Microwave Spectroscopic Identification of Atmospheric Contaminants

Status Report on NASA Grant NGR 25-001-008

Submitted by Gordon E. Jones
Principal Investigator

October, 1966
The purpose of this investigation is to employ the unique features of microwave spectroscopy in an attempt to furnish a simple and direct means of identification of small amounts of trace gases. The first phase of this work is the cataloging of the microwave spectra of gases which might possibly contaminate the atmosphere of a closed space capsule.

This second semiannual status report covers the period from March, 1966, through September, 1966. In brief, most of the necessary equipment has been received and is in working order. A first edition of the bibliography begun in February has been completed.

Figure (1) and Figure (2) show a block diagram of the spectrometer purchased from Hewlett-Packard. The heart of the spectrometer is the sweep oscillator. The sweep oscillator is an electrically tuned microwave signal source providing frequencies of 26-40 GHz. The source is a backward wave oscillator tube (BWO), which is a self-contained, voltage tunable oscillator. Three automatic linear sweeps are provided, two broad band and one narrow band. The two broad band sweeps have calibrated start and stop frequencies which are continuously adjustable over the entire oscillator frequency range. The narrow band sweep varies the frequency output upward through a 0 to 10 percent segment of the oscillator frequency range. Sweep times are continuously adjustable in four ranges from 1 to 10,000 seconds. The oscillator utilizes a closed loop feedback system to automatically level the frequency output power. Provisions are made for oscilloscope and graphic recorder displays.
The oscillator synchronizer provides a means of absolutely stabilizing voltage tunable oscillators. It operates on the principle of automatic phase control (APC), mixing a small sample of the sweep oscillator signal with a harmonic of the signal from a temperature stabilized crystal frequency reference oscillator to produce a 30 MHz signal. This signal is then phase compared to a reference signal. Once it is "locked," any attempt by the sweep oscillator to change frequency will produce a phase error and a phase compensator output voltage, which tunes the sweep oscillator, thereby stopping the frequency shift. Whenever the sweep oscillator is not locked, a "search" oscillator automatically sweeps the sweep oscillator through a frequency range to obtain a "locked-in" condition.

The oscillator coupler allows phase-locking the sweep oscillator to a crystal reference with the oscillator synchronizer. The oscillator coupler functions by providing the required impedance match, power gain, and loop stabilization network between the oscillator synchronizer and the sweep oscillator.

The reference oscillator is a very stable tunable oscillator used to control the frequency of the sweep oscillator. Part of the reference oscillator signal is removed by a directional coupler and fed into the sweep oscillator synchronizer. This synchronizer is in a phase-locked loop together with the reference oscillator, the oscillator coupler, and a sweep oscillator.

The amplifier is used to raise the power level of the output of the reference oscillator to a level sufficient to drive the multiplier.
The multiplier is a harmonic generator utilizing a stop-recovery diode. A stop-recovery diode is a diode which has stored minority carriers. When the diode is reverse biased, it continues to conduct due to the stored minority carriers until suddenly there are no more carriers, at which time it abruptly shuts off. When driven by a signal, this abrupt shut-off generates many harmonics. (The 100th harmonic is used in the 26.5 - 40.0 GHz range).

The prescaler converts the electronic counter into a direct reading counter. Prescaling is accomplished by transistor binary dividers.

The electronic counter is a general purpose high frequency counter, modified to give a direct readout in R-band frequency when used with the prescaler and a microwave frequency converter with a -30 MHz offset. The oscillator in the frequency converter is tuned to use the 100th harmonic. The counter then measures the oscillator frequency, multiplies by 100, adds 30 MHz (to account for the -30 MHz offset) and displays the R-band frequency.

The modulator control instrument supplies the Stark modulator with the 33.333 kHz square wave modulation used in the spectrometer, and controls and monitors the voltage (ground-to-base) and (base-to-peak). It also controls the phase and type of waveform (square-wave or quarter period sine-wave rise). The modulator control unit also supplies a 33.333 kHz reference frequency to the synchronous detector.

The preamplifier, together with an external mixer, form the microwave detector and preamplifier. The output goes to the synchronous
detector. Circuits are also provided which allow the crystal current to be measured.

   The crystal current mixer receives and measures the dc output from the microwave detector and preamplifier.

   The synchronous detector is a narrow band detection instrument in which the input signal is beat with a reference signal of nearly the same frequency, giving a dc output. The synchronous detector, which is a balanced mixer, is used to compare the two signals and give the dc output. The output of the synchronous detector can be adjusted for various time constants by adding capacitance. The output also goes to two recorder drivers for the recorder output jacks.

   The Stark modulator is a power supply used to supply a 33.333 kHz square wave into the Stark cell. The reference frequency and control voltages for the modulator are supplied by the modulator control unit.

   The strip chart recorder has a single servo-actuated ink pen drive and accommodates a single input module. The chart transport system has twelve instantly selectable speeds ranging from 1 inch/hr. to 2 inches/second. The recorder is equipped with a remote electrical pen-lift and a remotely-controlled event marker.

   The oscilloscope is a general purpose scope whose bandwidth extends from dc to 450 kc. It can be used with either internal or external sweeps which can be either internally or externally synchronized. A signal from the sweep oscillator is supplied to the horizontal display and a signal from the synchronous detector goes to the vertical display.
Many of the molecules to be investigated in the study have been studied by other investigators. A complete and comprehensive bibliography of all work done on these molecules would be very valuable. Several bibliographies have been published, but we know of no bibliography that includes research done in the last two years. In this investigation, we have assumed the task of compiling a bibliography that shall be complete through the middle of 1966. Our bibliography is not complete, but a portion of it has been put in final form for inclusion in this report.

We are disappointed that the investigation is moving somewhat more slowly than our original expectations. This is because the Hewlett-Packard Company was unable to deliver our spectrometer at the estimated date, which in turn was due to higher priority government orders for their equipment. However, our last piece of equipment, the vacuum system, is expected to arrive in two weeks so that we expect to begin frequency measurements by the end of the month.
BIBLIOGRAPHY OF STUDIES
OF
INORGANIC AND ORGANIC MOLECULES
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$</td>
<td>Electric dipole moment</td>
</tr>
<tr>
<td>$S$</td>
<td>Structure (bond distances, angles)</td>
</tr>
<tr>
<td>$A, B, C,$</td>
<td>Rotation constants</td>
</tr>
<tr>
<td>$H, D, _{C^{12,13}}, _{C^{16,18}}$, etc.</td>
<td>Isotopes</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Vibrational frequency</td>
</tr>
<tr>
<td>$eQq$</td>
<td>Quadrupole coupling constant</td>
</tr>
<tr>
<td>$V$</td>
<td>Barrier to internal rotation</td>
</tr>
<tr>
<td>$\chi, \eta$</td>
<td>Quadrupole coupling parameters</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Frequency</td>
</tr>
<tr>
<td>Int.</td>
<td>Intensity</td>
</tr>
<tr>
<td>$I$</td>
<td>Moment of Inertia</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Vibration-rotation interaction constant</td>
</tr>
<tr>
<td>$\lambda, \gamma$</td>
<td>Magnetic coupling constants</td>
</tr>
<tr>
<td>$D_{j}, D_{jk}$</td>
<td>Centrifugal distortion constants</td>
</tr>
<tr>
<td>$c$</td>
<td>Spin-rotation interaction constant</td>
</tr>
</tbody>
</table>
INORGANIC MOLECULES

Ammonia (NH₃)
V. S. Zuev, Optika i Spektroskopiya, 12, 641 (1962)
D, Int.

A. Ben-Reuven, Phys. Rev. Letters, 14(10), 349 (1965)
(Transition from resonant to nonresonant line shape).

B. Thaddeus and L. C. Krisher, and P. Cahill, J. Chem. Phys., 41(6), 1542 (1964)
D, eQq, S, v.

Cesium Bromide (CsBr)
B, α, β, γ, D₂, I, S, ω, ν, v, w.

Cesium Iodide (CsI)
B, α, β, γ, D₂, I, S, ω, ν, v, w, w, v, w.

Chlorine Dioxide (ClO₂)
(Hyperine coupling constants and electronic structure).

Dinitrogen Trioxide (N₂O₃)

Dioxygen Difluoride (F₂O₂)
S, μ, Int.

Fluorine Oxide (F₂O)
A, B, C, I, S.

Germanium Mono-Sulfide (GeS)
J. Hoeft, Z. Naturforsch (German), 20a, 826 (1965)
eQq, ν, B, S.

Germanyl Fluoride (GeH₃F)
S, eQq.

H Radical (H)
(Absorption lines of Cassiopeia A).

Hydrazine Molecule (N₂H₄)
Hydrogen Bromide (HBr)
Gordon Jones and Walter Gordy, Phys. Rev., 136(5A), 1229 (1964)
\[ e\phi q, B, S, v. \]

Hydrogen Chloride (HCl)
Gordon Jones and Walter Gordy, Phys. Rev., 136(5A), 1229 (1964)
\[ e\phi q, B, S, v. \]

Hydrogen Peroxide (H\(_2\)O\(_2\))
\[ A, C, S, D. \]

Hydrogen Selenide (H\(_2\)Se)
Takesi Oka and Vonezo Morino, J. Mol. Spectroscopy, 8, 300 (1962)
\[ D_{jk}, \alpha, S. \]

Hydrogen Sulfide (H\(_2\)S)
\[ (F\text{abry-Perot interferometer}). \]

Hydrazoic Acid (N\(_3\)H)
Roger Kewley, K. V. L. N. Sastry, and Manfred Winnewisser, J. Mol. Spectroscopy, 12, 387 (1965)
\[ A, C, D_{ij}, D, e\phi q. \]

Lead Mono-Sulfide (PbS)

Lithium Bromide (LiBr)
A. J. Herbert, F. W. Breivogel, and K. Street, J. Chem. Phys., 41(8), 2368 (1964)
\[ e\phi q, B, \mu, c, Br_{79,81}, (Molecular-Beam Electric Resonance Method). \]

\[ B, \alpha, \gamma, D_{ij}, I, S, \omega, v. \]

Lithium Chloride (LiCl)
\[ B, S, \alpha, \mu, \gamma, Cl_{35,37} \]

Lithium Iodide (LiI)
\[ B, \alpha, \gamma, D_{ij}, I, S, \omega, v. \]

Lithium Iodine (LI)
\[ B, e\phi q, \mu, c, \nu (Molecular-Beam Electric Resonance Method). \]
Nitric Acid (HNO₃)
Peter A. Cox and Jose M. Riverds, J. Chem. Phys., 42(9), 3106 (1965)
D, S, μ, c16,15, N14,15.

Nitrogen Di-Oxide (NO₂)
A, B, C, λ, γ, c (Electron Expectation Values, Reduced Spin-Rotation Coupling Constants are Discussed).

Nitrous Oxide (N₂O)
(Effects of Quadrupole Splitting and Centrifugal Distortion are Discussed).

Nitryl Chloride (NO₂Cl)
Yonezo Morino and Takehiko Tanaka, J. Mol. Spectroscopy, 16(1), 179 (1965)
A, B, C, eΩq.

OH Radical (OH)
(Absorption Lines of Cassiopeia A).

(Paramagnetic Resonance Spectra).

μ.

Oxygen (Atmospheric) (O₂)

Oxygen Molecule (O₂)

Phosphorus Tetra Chlorofluorides (PCl₄F)
S, μ.

Phosphorus Tri-Chloride (PCl₃)
Anna M. Mirri, Flavio Scappini and Paolo G. Favero, Spectrochim. Acta (Italy) 21(5), 965 (1965)
D₃, Djk.

Phosphorus Tri-Fluoride (PF₃)
Anna M. Mirri and Flavio Scappini, Spectrochim. Acta (Italy), 21(5), 965 (1965)
D₃, Djk.

Potassium Bromide (KBr)
B, α, γ, D₃, I, S, α, v.
Potassium Iodide (KI)
$B, \alpha, \gamma, J_j, I, S, \omega, \nu.$

Rubidium Bromide (RbBr)
$B, \alpha, \gamma, J_j, I, S, \omega, \nu.$

Rubidium Iodide (RbI)
$B, \alpha, \gamma, J_j, I, S, \omega_e, \nu.$

Silicon Di-Floride (SiF2)
$A, B, C, S, \mu, \nu.$

Silicon Selenium (SiSe)
J. Hoeft, Z. Naturforsch., 20a, 1122 (1965)
$S, \nu, Si_{28,29,30}, Se_{76,77,78,80,82}.$

Silicon Sulfide (SiS)
J. Hoeft, Z. Naturforsch., 20a, 1327 (1965)
$S, \nu, Si_{28,29,30}, S_{32,34}.$

Sodium Bromide (NaBr)
$B, \alpha, \gamma, J_j, I, S, \omega, \nu.$

Sodium Fluoride (NaF)
$\mu, \nu, B, c,$ (Molecular-Beam Electric Resonance Method).

Sodium Iodide (NaI)
$B, \alpha, \gamma, J_j, I, S, \omega, \nu.$

SO Radical (SO)
$\lambda, \gamma, B, \mu, S.$

Sulfur Dioxide (SO2)
$\mu,$ (Rate-of-growth Technique for the Measurement of Molecular Dipole Moments from Microwave Spectra at Weak Modulation Fields).

$S$ (Quadratic Force Constants).
Sulfur Dioxide (SO₂)
A. Bauer and J. Bellet, J. Phys. (Fr.), 25(8-9), 805 (1964)
S₃², S₃⁴, Int., ν.

Sulfur Mono-Fluoride (S₂F₂)
Robert Kuczkowski, J. Am. Chem. Soc., 86(18), 3617 (1964)
μ, S₃², S₃⁴, S.

E. Bright Wilson, Jr., and Robert L. Kuczkowski, Natl. Aero. Space Admin.,
Doc. N63-17725 (1964)
(prepd)

Sulfur Monoxide (SO)
Manfred Winnewisser, K.V.L.N. Sastry, R. L. Cook, and Walter Gordy,
J. Chem. Phys., 41(6), 1687 (1964)
B, λ, γ, δ.

Sulfur Tetra-Fluoride (SF₄)
S, μ.

Thallium Mono-Chloride (TlCl)
H. W. De Wijn, Physics, 31, 1193 (1965)
B, S, eq, α, Tl120, Cl205, Cl35, 37.

Tinous Sulfide (SnS)
J. Hoeft, Z. Naturforsch (German), 20a, 313 (1965)
S, B.

Water (H₂O)
D, ν, eqq.

(.7mm - 32cm Range).

Xenon Oxytetrafloride (XeOF₄)
O16, 18, A, B, C, S.
ORGANIC MOLECULES

Acetone (CH₃COCH₃)
R. Peter and H. Dreizier, Z. Naturforsch 20a, 301 (1965)
μ, I (Torsion Splitting).

Acetylacetylene
μ, A, B, C.

Acetylene-d (H-C=C-H)
J. S. Muenter and V. W. Laurie, J. Amer. Chem. Soc., 86(18), (1964)
B, D, μ (Polarizability Anisotropy).

Amine, Difluoro- (NF₂H)
D, A, B, C, S, εQq, μ.

Benzene, Bromo (C₆H₅Br)
A, B, C, S, h, εQq, D, Br, 79, 81.

Eli Rosenthal, Columbia University, Diss. Abs. Order No. 64-2784 (1963)
S, εQq.

Benzene, Chloro- (C₆H₅Cl)
Eli Rosenthal, Columbia University, Diss. Abs. Order No. 64-2784 (1963)
eQq, S.

Benzonitrile (C₆H₅CN)
Borge Bak and Daniel Christensen, William Dixon, and Lise Hansen-Nygaard,
I, S, (9 Isotropic Species are reported).

Butadiene, 1, 1 Difluoro- (C₄H₄F₂)

tert-Butyl Chloride [(CH₃)₃CCl]
A, B, C, S, εQq, Cl, 12, 13, Cl, 35, 37.

Butyronitrile [(CH₃(CH₂)₂CN]

Carbon Monoxide (CO)
Gordon Jones and Walter Gordy, Phys. Rev., 135(2A), 295 (1964)
B, E, v, \( \lambda = 43 \text{mm} \).
Carbonyl Chloride Fluoride (FClCO)
\( \text{Cl}^{35,37}, \text{A, B, C, D}_j, \text{D}_{jk}, \chi \).

Carbonyl Fluoride (COF_2)
\( \mu, \text{S, A, B, C, D}_16,18, \text{C}12,13 \).

Carbonyl Sulfide (COS)
\( \mu \) (Rate-of-growth technique for the measurement of molecular dipole moments from microwave spectra at weak modulation fields).

Chloromethylsilane (CH_2ClSiH_3)
Gerald Daniel Jacobs, Chemistry, Order No. 62-1655
\( I, \text{S, } \chi, \text{V, } \eta \).

cis-Crotononitrile (CH_2=CH:CWN)
\( V, \mu \).

Cyanamide (Diazirine) (HN=CN)
\( N^{14,15, S, } \mu, V \).

Cyanogen Chloride (CICN)
\( S, \text{Cl}^{35,37}, V \).

Cyclobutane, Bromo (C_4H_7Br)
Walter G. Rothschild, Chemistry Diss. Abs. Order No. 62-1925
\( A, B, C, D, S, \chi, \eta, \text{Br}^{79,81}, V \) (4 Isotopic Species Report).

Cyclobutane, Chloro (CH_2CH_2CH_2CHCl)
Hyunyong Kim, University Microfilms (Ann Arbor, Mich.) Diss. Abs. No. 64-13,

Cyclobutane, 1, 3, Cyclohexadiene (CH: CHCH: CH-CH=CH_2)
\( \mu, A, B, C \).

Cyclopentane, 1-1 Difluoro (CH_2=CH=CH_2CF_2)
Chadwich Tolman, Univ. Microfilms (Ann Arbor, Mich.), Diss. Abs. Order No. 64-13
Cyclopentene (CH:CHCH₂CH₂CH₃)

μ, S, Int., A, B, C.

Cyclopropyl Chloride (C₃H₅Cl)
Gerald Daniel Jacobs, Chemistry, Order No. 62-1655

Dimethyl Ether [(CH₃)₂O]
S, D, μ, c₁₂,₁₃, c₁₆,₁₈.

Dimethyl Sulfide [(CH₃)₂S]
μ, S, D, V (5 Isotopic Species Reported).

Ethane, 1-1 Dichloride (CH₂CHCl₂)
A, B, C, S, eΩ₂.

Ethane, Trifluoro- (F₂H=CH₂F)
I. A. Mukhtarov, Optic and Spectroscopy, 16(5), 494 (1964)
D, ν, Int. (Torsional vibration frequency).

Ethane, 1, 1, 2 Trifluoro- (CF₂HCF₂)
S, A, B, C, D, Isomers.

Ethyl Alcohol (C₂H₆O)
D, S.

L. M. Imanov, Ch. O. Kadzhar, and I. Dzh. Isaev, Optika i Spektroskopia, 18(5), 904 (1965)
A, B, C, I, D, Dᵣ, Dᵢᵣ.

Dᵣ, Dᵢᵣ, D, A, B, C, I, μ.

Ethyl Chloride (C₂H₅Cl)
Gerald Daniel Jacobs, Chemistry Diss. Abs. Order No. 62-1655
D, S, μ, η, ν.

Ethylene-, Difluoro (HFC=CHF)
D, S, A, B, C, c₁₂,₁₃.

Ethylene, Trifluoro (C₂HF₃)
I. A. Mukhtarov, Optics and Spectroscopy, 15(4), (1963)
A, B, C, μ, ν (The molecule is non-planar).
Ethylene, Trifluoro- \((\text{C}_2\text{HF}_3)\)
A, B, C, \(\mu\) (The molecule is non-planar).

Formaldehyde \((\text{H}_2\text{C} \overset{\text{O}}{\text{O}})\)
M. G. Krishna Pillai, J. Annamalai Univ. Pt. B25, 126 (1964)
A, B, C, S, D, 616,18

Takeshi Oka, Kojiro Takagi, and Yonezo Morino, J. Mol. Spectroscopy, 14(1), 27 (1964)
D, A, B, C, (Coriolis interaction discussed).

Formic Acid \((\text{HCOOH})\)
Hyunyong Kim, Univ. Microfilms (Ann Arbor, Mich.), Diss. Abs. No. 64-13,035

Furan \((\text{CH}:\text{CH}:\text{H})\)
George B. Brown, Daniel Christensen, William B. Dixon, and Lise Hansen-Nygaard,
S, A, B, C.

Ketone, Methyl Vinyl \((\text{CH}_3\text{H}_6\text{O})\)
V, \(\mu\).

Methane, Fluorobromo- \((\text{CH}_2\text{FBr})\)
A, B, C, S, \(\chi\) (Nuclear quadrupole coupling constants).

Methane, Trichlorofluoro- \((\text{CCl}_3\text{F})\)
S.

Methane, Trifluoronitro- \((\text{CF}_3\text{NO}_3)\)
\(\mu\), V, A, B, C.

Methyl Chloride \((\text{CH}_3\text{Cl})\)
B, e\(\chi\), S, D, Cl\(12,13\), Cl\(35,37\).

Methyl Bromide \((\text{CH}_3\text{Br})\)
\(\mu\) (Rate-of-growth technique for the measurement of molecular dipole from microwave spectra at weak modulation fields).

B, e\(\chi\), S, D, Br\(79,81\), Cl\(12,13\).
Methyl Ether \( [(CH_3)_2O] \)

S, D, \( \mu \), C\(^{12}\), C\(^{13}\), C\(^{16,18}\) (Six Isotopic Species Reported).

Methyl Isocyanate (CH\(_3\)NCO)

\( \nu \), \( \mu \), eqq, D.

N-Methyl Methyleneimine (CH\(_2\)NCH\(_2\))

\( \nu \), \( \chi \), \( \mu \).

Methyl Nitrite (CH\(_3\)ONO)
David Stelman, Chemistry Diss. Abs. Order No. 64-9094 (Univ. of California, 25(3)

\( \mu \), \( \chi \), \( \nu \), S.

Methyl Silylacetylene (CH\(_3\)CCSiH\(_3\))

\( \nu \).

Methyl Sulfide \((CH_2)_2S\)

\( \mu \), S, D, \( \nu \) (5 Isotopic species reported).

Methylthiocyanate (CH\(_3\)SCN)
S. Nakagawa, T. Kojima, S. Takahashi, and Chun C. Lin, J. Mol. Spectroscopy (Letter to Editor), 14, 201 (1964)

A, B, C, \( \mu \), \( \nu \), S.

Methyl Thionylamine (CH\(_3\)NSO)

\( \nu \), \( \mu \).

Methyl Vinyl Ketone (CH\(_3\)O)

\( \nu \), \( \mu \).

Phosphine, Dimethyl- \( [(CH_3)_2PH] \)

Propane, 2-Bromo- (C\(_3\)H\(_7\)Br)

S, \( \chi \), Br\(^{79,81}\), \( \lambda \).

Propane, 2-Chloro- (C\(_3\)H\(_7\)Cl)

(Tokyo), 313, (1962)

D, S, eqq, C\(^{12,13}\) (Eight isotopic species reported).
Propene, 2 Chloro- \((\text{CH}_3\text{CCl}:\text{CH}_2)\)
V, A, B, C, eQq, \(\text{Cl135},37\) (Double Resonance Spectra).

Propene, 3 Fluoro \((\text{C}_3\text{H}_2\text{F})\)
Elzi Hirota, J. Chem. Phys., 42(6), 2071 (1965)
A, B, C, S, \(\mu\), Int.

Propyl, Chloride \((\text{C}_3\text{H}_7\text{Cl})\)
A, B, C, Int., \(\chi\), \(\eta\).

Propylene \((\text{C}_3\text{H}_6)\)
S.

Silyl Cyanide \((\text{SiH}_3\text{CN})\)

Thiadiazole \(-1,2,5\) \((\text{C}_2\text{H}_2\text{N}_2\text{S})\)
Victor Dobyns, Sr., and Louis Pierce, Dept. of Chem., U. of Notre Dame, (7-12-63)
S, \(\mu\), Int. (Four isotopic species reported).

Thiocyanic Acid, Methyl Ester- \((\text{CH}_3\text{SCN})\)
(Letter to Editor), 14, 201 (1964)
A, B, C, \(\mu\), S, \(\nu\).

Trimethylamine \([\text{CH}_3]_3\text{N}\)
S, D.

Tri Methylene Sulfide \((\text{C}_3\text{H}_6\text{S})\)
\(\mu\), A, B, C, \(\nu\), Int. (K Ray's asymmetry parameter).

Vinylidene Fluoride \((\text{H}_2\text{C}=\text{CF}_2)\)