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$_2$F$_2$. 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. ©1996 American Institute of Physics and American Chemical Society.

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
the chlorine oxides 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 $D_{e}^{0}$ 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$_{2}$F$_{2}$. 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 13 fluorides and 9 isotopomers. 484 citations deal with O$_{2}$F$_{2}$, 133 deal with OF, 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. 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, 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 includes three oxygen fluorides (OF, FOO, FOF), whereas the 1989 version of the Thermochemical Properties of Individual Substances (TPIPS) only contains information on OF and FO. For the JANAF Thermochemical Tables, the data evaluations were actually performed in 1966 for O$_{2}$F and O$_{2}$F$_{2}$ and in 1969 for OF$_{2}$. For TPIPS, 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 FO 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 and its Russian counterpart by Gushenko and Medvedev listed values (C$_{p}^{m}$, H$_{m}^{o}$, S$_{m}^{o}$, and ΔH$_{f}^{o}$) at 298.15 K for OF(g) and O$_{2}$F$_{2}$(g), but only ΔH$_{f}^{o}$(298 K) for O$_{2}$F$_{2}$(g) and O$_{2}$F$_{2}$(g). In addition, Gushenko and Medvedev include an enthalpy of formation value for O$_{2}$F$_{2}$(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$_{2}$F, and O$_{2}$F$_{2}$ were listed by NASA-JPL. 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, 1992). 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, in 1959, gave a thorough review of the preparation properties of O$_{2}$F and O$_{2}$F$_{2}$ and discussed the existence of OF and O$_{2}$F$_{2}$. In 1986, as an update to the review of the oxygen fluorides for this Gmelin series, Jager et al. summarized the properties of OF, O$_{2}$F, O$_{2}$F$_{2}$, O$_{2}$F$_{3}$, O$_{2}$F$_{4}$, O$_{2}$F$_{5}$, O$_{2}$F$_{6}$, O$_{2}$F$_{7}$, O$_{2}$F$_{8}$, OF$_{3}$, OF$_{4}$, OF$_{5}$, OF$_{6}$, OF$_{7}$, OF$_{8}$.

In 1963, Schmeisser and Brandle summarized the status of four compounds (OF$_{2}$, O$_{2}$F$_{4}$, O$_{2}$F$_{5}$, O$_{2}$F$_{6}$). 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$_{2}$F$_{3}$, and O$_{2}$F$_{4}$.

In a review of advanced inorganic oxidizers, Lawless and Rowatt discussed eight oxygen fluorides, of which three were stated to be well characterized (O$_{2}$F, OF$_{2}$, O$_{2}$F$_{3}$). Additional reviews are provided by Allamagny and Nikitin and Rosolovskii.

After this article was written and reviewed, this author became aware of the existence of another review article by Wayne et al. 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.
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 (\(\text{OF}^2\)); FOO (\(\text{OF}^2\),\(\text{OF}^4\),\(\text{OF}^6\),\(\text{OF}^8\)); FOF; \(\text{OF}_2\); \(\text{OF}_3\); \(\text{OF}_4\); \(\text{OF}_5\); \(\text{OF}_6\); \(\text{OF}_7\); \(\text{OF}_8\); \(\text{OF}_{10}\).

Compounds that may exist (have not been isolated but some characterization available): OFO; \(\text{OF}_2\); \(\text{OF}_3\); \(\text{OF}_4\); \(\text{OF}_5\); \(\text{OF}_6\); \(\text{OF}_7\); \(\text{OF}_8\); \(\text{OF}_9\).

No conclusive confirmation as to existence: \(\text{OF}_2\); FFO; \(\text{OF}_2\); \(\text{OF}_3\); \(\text{OF}_4\); \(\text{OF}_5\); \(\text{OF}_6\); \(\text{OF}_7\); \(\text{OF}_8\).

In the following discussions, analyses and calculations, the 1993 atomic weights of the elements\(^{15}\) are used: \(\text{A}(\text{F}) = 18.9984032 \pm 0.0000009\); \(\text{A}(\text{O}) = 15.9994 \pm 0.0003\). 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: \(R = 8.314510 \pm 0.00007\) J·mol\(^{-1}\)·K\(^{-1}\). In comparison to the 1973 fundamental constants\(^{14}\), \(R\) has changed by +0.0001 J·mol\(^{-1}\)·K\(^{-1}\). Using the 1986 fundamental constants (instead of the 1973 fundamental constants), the \(S(298.15\text{ K})\) 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) 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 \(S^\circ\) and \(\Delta H^\circ\) are calculated using a propagation of errors approach.

The recommended data presented in the NIST-JANAF Thermochmical 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 Thermochmical Tables (Sec. 6) are calculated using the current atomic weights and fundamental constants, as well as the thermochmical tables for monatomic and diatomic fluorine and oxygen. These latter reference state thermochmical tables, as originally calculated, were based 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 thermochmical table for FO(g); this table was prepared jointly with this author.

1.1. References for the Introduction

2. Chemical Species Coverage

The following is a list of all oxygen fluoride species cited in the Chemical Abstracts 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, CICI0 and OCI0, however, do exist.

<table>
<thead>
<tr>
<th>Formula(a)</th>
<th>Name</th>
<th>Chemical Abstracts Registry Numbers</th>
<th>Deleted #</th>
<th>Current #(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OF(FO)</td>
<td>Oxygen fluoride</td>
<td>14986-71-1, 77318-95-7, 54974-35-7</td>
<td>—</td>
<td>1116-01-1</td>
</tr>
<tr>
<td>FO(OF)</td>
<td>Oxygen fluoride</td>
<td>99873-96-8, 903-10-8, 12207-32-3, 12020-93-8, 61825-17-0, 19061-71-1</td>
<td>—</td>
<td>38536-87-7</td>
</tr>
<tr>
<td>O(^{18})OF</td>
<td>Oxygen fluoride</td>
<td>15891-85-7</td>
<td>—</td>
<td>15891-85-7</td>
</tr>
<tr>
<td>O(^{17})OF</td>
<td>Oxygen fluoride</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O(^{16})OF</td>
<td>Oxygen fluoride</td>
<td>15891-85-7</td>
<td>—</td>
<td>15891-85-7</td>
</tr>
<tr>
<td>O(^{15})OF</td>
<td>Oxygen fluoride</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O(^{14})OF</td>
<td>Oxygen fluoride</td>
<td>15891-85-7</td>
<td>—</td>
<td>15891-85-7</td>
</tr>
<tr>
<td>OF(_2)(FO)</td>
<td>Oxygen fluoride</td>
<td>86100-45-0</td>
<td>—</td>
<td>7783-41-7</td>
</tr>
<tr>
<td>O(^{18})F(_2)(POF)</td>
<td>Oxygen fluoride</td>
<td>86100-45-0</td>
<td>—</td>
<td>7783-41-7</td>
</tr>
<tr>
<td>O(^{17})F(_2)(POF)</td>
<td>Oxygen fluoride</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O(^{16})F(_2)(POF)</td>
<td>Oxygen fluoride</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>OF(_2)(FPO)</td>
<td>Fluorosyl fluoride</td>
<td>—</td>
<td>—</td>
<td>86825-57-2</td>
</tr>
<tr>
<td>O(^{18})F(_2)(FPOOF)</td>
<td>Oxygen fluoride</td>
<td>—</td>
<td>—</td>
<td>86825-57-2</td>
</tr>
<tr>
<td>O(^{17})F(_2)(FPOOF)</td>
<td>Oxygen fluoride</td>
<td>—</td>
<td>—</td>
<td>86825-57-2</td>
</tr>
<tr>
<td>O(^{16})F(_2)(FPOOF)</td>
<td>Oxygen fluoride</td>
<td>—</td>
<td>—</td>
<td>86825-57-2</td>
</tr>
<tr>
<td>O(^{15})F(_2)(FPOOF)</td>
<td>Oxygen fluoride</td>
<td>—</td>
<td>—</td>
<td>86825-57-2</td>
</tr>
<tr>
<td>O(^{14})F(_2)(FPOOF)</td>
<td>Oxygen fluoride</td>
<td>—</td>
<td>—</td>
<td>86825-57-2</td>
</tr>
<tr>
<td>OF(_2)</td>
<td>Hexafluorodifluoride</td>
<td>—</td>
<td>—</td>
<td>12191-80-9</td>
</tr>
<tr>
<td>OF(_2)(O(^{18})F—O—FO(_1))</td>
<td>Fluorine oxide</td>
<td>—</td>
<td>—</td>
<td>106996-21-8</td>
</tr>
<tr>
<td>OF(_2)</td>
<td>Difluorooxide</td>
<td>—</td>
<td>—</td>
<td>153851-83-3</td>
</tr>
<tr>
<td>OF(_2)</td>
<td>Oxygen trifluoride</td>
<td>—</td>
<td>—</td>
<td>12434-38-7</td>
</tr>
<tr>
<td>OF(_2)</td>
<td>Oxygen tetrafluoride</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>OF(_2)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\(a\) A secondary formula is intended to suggest the assigned structure. If there is no 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. The references referred to a reaction of F₂ and O₂ 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, OF₂, O₂F₂, and O₃F₂.

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 OF₂. 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, O₂F₂, and O₃F₂ were studied.

For the time period 1962 to 1971 (the 7th and 8th Collective Indices), 348 references were cited. Not including isomers, 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 isomers) mentioned. In all cases, the dominant studies involved spectroscopic and bond energy investigations. There were however, numerous studies involving the formation, 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 additives involving the oxygen fluorides.

For the 11th and 12th Collective Indices (1982–1991), there was one reference dealing with the formation of O₂F₂, but many dealing with OF, OF₂, O₂F₂, and O₃F₂. 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, FOF, and O₂F₂). 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


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 FO₂, FOF and O₂F₂. 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 O₂F₂.

For any 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 (OF₂, O₂F₂, O₃F₂).

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 phases. 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 —

- [65SNEU/VAN], [72LEV]

3. Dipole moment —

- [83LAN/BAU], [83MCK]

4. Formation/preparation/decomposition —

- [33RUJ], [34RUJ/MEN], [34RUJ/MEN], [36FRI/SCH], [36FRI/SCH2], [61VIS], [62STA/SIC], [63HAM/IVE], [63WAL], [65KIR], [65MAC], [65SNEU/VAN], [68SOL/KAC], [74SMA/FOX], [74SMA/FOX2]

5. Kinetics —

- [60GRE/LIN], [69LIN/BAU], [70HOM/SOL], [71CLY/WAT], [71WAG/WAR], [72HOU/ASM], [72LIE], [72WAG/SET], [73CHE/TUP], [73POL/POL], [74CLY/WAT], [74WIG/BRI], [76ALE/NIK], [78AMY/CLY], [79GAR/TUR], [80BAU/COX], [81RAY/WAT], [82ANT], [82BAU/COX], [82LER/PC], [86DOS/CAS], [86PAT/SHA], [86SWE], [86THA/SHA], [88FRA/GOL], [88RAH/BE], [88SYM/ROS], [92BED/MAR], [92BED/MAR2], [92FRA], [93BED/MAR], [93BED/MAR2], [93BED/MAR3], [93FRA/SU2]

6. Dissociation energy —

- Experimental — [34KOB/SCH], [57DIB/REI], [59HIL], [65ARK/REI2], [67MAL/MCG], [67OGD/TUR], [69ARK], [71CLY/WAT], [72CZA/SCH], [72LEV], [73BER/DEH], [94ZHA/KTO]
- Calculations — [48GLO], [49GLO], [50SCH], [62PRI/HAR], [63PRI/PAS], [65MOR], [69ION/ION], [70OHA/WAH], [70OHA/WAH2], [70OHA/WAH3], [72LIE], [77GLI], [78DEW/RZ], [78DEW/RZ2], [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], [70-1], [73BEN], [79HUB/HER], [82WAG/EVA]

7. Review —

- [60GEO], [68TUR], [72BRI], [80SOL]

8. Miscellaneous —

- [62SVE], [65ARK/REI], [73ROZ/GUT], [80HAR/BLI], [81LEN/FAJ], [83ALE/PED], [84ALE/VO], [84DM/YY], [84SAU/TAT], [85CHA/CAN], [86JAF/AKE], [87HER], [87KAR], [88MAL/PER], [89THA/PED], [90C/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’I(12) (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 \omega_e values. The vibrational and rotational structure of OF was first fully described by [86BUR/HAM]. Earlier work determined in part the vibrational (only \omega_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.

[65SNEU/VAN]: Possible formation/identification of OF in the irradiation of pure liquid OF_2 at -196 °C and OF_2 in CFC_1 matrix; observed an isotopic doublet.

[72LEV]: Observed reaction (H + OF_2 -> 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]: Electron negativity
[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/CA]: Vibrational lifetimes
[91XIE/XIA]: Laser emission (article not obtained)
[92MCI/AN]: IR spectra of OF complexes
[92XIE/LIU]: Calculation of oscillator strength
[93XIE/XIA]: Six electronic states at MRSDCI level

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**Table 5.1.1. Vibrational/rotational structure, cm⁻¹**

<table>
<thead>
<tr>
<th>Source</th>
<th>State</th>
<th>A</th>
<th>ω₀</th>
<th>ω₀B₀/α₀</th>
<th>B₀</th>
<th>α₀</th>
<th>rₑ(Å)</th>
<th>Comments</th>
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<tbody>
<tr>
<td>Experimental Values</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>58DUR/RAM</td>
<td>65ARK/REI</td>
<td>1028</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>69ARK</td>
<td>O²⁺F</td>
<td>1028.6±0.3</td>
<td>997.7±0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>71AND/RAY</td>
<td>O³⁻F</td>
<td>1028.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>72AND</td>
<td>O²⁺F</td>
<td>1028.0±0.5</td>
<td>998.4±0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>72YAN</td>
<td>O³⁻F</td>
<td>916</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>74SMA/FOX</td>
<td>X²⁺I</td>
<td>−177.3</td>
<td>1044</td>
<td>1.05955± 0.00019</td>
<td>0.013475± 0.00035</td>
<td>1.35789± 0.00025</td>
<td>1.36±0.03</td>
<td>Matrix infrared spectrum (argon matrix Raman study)</td>
</tr>
<tr>
<td>79MCK</td>
<td>X²⁺I</td>
<td>−177.3</td>
<td>1044</td>
<td>1.05955± 0.00019</td>
<td>0.013475± 0.00035</td>
<td>1.35789± 0.00025</td>
<td>1.36±0.03</td>
<td>Matrix infrared spectrum (argon matrix Raman study)</td>
</tr>
<tr>
<td>80AND</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80DYK/ION</td>
<td>−160±30</td>
<td>1044</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>83MCK/YAM</td>
<td>²¹¹₂</td>
<td>−177.3</td>
<td>1033.4829</td>
<td>**1.05285± 0.00009</td>
<td>1.05286± 0.00009</td>
<td>1.35412</td>
<td>1.35789</td>
<td>He(I) photoelectron spectrum ionization of OF((X²⁺I); estimated splitting of ground state; rₑ and ω₀ values were taken from 79MCK</td>
</tr>
<tr>
<td>86BUR/HAM</td>
<td>²¹¹₂</td>
<td>−198.3</td>
<td>1053.42</td>
<td>10.23</td>
<td>1.052869</td>
<td>0.01325</td>
<td>1.35412</td>
<td>High resolution Fourier transform spectroscopy</td>
</tr>
<tr>
<td>88HAM/SIN</td>
<td>−193.80</td>
<td>1052.99</td>
<td>9.9003</td>
<td>1.05870547</td>
<td>0.0010881</td>
<td>0.0002945</td>
<td>1.337</td>
<td>High resolution IR chemiluminescence (emission); ω₀β₀, α₀β₀ and ω₀α₀ values</td>
</tr>
</tbody>
</table>

**Calculated Values**

63TAN

74LAT/CUR

---

Molecular orbital theory (3 electron bond discussion)

### Table 5.1.1. Vibrational/rotational structure, cm\(^{-1}\) — Continued

<table>
<thead>
<tr>
<th>Source</th>
<th>State</th>
<th>(A)</th>
<th>(\omega_x)</th>
<th>(\omega_x\alpha_x)</th>
<th>(B_x)</th>
<th>(\alpha_x)</th>
<th>(r_x(\text{Å}))</th>
<th>Comments</th>
</tr>
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<tbody>
<tr>
<td>89SUN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Article not available at this time</td>
</tr>
<tr>
<td>90FRA/GOL</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>Ab initio molecular orbital theory</td>
</tr>
<tr>
<td>91HAA</td>
<td></td>
<td>1017</td>
<td>12.21</td>
<td></td>
<td></td>
<td></td>
<td>1.344</td>
<td>QCISD(T) calculation; (\omega_x) and (\omega_x\alpha_x) values given at 4 different levels of calculation</td>
</tr>
<tr>
<td>92KOB/SCH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.5058</td>
<td>Ab initio molecular orbital method</td>
</tr>
<tr>
<td>93FRA/SU2</td>
<td></td>
<td>1542</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.344</td>
<td>Ab initio calculations; (r_x) values derived from UMP2/6-31G(d) and UMP2/6-311G(\text{Dp})</td>
</tr>
<tr>
<td>94CHO</td>
<td></td>
<td>1156</td>
<td>8.29</td>
<td>0.01070</td>
<td></td>
<td></td>
<td></td>
<td>Calculations based on deMon density functional program</td>
</tr>
<tr>
<td>94FRA</td>
<td></td>
<td>1542</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.323</td>
<td>Ab initio method; UMP2/6-31G(d)</td>
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### Table 5.1.2. Dissociation energy/enthalpy or formation, kJ/mol

<table>
<thead>
<tr>
<th>Source</th>
<th>(D_0(\text{FO}))</th>
<th>(\Delta H)</th>
<th>Temperature</th>
<th>Comments (as reported values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>34KOB/SCH</td>
<td>240.58</td>
<td></td>
<td></td>
<td>Kinetic study of thermal decomposition of OF(_2) between 250–270 °C; dissociation energy based on average bond energy of OF(_2); 57.5 kJ/mol(^{-1})</td>
</tr>
<tr>
<td>57DIB/REE</td>
<td>106.3</td>
<td></td>
<td></td>
<td>Electron impact study; direct calculation not feasible from ion data; (D(\text{F}–\text{O})) calculated from known (\Delta H(\text{OF}_2\text{g})) and (\Delta H(\text{F})); experiment suggested (D(\text{OF})+D(\text{F})–F=3.9\pm0.1) eV with (D(\text{FOF}–\text{F})=2.8, D(\text{OF})=1.1) eV</td>
</tr>
<tr>
<td>59HIL</td>
<td>135.6±42</td>
<td>298 K</td>
<td></td>
<td>Value derived from (\Delta H) of OF(_2); 32.4±10 kJ/mol(^{-1})</td>
</tr>
<tr>
<td>65ARK/REI2</td>
<td>−236.4</td>
<td></td>
<td></td>
<td>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(\text{F}–\text{O})) may be higher than the average energy in OF(_2); similar results for the chlorine molecules; suggested 48GLO reasonable; −2.45 eV</td>
</tr>
<tr>
<td>67MAL/MCG</td>
<td>126</td>
<td></td>
<td></td>
<td>Mass spectrometric investigation of OF(_2): no specific (\Delta H) value given; however (\Delta H) values are given for the reactions from which (\Delta H(\text{OF}_2\text{g})\sim30) kJ/mol(^{-1}) Based on kinetic description of the photolysis of fluorine with (N_2) or (O_2) mixtures; observations supported a lower limit for the dissociation energy, (D(\text{OF})\sim40) kJ/mol(^{-1}); 69ARK suggested presence of (\text{OF}); in fluorine sample might have caused a problem in the absorption spectra</td>
</tr>
<tr>
<td>67OCH/TUD</td>
<td>−167.4</td>
<td></td>
<td></td>
<td>Based on kinetic description of the photolysis of fluorine with (N_2) or (O_2) mixtures; observations supported a lower limit estimate, (D(\text{OF})&gt;40) kJ/mol(^{-1})</td>
</tr>
<tr>
<td>69ARK</td>
<td>&gt;167.4</td>
<td></td>
<td></td>
<td>Photolysis of OF(_2)--(N_2) or OF(_2)--CO(_2) mixtures; observations supported a lower limit estimate, (D(\text{OF})&gt;40) kJ/mol(^{-1})</td>
</tr>
<tr>
<td>71CLY/WAT</td>
<td>215±17</td>
<td></td>
<td></td>
<td>Molecular beam study; measurement of appearance potential of OF(_2) from OF and OF(_2); (D^\ast) dependent on enthalpy of atomization for OF(_2); 2.25±0.15 eV</td>
</tr>
<tr>
<td>72CZA/SCH</td>
<td>212.5±8.4</td>
<td></td>
<td></td>
<td>Thermal decomposition of OF(_2) using a method; (D(\text{O}–\text{F})) calculated from known (\Delta H(\text{F}_2\text{g})) and the activation of an observed reaction</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Source</th>
<th>$D(\text{FO})$</th>
<th>$\Delta H$</th>
<th>Temperature</th>
<th>Comments (as reported values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>72LEV</td>
<td>243.2±17.4</td>
<td></td>
<td></td>
<td>EPR study; $2.34\pm0.27$ eV; $2.52\pm0.18$ eV is the recommended dissociation value</td>
</tr>
<tr>
<td>73BER/DEH</td>
<td></td>
<td>109.3±20.9</td>
<td>0 K</td>
<td>Enthalpy of formation obtained from photoionization study; $26.11\pm2.3$ kcal mol$^{-1}$</td>
</tr>
<tr>
<td>94ZHA/KUO</td>
<td></td>
<td>109.5±8.0</td>
<td></td>
<td>Calculated from photoionization efficiency spectra and a previous appearance energy measurement</td>
</tr>
<tr>
<td><strong>Calculated Values</strong></td>
<td></td>
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<tr>
<td>48GLO</td>
<td>736.4</td>
<td></td>
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</tr>
<tr>
<td>49GLO</td>
<td>265.9</td>
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<tr>
<td>50SCH</td>
<td>169.5±12.6</td>
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<tr>
<td>62PRI/HAR</td>
<td>212.3</td>
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<tr>
<td>63PRI/PAE</td>
<td>217.1</td>
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<tr>
<td>65MOR</td>
<td>209.6</td>
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</tr>
<tr>
<td>69ION/ION</td>
<td></td>
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</tr>
<tr>
<td>700HA/WAH</td>
<td>290±30°~80</td>
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<td></td>
<td>Hartree-Fock wave functions; calculation dependent on auxiliary information for OF$_2$, O and F; $3.0\pm0.3$, $-0.8$ eV</td>
</tr>
<tr>
<td>700HA/WAH2</td>
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<td></td>
<td>Hartree-Fock wave functions; OF mentioned only in comparison to SF and SF</td>
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<tr>
<td>700HA/WAH3</td>
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<td>Hartree-Fock wave functions; $-174.19502$</td>
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<td>72LIE</td>
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<td></td>
<td>Hartree-Fock wave functions; $-174.19502$</td>
</tr>
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<td>77GLI</td>
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<td>113.4</td>
<td></td>
<td>Source of this experimental value not identified</td>
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<tr>
<td>78DEW/RZE</td>
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<td>109.2</td>
<td></td>
<td>Observed and calculated enthalpy of formation values respectively, $26.1$ kcal mol$^{-1}$, $32.5$ kcal mol$^{-1}$; observed value taken from 73BER/DEH</td>
</tr>
<tr>
<td>78DEW/RZE2</td>
<td></td>
<td>90.8</td>
<td></td>
<td>MNDO semiempirical SCF-MO method; $21.7$ kcal mol$^{-1}$</td>
</tr>
<tr>
<td>80GLI</td>
<td></td>
<td>106</td>
<td>0 K</td>
<td>Study directed at use of MNDO approximation for other oxygen fluorides</td>
</tr>
<tr>
<td>80JUG/NAN</td>
<td></td>
<td>135.9</td>
<td>298 K</td>
<td>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, $\Delta H$) and $1.4$ kcal mol$^{-1}$ (SINDO; $E_a$)</td>
</tr>
<tr>
<td>80NAN/JUG</td>
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<td>No value given</td>
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Table 5.1.2. Dissociation energy/enthalpy of formation, kJ/mol — Continued

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<thead>
<tr>
<th>Source</th>
<th>$D^0(FO)$</th>
<th>$\Delta H$</th>
<th>Temperature</th>
<th>Comments (as reported values)</th>
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</thead>
<tbody>
<tr>
<td>86MEL</td>
<td>102.1</td>
<td>0 K</td>
<td></td>
<td>BAC/MPP4 calculation of enthalpy of formation; 24.4 kcal/mol $^{11}$</td>
</tr>
<tr>
<td>90ZHA/FRA</td>
<td>116.3±4.2</td>
<td></td>
<td></td>
<td>Ab initio studies using MP theory up to the fourth order; enthalpy of formation calculated using no benchmark reactions above; 27.0±1 kcal/mol $^{1}$</td>
</tr>
<tr>
<td>91BRA/WRI</td>
<td>225.8</td>
<td></td>
<td></td>
<td>7 different calculations using MRD-CI potential surfaces; refers to the experimental value of 71CLY/WAT; 1.007 – 3.11 eV, 2.29 eV, 2.34 eV; the last value is designated as the best value</td>
</tr>
<tr>
<td>93FRA</td>
<td>116.3</td>
<td></td>
<td></td>
<td>Ab initio calculations to investigate stability of MOOP in the reaction of MO with OP, refers to an enthalpy of formation value of 90ZHA/FRA; 27.8 kcal/mol $^{1}$</td>
</tr>
<tr>
<td>93FRA/SU</td>
<td>116.3±4.2</td>
<td></td>
<td></td>
<td>Enthalpy of formation; value taken from 90ZHA/FRA; 27.8±1 kcal/mol $^{1}$</td>
</tr>
<tr>
<td>94CHO</td>
<td>403.7±188.5</td>
<td></td>
<td></td>
<td>Local density calculation; 4.184±1.954 eV</td>
</tr>
<tr>
<td>Review</td>
<td></td>
<td></td>
<td></td>
<td>Review, no value given</td>
</tr>
<tr>
<td>50SCH2</td>
<td>144.7±48.2</td>
<td></td>
<td></td>
<td>Value based on results of 48GLO; using (DF) 1 eV this gives 1.5 eV for OF; 1.5±0.5 eV, 0.35 kcal/mol $^{11}$</td>
</tr>
<tr>
<td>58BRE</td>
<td>167.56</td>
<td></td>
<td></td>
<td>Review; recommended a value of 40 kcal/mol $^{11}$</td>
</tr>
<tr>
<td>62VED/GUR</td>
<td>184±42</td>
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<td></td>
<td>Assumed $D^0$(OF) = 1/2D$(OF_2)$</td>
</tr>
<tr>
<td>65GAY</td>
<td>100.1</td>
<td>184.1±41.8</td>
<td>0 K</td>
<td>The recommended dissociation value was based on the assumption $D^0$(OF) = 1/2D$(OF_2)$; 44±10 kcal/mol $^{11}$; refers to electron impact data of 57DHE/BEE</td>
</tr>
<tr>
<td>68GAY</td>
<td>231.6±38.6</td>
<td></td>
<td></td>
<td>Review; refers to 5 studies with values ranging from 1.1 to 2.45 eV; 2.4±0.4 eV (55 kcal/mol $^{11}$)</td>
</tr>
<tr>
<td>69BRE/ROS</td>
<td>230±40</td>
<td>0 K</td>
<td></td>
<td>Dissociation energy values; refer to numerous studies, preferred results of 65ARK/REI and 48GLO; 55 kcal/mol $^{11}$</td>
</tr>
<tr>
<td>69FRA/DIL</td>
<td>171.5</td>
<td>298 K</td>
<td></td>
<td>Value taken from Wagman et al. (1968); 41 kcal/mol $^{11}$; reprinted value in 1982 is different</td>
</tr>
<tr>
<td>70DAR</td>
<td>115±13</td>
<td></td>
<td></td>
<td>Based on three studies, 57DHE/BEE, 62VED/GUR, and 68WAGE/GEVA (reprinted as 62WAGE/GEVA; $\gamma_{2,3}$ kcal/mol $^{11}$)</td>
</tr>
<tr>
<td>76BEN</td>
<td>108.8±4.2</td>
<td>300 K</td>
<td></td>
<td>Review; 26±1 kcal/mol $^{11}$</td>
</tr>
<tr>
<td>79HUB/HER</td>
<td>215.2</td>
<td></td>
<td></td>
<td>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 70HAHA/WAH and 72LEV; 22.3 eV</td>
</tr>
<tr>
<td>87WAGE/GEVA</td>
<td>108.78</td>
<td>0 K</td>
<td></td>
<td>Reprint of 1968 edition; based on consideration of four studies by 66MAL/MCG, 71CLY/WAT, 72LEV and 73BER/DEH</td>
</tr>
</tbody>
</table>

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 $^{18}$OF and $^{16}$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 $^{18}$OF and $^{16}$OF free radicals.

5.3. O$_2$F (FOO)

All references dealing with O$_2$F 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], [69GUL/HAY], [69OHAR], [69ARK/MAC], [74SIN/NAG], [75BIS/VAL], [75MCC/PAL], [79PAN/CHA], [80GLI], [80HIN], [80TH/ STUR], [84YAM/HIR], [85GOS/RAG], [86MEI], [87MCK/BUR], [89BOG/DAY], [90FRA/GOL], [91BLE/DAY], [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], [881JAC], [89JYM], [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], [76CHE/STIR], [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], [70MAT/TUP], [77SLI], [78DEW/RZ], [79SIA/KOT], [80GLI], [80THY/SUB], [84FRE], [85GOS/RAG], [86MEI], [87PAG/RAT], [88CAM], [88LYM/HOL], [89JYM], [90FRA/GOL], [92FRA/ZHA], [94ELL/SEH], [95CAM/CRO]

5. Kinetics —
   [37SCH/FRI], [68SO/LKE], [73CHE/TUP], [73ZET], [76MAT/TUP], [78CHE/TUP], [79CIO/HOR], [79SIA/KOT], [80BAC/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], [75ALE/NIK], [78COO/PIL], [78LEW/MAK], [80GRI/DIS], [80SMI/WRI], [80SOL], [81SLI/SOL], [81SMI/WRI], [83BAS/VAG], [83TEM/WAG], [86YU], [87FIT/DUN], [88MAL/PET], [89TIM/PUR], [90FRA/GOL], [92CIIR], [92LIU/DAV]

7. Reactions —
   [68SOL], [69GOE/CAM], [77COO/PRI], [79COO/HOR], [80COO/HOR], [82COO/HOR], [88SYM/ROE], [89APP/DOW], [91LUT/STA], [92ALM/HOL], [92MAR/SZE], [94SEH/SEH]

8. Review —
   [61MCG], [68TUR], [70DAR], [72BRI], [84BUR/LAW], [88JAC], [89JYM], [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/DAY] 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 $^{18}$O$_2$F, $^{16}$O$_2$F, $^{18}$O$_2$OF, and $^{18}$O$_4$OF. The results are summarized in Table 5.3.3. There is some confusion in the literature due to the assignments of $\nu_2$ and $\nu_1$ as to which one is the bending frequency. $\nu_1$ 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 66SPV/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/DAY].

There are numerous EPR studies on the oxygen fluorides, including FO. In most of these studies, a spectra was associated with the radical FO 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$_2$F 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 \( \Delta H^\circ \) (FOO, g, 298.15 K) = 23 kJ mol\(^{-1}\).

### Table 5.3.1. EPR spectra assigned to FOO

<table>
<thead>
<tr>
<th>Source</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>65KAS/KIR</td>
<td>EPR spectra of ( \text{F}_2\text{O}_3 ) and ( \text{F}_2\text{O} )</td>
</tr>
<tr>
<td>65NEUVAN</td>
<td>EPR spectra of the decomposition of ( \text{FSO}_2\text{OOF} )</td>
</tr>
<tr>
<td>66FES/SCH</td>
<td>EPR spectra during electron irradiation of liquid ( \text{CF}_2\text{O} )</td>
</tr>
<tr>
<td>66KIR/STR</td>
<td>EPR spectra of ( \text{O}_2\text{F}_3, \text{O}_2\text{F}_2 ) and ( \text{OF}_2 )</td>
</tr>
<tr>
<td>66LAW/OGD</td>
<td>EPR NMR spectra of ( \text{O}_2\text{F}_2 ) in ( \text{CF}_2\text{Cl} )</td>
</tr>
<tr>
<td>66MET/WEL</td>
<td>EPR study of liquid ( \text{OF}_2 ) with photolysis, observed a radical classified ( \text{O}_2\text{F} )</td>
</tr>
<tr>
<td>66WEL/MET</td>
<td>EPR spectra of ( \text{O}_2\text{F}_2 ); isotopic species (( ^{18}\text{OOF}, ^{18}\text{O}^\text{OF}, ^{18}\text{O}_2\text{F} )) contributed to the paramagnetism</td>
</tr>
<tr>
<td>67ADR</td>
<td>IR and EPR spectra of ( ^{18}\text{O} )</td>
</tr>
<tr>
<td>68LAW/OGD</td>
<td>EPR-NMR spectra of ( \text{O}_2\text{F}_2 )</td>
</tr>
<tr>
<td>70VED/GUR</td>
<td>EPR study of F–O system</td>
</tr>
<tr>
<td>73CHE/TUP</td>
<td>IR spectroscopy and EPR spectra of ( \text{OF}, \text{O}_2\text{F} ) and ( \text{O}_2\text{F}_2 )</td>
</tr>
<tr>
<td>75MCC/PAL</td>
<td>SCF-MO calculations, EPR spectra of FOO</td>
</tr>
<tr>
<td>76CHR/WIL</td>
<td>EPR study of dioxynyl salts; spectra in excellent agreement with other FOO studies</td>
</tr>
<tr>
<td>70MAT/TUP</td>
<td>Electronic absorption spectra and EPR of ( ^{18}\text{O}_2\text{F} ) and ( ^{18}\text{O}_2\text{F}_2 )</td>
</tr>
<tr>
<td>76TUP/MAT</td>
<td>EPR spectrum of FOO</td>
</tr>
<tr>
<td>84GLI</td>
<td>Calculated spin density and hyperfine coupling constants; refers to 67ADR</td>
</tr>
</tbody>
</table>

### Table 5.3.2. Rotational constants/structure

<table>
<thead>
<tr>
<th>Source</th>
<th>Rotational constants, cm(^{-1})</th>
<th>Bond distance, r(Å)</th>
<th>Bond angle</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \alpha ) ( \beta ) ( \gamma )</td>
<td>(( r(\text{F}–\text{O}) )) (( r(\text{O}–\text{O}) ))</td>
<td>( \theta )</td>
<td></td>
</tr>
<tr>
<td>65ARK</td>
<td>1.63 1.22 100.1</td>
<td>( \text{IR spectra in matrix (Ar, O}_2, \text{N}_2 ) isolated ( \text{FO}_2 ) at 4 K )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>66SPR/PIM</td>
<td>1.575 1.217 109.5</td>
<td>( \text{IR spectra of N}_2, \text{Ar, and O}_2 ) matrix isolated ( \text{FO}_2 ) at 77 K; molecular parameters are analogous to those of ( \text{O}_2\text{F}_2 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>67ADR</td>
<td>1.575 1.22 90.5</td>
<td>Assumed bond angle; bond distances are taken from ( \text{O}_2\text{F}_2 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>67ATH/HIN</td>
<td>bent</td>
<td>Unrestricted Hartree-Fock method with CNDO/2 approximation; authors assumed molecule was bent; no quantitative geometry given</td>
<td></td>
<td></td>
</tr>
<tr>
<td>68GOR/POP</td>
<td>1.19 1.19 110.6</td>
<td>Calculated geometry via INDO self-consistent theory; no experimental data available for comparison</td>
<td></td>
<td></td>
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<tr>
<td>69GOL/HAY</td>
<td>1.63 1.23 128°22</td>
<td>Nonempirical LCAO-MO-SCF calculations to determine the relative stability of FOO and OFO; estimated geometry; the bond distances are taken from 65ARK</td>
<td></td>
<td></td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Source</th>
<th>Rotational constants, cm⁻¹</th>
<th>Bond distance, r(Å)</th>
<th>Bond angle</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>(F-O)</td>
</tr>
<tr>
<td>70HAR</td>
<td></td>
<td></td>
<td>bent</td>
<td></td>
</tr>
<tr>
<td>74CAR/MAC</td>
<td></td>
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<td>1.195</td>
<td>1.220</td>
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<tr>
<td>74SIN/NAG</td>
<td></td>
<td></td>
<td>1.575</td>
<td>1.217</td>
</tr>
<tr>
<td>75BIS/VAL</td>
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<td>1.19</td>
<td>1.195</td>
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<tr>
<td>75MCC/PAL</td>
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<td>*1.575</td>
<td>*1.217</td>
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<tr>
<td>79PAN/CHA</td>
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<td>80GLI</td>
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<td>1.496</td>
<td>1.211</td>
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<td>80HIN</td>
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<td>1.43</td>
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<td>80THY/SUB</td>
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<tr>
<td>84VAKISHIB</td>
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<td>1.649±</td>
<td>1.700±</td>
</tr>
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<td></td>
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<td>0.013</td>
<td>0.013</td>
</tr>
<tr>
<td>85GOS/RAG</td>
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<td>1.4402</td>
<td>1.3328</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>1.4280</td>
<td>1.4586</td>
</tr>
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<td></td>
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<td></td>
<td>1.2010</td>
<td>1.2547</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.3606</td>
<td>1.3792</td>
</tr>
<tr>
<td>86MeL</td>
<td></td>
<td></td>
<td>1.55</td>
<td>1.254</td>
</tr>
<tr>
<td>87MCK/BUR</td>
<td></td>
<td></td>
<td>2.613396</td>
<td>0.333987</td>
</tr>
<tr>
<td>89DOOC/DDAV</td>
<td></td>
<td></td>
<td>2.616116</td>
<td>0.334072</td>
</tr>
<tr>
<td>90FRA/GOL</td>
<td></td>
<td></td>
<td>1.380</td>
<td>1.437</td>
</tr>
<tr>
<td>91BLE/DAV</td>
<td></td>
<td></td>
<td>1.383</td>
<td>1.250</td>
</tr>
<tr>
<td>92FRA/ZHA</td>
<td></td>
<td></td>
<td>1.709</td>
<td>1.198</td>
</tr>
</tbody>
</table>

### Table 5.3.3. Vibrational frequencies, cm⁻¹

<table>
<thead>
<tr>
<th>Source</th>
<th>ν₁</th>
<th>ν₂</th>
<th>ν₃</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>65ARK</td>
<td>1494</td>
<td>584</td>
<td></td>
<td>IR spectra of matrix (Ar, O₂, N₂) isolated FOO at 4 K</td>
</tr>
<tr>
<td>66NOB/PIM</td>
<td>1495.0</td>
<td>584.5</td>
<td>376.0</td>
<td>IR spectra of N₂ matrix isolated FOO are based on the measurements of 4 isotopic species; ν₁ is the bending frequency</td>
</tr>
<tr>
<td>66SPR/PIM</td>
<td>1453.9</td>
<td>563.4</td>
<td></td>
<td>Discarded possible bonding in FOO but relies on earlier data</td>
</tr>
<tr>
<td>66SPR/TUR</td>
<td>1457.7</td>
<td>586.4</td>
<td>376.0</td>
<td>IR spectra of the N₂, Ar, and O₂ matrix isolated FOO at 77 K is based on measurements of 4 isotopic species; electronic ground state is a doublet and ν₂ is the bending frequency</td>
</tr>
<tr>
<td>71GAR/LAW</td>
<td>1411.7</td>
<td>560.1</td>
<td>366.6</td>
<td>Prime measurement was the IR and Raman spectra of solid and matrix isolated O₂F₂, observed the decomposition to O₂F</td>
</tr>
<tr>
<td>74SIN/NAG</td>
<td>1499.7</td>
<td>586.4</td>
<td>376.0</td>
<td>Used values of 66SPR/TUR and 66NOB/PIM</td>
</tr>
<tr>
<td>80JAC</td>
<td>1490</td>
<td>583.5</td>
<td></td>
<td>Ar matrix spectroscopy; agree well with results of 65ARK and 66SPR/TUR</td>
</tr>
<tr>
<td>84JAC</td>
<td>1490</td>
<td>376</td>
<td>579.32</td>
<td>Review; ν₁ and ν₂ values are based on IR spectra of matrix isolated (Ar or N₂) studies of 65ARK, 80JAC and 66SPR/TUR respectively; ν₃ is based on the Raman laser phase study of 84YAM/HIR</td>
</tr>
<tr>
<td>84YAM/HIR</td>
<td></td>
<td></td>
<td>579.32</td>
<td>Gas phase IR diode laser spectroscopy</td>
</tr>
<tr>
<td>85KIM/CAM</td>
<td>1489</td>
<td></td>
<td></td>
<td>Laser flash photolysis of the gas phase O₂F radical</td>
</tr>
<tr>
<td>87MCK/BUR</td>
<td>1487</td>
<td></td>
<td>579.32</td>
<td>Fourier transform IR spectra of O₂F, ν₃=2ν₁=940 cm⁻¹, 2ν₁=1142 cm⁻¹, ν₁+ν₂=1496 cm⁻¹, 2ν₁=2948 cm⁻¹</td>
</tr>
<tr>
<td>88CAM</td>
<td>1490</td>
<td></td>
<td></td>
<td>FTIR study of equilibrium between O₂F and O₂F₂ and O₂</td>
</tr>
<tr>
<td>88JAC</td>
<td>1486.96</td>
<td>376</td>
<td>579.32</td>
<td>ν₁ and ν₂ are based on the gas phase IR studies of 85KIM/CAM, 87MCK/BUR and 84YAM/HIR; ν₃ is based on the N₂ matrix infrared study of 66SPR/TUR</td>
</tr>
<tr>
<td>89LYM</td>
<td>1490.0</td>
<td>376.0</td>
<td>579.3</td>
<td>Based on the laser flash photolysis results of 85KIM/CAM, the IR diode laser studies of 84YAM/HIR, the IR results of 66NOB/PIM and the argon matrix study of 80JAC</td>
</tr>
<tr>
<td>94JAC</td>
<td>1486.93</td>
<td>1500</td>
<td>586</td>
<td>Review; ν₁ 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 N₂ matrix, and 3rd line is Ar matrix studies</td>
</tr>
</tbody>
</table>

### Table 5.3.4. Enthalpy of formation, kJ·mol⁻¹

<table>
<thead>
<tr>
<th>Source</th>
<th>ΔH°(FOO, g, 0 K)</th>
<th>Reaction</th>
<th>Comments (as reported values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>61ARM/KRI</td>
<td>&gt;154.3</td>
<td>FO₂(g)=F(g)+2O(g)</td>
<td>Review; estimate taken from 61BRE/ROS</td>
</tr>
<tr>
<td>61BRE/ROS</td>
<td>&gt;154.3</td>
<td>MO₂(g)=M(g)+2O(g)</td>
<td>Estimated enthalpy of formation based on trends in atomization energies; this value may refer to O₂F (rather than FOO); ΔH°(298 K)=&lt;19 kcal·mol⁻¹</td>
</tr>
<tr>
<td>65LEV/COP</td>
<td>14.5</td>
<td>FOO→F+O₂</td>
<td>Calculated ΔH=3.5 kcal·mol⁻¹ from an estimated ΔH=17.3 kcal·mol⁻¹ for O₂F=FOO+F; assumed enthalpy of formation of O₂F was 4.73 kcal·mol⁻¹ from 59KIR/GOO, this led to ΔH°(F-O₂)=15 kcal·mol⁻¹</td>
</tr>
<tr>
<td>65MAL/MCG</td>
<td>0.1</td>
<td>FOO→F+O₂</td>
<td>Mass spectrometry; enthalpy of formation was derived from dissociation energy values; assumed ΔH°(F-O₂)=0.8 eV, ΔH°(O=O)=8.45 kcal·mol⁻¹; ΔH°(O-OF)=4.8 eV, 110 kcal·mol⁻¹ [these two values are not at all consistent with the currently adopted ΔH°(FO)]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Source</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>Reaction</th>
<th>Comments (as reported values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>66MAL/MCG</td>
<td>0.1</td>
<td>FOO $\rightarrow$ F + O$_2$</td>
<td>Mass spectrometry; enthalpy of formation was derived from dissociation energy values; assumed $D(F-O) = 0.8$ 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</td>
</tr>
<tr>
<td>66SPR/TUR</td>
<td></td>
<td></td>
<td>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</td>
</tr>
<tr>
<td>67ADR</td>
<td>$-73.34$</td>
<td>FOO $\rightarrow$ F + O$_2$</td>
<td>Derived bond order from EPR results, estimated $D(F-O) = -36$ kcal mol$^{-1}$</td>
</tr>
<tr>
<td>67MAL/MCG</td>
<td></td>
<td></td>
<td>Mass spectrometry; reaction scheme and enthalpies given for the decomposition of O$_2$F$_2$; described in terms of POO radical; no enthalpy of formation given</td>
</tr>
<tr>
<td>68LEV/COP</td>
<td>14.5</td>
<td>FOO $\rightarrow$ F + O$_2$</td>
<td>Discussed stability; suggests the F-O$_2$ bond is approximately 15 kcal mol$^{-1}$ as in 65LEV/COP</td>
</tr>
<tr>
<td>69FRA/DIL</td>
<td>14.401</td>
<td></td>
<td>Review; value taken from JANAF (1967); $\Delta H^\circ(298$ K) $= 3.0$ kcal mol$^{-1}$</td>
</tr>
<tr>
<td>69MAT/TUP</td>
<td></td>
<td></td>
<td>Could calculate a limiting value based on the photochemical decomposition of O$_2$F$_2$; F$_2$ + 2O; discussion mentions dissociation values from 65MAL/MCG</td>
</tr>
<tr>
<td>77OLI</td>
<td>14.401</td>
<td></td>
<td>Value extracted from JANAF (1967); $\Delta H^\circ(298$ K) $= 3.0$ kcal mol$^{-1}$</td>
</tr>
<tr>
<td>78DEW/RZE</td>
<td>102.6</td>
<td></td>
<td>$\Delta H^\circ(298$ K) $= 24.1$ kcal mol$^{-1}$; calculated enthalpy of formation by the half-equation method; refers to a value of 3.0 kcal mol$^{-1}$ from the JANAF Tables 2nd Edition</td>
</tr>
<tr>
<td>79SHA/KOT</td>
<td>23.44</td>
<td></td>
<td>EPR measurement of rate constants</td>
</tr>
<tr>
<td>80CI I</td>
<td></td>
<td></td>
<td>MINDO approximation; total energy is $\sim 1005$ kcal mol$^{-1}$</td>
</tr>
<tr>
<td>80THY/SUB</td>
<td>$-1.9$</td>
<td>FOO(g) $\rightarrow$ F(g) + 2O(g)</td>
<td>Calculated the enthalpy of atomization (136.9 kcal mol$^{-1}$) based on force constants data; refers to 66SPR/TUR value of 135.0 $\pm$ 5 kcal mol$^{-1}$</td>
</tr>
<tr>
<td>84FRE</td>
<td>52.14</td>
<td>O$_2$ + F$_2$ $\rightarrow$ O$_2$F + F</td>
<td>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;</td>
</tr>
<tr>
<td>85GOS/RAG</td>
<td></td>
<td></td>
<td>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</td>
</tr>
<tr>
<td>86MEL</td>
<td>99.6</td>
<td></td>
<td>BAC MP4 theory; 23.2 and 23.8 kcal mol$^{-1}$ given for 298 and 0 K respectively</td>
</tr>
<tr>
<td>87PAG/RAT</td>
<td>27.94 $\pm$ 2</td>
<td>F + O$_2$ $\rightarrow$ FO$_2$</td>
<td>Spectrokinetic study (295$-$359 K) = $-12.62 \pm 0.5$ kcal mol$^{-1}$; gas phase equilibrium; led to $D(F-O) = 11.68 \pm 0.5$ kcal mol$^{-1}$</td>
</tr>
<tr>
<td>88CAM</td>
<td>18.9</td>
<td>2O$_2$F $\rightarrow$ O$_2$F + O$_2$</td>
<td>Gas equilibrium; FTIR study; yielded K$=22$ at 286 K</td>
</tr>
<tr>
<td>88LYM/HOL</td>
<td>24.81 $\pm$ 1.7</td>
<td></td>
<td>Derived from a kinetic study of reactions of fluorine atoms with oxygen; derived $\Delta H(298$ K) = $5.49 \pm 0.4$ kcal mol$^{-1}$</td>
</tr>
<tr>
<td>89LYM</td>
<td>24.73 $\pm$ 1.7</td>
<td></td>
<td>$5.47 \pm 0.4$ kcal mol$^{-1}$; recommended value based on mean of three studies; $5.49 \pm 0.4$ 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</td>
</tr>
<tr>
<td>90FRA/GOL</td>
<td></td>
<td></td>
<td>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</td>
</tr>
</tbody>
</table>
5.4. O\textsuperscript{17}OF

Welsh et al. [66WEL/MET] studied the EPR spectra of the three O\textsubscript{2}F\textsuperscript{17} isotopic species (O\textsuperscript{17}OF, O\textsuperscript{18}OF, O\textsubscript{2}F\textsuperscript{18}). 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. O\textsuperscript{18}OF

Welsh et al. [66WEL/MET] studied the EPR spectra of the three O\textsubscript{2}F isotopic species (O\textsuperscript{16}OF, O\textsuperscript{17}OF, O\textsubscript{2}F\textsuperscript{18}). 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. O\textsuperscript{17}OF

Welsh et al. [66WEL/MET] studied the EPR spectra of the three O\textsubscript{2}F isotopic species (O\textsuperscript{16}OF, O\textsuperscript{17}OF, O\textsubscript{2}F\textsuperscript{18}). 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\textsuperscript{18}OF

Singh and Nagarajan [74SIN/NAG] surveyed the vibrational spectra studies on four isotopic species (\textsuperscript{16}O\textsuperscript{16}O\textsuperscript{16}F, \textsuperscript{16}O\textsuperscript{16}O\textsuperscript{17}F, \textsuperscript{16}O\textsuperscript{17}O\textsuperscript{16}F, \textsuperscript{17}O\textsuperscript{16}O\textsuperscript{16}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]; \(r(O-F) = 1.575\text{\AA}, r(O-O) = 1.217\text{\AA}, \angle(OOF) = 109\text{.3°}\). The structure data is included in Table 5.3.2, whereas the vibrational frequency information is noted in Table 5.3.3.

5.8. O\textsuperscript{17}OF

Singh and Nagarajan [74SIN/NAG] surveyed the vibrational spectra studies on four isotopic species (\textsuperscript{16}O\textsuperscript{16}O\textsuperscript{16}F, \textsuperscript{16}O\textsuperscript{16}O\textsuperscript{17}F, \textsuperscript{16}O\textsuperscript{17}O\textsuperscript{16}F, \textsuperscript{17}O\textsuperscript{16}O\textsuperscript{16}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]; \(r(O-F) = 1.575\text{\AA}, r(O-O) = 1.217\text{\AA}, \angle(OOF) = 109\text{.3°}\). 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 ap basis set SCF total energy calculations as a function of OFO bond angle (assumed O-F bond distance of 1.19\text{\AA}), predicted the ground state to be\textsuperscript{\textsuperscript{2}}B\textsubscript{1} with a bond angle of 128.22°. Using the authors results for ClO\textsubscript{2} one would estimate the uncertainty of this bond angle is of the order \(\pm 4°\). The non-empirical LCAO-MO-SCF calculations on OFO indicated that OFO was thermodynamically unstable relative to FOO by over 100 kcal-mol\textsuperscript{-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 \textsuperscript{\textsuperscript{2}}B\textsubscript{1}, \textsuperscript{1}B\textsubscript{2}, \textsuperscript{1}A\textsubscript{1}, and \textsuperscript{1}A\textsubscript{2} states of UP(U) and the \textsuperscript{1}A and \textsuperscript{1}A\textsubscript{2} states of UP(O) was carried out at the RHF-SCF level with 6-31G and 6-31G* basis sets [85GOS/RAG]. These calculations predicted the \textsuperscript{2}B\textsubscript{1} and \textsuperscript{1}B\textsubscript{2} states of OFO to lie close in energy, with the \textsuperscript{2}B\textsubscript{2} state lying approximately 3 kcal-mol\textsuperscript{-1} lower and designated as the ground state. These calculations yielded the result that FOO was more stable than OFO by 85 kcal-mol\textsuperscript{-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 1.5591\text{\AA} and a bond angle of 76.75°. No information is given on the vibrational frequencies.

5.10. O\textsubscript{2}F

The photochemical reaction between fluorine and ozone was stated to produce O\textsubscript{2}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\textsubscript{2} and O\textsubscript{3} using a water filter, Arkell [65ARK] tentatively assigned a band at 1503 cm\textsuperscript{-1} to O\textsubscript{2}F. No other information was given on this radical.

The EPR spectra obtained by Kasai and Kirshenbaum [65KAS/KIR] on O\textsubscript{2}F\textsubscript{2} and O\textsubscript{2}F\textsubscript{3} were identical. Although the
spectra was attributed to FOO, a later reference [72MCC/PAL] suggested that the radical was really O₂F.

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 O₂F.

Glidewell [80GLI], using MINDO approximation, calculated the geometry and enthalpy of formation (+107.69 kJ mol⁻¹), and predicted an asymmetric molecular structure of F⁻⁻O₁⁻⁻O₂⁻⁻O₃ for O₂F: r(F⁻⁻O₁⁻⁻O₂⁻⁻O₃) = 1.314 Å. r(O₁⁻⁻O₂⁻⁻O₃) = 1.257 Å. ∠(F⁻⁻O₁⁻⁻O₂⁻⁻O₃) = 116.2°. ∠(O₁⁻⁻O₂⁻⁻O₃) = 124.2°. ∠(F⁻⁻O₁⁻⁻O₂⁻⁻O₃) = 53.1°. It is important to note that this compound does not have a pyramidal structure, in contrast to the other halogen oxides (XO₃) which are thought to have a pyramidal structure. No vibrational frequencies were provided.

5.11. O₂F

In examining the irradiation of a mixture of F₂ and O₂ using a water filter, Arkell [65ARK] tentatively assigned a band at 1312 cm⁻¹ to O₂F. The author proposed the formation of O₂F from the decomposition of O₂F. No other data as to the structure or vibrational frequencies were provided.

Spratley and Pimentel [66SPR/PIM] discussed the bonding in fluorine oxide compounds. Although the O₂F 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. [69GOET/CAN], in their radiolysis of O₂F₂ mixtures, briefly mentioned that the existence of O₂F 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 O₂F. No spectroscopic or thermodynamic information was provided.

Glidewell [80GLI], using MINDO approximation, calculated the geometry and enthalpy of formation (+134.01 kJ mol⁻¹), and predicted the structure F⁻⁻O₁⁻⁻O₂⁻⁻O₃ for O₂F: r(F⁻⁻O₁⁻⁻O₂⁻⁻O₃) = 1.488 Å. r(O₁⁻⁻O₂⁻⁻O₃) = 1.317 Å. r(O₁⁻⁻O₂⁻⁻O₃) = 1.439 Å. r(O₁⁻⁻O₂⁻⁻O₃) = 1.253 Å. ∠(F⁻⁻O₁⁻⁻O₂⁻⁻O₃) = 110.1°. ∠(O₁⁻⁻O₂⁻⁻O₃) = 112.0°. ∠(O₁⁻⁻O₂⁻⁻O₃) = 123.8°. ∠(F⁻⁻O₁⁻⁻O₂⁻⁻O₃) = 80.4°. ∠(O₁⁻⁻O₂⁻⁻O₃) = 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 (XO₃) halogen oxides. No vibrational frequencies were provided.

5.12. OF₂

As mentioned in the introduction, the following does not represent a complete coverage of all references dealing with OF₂. As a result, coverage in the areas dealing with preparation, reaction, 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 OF₂ are listed in the following ten categories:
[74SIM/NOV], [75DIA/SIM], [75SPE/SPI],
[76ALL/RAL], [76GIR/SAS], [77VIZ/SEB],
[80VIZ/SEB], [83DUI], [84CY/TVV],
[84WAS/MOO], [87KEX], [90AND/PAL],
[93ALL/CSA]
Electronic spectra — [34GLI/SCH], [35HET/POH], [83BUS/SIB],
Miscellaneous — [46GOR], [53ARO], [57LIC/LIN], [60WUL], [61DUR/BAT], [61PIE/JAC],
[63PIE/DIC], [67STR/STR], [67NEB/ME], [68PET/SCR], [69BON/PET],
[69GOC/STO], [70DAR/BUR],
[71HOL], [71RAD/HEH], [72ROB/KUE],
[74MIN/MIT], [79NIE], [79SUG/KAU],
[80HAY], [81ZHI/KOL], [83SCH/KAT],
[84MAI], [85TAN/HER], [89MAI],
[92MCI/AND], [93MAI], [93WAT],
[94L/HON]
6. Dissociation energy/ionization potential —
[52PAU], [44GLI/SCH], [45SUK], [46WIC],
[49GLOC], [49GLOC], [49DEP], [50SCH],
[52AOK], [57DIB/REE], [63PRI/PAS], [63SCH],
[65MOR], [66VEV/GER], [67DRO/WAG],
[70DAR], [71C/LY/WAT], [71C/RFO],
[72BRO/ROB], [72CZA/SCH], [73BER/DEH],
[73ROT/SCH], [77GLI], [78CH/HER],
[78LEO/LEO], [80VAV/VAS], [81LAN/CHO],
[84ALE/VOL], [92CHO]
7. Geometry/structure:
Experimental — [35BOE], [35BOE2], [35HET/POH], [35HET/POH2], [35SUT/BRO],
[36POH/SCH], [50BRE/POW], [53BIE/SCH], [61HIL/JAC], [61PIE/JAC], [63PIE/DIC],
[66MOR/SAI], [71TRE/SAV],
[83TAU/JON],
Theoretical — [51DUC/BUR], [63SCH2],
[66DOU/DEY], [66POP/SEG], [66SFT/PIM],
[70NEW/LAT], [73SIC], [74MIN/MIT],
[75BEN/DEW], [76PLE/KOC], [79SCH/CRU],
[80GLI], [80L/AV/VAS], [80VAV/VAS],
[82ALP/TAY], [82MAR/RAO],
[82ZHU/MUR], [83DEK/JAS], [83DUI],
[83MAR/DIX], [84DUI], [85MEL],
[87REE/SCH], [88THI/SCU], [89BHA],
[90SAA/KAU], [92GIL/ROB], [94GIM/7HA]
Review — [36BRO], [37STU], [40MAX],
[76CAL/HIR], [79HAR/LAU]

8. Review —
[33YS/HAT], [36BIC/ROS], [36BRO], [40SID/Pow],
[41SIC/STE], [46WIC], [50BRE/BRO],
[52SRO/WAG], [54COU], [55EVA/MUN],
[60GEO], [61ARM/KRI], [63STR], [66FOV/JAC],
[66RED/GUR], [68TUR], [69FRA/DIL],
[70DAR], [72BRI], [78LEO/LEO], [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/FRI], [83KOL/SHC],
[89LIV/TAK]
10. EPR —
[65SIT/Y], [65SIT/VIA/VAI], [661 AW/OGD],
[66MET/WEL], [72LEV]

The geometry and vibrational frequencies of UF₅ 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 geometry and structure data is summarized in Table 5.12.2.

Since this symmetric molecule is bent, the point group is C₂ᵥ. 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/MLI, 65BIS/IAM, 65BIS/HAM]. 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 PO. These studies have all been summarized in Table 5.12.1, 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 POF.
<table>
<thead>
<tr>
<th>Source</th>
<th>$\nu_1$</th>
<th>$\nu_2$</th>
<th>$\nu_3$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>35HET/POH</td>
<td>870</td>
<td>1280</td>
<td>1740</td>
<td>IR spectra between 1 and 27$\mu$</td>
</tr>
<tr>
<td>35HET/POH2</td>
<td>833</td>
<td>492</td>
<td>1110</td>
<td>IR spectra; vibrational frequencies observed but assignments for the 3 specific frequencies not made</td>
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<tr>
<td>36PHT/SCH</td>
<td>929</td>
<td>461</td>
<td>828</td>
<td>IR spectra of OF2(g)</td>
</tr>
<tr>
<td>51JON/KIR</td>
<td>928</td>
<td>461</td>
<td>831</td>
<td>IR spectra; comparisons made with 35HET/POH2; $\nu_3$ not directly observed</td>
</tr>
<tr>
<td>51NIE</td>
<td></td>
<td></td>
<td></td>
<td>Explanation of history of some previous studies; no data given</td>
</tr>
<tr>
<td>62AGA/GRA</td>
<td>929</td>
<td>461</td>
<td>826</td>
<td>Matrix IR studies; values from another unnamed source</td>
</tr>
<tr>
<td>65ARK/REI2</td>
<td>945.1</td>
<td>470.4</td>
<td>858.8</td>
<td>IR spectrum; re-investigation of Fermi resonance; harmonic frequencies and harmonic constants also given</td>
</tr>
<tr>
<td>66SPE/TUR</td>
<td>925.2</td>
<td>461.1</td>
<td>821</td>
<td>IR spectra of products of photolysis of F and O in a matrix; observed frequencies assigned to OF2; $\nu_2$ not observed; no assignments made</td>
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<tr>
<td>67MOR/YAM</td>
<td>898</td>
<td>457</td>
<td>794</td>
<td>IR spectra; attempt to examine the Fermi resonance between $\nu_1$ and 2$\nu_2$ states; rotational constants given</td>
</tr>
<tr>
<td>67OGD/TUR</td>
<td>925.1</td>
<td>461</td>
<td>821</td>
<td>IR matrix spectra of $^{16}$OF2 and $^{18}$OF2 in argon; the 2 values for $\nu_1$ refer to the Fermi doublet</td>
</tr>
<tr>
<td>71AND/RAY</td>
<td>925.2</td>
<td>461.1</td>
<td>821.1</td>
<td>Matrix IR spectra of OF2 or $^{18}$OF2 in Ar; main emphasis is on the formation of LOF rather than the examination of OF2</td>
</tr>
<tr>
<td>71BRE/SAV</td>
<td>412–416</td>
<td>456–462</td>
<td>812–845</td>
<td>Raman spectra of liquid OF2; polarization studies confirm earlier IR assignments and support existence of Fermi resonance</td>
</tr>
<tr>
<td>71BRE/SAV</td>
<td>412–416</td>
<td>456–462</td>
<td>812–845</td>
<td>Raman and IR spectra of OF2 (cr)</td>
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<tr>
<td>72AND</td>
<td>920</td>
<td>465</td>
<td>825</td>
<td>Ar matrix Raman spectra</td>
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<td>79KOL/KON</td>
<td>918.0±0.8</td>
<td>459.8±0.8</td>
<td>823.0±0.5</td>
<td>Absorption spectra in liquid N2 at 80 K; Fermi resonance; also presents harmonic frequencies and anharmonicity constants</td>
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<td>81POP/SCH</td>
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<td>480</td>
<td>1227</td>
<td>Ab initio calculations HF3–21G; harmonic frequencies given</td>
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<td>82MAR/RAO</td>
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<td>493.5</td>
<td>1081.4</td>
<td>Ab initio SCF calculations at the 4-31G level; harmonic frequencies given (source of frequencies not given)</td>
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<td>83TAU/3JON</td>
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<td>Fermi diad at 928 cm$^{-1}$ studied by IR-MW double resonance</td>
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<td>86TAU/3JON</td>
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<td>Fermi resonance; diode laser spectra to resolve the true vibrational center for $\nu_1$ and 2$\nu_2$</td>
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<td>87BMT/SCH</td>
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<td>475</td>
<td>923</td>
<td>A, B, C, and ground state calculated</td>
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<td>87TAU</td>
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<td>832</td>
<td>IR diode laser spectroscopy; $\nu_1$ frequency range examined; Coriolis coupling</td>
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<td>88THI/SCU</td>
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<td>843.86</td>
<td>Ab initio prediction at the SCF, CISD and CCSD levels, using DZP and TZVP basis sets; results listed for TEP CCSD/D2C</td>
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<td>90AND/PAL</td>
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<td>843.86</td>
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<td>90SAA/KAU</td>
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<td>Curvilinear internal coordinate Hamiltonian; harmonic frequencies calculated</td>
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<td>Bond angle(*)</td>
<td>Comments</td>
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<td>35BOE</td>
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<td>Electron interference technique; 35BOE2 assumed to be the same article</td>
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<td>35HET/POH</td>
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<td></td>
<td>IR spectra supports bent structure</td>
<td></td>
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<tr>
<td>35HET/POH2</td>
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<td>105±5</td>
<td>Electron diffraction study</td>
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<td>35SUT/BRO</td>
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<td>100±3</td>
<td>Review based on 3 studies [35SUT/BRO, 35BOE, 35BOE2]</td>
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<td>36BRO</td>
<td>1.4</td>
<td>105±5</td>
<td>Recalculated values based on data of 35BOE</td>
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<tr>
<td>36POH/SCH</td>
<td>1.41±0.5</td>
<td>100+3</td>
<td>Review of electron diffraction data based on three studies: 35BOE, 35BOE2, 35SUT/BRO</td>
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<td>50BER/POWER</td>
<td>1.38±0.3</td>
<td>101.5±1.5</td>
<td>IR spectra of OF(2)</td>
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<tr>
<td>51DUC/BUR</td>
<td>101.30</td>
<td></td>
<td>No mention as to the source of this value</td>
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<tr>
<td>53HBE/SCH</td>
<td>1.413±0.019</td>
<td>103.8±1.5</td>
<td>Electron diffraction study; *recommended values based on present work and 3 other studies</td>
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<tr>
<td>61HIL/JAC</td>
<td>1.3896</td>
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<td>Microwave spectroscopy; derived 3 average rotational constants; also derived centrifugal distortion constants</td>
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<tr>
<td>61PIE/JAC</td>
<td>1.409</td>
<td>103.18</td>
<td>Microwave spectrum; dipole moment and inertial defect determined</td>
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<tr>
<td>63PIE/DIC</td>
<td>1.4124</td>
<td>103.10</td>
<td>Microwave spectroscopy; derived average structure</td>
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<tr>
<td>63SCH</td>
<td></td>
<td></td>
<td>** Note: use of various basis sets (a simple MOL/LAU calculation with Slater functions and LCAO-MO-SCF calculations; correlate the intermolecular angle with orbital energies)</td>
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<tr>
<td>66BUE/PEY</td>
<td>1.4053±0.0004</td>
<td>103.4°±3°</td>
<td>Microwave spectroscopy; determined equilibrium structure</td>
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<td>66MOR/SAI</td>
<td>1.410</td>
<td>99.2</td>
<td>SCF-MO-CND2, SCF-MO-CND2/2 calculations; refers to 53HBE/SCH</td>
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<tr>
<td>66SPR/PIM</td>
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<td>103.10</td>
<td>Prediction of structures of molecules; only data for OF(2) implies a bent structure</td>
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<tr>
<td>71TRE/SIAV</td>
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<td>106.8</td>
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<td>71TRE/SIAV</td>
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<td>99.2</td>
<td>SCF-MO calculation</td>
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<tr>
<td>73SIC</td>
<td>1.439</td>
<td>55.2</td>
<td>MINDO3 calculations</td>
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<tr>
<td>74MIN/MIT</td>
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<td>103.067±0.50</td>
<td>Review; based on four studies</td>
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<td>76CAL/HIR</td>
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<td>102.91</td>
<td>Ab initio MO theory (STO-3G, STO-4G)</td>
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<tr>
<td>76PLE/KOC</td>
<td>1.409</td>
<td>103.3</td>
<td>Review; values based on 63PIE/DIC and 66MOR/SAI; 3 sets of values, refer to effective geometry, average geometry, and equilibrium geometry respectively</td>
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<td>79HAR/LAU</td>
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<tr>
<td>79SCH/CRU</td>
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<td>102.0</td>
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<td>80GLI</td>
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<td>MINDO calculation</td>
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<tr>
<td>80LAW/VAS</td>
<td>1.40</td>
<td>103.0</td>
<td>Orbital exponents were optimized for bond functions (Gaussian s and p orbitals based; human model); 3 different levels of calculation, DZ, DZD and DZD</td>
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<td>80VAI/VAS</td>
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<td>103.0</td>
<td>SCF-CI studies (DZ-SCF, DZP-SCF, DZP-CI)</td>
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<tr>
<td>82AHL/TAY</td>
<td>1.393</td>
<td>103.7</td>
<td>High quality correlated wave functions (SCF, CEPA 3 different types of frozen orbitals)</td>
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<tr>
<td>82MAR/RAO</td>
<td>1.40</td>
<td>103.5</td>
<td>Ab initio SCF calculations at the 4-31G level</td>
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<tr>
<td>82ZHOU/MUR</td>
<td>1.335</td>
<td>103.01</td>
<td>SCF calculations 6-31G and 6-31G**; refers to data of 66MOR/SAI and 79SCH/CRU</td>
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### TABLE 5.12.2. Geometry and structure — Continued

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<td>SINDO calculations</td>
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<td>83MAR/DIX</td>
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<td>Ab initio SCF calculations (3G, 4–31G, STO1); refers to 66MOR/SAI</td>
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<td>1.422</td>
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<td>83TAU/JON</td>
<td>1.271</td>
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<td>Fermi resonance; IR-MW double resonance</td>
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<td>83MEL</td>
<td>1.3484</td>
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<td>Critical review: BAC/MP4 method using geometries optimized at HF-6-31G*: value</td>
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<td>measured at 0 K</td>
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<tr>
<td>87REE/SCH</td>
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<td>Ab initio 6-31G* calculations; optimized geometries with respect to E(Lewis)</td>
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<td>1.408</td>
<td>97.1</td>
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<td>88THI/SCU</td>
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<td>Ab initio prediction at the SCF, CISD and CCSD levels</td>
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<td>1.4085</td>
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<td>89BAI</td>
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<td>102</td>
<td>Ab initio MO calculations (STO-3G); values extracted from a graph</td>
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<td>90SAA/KAU</td>
<td>1.4052</td>
<td>103.07</td>
<td>Equilibrium geometry calculated from 66MOR/SAI, 86TAU/JON, 87BUR/SCH</td>
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<tr>
<td>92GIL/ROB</td>
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<td></td>
<td>Only provides bond distance; relies on other sources for numeric values</td>
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<tr>
<td>94GIM/ZHA</td>
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<td>Ab initio SCF-MO calculations at the RHF and MP2 levels using the 6-31G** basis set</td>
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<td>102.61</td>
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### TABLE 5.12.3. Dissociation energy

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<tr>
<td>34GLI/SCH</td>
<td>Absorption maximum attributed to OF$_2$ dissociation to 2F+O; &lt;2100-</td>
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<tr>
<td>45SKI</td>
<td>Review; bond energy values from $\Delta H$ from 36BIC/ROS; 117.0 kcal-mol$^{-1}$</td>
</tr>
<tr>
<td>46WIC</td>
<td>Review; $D_{1u}$(OF)+1/2$D_{2v}$(OF)$_2$+115 kcal-mol$^{-1}$; no reference as to the origin of the value</td>
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<tr>
<td>49POT</td>
<td>No value recommended; refers to 3 earlier experimental enthalpy of formation studies</td>
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<tr>
<td>55AOK</td>
<td>Used Mulliken's magic formula (calculation); 5.62 eV</td>
</tr>
<tr>
<td>65MOR</td>
<td>Three-dimension Hückel calculations; refers to an observed value of 95 kcal-mol$^{-1}$ (no source of value given); 94.9 kcal/cal</td>
</tr>
<tr>
<td>67TRO/WAG</td>
<td>Source of value not clear but presumably derived from kinetic study; $D_{2v}$(FO)$\rightarrow$F$=37\pm1$ kcal-mol$^{-1}$</td>
</tr>
<tr>
<td>70DAR</td>
<td>Review; recommended value taken from 68WAG/EVA; 268±13 (T/K=0) kcal-mol (64±3, T/K=0, kcal-mol$^{-1}$)</td>
</tr>
<tr>
<td>71COR/FRO</td>
<td>Photoionization of OF$_2$; no dissociation energy value given</td>
</tr>
<tr>
<td>72BRU/ROB</td>
<td>Comparison of ionization potentials and MO calculations; no dissociation energy value given</td>
</tr>
<tr>
<td>73ROT/SCH</td>
<td>SCF calculations for the electronic ground state; a contracted Gaussian basis set of double zeta plus polarization quality; –1.52 eV</td>
</tr>
<tr>
<td>77GLI</td>
<td>Calculation of dissociation energies from an experimentally reported $\Delta H$ value</td>
</tr>
<tr>
<td>78CHO/HER</td>
<td>Refers to earlier work on OF$_2$ by Chong; no dissociation energy given</td>
</tr>
<tr>
<td>78LEO/MED</td>
<td>Critical review; values based on analysis (with current 1978 auxiliary data) of 30RUF/MEN, 30WAR/KLI, 66BIS/HAM and 68KIN/ARM; $\Delta H$(OF$\rightarrow$F$)=38\pm2$ kcal-mol$^{-1}$, $\Delta H$(O+O$\rightarrow$=21±4 kcal-mol$^{-1}$</td>
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<tr>
<td>80VAL/VAS</td>
<td>PCS-CI-DZ studies; ionization potentials; no dissociation energy value given</td>
</tr>
<tr>
<td>81LAN/CHO</td>
<td>Ionization potentials; no dissociation energy value given</td>
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<tr>
<td>84ALE/VOL</td>
<td>Ionization potentials; no dissociation energy value given</td>
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<tr>
<td>92CHO</td>
<td>Ionization potentials; no dissociation energy value given</td>
</tr>
<tr>
<td>Source</td>
<td>$\Delta H(298.15 \text{ K})$ (kJ·mol$^{-1}$)</td>
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<tr>
<td>-----------------</td>
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<tr>
<td>30RU/MEN</td>
<td>10.9±8</td>
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<td>30WAR/KLI</td>
<td>46.0±8</td>
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<tr>
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<td>31WAR</td>
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<td>33YOS/HAT</td>
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<td>36BIC/ROS</td>
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<td>50BRE/BRO</td>
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<td>50LUF</td>
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<tr>
<td>50SCH2</td>
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<tr>
<td>52ROS/WAG</td>
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<td>54COU</td>
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<td>55EVA/MUN</td>
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<td>61ARM/KRI</td>
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<td>66BIS/HAM</td>
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<td>66BIS/HAM2</td>
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<td>66VED/GUR</td>
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<td>67TRO/WAG</td>
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<tr>
<td>68KIN/ARM</td>
<td>24.52±1.59</td>
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<tr>
<td>69FRA/DIL</td>
<td>21.72</td>
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<td>71CILY/WAT</td>
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<td>72HOU/ASM</td>
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<td>76BIN/DEW</td>
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<td>76KOE/JOL</td>
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<td>87HER</td>
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<tr>
<td>89LIV/AAR</td>
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<tr>
<td>90VAN/KEL</td>
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</tbody>
</table>

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$^{16}$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$^{16}$F$_2$ and O$^{18}$F$_2$.

5.15. FFO

83DEK/JAS, using the MNDO method, calculated an enthalpy of formation of FFO, and reported a value of 356.3 kJ mol$^{-1}$. Similar calculations on OF$_2$ suggested that FFO was less stable by 509 kJ mol$^{-1}$. However, the absolute values presented may be too high by 51 kJ mol$^{-1}$ (in comparison to experimental data for FOF). No references to previous work on this species were cited.

5.16. O$_2$F$_2$

All references dealing with O$_2$F$_2$ are listed in the following nine categories. Of prime interest are the spectroscopic, geometry and enthalpy of formation studies.

1. Vibrational frequencies/spectroscopy —
   [37BAO/FRI], [65ARK], [65BRO], [65SPP/ TUR], [67LAW], [67SPP], [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/RAU], [80GIL], [82AHL/ 1AY], [84BUR/LAW], [86MEL], [86KOH/ HAY], [88HED/HED], [88MAC/OBE], [89LEE/ RIC], [90MAC/OBE], [89RAG/TRU],
   [90MCG/CTE], [93AMO/MUR], [94JAC/71H]

3. EPR/NMR —
   [65KAS/KIR], [65NEU/VAN], [66LAW/OGD],
   [66WEL/MET], [67NEB/MET], [68LAW/OGD],
   [68SOL/KEI], [71SOL/RAN], [72SUG/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], [36FRS/SCH],
   [36FRS/SCH2], [37FRS/SCH], [37FRS/SCH2],
   [37SCH], [37SCH/FRI], [38AOY/SAK],
   [41AOY/SAK], [58BAI/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], [73MIN/ MIN], [81SUL/SUL], [83FUR/MAJ], [84FUR],
   [84TAK/HOS], [84YAM/HIR], [85BEA],
   [87CLA/SCH], [88KIS/POP], [88KIS/POL2],
   [88LYL/LOI], [88MAL/PBE], [91AOM/SOD],
   [91DIX/AND], [91RAS/COC], [92RAS/BAG],
   [94SAM/MAS]

6. Density/vapor pressure —
   [58KIR/AST], [59KIR/GRO]

7. Review —
   [33RUF], [50SCH], [60GOE], [61ARM/KRI],
   [61MCG], [62STR], [66FOX/JAC], [66VED/ GUR], [68TUR], [70DAR], [72BRJ], [76CAL/ HIR], [79HAR/RAU], [84BUR/LAW], [85LYM],
   [94JAC]

8. Kinetics/reaction —
   [36FRS/SCH], [37SCH/FRI], [62HOL/COH],
   [62STR/GRO], [62STR/GRO2], [62STR/GRO3],
   [63STR], [63STR/KIR], [63STR/KIR2],
   [64SOL], [65MOR/YOU], [65SOL], [66SOL2],
   [67JOL], [67OL], [68BAN/SUK], [68LAW/ TUR], [68SOL], [68SOL/KAC], [68SOL/KAC2],
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   [69SOL/KEI], [70SOL], [71STR], [73CHE/TUP],
   [73CHE/TUP2], [73NIK/DUD], [74SOL/KEI],
   [75LEU], [75MA/LUT], [78STR/BEZ],
   [78CHE/TUP], [79JAC], [80SOL], [82DAV/ TEM], [82DAV/TEM2], [82DAV/TEM3],
   [84ASP/EL1], [84EL1/MAL], [84MAL/EL1],
   [84PAR/MOR], [85PVEL/RAR], [85KHM/CAM3],
   [85KIN/ASP], [86ASP/KIN], [87BAS/BAI],
   [87BAS/BAI2], [87EL/PEN], [87HER],
   [88LYL/HUL], [90AMJ], [90AMJ/UK],
   [90LEE/REN], [90NIE/KIN], [91BE], [91LUT/ SMA], [91NIL], [91SCU], [92ALM/HOL]

9. References in [65STR] —
   [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 [57GLD/DAK, 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.

Brodersen et al. [37BRO/FRI] measured the absorption spectra and extinction coefficients between 2000 and 10000 Å. [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 UF3 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 O2F2 is yellow, melts sharply at 119 K and is diamagnetic.

Jacoby [94IAC] provided recommended data for FOOF as follows: a C3v 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 ν1 through ν5.

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<th>ν4 (cm⁻¹)</th>
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<td>621</td>
<td>369</td>
<td>205</td>
<td>615</td>
<td>457</td>
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<td></td>
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<td>595</td>
<td>362</td>
<td>195</td>
<td>586</td>
<td>444</td>
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<tr>
<td>70LOO/GOE</td>
<td>*1306</td>
<td>621</td>
<td>369</td>
<td>205</td>
<td>615</td>
<td>457</td>
</tr>
<tr>
<td></td>
<td>1239</td>
<td>595</td>
<td>362</td>
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<td>586</td>
<td>444</td>
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<tr>
<td>71GAR/LAW</td>
<td>1270</td>
<td>618</td>
<td>364</td>
<td>–</td>
<td>612</td>
<td>468</td>
</tr>
<tr>
<td>72MEL/AND</td>
<td>~1300</td>
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<td></td>
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<tr>
<td>73BUR/GAR</td>
<td>1290</td>
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<td>366</td>
<td>195.6</td>
<td>624</td>
<td>459</td>
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<td>78GRU/EDW</td>
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<td>80JAC</td>
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<td></td>
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<td>612</td>
<td>366</td>
<td>195</td>
<td>627</td>
<td>466</td>
</tr>
<tr>
<td></td>
<td>1250</td>
<td>608.5</td>
<td>367.1</td>
<td>194.7</td>
<td>627.5</td>
<td>466.9</td>
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<tr>
<td></td>
<td>1214.9</td>
<td>592.2</td>
<td>361.4</td>
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<td>620.1</td>
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<td>–</td>
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<tr>
<td></td>
<td>1178.6</td>
<td>585.8</td>
<td>355.9</td>
<td>192.0</td>
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<td>450.4</td>
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<td>85KIM/CAM</td>
<td>1210</td>
<td>639</td>
<td>360</td>
<td>707</td>
<td>614.4</td>
<td>471</td>
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<td>85KIM/CAM2</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Values quoted by other authors, refer to the natural abundance molecule; IR spectra of solid, preliminary announcement of data reported in 71GAR/LAW.

IR spectra of solid isotopic species

Matrix infrared study; observed ν(OF asymmetric stretch) of 624 cm⁻¹; assignment was made by 65BRO

Absorption spectra; observed 4 frequencies (624.4, 612.0, 461.9, 368.1) from the photolysis of nitrogen-oxygen mixtures

ν is ν1 (cm⁻¹) for O–O stretching frequency in fluoro-peroxides; refers to results by 65BRO, 66SPR/TUR, 65ARK, 68LOO/GOE, 67LAW, 61SPR.

Studied the O–O stretching frequency in fluoro-peroxides; refers to results by 65BRO, 68LOO/GOE, 71GAR/LAW.

Raman spectra in CF3F solution; detailed discussion as to the assignment of vibrational frequencies

Raman study of solid

IR spectra of Ar matrix; observed and calculated values given respectively

PTIR (ν = 1 cm⁻¹) ν2 and ν3 are different from those presented in 80JAC; no numerical structure information; observed all six vibrational frequencies

Laser flash photolysis; examined the equilibrium existence between O2P and O2F2 compared O–F stretch and O–O stretching in both molecules

### Table 5.16.1 Vibrational frequencies, cm⁻¹ — Continued

<table>
<thead>
<tr>
<th>Source</th>
<th>ν₁</th>
<th>ν₂</th>
<th>ν₃</th>
<th>ν₄</th>
<th>ν₅</th>
<th>ν₆</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>87WOO/LAR</td>
<td>1281</td>
<td>607</td>
<td>373</td>
<td>197</td>
<td>623</td>
<td>461</td>
<td>Condensed phase Raman spectrum</td>
</tr>
<tr>
<td>88CAM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IR intensity study of equilibrium between O₂F₂, O₂F and O₂ sore</td>
</tr>
</tbody>
</table>

#### Calculated Values

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

---

### Table 5.16.2 Geometry and structure

#### Experimental Values

<table>
<thead>
<tr>
<th>Source</th>
<th>Bond distance (Ǻ)</th>
<th>dihedral°</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>r – O</td>
<td>o – o</td>
<td></td>
</tr>
<tr>
<td>62JAC</td>
<td>1.575 ±0.003</td>
<td>1.217 ±0.03</td>
<td>109.50 ±0.5 87.5 87.5 Microwave spectroscopy of 3 isomers, ¹⁰O₂F₂, ¹⁸O₂F₂, and ¹⁰O¹⁸OF₂; 9r structure</td>
</tr>
<tr>
<td>73MIN/MIN</td>
<td></td>
<td></td>
<td>87.5 Refers to a dihedral angle; extended Huckel calculation; the experimental value is the same and refers to 68WIN/WIN</td>
</tr>
<tr>
<td>88HED/HED</td>
<td>1.586</td>
<td>1.216</td>
<td>109.2 88.1 Electron diffraction study at -42°C; r₅ structure</td>
</tr>
</tbody>
</table>

#### Calculated Values

<table>
<thead>
<tr>
<th>Source</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>62WIL</td>
<td>Quantum calculations of 62JAC</td>
</tr>
<tr>
<td>63LIN</td>
<td>Refers to geometry given by 62JAC; discussed bonding</td>
</tr>
<tr>
<td>67TUR/HAR</td>
<td>MO treatment of bonding; structure assumed to be FOOF; 4 calculations assuming different bond distances; VESCF</td>
</tr>
<tr>
<td>69GOR/POP</td>
<td>INDO calculation of geometry</td>
</tr>
<tr>
<td>69GOR</td>
<td>Refers to 62JAC values; CNDO/2 calculations; barriers to internal rotations</td>
</tr>
<tr>
<td>70GIM</td>
<td>Reported a C₂ symmetry; extended Huckel calculations</td>
</tr>
<tr>
<td>70LOO/DOE</td>
<td>Structure adopted from 62JAC microwave work</td>
</tr>
<tr>
<td>70NEW/LAT</td>
<td>Refers to 62JAC values; STO-3G, INDO</td>
</tr>
<tr>
<td>73LEI</td>
<td>Results in part based on 62JAC, CNDO/2</td>
</tr>
<tr>
<td>75CAL/MAH</td>
<td>Data taken from 62JAC</td>
</tr>
<tr>
<td>76PLE/KOC</td>
<td>Refers to the results of 62JAC; ab initio calculations; STO-2G, STO-4G</td>
</tr>
<tr>
<td>78LUC/SCH</td>
<td>Comparison with the experimental data of 62JAC; quantum-mechanical calculations RHF/4-31G, RHF/DZ, RHF/DZP(O); RHF/DZP(OF), CVDZ, CV/DZP(O); a C₂ symmetry constraint (RHF/4 31G), a C₂v symmetry constraint (RHF/4 31G)</td>
</tr>
<tr>
<td>780LS</td>
<td>Ab initio calculations; rigid-rotor calculations on O₂F₂, 4-31G</td>
</tr>
<tr>
<td>79HAR/LAU</td>
<td>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</td>
</tr>
<tr>
<td>80GIL</td>
<td>MINDO calculations</td>
</tr>
<tr>
<td>81AHL/TAY</td>
<td>Quantum-mechanical calculation; calculated results compared with those of 62JAC performed; SCF, ODC, CEPA, CI(SD), MR CI(SD)</td>
</tr>
<tr>
<td>84BUR/LAW</td>
<td>Selected from 62JAC, 73BUR/GAR, 80JAC; no bond angle is given</td>
</tr>
<tr>
<td>86MEL</td>
<td>BAC/MP4 calculation</td>
</tr>
<tr>
<td>87ROH/HAY</td>
<td>Quantum-mechanical calculation; comparison with 62JAC; DZP: RHF, CI, CEPA; 6-31G*: RHF, MP2, 92-CAS/CCI, 92-CAS/CCI+DZP, 92-CAS/CCI+DZP: Diffuse: RHF/6-31G*, MP2/6-31G*, MP3/6-31G*, MP4SDQ/6-31G*, RHF/D95*, MP2/D95*, MP4SDQ/D95*</td>
</tr>
</tbody>
</table>

---

TABLE 5.16.2 Geometry and structure — Continued

<table>
<thead>
<tr>
<th>Source</th>
<th>Calculational Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>88MAC/OBE</td>
<td>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**</td>
</tr>
<tr>
<td>89LEE/RIC</td>
<td>Comparison to 62JAC; quantum-mechanical; MP2, CISD, CPF, CCSD</td>
</tr>
<tr>
<td>89MAC/OBE</td>
<td>Article not available</td>
</tr>
<tr>
<td>89RAG/TRU</td>
<td>Quantum-mechanical calculations; 6-31G*: HF, MP2, CAS+Cl+D, QCISD(T); 6-31G(sp): HF, MP2, CAS+Cl+D, QCISD(T)</td>
</tr>
<tr>
<td>90MCG/CLE</td>
<td>Quantum-mechanical calculation; HF/6-31G*, MP2/6-31G*</td>
</tr>
<tr>
<td>93AMO/MUR</td>
<td>Quantum-mechanical calculation; comparison with 62JAC and 85KIM/CAM; TZ2P/SCF, TZ2P/LDA, TZ2P/BLYP, TZ2P/LDA, TZ2P/BLYP, TZ2P/CCSD(T)</td>
</tr>
<tr>
<td>94GIM/ZHA</td>
<td>Ab initio SCF-MO calculations; a C$_3$ symmetry is proposed; RHF/6-31G**, MP2/6-31G**</td>
</tr>
</tbody>
</table>

There are numerous references to the enthalpy of formation of O$_3$F$_4$(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>
<thead>
<tr>
<th>Source</th>
<th>$\Delta H$(298.15 K)</th>
<th>Comments (as reported values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>58KIR/AST</td>
<td>20.9±1.7</td>
<td>Measured the enthalpy of decomposition at 100K calorimetrically; 5.00±0.40 kcal·mol$^{-1}$</td>
</tr>
<tr>
<td>59KIR/GRO2</td>
<td>19.8±1.3</td>
<td>4.73±0.30 kcal·mol$^{-1}$</td>
</tr>
<tr>
<td>61ARM/KRI</td>
<td>19.8±1.3</td>
<td>From 59KIR/GRO2 (4.73±0.3 kcal·mol$^{-1}$), although referenced as the source of this value, the quoted value really comes from 59KIR/GRO2; from 61WAG (4.65 kcal·mol$^{-1}$) estimated $\Delta_{in}H$ and calculated $\Delta H$; from 50SIM and 54SIM; discussed dissociation energy; from 57LO/DAW, 16.0 kcal·mol$^{-1}$</td>
</tr>
<tr>
<td>65MAL/MCG</td>
<td>19.5</td>
<td>Estimated value [0.8 eV], assuming $D$(F–O$_2$F)+D(O$_2$F); the second value, $D$(FO–OF)=4.5±0.2 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</td>
</tr>
<tr>
<td>65MOR</td>
<td>66.9</td>
<td>Three-dimensional Huckel MO calculations; $E_{tot}$=156.5 kcal·mol$^{-1}$ (obs.); -151.6 kcal·mol$^{-1}$ (calc.); no reference as to the observed value</td>
</tr>
<tr>
<td>65MAL/MCG</td>
<td>19.8±1.3</td>
<td>Refers to a mass spectrometrically derived value, presumably in 65MAL/MCG; quotes a value $D$(F–O$_2$F)=0.8 eV</td>
</tr>
<tr>
<td>65VED/GUR</td>
<td>19.8±1.3</td>
<td>Review; from 59KIR/GRO2; 4.73±0.30 kcal·mol$^{-1}$</td>
</tr>
<tr>
<td>68TUR</td>
<td>19.8±1.3</td>
<td>Review; refers to mass spectral study of 65MAL/MCG; FOOF→FO+OF, 103 kcal·mol$^{-1}$; FOOF→F+OF$^+$, 18 kcal·mol$^{-1}$</td>
</tr>
<tr>
<td>69FRA/DIL</td>
<td>18</td>
<td>From 270–3; 4.3 kcal·mol$^{-1}$</td>
</tr>
<tr>
<td>70DAR</td>
<td>18</td>
<td>From 66MAL/MCG; FOOF→FO$_2$+F; $\Delta H$/(0K)=18.4 kcal·mol$^{-1}$</td>
</tr>
<tr>
<td>86MEL</td>
<td>61.5</td>
<td>$\Delta H$/(0K)=14.7 kcal·mol$^{-1}$</td>
</tr>
<tr>
<td>89LYM</td>
<td>19.2±0.8</td>
<td>Review; corrected 59KIR/GRO; 4.58±0.20 kcal·mol$^{-1}$</td>
</tr>
</tbody>
</table>

Kirshenbaum et al. [59KIR/GRO, 59KIR/GRO2] studied the decomposition of O$_2$F$_2$ and O$_2$F$_2$ calorimetrically at 90 and 121 K respectively. From these values, the $\Delta H$ (298 K) for the two gases were calculated: O$_2$F$_2$ = +4.73 ± 0.30 kcal·mol$^{-1}$ and O$_2$F$_2$ = 6.24 ± 0.75 kcal·mol$^{-1}$. Auxiliary information was required to convert the measured data at low temperatures to 298.15 K. The authors estimated $\Delta C_p$ for O$_2$, F$_2$ and O$_2$F$_2$ 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 $\Delta H$ = 4.58 ± 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$_2$F$_2$

Welsh et al. [66WEL/MET] studied the EPR spectrum of liquid O$_2$F$_2$. The authors suggested that the paramagnetism is due to the O$_2$F radicals. The EPR spectrum was measured using solid O$_2$F$_2$ and solid enriched$^{17}$O$_2$F$_2$.

5.18. $^{18}$O$_2$F$_2$

Jackson [62JAC] examined the rotational spectra of three isotopically substituted O$_2$F$_2$ compounds: $^{16}$O$_2$F$_2$, $^{18}$O$^{16}$OF$_2$, and $^{18}$O$_2$F$_2$. From this microwave data, the author calculated the moments of inertia and the resulting structure of O$_2$F$_2$ (see Table 5.16.2).

Loos et al. [68LOO/GOE] observed and analysed the IR spectra of solid$^{17}$O$_2$F$_2$ and $^{18}$O$_2$F$_2$. 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 $^{18}$O$^{16}$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$_2$F$_2$

The more recent articles suggest that O$_2$F$_2$ does not exist. Instead, the compound observed is a mixture of O$_2$F$_2$ and O$_2$F$_2$. Since 1976, there are only two citations dealing with this presumed compound — both are calculations involving the molecular structure.

Summary comments in numerous reviews have shifted from O$_2$F$_2$ 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$_2$F$_2$ does not exist as a distinct molecular entity. Thus, discussions of the following articles must be interpreted in the light of O$_2$F$_2$ not existing as a separate entity.

All references dealing with O$_2$F$_2$ 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], [59R,h], [61GRO/STR], [63MCC], [65MAL/MCG], [65STR/STR], [66STR/STR], [67JOL], [67MAL/MCG], [70MEI/GEN]

2. Enthalpy of formation/vaporization/dissociation —
   [58KIR/AST], [59KIR/GRO], [61KIR/AST], [63PRH/PAS], [66MOR], [66VED/GUR], [69RIP/ZER], [76CLE/PKC], [80GLO]

3. Structure —
   [65MAG], [67NEB/MET], [67SOL/RAN], [68SOL/KHE], [76CLE/PKC], [80GLO], [94GIM/ZHA]

4. Properties —
   [61KIR/AST], [61KIR/STR], [62R/PER], [64AMS/CAP], [64SOL], [65MAG], [65STR/STR], [66STR]

5. EPR —
   [65KAS/KIR], [65NEU/VAN]

6. Review —
   [60GEO], [61ARM/KRI], [61MCC], [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$_2$F$_2$ 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$_2$F$_2$ and O$_2$F$_2$ calorimetrically at 90 and 121 K respectively. From these values, the $\Delta H$ (298 K) for the two gases were calculated: O$_2$F$_2$ = +4.73 ± 0.30 kcal·mol$^{-1}$ and O$_2$F$_2$ = 6.24 ± 0.75 kcal·mol$^{-1}$. Auxiliary 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, $\Delta H$(0K) = 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 of dissociation study by [59KIR/GRO2].

— Rips et al. [69RIP/ZEK], using the method of correlating increments, calculated the enthalpy of vaporization of O$_2$F$_2$ as well as critical properties.

— Plesnicar et al. [76FLE/KOC], using ab initio molecular orbital theory (STO-2G and STO-4G), calculated the total energy and the decomposition energies to F$_2$ and O$_2$F$_2$.

— Glidewell [80GLO], using MINDO approximation, calculated the heat of formation of O$_2$F$_2$ to be −11.23 kcal·mol$^{-1}$.

Although O$_2$F$_2$ 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_2F_2. Their calculated values were: \( r(F-O) = 1.3564 \text{Å}, \quad r(O-O) = 1.4069 \text{Å}, \quad \angle(FOO) = 103.77^\circ, \quad \angle(OOO) = 102.76^\circ, \quad \angle(OOF) = 103.77^\circ, \) and the dihedral \( \angle = 88.37^\circ \). There was no experimental data available at the time with which to compare these calculations. No information on the vibrational frequencies was provided.

Gidewell [80GIL], using MINDO approximation, calculated the energy and structure of O_2F_2. The geometry was given as: \( r(F-O) = 1.4811 \text{Å}, \quad r(O-O) = 1.3311 \text{Å}, \quad \angle(FOO) = 112.7^\circ, \quad \angle(OOO) = 120.2^\circ, \) and the dihedral \( \angle = 71.1^\circ \). No vibrational frequency information was provided.

Gimarc and Zhao [94GIM/ZA] calculated the geometry optimized total energies of O_2F_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:

<table>
<thead>
<tr>
<th>RHF</th>
<th>MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(O-O)</td>
<td>1.3399</td>
</tr>
<tr>
<td>(O-F)</td>
<td>1.3640</td>
</tr>
<tr>
<td>( \angle ) OOO</td>
<td>108.12</td>
</tr>
<tr>
<td>( \angle ) FOO</td>
<td>105.28</td>
</tr>
<tr>
<td>( \angle ) OOF</td>
<td>81.47</td>
</tr>
</tbody>
</table>

No vibrational frequency information was provided.


de data has been estimated via quanum mechanical means. The structure and vibrational frequencies of O_2F_2 have not been completely and definitively determined. The structure was assumed to be FOOOF. There are two calculational studies which propose the structure. There are spectroscopic studies which have proposed a tentative assignment for these vibrational frequencies (there are 12 vibrations to be assigned in O_2F_2). It is interesting to note that the most recent experimental study intended to characterize the properties of O_2F_2 was the Raman solution experiments of Gardner 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_2F_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], [69FIP/ZEI]

3. EPR/NMR —
   - [66FES/SCH], [66KIR/STR], [67SOL/RAN],
   - [68LAW/OGD], [68SOL/KEI]

4. Spectroscopy/structure —
   - [69KIR/HAR], [65ARK], [65STR/STR],
   - [66SOL], [66SPR/TUR], [69GOE/CAM],
   - [71GAR/LAW], [71GAR/TUR], [76PLE/KOC],
   - [80GIL], [94GIM/ZA]

5. Review —
   - [61ARM/KRI], [61MCG], [63STR], [66FOX/JAC],
   - [68TUR], [72BRI]

6. Reaction —
   - [68KEI/SOL], [71SOL/KAC]

The preparation of O_2F_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 property references [61GRO/STR, 61KIR/AST, 64SOL, 66STR, 69FIP/ZEI], presented limited vapor pressure data, thermal stability, some solubility information, and values for melting and boiling points of O_2F_2.

Kirschbaum and Streng [66KIR/STR] measured the EPR spectrum of O_2F_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 or 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_{2}F_{2}.
Solomon et al. [67SOL/RAN] studied the $^{18}$O and $^{18}$F NMR spectra of O$_2$F$_2$ and the presumed O$_2$F$_2$. The NMR results showed conclusively that what was once called O$_2$F$_2$ was truly a mixture of O$_2$F$_2$ and O$_3$F. It was suggested that the latter is O$_3$F$_3$, which probably existed as O$_2$F and O$_2$F$_2$. Although not conclusive, the structure was assumed to be FOFOOF.

Three additional studies refer to O$_2$F$_2$ 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 $r(O-F) = 1.63\overline{A}$, $r(O-O) = 1.22\overline{A}$, and $\angle(OF) = 100^\circ$. Force constants were calculated for two of the bonds. No prior structural data was available.

Streng and Steng [65STR/STR] measured molar extinction coefficients from 350 to 750\mu m.

Spratley et al. [66SPR/1UK] proposed a tentative assignment of O$_2$F$_2$ 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$_2$F$_2$. 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$_2$F$_2$. The authors assumed the molecule is diamagnetic and that at 80–90\degree C, the dissociation energy of O$_2$F$_2$ 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$_2$F$_2$ is a red unstable solid with a melting point at 82 K, and its spectrum being very little different from O$_2$F. There was strong evidence that the O$_2$F$_2$ 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 $\delta(O-O-F) = 376.8 \pm 1$ 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$_2$F$_2$ to O$_2$F and O$_2$. Their calculated values were: $r(F-O) = 1.3564\overline{A}$ (taken from H$_2$O and O$_2$F$_2$) and $r(O-O) = 1.4064\overline{A}$.

Gldowell [80GLO], using MINDO approximation, calculated the energy and geometry of O$_2$F$_2$. The geometry was given as: $r(F-O) = 1.48\overline{A}$, $r(O-O) = 1.51\overline{A}$, $r(O_2=O_2) = 1.42\overline{A}$, $\angle(FOO) = 112^\circ$, $\angle(OOO) = 121.0^\circ$, dihedral $\angle(FOOO) = 79.6^\circ$, and dihedral $\angle(OOOO) = 53.3^\circ$. The enthalpy of formation of O$_2$F$_2$ was calculated to be $\Delta H^\circ = +36.2$ kcal-mol$^{-1}$.

Gimarc and Zhao [94GIM/ZHA] calculated the geometry optimized total energies of O$_2$F$_2$ 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 were calculated and were presented in the paper as:

<table>
<thead>
<tr>
<th>RHF calculations</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$r(O-O)$</td>
<td>1.3346</td>
</tr>
<tr>
<td>$r(O=O)$</td>
<td>1.3669</td>
</tr>
<tr>
<td>$r(O-F)$</td>
<td>1.3650</td>
</tr>
</tbody>
</table>

No vibrational frequency information was available.

5.21 O$_2$F$_2$

Schumacher [50SCH] in 1930 questioned the existence of O$_2$F$_2$.

[61ARM/KRI, 62ARM/KRI], in their review of the inorganic fluoride compounds, list an estimated enthalpy of formation of O$_2$F$_2$ of $\Delta H(298.15K) = -53.6$ 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$_2$F$_2$ by mixing O$_2$ and F$_2$ in an electrical discharge apparatus and found it to be stable at 60 K. On warming, O$_2$F$_2$ 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$_2$F$_2$.

5.22. FOFOOF

Gimarc and Zhao [94GIM/ZHA] calculated the geometry optimized total energies of O$_2$F$_2$ 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$_2$F$_2$ was assumed to have a chain structure.

5.23. O$_2$F$_2$

Streng and Grosse [66STR/GRO] prepared O$_2$F$_2$ by mixing O$_2$ and F$_2$ in an electrical discharge apparatus and found it to be stable at 60 K. On warming, O$_2$F$_2$ 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$_2$F$_2$.
Goetschel et al. [68GOE/CAM, 69GOE/CAM], aware of the early work by [66STR/GRO], examined the radiolysis of liquid mixtures of O₂ and F₂ at 77 K. Although there was some evidence of higher oxygen fluorides being produced, there was no conclusive evidence that O₃F₂ was formed.

Briston [72BRI], in a 1972 review, stated that sufficient data was not available to reach any definite conclusion as to the existence of O₃F₂ or its unknown structure.

5.24. FOOOOOF

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 O₄F₄(n = 2 – 8), converting cyclic O₄F₄(n = 2 – 8) to chain-like O₄F₄.

5.25. O₄F₂

[85WEI/WEI], using quantum mechanical calculations compared the results of O₃F₂ and ClₓOₓ. CNDO-2 MNDO geometry optimizations were conducted, where the structures were assumed to be Oₓ–X–Oₓ. The results indicated that O₃F₂ 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 O₄F₄(n = 2 – 8), converting cyclic O₄F₄(n = 2 – 8) to chain-like O₄F₄.

5.26. O₃F₂

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 O₄F₄(n = 2 – 8), converting cyclic O₄F₄(n = 2 – 8) to chain-like O₄F₄.

5.27. OF₃

Price et al. [63PRA/PAS] have estimated the dissociation energy of OF₃ through a comparison of all dissociation energies of the fluorides of all the first row elements and their ions, D(F – O – F) = 0.7 eV. Although not specifically stated, the structure would appear to be planar (D₃h), not pyramidal (C₃v).

6. NIST-JANAF Thermochemical Tables

NIST-JANAF Thermochemical Tables for OF(g) (Sec. 6.1), FOO(g) (Sec. 6.2), OOF(g) (Sec. 6.3), FOF(g) (Sec. 6.4), and O₃F₂ (g) (Sec. 6.5) are presented on the following pages.


\[ \Delta H_f^\circ (0^\circ C) = 108 \pm 10 \text{ kJ mol}^{-1} \]

\[ \Delta H_f^\circ (298.15 \text{ K}) = 109 \pm 10 \text{ kJ mol}^{-1} \]

**Electronic Levels and Molecular Constants \((i^\circ C)\), cm\(^{-1}\)**

<table>
<thead>
<tr>
<th>State</th>
<th>(T, ^\circ C)</th>
<th>(\omega_i)</th>
<th>(\omega_{i\ast})</th>
<th>(B_i)</th>
<th>(\alpha_i)</th>
<th>(L_i 10^{\circ C})</th>
<th>(\lambda)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X'H(_2)F</td>
<td>0, 2</td>
<td>1052.9756</td>
<td>9.00930</td>
<td>1.0587054</td>
<td>-0.0038105</td>
<td>428739</td>
<td>35442</td>
</tr>
<tr>
<td>X'H(_2)F</td>
<td>391.80</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Enthalpy of Formation**

The enthalpy of formation is given by the following equation:

\[ \Delta H_f^\circ = H_f^\circ (\text{products}) - H_f^\circ (\text{reactants}) \]

The values are derived from various experiments and calculations. The enthalpies of formation of related compounds are also provided for comparison.

**Heat Capacity and Entropy**

The heat capacity and entropy values are also listed for different temperatures. These values are important for thermodynamic calculations and are derived from experimental measurements.

**References**

A list of references is provided at the end of the page, which includes scientific articles and sources used in the calculations and experiments.
Enthalpy of Formation

The enthalpy of formation of O(FOO) at 298.15 K 25.4 ± 2 kJ·mol⁻¹, is based on six experimental results. Two earlier studies are not included in this analysis. The review by Lyman recommended an enthalpy of formation value based on three experimental studies.

These six experimental studies and their recommended values are:

<table>
<thead>
<tr>
<th>Author</th>
<th>Technique</th>
<th>ΔH°(298 K), kJ·mol⁻¹</th>
<th>T/K of study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lyman and Holland</td>
<td>Kinetic study of reaction F=O ≈ 0</td>
<td>298 K</td>
<td></td>
</tr>
<tr>
<td>Holland</td>
<td>Unpublished; kinetic study of reaction F=O ≈ 0</td>
<td>298 K</td>
<td></td>
</tr>
<tr>
<td>Shaminina and Koto</td>
<td>ERP measurement of rate constants</td>
<td>298 K</td>
<td></td>
</tr>
<tr>
<td>Lyman</td>
<td>Review</td>
<td>298 K</td>
<td></td>
</tr>
<tr>
<td>Poggeby et al.</td>
<td>Spectroscopic study</td>
<td>298 K</td>
<td></td>
</tr>
<tr>
<td>Campanuţu-Joţ et al.</td>
<td>Spectroscopic study</td>
<td>298 K</td>
<td></td>
</tr>
</tbody>
</table>

Heat Capacity and Entropy

The uncertainties of the molecule are best fitted with a F-O-O angle of 112° based on the diode-laser experiment as obtained by Yamada and Hidaka. The bond length is F-O=1.94 Å and O-O=1.19 Å. Supporting structural information is available from the infrared study of McKellar et al., a microwave study by Bogy et al., and a laser magnetic resonance study by Bley et al. The principle moments of inertia (in g cm²) are:

\[ \begin{align*}
 I_x &= 1.67(4) \\
 I_y &= 3.55(2) \\
 I_z &= 9.4(1) 
\end{align*} \]

There are numerous studies from which vibrational frequencies derived: Yamada and Hidaka, McKellar et al., Ackerl, Noble and Fintenel, Spratley et al., Jacobson, Fintenel, and Campbell. We adopt the recommendations of Jacobson, using gas phase values for ν and ν2 and the normal mode values recommended by Jacobson in an earlier review.

Lyman stated that published absorption spectra of O(FF) and Schumacher and Machtch et al. indicated no electronic states at energies below the dissociation energy of the molecule. Jacobson revised the four absorption studies in which a maximum has been observed at 220 nm by Chegodaev and Tupikov, 240 nm by Frosendahl and Sauer, and 446 nm by Machuch et al. Jacobson observed the onset of dissociation near 400 nm only and both A states are used in the calculation.

References


In 1991, a further study by the Lyman group recommended an enthalpy of formation value based on three experimental studies. The recommendation was 298.15 K 25.4 ± 2 kJ·mol⁻¹.
Oxygen Fluoride (OFO) | Ideal Gas
---|---
$\Delta H^0(298 \text{ K}) = [170 \pm 5] \text{ kJ mol}^{-1}$
$\Delta H^0(298 \text{ K}) = [211 \pm 1] \text{ kJ mol}^{-1}$

Electronic Levels and Quantum Weights

<table>
<thead>
<tr>
<th>State</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1B_2$</td>
<td>0</td>
</tr>
<tr>
<td>$^3B_2$</td>
<td>[10,9,3]</td>
</tr>
</tbody>
</table>

Vibrational Frequencies and Degeneracies

- $\nu$, cm$^{-1}$
- $\sigma$ = 2
- Bond Distance: $r_{O-O}$ = [1.559 Å]
- Bond angle: O-F-O = [76.75°]
- $\text{Produc of the Moments of Inertia: } I_{33} = 116.832 \times 10^{-22} \text{ g cm}^2$ |

Enthalpy of Formation

The enthalpy of formation was calculated based on the molecular geometry optimization of Gosavi et al. This calculation yielded the result $\Delta H^0(298 \text{ K}) - \Delta H^0(0 \text{ K}) = -356 \text{ kJ mol}^{-1}$. It is assumed that this calculated difference referred to 0 K. In contrast, Gole and Hayes' earlier calculation difference of -418 kJ mol$^{-1}$.

Heat Capacity and Entropy

The molecular geometry adopted here is that used by Gosavi et al., 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 [1.559 Å].

References

Oxygen Fluoride (FOF)  

\[ \Delta H^o(\text{FO}) = 26.8 \pm 2 \text{ kJ mol}^{-1} \]

\[ \Delta H^o(\text{FO}) = 24.5 \pm 2 \text{ kJ mol}^{-1} \]

<table>
<thead>
<tr>
<th>Electronic Level and Quantum Weight</th>
<th>State</th>
<th>e⁻ cm⁻¹</th>
<th>g</th>
<th>[W/A]</th>
<th>0.0</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>928(1)</td>
<td>46(1)</td>
<td>81(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Vibrational Frequencies and Degeneracies

Point Group: \( C_2 \)

Bond Distance: \( F-O = 1.412 \text{ Å} \)

Bond angle: \( F-O-F = 103.1^\circ \)

Produce of the Moments of Inertia: \( I_{FDO} = 1.8136 \times 10^{-12} \text{ g cm}^2 \)

Enthalpy of Formation

King and Armstrong\(^\text{1}\) have established the enthalpy of formation with a series of reactions of \( h \) to a flame calorimeter. They turned \( F_2 \) in hydrogen and \( C_2 \) in hydrogen so that the enthalpy of formation, \( 2.53 \text{ kJ mol}^{-1} \), was directly obtained. This value was in good agreement with the recalculated values of Vartenberg and Klink\(^2\), 2.385 \pm 0.7 \text{ kJ mol}^{-1} , and of Ruff and Mennel, 19.66 \pm 8.4 \text{ kJ mol}^{-1} but differed from that of Bieble et al., -16.99 \pm 8.4 \text{ kJ mol}^{-1} . There are several factors in the experiments of Bieble et al. that might cause the enthalpy of formation to be too negative. We adopt the value of 2.52 \text{ kJ mol}^{-1} , reported by King and Armstrong.\(^\text{2}\)

Heat Capacity and Entropy

The structural parameters are those reported by Pierce et al.\(^\text{3}\) for the average ground state molecule from the microwave spectrum. Earlier measurements of Hilton et al.\(^\text{4}\) disagree but according to Pierce et al., the line assignments used by Hilton et al. are incorrect. The microwave studies of Morino and Sato\(^\text{5}\) yielded \( \tau = 1.4053 \text{ Å} \) and an angle of 103.6\(^\circ\) which is in agreement with our adopted values. The principle moments of inertia (in g cm\(^2\)) are: \( I_{xx} = 1.3492 \times 10^{-12} \text{g cm}^2 \), \( I_{yy} = 7.7225 \times 10^{-12} \text{g cm}^2 \), and \( I_{zz} = 9.1617 \times 10^{-12} \text{g cm}^2 \). We adopt the vibrational frequencies reported by Jones et al.\(^\text{3}\) and several other investigators reported similar values.\(^\text{6,7,8,9,10,11}\) Netgen et al.\(^\text{12}\) observed 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.

References

Enthalpy of Formation

A critical measurement for the calculation of thermodynamic functions for both OOF and OOF₂ is the standard enthalpy of formation of OOF₂ by Kirkham et al. 1 These authors made a calorimetric measurement at 15K for decomposition of OOF₂ into O₂ and F₂. Conversion of that measurement from 19K to the standard enthalpy of formation at 298 K required knowledge of the difference in constant-volume heat capacity between the reactant (OOF₂) and the products (O₂ and F₂). The authors assumed that difference to be zero over the entire range. With the published heat capacities for fluorine and oxygen, plus that for OOF₂ reported here, we find that the average heat capacity difference over the 190 K – 298 K temperature range is 1.404 cal K⁻¹ mol⁻¹. The standard enthalpy of formation of the Kirkham et al. reported was ΔH(298 K) = 291.5 ± 2.0 cal mol⁻¹. With the lower heat capacity correction suggested by Lymn, 2 it becomes ΔH(298 K) = 291.5 ± 0.84 cal mol⁻¹ as suggested by Lymn. 

Heat Capacity and Entropy

The structure of this molecule is estimated to be a nonlinear chain with an O-C-F bond angle of 109°30' and a dixedral angle 97°30'. The adopted bond lengths are r(F-O) = 1.575 Å and r(O-F) = 1.217 Å from the microwave study of Jackson. 1 The principal moments of inertia (in gm² cm⁻²) are: 

Iₐ = 4.149 x 10⁻¹⁰ gm² cm⁻², Iₐ = 1.674 x 10⁻¹⁰ gm² cm⁻², Iₐ = 1.92 x 10⁻¹⁰ gm² cm⁻². 

The vibrational frequencies are those recommended in the review by Jacor. 9 For νₐ and νₐ, the gas phase results (rather than the matrix isolation matrix) of Kim and Campbell. 3 For νₐ and νₐ, the more extensive matrix isolation studies agree within 6 cm⁻¹ of the gas phase results. The matrix isolation results of Angier et al. 4 and Blackwood et al. 5 are in support of these values.

References

7. Conclusions

Of the oxygen fluorides mentioned in the literature, only four have been isolated and characterized: FO(g), FO0(g), \text{FOF}(g), and \text{FOOF}(g). Although two isomers have not been observed (\text{OFO} and \text{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 \text{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 \text{OF}. Independent confirmatory information is required for \text{FOF} and \text{O}_2\text{F}_2. For all of the polyatomic gaseous species, except \text{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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>0 K $\Delta H^\circ$</th>
<th>$\Delta G^\circ$</th>
<th>$C_p^\circ$</th>
<th>$S^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{OF}(g)</td>
<td>108±10 kJ mol$^{-1}$</td>
<td>105</td>
<td>32.0</td>
<td>216.40±0.3 J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>\text{FO0}(g)</td>
<td>27.2±2 kJ mol$^{-1}$</td>
<td>25.4±2</td>
<td>39.4</td>
<td>44.5</td>
</tr>
<tr>
<td>\text{OFO}(g)</td>
<td>[381.2±20] kJ mol$^{-1}$</td>
<td>[378.6±20]</td>
<td>[395]</td>
<td>[41.1]</td>
</tr>
<tr>
<td>\text{FOF}(g)</td>
<td>26.8±2 kJ mol$^{-1}$</td>
<td>24.5±2</td>
<td>41.8</td>
<td>13.3</td>
</tr>
<tr>
<td>\text{O}_2\text{F}_2(g)</td>
<td>22.9±0.8 kJ mol$^{-1}$</td>
<td>19.2±0.8</td>
<td>58.2</td>
<td>62.1</td>
</tr>
</tbody>
</table>

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.

The author is particularly grateful for the help of Sabina Crisen who confirmed the completeness of the annotated bibliographies, created the numerous tables which summarize the reported experimental and theoretical studies, and obtained copies of the pertinent articles. The contribution of Stanley Abramowitz in discussions on the spectroscopic properties of the triatomic molecules is greatly appreciated. The FO calculations were performed by David Neumann.
9. References – Annotated Bibliography

The following articles are a combination of all references dealing with the oxygen fluorides. Where possible, we have tried to include all authors, title, journal, a citation to Chemical Abstracts, and an annotation indicating the type of study. In general, dissertations (especially non-US) have not been obtained nor read.

27BRA B. Brauner, Oxide of fluoride or fluoride of oxygen 7, Nature 130, 842 (1937); CA 22 756(9); formation.

27LEB/DAM P. Lebeau and A. Daniens, The existence of an oxygen compound of fluorine, Compt. rend. 185, 652-4 (1927); CA 22 20022; preparation.

29LEB/DAM P. Lebeau and A. Daniens, A new method for the preparation of the fluoride oxide, Compt. rend. 188, 1253-5 (1929); CA 23 36878; preparation.

30RU/CLU O. Ruff and K. Clusius, Melting points of oxygen difluoride and nitrogen trifluoride, Z. anorg. Chem. 190, 267-69 (1930); CA 24 34145 Y; 1 p.

30RU/FMEN O. Ruff and W. Menzel, Oxide of fluoride, F,O, Z. anorg. allgem. Chem. 190, 257-66 (1930); CA 24 37223; enth.

30RU/FMEN O. Ruff and W. Menzel, Oxide of fluoride, F,O, Z. anorg. allgem. Chem. 190, 257-66 (1930); CA 24 37223; enth.

30WAR H. von Wartenberg and G. Klinkott, Heat of formation of oxygen fluoride, Z. anorg. allgem. Chem. 192, 409-19 (1930); CA 25 5636(3); enth.

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