an O–O–F bond angle of 109°30' and a dihedral angle 87°30'. The adopted bond lengths are r(F–O) = 1.575 Å and r(O–O) = 1.217 Å from the microwave study of Jackson.[3] The principle moments of inertia (in g cm^2) are: $I_A = 4.1409\times10^{-39}$, $I_B = 1.6747\times10^{-38}$, $I_C = 1.9247\times10^{-38}$.

The vibrational frequencies are those recommended in the review by Jacox.[4] For $\nu_1-\nu_5$ we adopt the gas phase results (rather than the matrix isolation matrix) of Kim and Campbell.[5] For ν_6 we adopt the results of Spratley *et al.*[6] which were derived from oxygen matrix isolation studies. For ν_2, ν_3 and ν_5, these matrix isolation studies agree within 6 cm^{-1} of the gas phase results. The matrix isolation results of Arkell[7], Gardiner *et al.*[8] and Jacox[4] are in support of these values.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−13.778	22.930	22.930	INFINITE
50	34.134	197.692	439.855	−12.108	21.699	26.981	−28.187
100	39.458	222.827	325.625	−10.280	20.617	32.702	−17.082
150	46.225	240.092	294.354	−8.139	19.844	38.925	−13.555
200	52.643	254.291	282.610	−5.664	19.393	45.362	−11.847
250	57.967	266.632	278.206	−2.894	19.203	51.881	−10.840
298.15	62.073	277.206	277.206	.000	19.200	58.177	−10.192
300	62.213	277.591	277.207	.115	19.203	58.419	−10.172
400	68.291	296.385	279.729	6.663	19.560	71.448	−9.330
500	72.244	312.079	284.673	13.703	20.176	84.352	−8.812
600	74.896	325.500	290.386	21.068	20.908	97.119	−8.455
700	76.732	337.192	296.256	28.655	21.689	109.760	−8.190
800	78.040	347.528	302.031	36.397	22.484	122.287	−7.985
900	78.997	356.778	307.609	44.251	23.279	134.715	−7.819
1000	79.716	365.140	312.951	52.189	24.064	147.054	−7.681
1100	80.267	372.764	318.047	60.189	24.836	159.316	−7.565
1200	80.697	379.768	322.903	68.238	25.590	171.508	−7.466
1300	81.039	386.241	327.529	76.326	26.325	183.638	−7.379
1400	81.316	392.257	331.940	84.444	27.039	195.712	−7.302
1500	81.542	397.875	336.151	92.587	27.731	207.736	−7.234
1600	81.729	403.144	340.175	100.751	28.398	219.714	−7.173
1700	81.885	408.104	344.026	108.932	29.042	231.652	−7.118
1800	82.017	412.788	347.717	117.127	29.662	243.552	−7.068
1900	82.130	417.225	351.260	125.334	30.258	255.418	−7.022
2000	82.226	421.441	354.664	133.552	30.832	267.254	−6.980
2100	82.310	425.455	357.941	141.779	31.387	279.061	−6.941
2200	82.383	429.285	361.097	150.014	31.924	290.843	−6.905
2300	82.446	432.949	364.142	158.256	32.446	302.600	−6.872
2400	82.502	436.459	367.083	166.503	32.958	314.334	−6.841
2500	82.552	439.828	369.926	174.756	33.461	326.048	−6.812
2600	82.596	443.066	372.677	183.013	33.960	337.742	−6.785
2700	82.635	446.184	375.342	191.275	34.458	349.417	−6.760
2800	82.671	449.190	377.926	199.540	34.958	361.073	−6.736
2900	82.703	452.092	380.434	207.809	35.463	372.710	−6.713
3000	82.731	454.896	382.869	216.081	35.977	384.331	−6.692
3100	82.757	457.609	385.237	224.355	36.501	395.935	−6.671
3200	82.781	460.237	387.540	232.632	37.038	407.520	−6.652
3300	82.802	462.785	389.781	240.911	37.590	419.089	−6.634
3400	82.822	465.257	391.965	249.192	38.160	430.641	−6.616
3500	82.840	467.658	394.094	257.475	38.747	442.176	−6.599
3600	82.857	469.992	396.170	265.760	39.354	453.695	−6.583
3700	82.872	472.262	398.196	274.047	39.982	465.195	−6.567
3800	82.886	474.473	400.174	282.335	40.631	476.679	−6.552
3900	82.899	476.626	402.107	290.624	41.301	488.146	−6.538
4000	82.911	478.725	403.996	298.914	41.994	499.594	−6.524
4100	82.922	480.772	405.844	307.206	42.709	511.025	−6.511
4200	82.933	482.771	407.652	315.499	43.446	522.439	−6.497
4300	82.943	484.722	409.421	323.793	44.204	533.835	−6.485
4400	82.952	486.629	411.155	332.087	44.984	545.212	−6.472
4500	82.960	488.493	412.853	340.383	45.786	556.572	−6.461
4600	82.968	490.317	414.517	348.679	46.607	567.913	−6.449
4700	82.975	492.101	416.149	356.977	47.447	579.237	−6.438
4800	82.982	493.848	417.749	365.274	48.306	590.543	−6.426
4900	82.989	495.559	419.320	373.573	49.182	601.831	−6.416
5000	82.995	497.236	420.861	381.872	50.074	613.101	−6.405
5100	83.001	498.879	422.375	390.172	50.981	624.352	−6.395
5200	83.006	500.491	423.862	398.472	51.902	635.585	−6.385
5300	83.012	502.072	425.323	406.773	52.835	646.802	−6.375
5400	83.016	503.624	426.758	415.075	53.779	657.999	−6.365
5500	83.021	505.147	428.170	423.377	54.732	669.179	−6.355
5600	83.025	506.643	429.558	431.679	55.693	680.343	−6.346
5700	83.030	508.113	430.923	439.982	56.659	691.488	−6.337
5800	83.033	509.557	432.267	448.285	57.630	702.618	−6.328
5900	83.037	510.976	433.589	456.588	58.604	713.729	−6.319
6000	83.041	512.372	434.890	464.892	59.578	724.825	−6.310

PREVIOUS: CURRENT: September 1995 (1 bar)

Oxygen Fluoride (FOOF) $F_2O_2(g)$

7. Conclusions

Of the oxygen fluorides mentioned in the literature, only four have been isolated and characterized: FO(g), FOO(g), FOF(g), and FOOF(g). Although two isomers have not been observed (OFO and FFO), we include an estimated table for OFO since calculations exist which describe the vibrational frequencies, geometry and enthalpy of formation. A calculation exists for the enthalpy of formation of FFO. All indications are that these two molecules are extremely unstable.

In the following table, a summary of the recommended thermodynamic properties at ambient conditions for five oxygen fluorides are given. The brackets indicate estimated values. The recommended values contain a significant uncertainty only for OFO(g). However, this species has not been observed in the gas phase and may not be important in any practical problems. The prime effort should be directed at confirming the dissociation energy of FO. It is necessary to obtain a dissociation energy of FO independent of the value of the enthalpy of formation of OF_2. Independent confirmatory information is required for FOF and O_2F_2. For all of the polyatomic gaseous species, except OFO, spectroscopic measurements for the geometry and vibrational frequencies are sufficiently reliable that the uncertainties in the resulting thermal functions are acceptable.

Additional confirmation is needed as to the existence of the condensed phases, although this a much lower priority. Heat capacity and enthalpy measurements are not necessary at this time.

7.1. Thermodynamic Properties of the Oxygen Fluorides

		298.15 K			
Compound	0 K Δ_fH°	Δ_fH°	Δ_fG°	C_p°	S°
		kJ·mol^{-1}		J·mol^{-1} K^{-1}	
OF(g)	108±10	109±10	105	32.0	216.40±0.3
FOO(g)	27.2±2	25.4±2	39.4	44.5	259.5±0.2
OFO(g)	[381.2±20]	[378.6±20]	[395]	[41.1]	[251±1]
FOF(g)	26.8±2	24.5±2	41.8	43.3	247.5±0.4
O_2F_2(g)	22.9±0.8	19.2±0.8	58.2	62.1	277.2±0.2

8. Acknowledgments

This work was undertaken as part of a larger study to provide JANAF Thermochemical Tables for as many halogen oxide species as possible. This particular study for the oxygen fluorides was supported by the Standard Reference Data Program at the U.S. National Institute of Standards and Technology.

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