COPY 2 of 3 COPIES

SSD-TDR-64-144

AD 604051

The Infrared Spectra of Perfluorocyclopropane and Cis- and Trans-Perfluorobutene-2

24 JULY 1964

Prepared by JULIAN HEICKLEN, FRANCIS WACHI, and VESTER KNIGHT
Materials Sciences Laboratory

Prepared for BALLISTIC SYSTEMS AND SPACE SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
Los Angeles, California

LABORATORY OPERATIONS • AEROSPACE CORPORATION
CONTRACT NO. AF 04(695)-269

S:

CLEARINGHOUSE FOR FEDERAL SCIENTIFIC AND TECHNICAL INFORMATION CFSTI
DOCUMENT MANAGEMENT BRANCH 410.11

LIMITATIONS IN REPRODUCTION QUALITY

ACCESSION # AD 604051

☐ 1. WE REGRET THAT LEGIBILITY OF THIS DOCUMENT IS IN PART UNSATISFACTORY. REPRODUCTION HAS BEEN MADE FROM BEST AVAILABLE COPY.

☑ 2. A PORTION OF THE ORIGINAL DOCUMENT CONTAINS FINE DETAIL WHICH MAY MAKE READING OF PHOTOCOPY DIFFICULT.

☐ 3. THE ORIGINAL DOCUMENT CONTAINS COLOR, BUT DISTRIBUTION COPIES ARE AVAILABLE IN BLACK-AND-WHITE REPRODUCTION ONLY.

☐ 4. THE INITIAL DISTRIBUTION COPIES CONTAIN COLOR WHICH WILL BE SHOWN IN BLACK-AND-WHITE WHEN IT IS NECESSARY TO REPRINT.

☐ 5. LIMITED SUPPLY ON HAND: WHEN EXHAUSTED, DOCUMENT WILL BE AVAILABLE IN MICROFICHE ONLY.

☐ 6. LIMITED SUPPLY ON HAND: WHEN EXHAUSTED DOCUMENT WILL NOT BE AVAILABLE.

☐ 7. DOCUMENT IS AVAILABLE IN MICROFICHE ONLY.

☐ 8. DOCUMENT AVAILABLE ON LOAN FROM CFSTI (TT DOCUMENTS ONLY).

☐ 9.

PROCESSOR: *[illegible]*

TSL-107-10/64

SSD-TDR-64-144

Report No.
TDR-269(4240-20)-5

THE INFRARED SPECTRA OF PERFLUOROCYCLOPROPANE AND CIS- AND TRANS-PERFLUOROBUTENE-2

Prepared by

Julian Heicklen, Francis Wachi, and Vester Knight
Materials Sciences Laboratory

Laboratory Operations
AEROSPACE CORPORATION
El Segundo, California

Contract No. AF 04(695)-269

24 July 1964

Prepared for

BALLISTIC SYSTEMS AND SPACE SYSTEMS DIVISIONS
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
Los Angeles, California

SSD-TDR-64-144

Report No.
TDR-269(4240-20)-5

THE INFRARED SPECTRA OF PERFLUOROCYCLOPROPANE AND CIS- AND TRANS-PERFLUOROBUTENE-2

Prepared by

Julian Heicklen

Francis Wachi

Vester Knight

Approved by

W. C. Riley, Head
Applied Science Department

J. E. Hove, Director
Materials Sciences Laboratory

This technical documentary report has been reviewed and is approved for publication and dissemination. The conclusions and findings contained herein do not necessarily represent an official Air Force position.

For Space Systems Division
Air Force Systems Command

W. J. Iller
Major, USAF

ABSTRACT

The infrared spectra in the NaCl region of cC_3F_6, cis-C_4F_8-2, and trans-C_4F_8-2 are reported. Partial vibration assignments are discussed.

THE INFRARED SPECTRA OF PERFLUOROCYCLOPROPANE AND CIS- AND TRANS-PERFLUOROBUTENE-2

We wish to report the infrared spectra in the NaCl region of three simple fluorocarbons. The preparation and purification procedure of the compounds cC_3F_6, cis-C_4F_8-2, and trans-C_4F_8-2 is described by Greene and Wachi (Ref. 1). For the cis and trans compounds, it was necessary that we perform the purification procedure twice for complete separation. The spectra were obtained on a Perkin-Elmer 21 infrared spectrometer and are shown in Fig. 1. The bands and their relative intensities are listed in Table I.

The infrared spectrum of cC_3F_6 has not been previously reported. The molecular symmetry is D_{3h}, and the only allowed infrared fundamental vibrations are the two A_2'' and the four E' bands. The two intense bands at 1368 and 1272 cm^{-1} must consist mainly of C—F stretching motions. Thus, one of these is an A_2'' band and the other an E' band. It is not clear which is which. However, there are some indications to suggest that the 1368 cm^{-1} band has A_2'' symmetry and the 1272 cm^{-1} band has E' symmetry. The A_2'' band involves the asymmetric stretching motion of the CF_2 group, whereas the E' band involves the symmetric stretching motion. Usually the asymmetric mode has higher frequency, which corresponds to the assignments of cC_3H_6 (Refs. 2, 3). Furthermore, if the 2532 cm^{-1} band is the overtone of the 1272 cm^{-1} band, then the latter band must be of E' symmetry as the overtones of A_2'' bands are symmetry forbidden. The disturbing feature is that asymmetric bands usually are more intense, but our assignment requires the reverse.

The strong band at 859 cm^{-1} corresponds undoubtedly to the CF_2 deformation of E' symmetry. The two bending frequencies associated with the motion of the CF_2 groups relative to the carbon skeleton lie below 650 cm^{-1} and are not observed. The E' ring deformation frequency of cyclopropyl compounds usually lies within 25 cm^{-1} of 1025 cm^{-1} (Ref. 4). No such band appears in our spectrum; thus, from this point of view, cC_3F_6 must be considered atypical. We tentatively assign the 978 cm^{-1} band to this mode.

The weak band at 2532 cm^{-1} must be either a combination or an overtone of C—F stretching modes. Only seven such possibilities are consistent with the symmetry selection rules: These are the overtones of the E' or E'' bands or the five combinations $A_1' \times A_2''$, $E' \times A_1'$, $E'' \times A_2''$, $E' \times E'$, and $E' \times E''$. The overtone of the E' band seems very attractive as 2532 is almost twice 1272, a result that would be expected if anharmonicity were considered.

The infrared spectrum has been reported for mixtures of cis- and trans-C_4F_8-2 (Refs. 5,6) but not for the pure geometric isomers. If the internal rotations of the CF_3 groups are nearly free, then the trans and cis compounds have C_{2h} and C_{2v} symmetry, respectively. Table II gives the symmetry classes and approximate descriptions of the vibrations.

For the trans molecule, all the gerade vibrations are symmetry forbidden in the infrared spectrum. Thus, there are five stretching modes that should be active. Three of these are surely the intense bands at 1193, 1242, and 1292 cm^{-1}. The band at 882 cm^{-1} also might correspond principally to stretching motions. At least one (and maybe two) of the stretching bands is not readily discernable, it is probably completely or partially obscured by the other bands. All the observed overtone bands must be combinations of gerade and ungerade bands. As a result, the C=C stretch must participate in the overtone bands at 2932 and 3003 cm^{-1} (except in the unlikely event that they are triple combinations). If the intense bands at 1242 and 1292 cm^{-1} are respectively the other participating bands, then the differences are 1711 and 1690 cm^{-1} respectively in reasonably close agreement. Allowing for some anharmonicity sets the C=C stretching frequency at 1710 ±20 cm^{-1}, which correlates nicely with the corresponding frequency in the cis molecule.

For cis-C_4F_8-2, all bands are allowed in the infrared spectrum, though some may be weak. The band at 1724 cm^{-1} is the double bond stretch. Of the remaining ten stretching modes, at leave five are observed at 1111, 1193, 1224, 1245, and 1350 cm^{-1}. The band at 952 cm^{-1} is also likely to contain considerable stretching motion. The other four stretching motions either are weak bands or are completely or partially obscured.

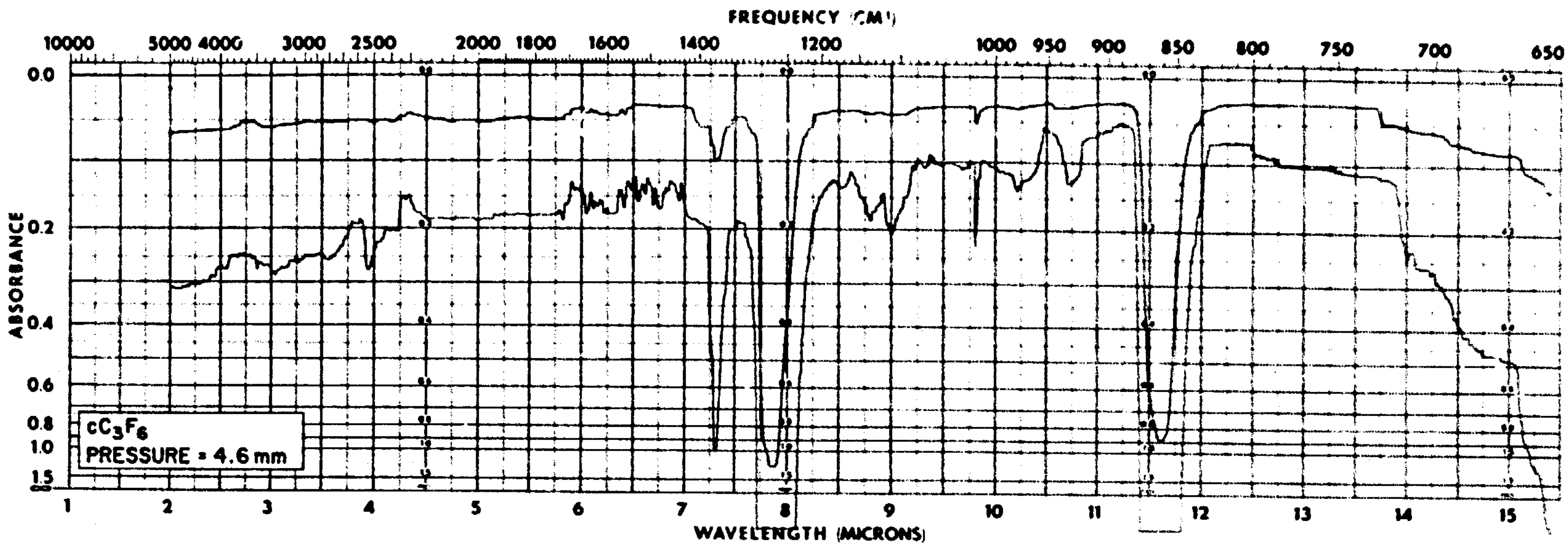

Fig. 1. Infrared spectra.

Path length 10 cm. Discontinuity at 9.82 μ due to change in optical system. For the curve with more intense absorption, the ordinate has been magnified five times.

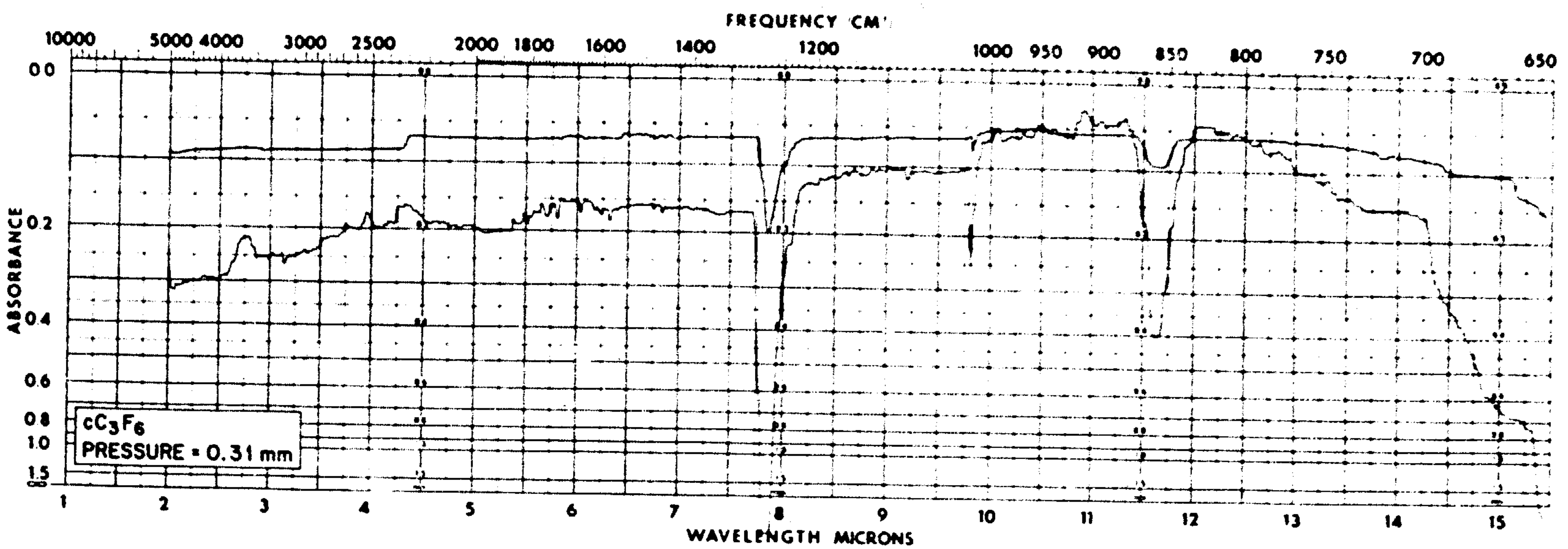

Fig. 1. Infrared spectra. (Continued)

Path length 10 cm. Discontinuity at 9.82 μ due to change in optical system. For the curve with more intense absorption, the ordinate has been magnified five times.

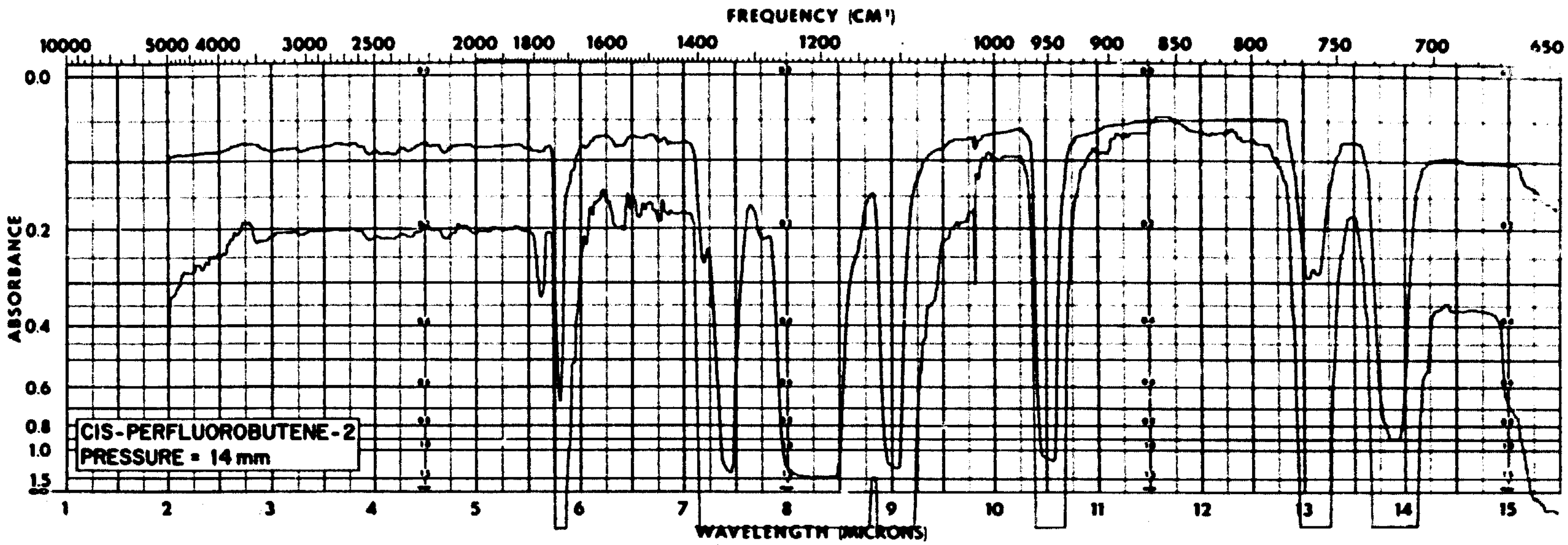

Fig. 1. Infrared spectra. (Continued)

Path length 10 cm. Discontinuity at 9.82 μ due to change in optical system. For the curve with more intense absorption, the ordinate has been magnified five times.

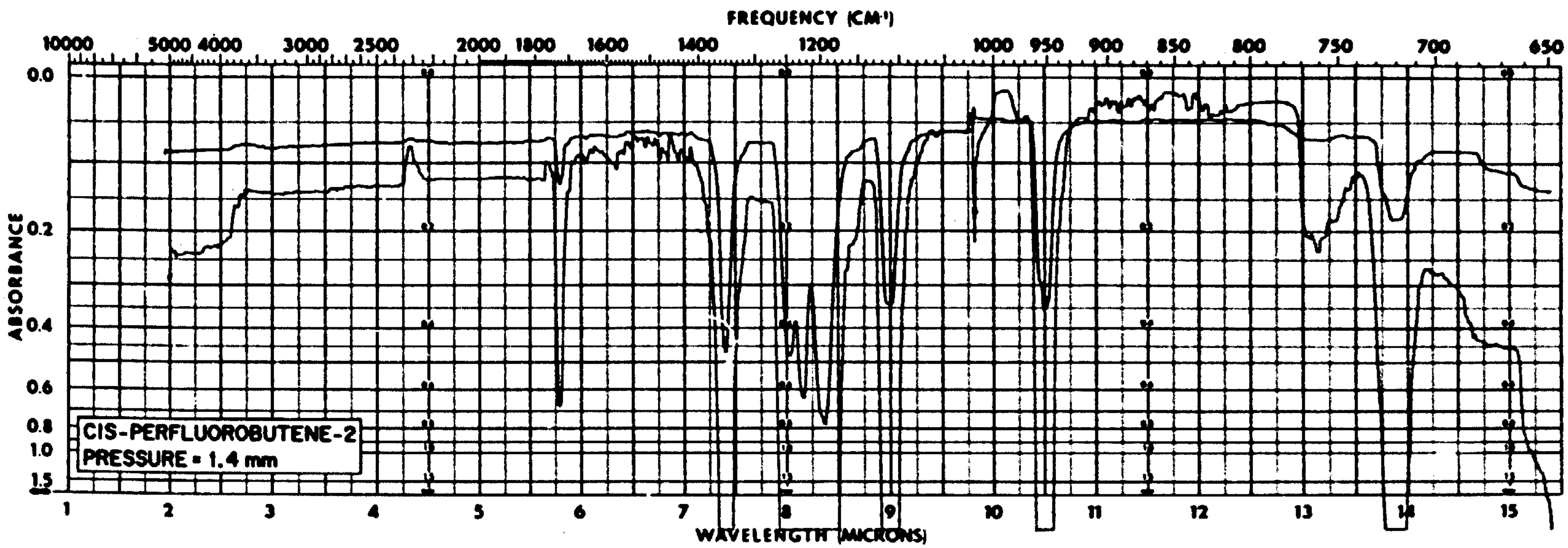

Fig. 1. Infrared spectra. (Continued)

Path length 10 cm. Discontinuity at 9.82 μ due to change in optical system. For the curve with more intense absorption, the ordinate has been magnified five times.

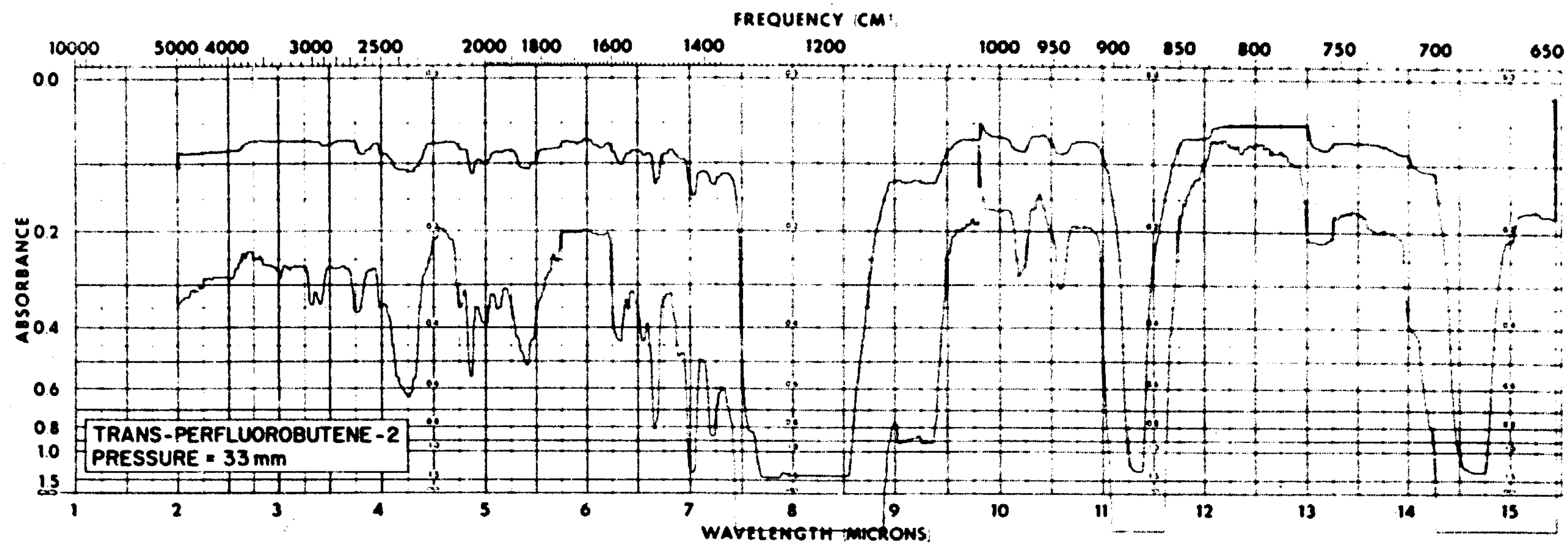

Fig. 1. Infrared spectra. (Continued)

Path length 10 cm. Discontinuity at 9.82 μ due to change in optical system. For the curve with more intense absorption, the ordinate has been magnified five times.

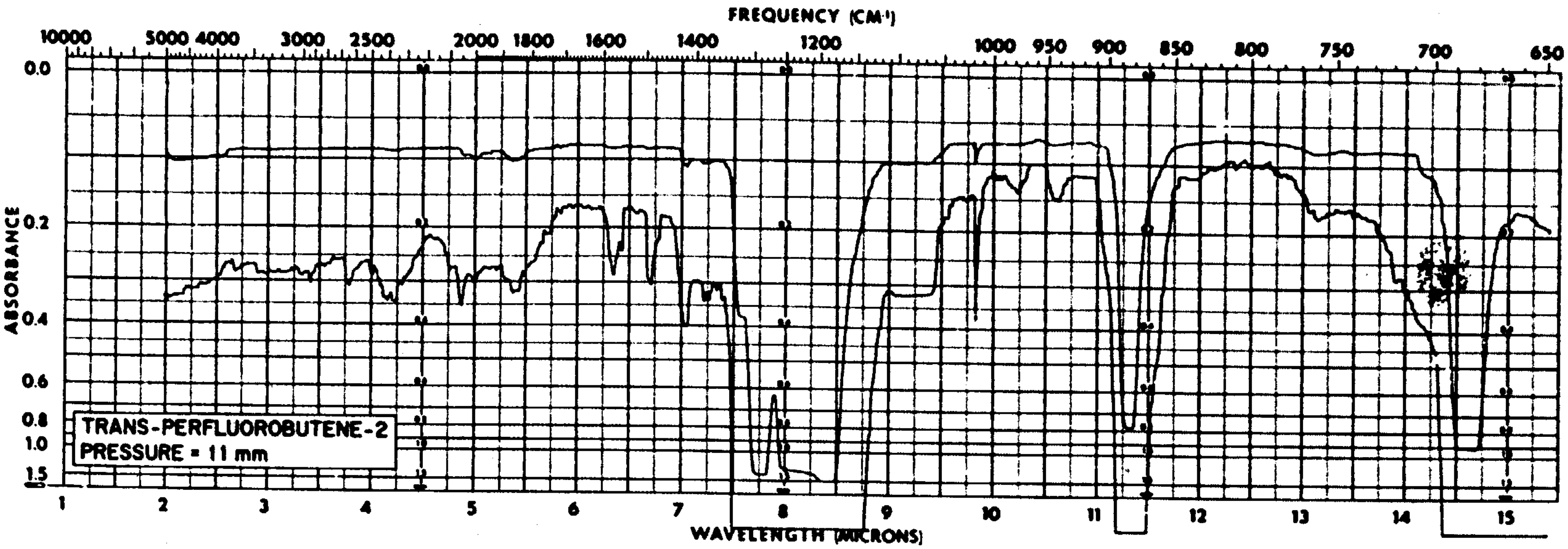

Fig. 1. Infrared spectra. (Continued)

Path length 10 cm. Discontinuity at 9.82 μ due to change in optical system. For the curve with more intense absorption, the ordinate has been magnified five times.

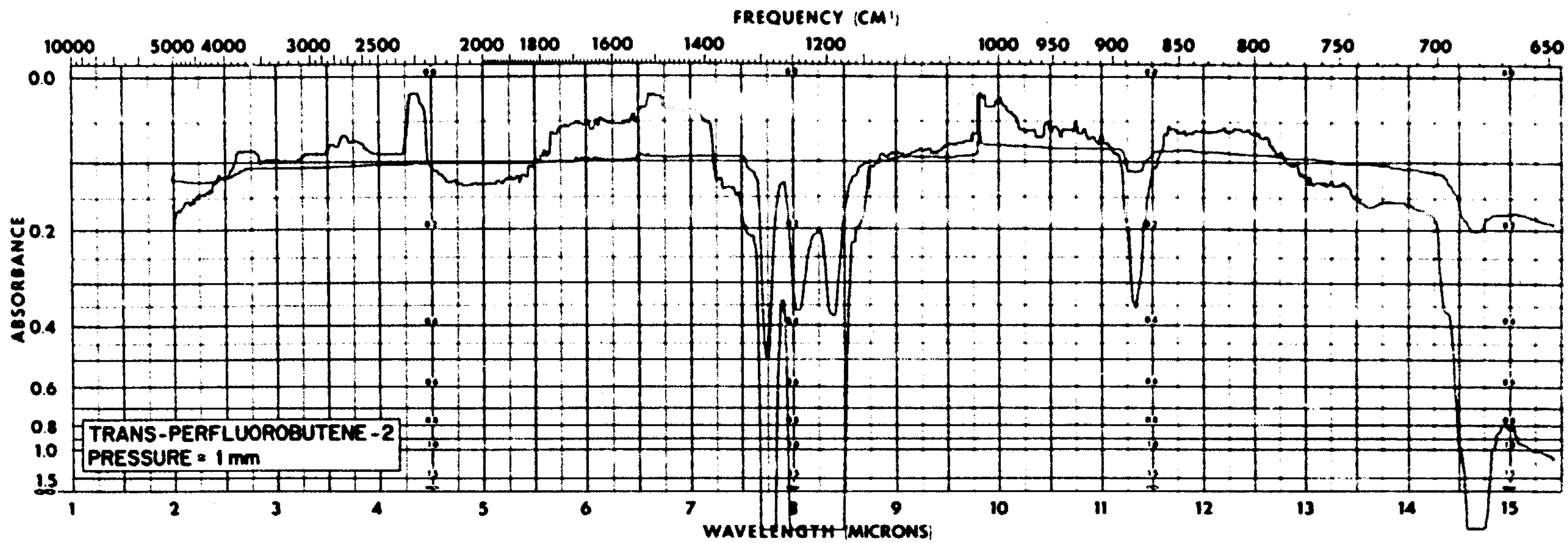

Fig. 1. Infrared spectra. (Continued)

Path length 10 cm. Discontinuity at 9.82 μ due to change in optical system. For the curve with more intense absorption, the ordinate has been magnified five times.

Table I. Infrared frequencies.

ν, cm^{-1}	Relative intensity	ν, cm^{-1}	Relative intensity
		cC_3F_6	
859	s	1172	vw
932	w	1272	vs
978	w	1368	s
1111	w	2532	w
1135	w		
		Cis-C_4F_8-2	
719	vs	1224	vs
726	sh	1245	vs
760	m	1287	m
766	m	1350	vs
905	vw	1389	m
952	vs	1481	vw
956	sh	1524	vw
1064	sh	1562	w
1111	vs	1686	sh
1156	sh	1724	s
1166	sh	1779	m
1193	vs		

Table I. Infrared frequencies. (Cont nued)

ν, cm^{-1}	Relative intensity	ν, cm^{-1}	Relative intensity
		Trans-C_4F_8-2	
682	vs	1387	m
696	sh	1424	m
712	m	1451	vw
730	vw	1499	m
760	m	1527	w
875	sh	1560	w
878	sh	1582	m
882	s	1751	w
890	sh	1848	m
945	m	1953	w
962	m	2000	w
1070-1105	m	2053	m
1149	sh	2105	w
1163	sh	2353	m
1193	vs	2512	w
1242	vs	2652	w
1292	vs	2932	w
1321	sh	3003	w

s = strong, m = medium, w = weak, v = very, sh = shoulder

Table II. Vibrations of cis- and trans-C_4F_8-2.

Description	Trans symmetry	Cis symmetry
	In-plane motions	
C=C stretch	Ag	A_1
C-F stretch	Ag	A_1
C-C stretch	Ag	A_1
CF_3 symmetric stretch	Ag	A_1
CF_3 asymmetric stretch	Ag	A_1
C-F bend	Ag	A_1
C-C bend	Ag	A_1
CF_3 symmetric bend	Ag	A_1
CF_3 asymmetric bend	Ag	A_1
CF_3 coupling wag	Ag	A_1
C-F stretch	Bu	B_1
C-C stretch	Bu	B_1
CF_3 symmetric stretch	Bu	B_1
CF_3 asymmetric stretch	Bu	B_1
C-F bend	Bu	B_1
C-C bend	Bu	B_1
CF_3 symmetric bend	Bu	B_1
CF_3 asymmetric bend	Bu	B_1
CF_3 coupling wag	Bu	B_1

Table II. Vibrations of cis- and trans-C_4F_8-2. (Continued)

Description	Trans symmetry	Cis symmetry
	Out-of-plane motions	
CF_3 asymmetric stretch	Au	A_2
Skeletal bend	Au	A_2
Skeletal bend	Au	A_2
CF_3 asymmetric bend	Au	A_2
CF_3 coupling wag	Au	A_2
CF_3 asymmetric stretch	Bg	B_2
Skeletal bend	Bg	B_2
CF_3 asymmetric bend	Bg	B_2
CF_3 coupling wag	Bg	B_2

REFERENCES

1. S. A. Greene and F. M. Wachi, Anal. Chem. 35, 928 (1963).
2. Hs. H. Günthard, R. C. Lord, and T. K. McCubbin, Jr., J. Chem. Phys. 25, 768 (1956).
3. H. E. Duckworth, Can. J. Phys. 34, 1448 (1956).
4. L. J. Bellamy, The Infrared Spectra of Complex Molecules (John Wiley and Sons, Inc., New York, 1958), p. 29.
5. T. J. Brice, J. D. La Zerte, L. J. Hals, and W. H. Pearlson, J. Am. Chem. Soc. 75, 2698 (1953).
6. R. N. Haszeldine, J. Chem. Soc. 4423 (1952).

DISTRIBUTION

Internal

W. Barry
P. Breisacher
H. Claflin
N. Cohen
J. Colwell
E. Cook
G. Cook
F. Fitzgerald
W. Gamber
R. Geidt
S. A. Greene
R. Hartunian
J. Heicklen
B. Henshall
T. Jacobs
R. Johnson
H. Judeikis
V. Knight
T. Lee
J. Logan
D. Marsh
S. Mayer
H. Myers
M. T. O Shaughnessy
R. Peterson
P. Propp
J. Quinville
W. Riley
D. Saunders
L. Schieler
B. Siegel
S. Siegel
J. Slaughter
E. Smith
H. Takimoto
W. Thompson
F. Wachi
A. Whittaker
R. Wilkins

External

K. Wray
Avco Research Company
Everett, Mass.

M. Camac
Avco Research Company
Everett, Mass.

DISTRIBUTION (Continued)

R. Taylor
Avco Research Company
Everett, Mass.

D. Teare
Avco Research Company
Everett, Mass.

J. Zelinsky
Avco Research Company
Everett, Mass.

W. Browne
General Electric Company
Valley Forge, Pa.

A. Modica
Avco Manufacturing Co.
Res. and Adv. Development Div.
Wilmington, Mass.

T. Wentink
Avco Manufacturing Co.
Res. and Adv. Development Div.
Wilmington, Mass.

Defense Documentation Center (DDC)
Attn: TISIA
Cameron Station
Alexandria, Va.

RTD (MAG)
Wright-Patterson AFB, Ohio

FTD
Wright-Patterson AFB, Ohio

RTD
Bolling AFB 25, D.C.

Hq USAF (Dir. Research and Dev't)
Washington 25, D.C.

AFFTC
Edwards AFB, Calif.

J. Keck
Avco Research Company
Everett, Mass.

A. Fairbairn
Avco Research Company
Everett, Mass.

W. Kaskan
General Electric Company
Valley Forge, Pa.

M. H. Bortner
General Electric Company
Valley Forge, Pa.

L. Isaacson
Avco Manufacturing Co.
Res. and Adv. Development Div.
Wilmington, Mass.

Prof. F. W. Dalby
Dept. of Physics
University of British Columbia
Vancouver, British Columbia

Commanding General
U. S. Army Ballistic Missile Agency
Technical Information Branch
ORDAM--IKE
Redstone Arsenal, Alabama

AFCRL
L G Hanscom Field
Bedford, Mass.

ARSC
Andrews AFB
Washington 25, D.C.

OAR (Tech. Library)
Building T-D
Washington 25, D.C.

DISTRIBUTION (Continued)

Office, Chief of Ordnance
Dept. of the Army
Attn: ORDTB, Materials
Washington 25, D.C.

DMIC
Battelle Memorial Institute
505 King Avenue
Columbus 1, Ohio

Scientific and Tech. Info. Facility
Attn: NASA Rep. (SAK/DL-814)
P. O. Box 5700
Bethesda, Maryland, 20014

R. Bryan Erb, Chief of
Thermostructures Branch
NASA
Manned Spacecraft Center
Houston, Texas

Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, Calif.

Ordnance Materials Research Office
Watertown Arsenal, RPD
Watertown 72, Mass.

USNRL
Anacostia Station
Washington 25, D.C.

NASA
Huntsville, Alabama

NASA
Langley Research Center
Langley Field, Va.

Library
NASA
Manned Spacecraft Center
Houston, Texas

National Bureau of Standards
Boulder Labs
Boulder, Colorado

cy