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

24 JULY 1964

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

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

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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

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Major, USAF
ABSTRACT

The infrared spectra in the NaCl region of cC₃F₆, cis-C₄F₈-2, and trans-C₄F₈-2 are reported. Partial vibration assignments are discussed.
THE INFRARED SPECTRA OF PERFLUOROCYCLOPROPA N E
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 $\text{cC}_3\text{F}_6$, cis-$\text{C}_4\text{F}_8$-2, and trans-$\text{C}_4\text{F}_8$-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 $\text{cC}_3\text{F}_6$ has not been previously reported. The molecular symmetry is $D_{3h}$, and the only allowed infrared fundamental vibrations are the two $\text{A}''_2$ and the four $\text{E}''$ 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 $\text{A}''_2$ band and the other an $\text{E}''$ band. It is not clear which is which. However, there are some indications to suggest that the 1368 cm$^{-1}$ band has $\text{A}''_2$ symmetry and the 1272 cm$^{-1}$ band has $\text{E}''$ symmetry. The $\text{A}''_2$ band involves the asymmetric stretching motion of the $\text{CF}_2$ group, whereas the $\text{E}''$ band involves the symmetric stretching motion. Usually the asymmetric mode has higher frequency, which corresponds to the assignments of $\text{cC}_3\text{H}_6$ (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 $\text{E}''$ symmetry as the overtones of $\text{A}''_2$ 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\(_3\)F\(_6\) 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\(_1\) × A\(_{\nu}\), E' × A\(_1\), E'' × A\(_{\nu}\), E' × E', and E' × 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\(_4\)F\(_8\) (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 discernible, 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\(_4\)F\(_8\)-\(\zeta\), 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 least 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)

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Fig. 1. Infrared spectra. (Continued)

Path length 10 cm. Discontinuity at 9.82 \( \mu \) due to change in optical system. For the curve with more intense absorption, the ordinate has been magnified five times.
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<th>$v$, cm$^{-1}$</th>
<th>Relative intensity</th>
<th>$v$, cm$^{-1}$</th>
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<td>$s$</td>
<td>1172</td>
<td>vw</td>
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<td>932</td>
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<td>vs</td>
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<tr>
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<td>$w$</td>
<td>1368</td>
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<tr>
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<td>vs</td>
<td>1224</td>
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<tr>
<td>1193</td>
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Table I. Infrared frequencies. (Cont nued)

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<td>1321</td>
<td>sh</td>
<td>3003</td>
<td>w</td>
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$s =$ strong, $m =$ medium, $w =$ weak, $v =$ very, $sh =$ shoulder
Table II. Vibrations of cis- and trans-$C_4F_8^-2$.

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<tr>
<th>Description</th>
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<td>C-F stretch</td>
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<tr>
<td>C-C stretch</td>
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<td>CF$_3$ symmetric stretch</td>
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<td>CF$_3$ asymmetric stretch</td>
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<td>$A_1$</td>
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<td>C-F bend</td>
<td>$A_g$</td>
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<td>C-C bend</td>
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<td>CF$_3$ symmetric bend</td>
<td>$A_g$</td>
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<td>C-F stretch</td>
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Table II. Vibrations of cis- and trans-$C_4F_8-2$. (Continued)

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