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# THE INFRARED AND RAMAN SPECTRA OF PENTAFLUOROPROPIONITRILE

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## SUMMARY

The infrared spectrum of $C_2F_5CN$ gas has been recorded between 4000 and 70 $cm^{-1}$. The Raman spectra of $C_2F_5CN$ in both gas and solid states have also been obtained between 2400 and 20 $cm^{-1}$. Frequencies have been assigned to the 21 fundamental modes with the aid of an approximate normal coordinate calculation and the gas-phase infrared band contours. The thermodynamic properties, heat capacity, enthalpy, entropy and free energy, have been calculated for several temperatures.

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## INTRODUCTION

The present study on pentafluoropropionitrile ($C_2F_5CN$) was undertaken as an extension of some of our previous work on trifluoroacetonitrile, $CF_3CN$[1-3]. It was hoped to obtain further information on the hot bands which are frequently found to be associated with C≡N or C≡C stretching fundamentals. Such bands were observed for $CF_3CN$[1]. It was also hoped that the force field obtained for $CF_3CN$[2] could be transferred to $C_2F_5CN$. It will be seen that unfortunately neither of these hopes was realized in this work. However, it appears that the only previous spectroscopic work on $C_2F_5CN$ is the publication of a gas-phase infrared survey spectrum without tabulation of frequencies or assignments[4]. We have recorded infrared and Raman spectra of $C_2F_5CN$ in both gas and solid states in order to locate the 21 fundamentals of the molecule. A normal co-ordinate calculation and calculations of gas-phase band contours have aided in making the assignments. We have also calculated thermodynamic properties for $C_2F_5CN$ for two possible models in which internal rotation of the $CF_3$ group is either allowed or not.

## EXPERIMENTAL

Several samples of pentafluoropropionitrile gas were obtained from Peninsular Chemresearch Inc. and were used without further purification. In some samples the presence of $CF_3CFHCN$ impurity was detected by comparison with the reported infrared spectrum of this compound[4].

Infrared survey spectra were run on Beckman IR 10 and Perkin–Elmer 21 spectrometers. High-resolution infrared spectra were recorded on Perkin–Elmer single-beam Ebert and model 180 spectrometers. The far-infrared spectrum of the gas was recorded in the laboratory of Dr. E. Whalley at the National Research Council in Ottawa on a Perkin–Elmer model 301 spectrometer. The Raman spectra of $C_2F_5CN$ were recorded in the laboratory of Dr. H. J. Bernstein, at the National Research Council in Ottawa, on a Spex Industries Model 1400 monochromator using photon counting system. The spectra were excited by the 4880 Å line of an argon ion laser operating at a power of 500 MW. The gas was in a rectangular glass cell 5 cm long and 1 cm cross-section at a pressure of 2 atm. A single pass of the laser beam was sufficient to excite the Raman spectrum. The Raman spectrum of solid $C_2F_5CN$ was 77°K was obtained using the low-temperature cell described previously[5].

## RESULTS AND DISCUSSION

The infrared and Raman spectra of gaseous pentafluoropropionitrile are shown in Figures 1–5, while the Raman spectrum of the solid is shown in Figures 6 and 7. The observed frequencies and assignments of the fundamentals are recorded in Table 1. Table 2 lists the frequencies and assignments of overtone and combination bands.

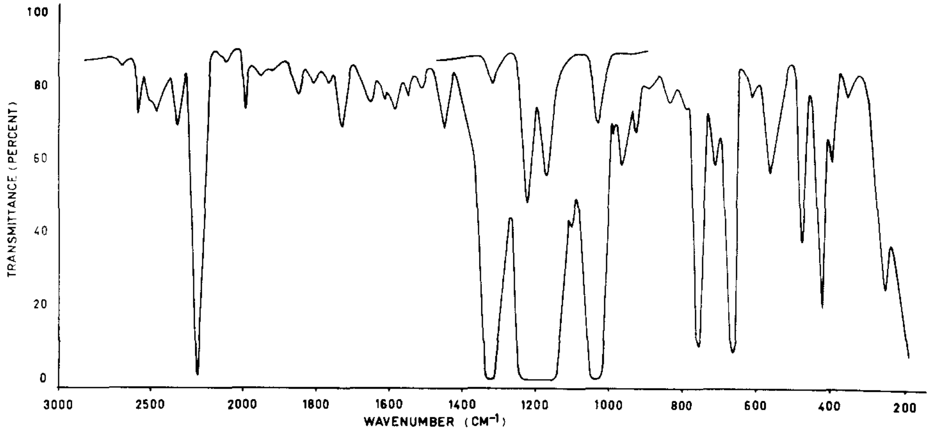

Fig. 1. The infrared spectrum of $C_2F_5CN$ gas between 3000 and 200 $cm^{-1}$. The main trace was obtained using 10 cmHg pressure of $C_2F_5CN$ in a 10 cm cell. The weaker trace between 1400 and 1000 $cm^{-1}$ was obtained from 1 cmHg pressure.

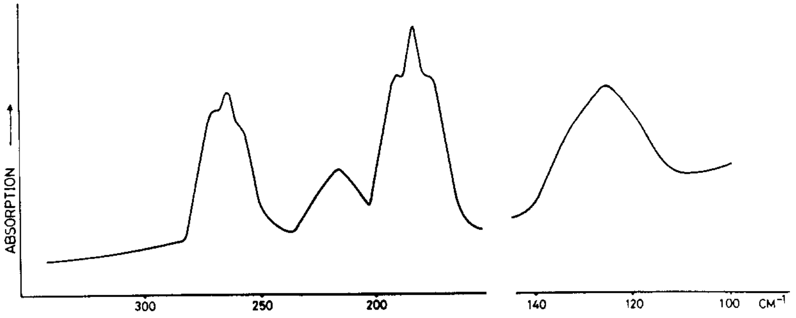

Fig. 2. The far infrared spectrum of $C_2F_5CN$ gas, using 20 cmHg pressure of $C_2F_5CN$ in a 10 cm cell with polyethylene windows.

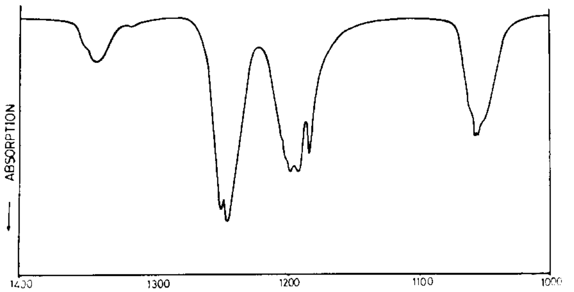

Fig. 3. The infrared spectrum of $C_2F_5CN$ gas, between 1400 and 1000 cm$^{-1}$. A 10 cm cell and 2 cmHg pressure of $C_2F_5CN$ gas was used.

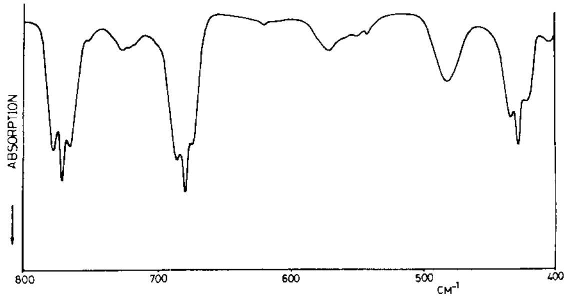

Fig. 4. The infrared spectrum of $C_2F_5CN$ gas, between 800 and 400 cm$^{-1}$. A 10 cm cell and 10 cmHg pressure of $C_2F_5CN$ gas was used.

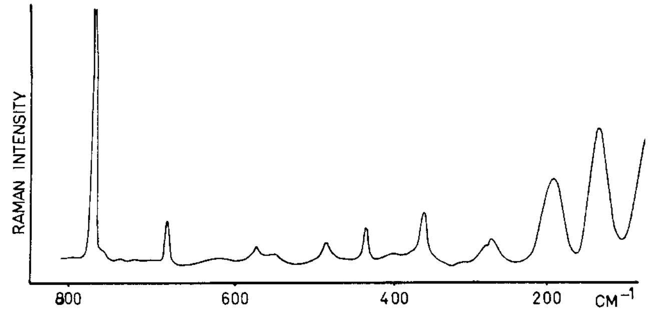

Fig. 5. The Raman spectrum of $C_2F_5CN$ gas at 2 atm pressure, excited by a single pass of the 4880 Å line of an argon ion laser operating at 500 MW.

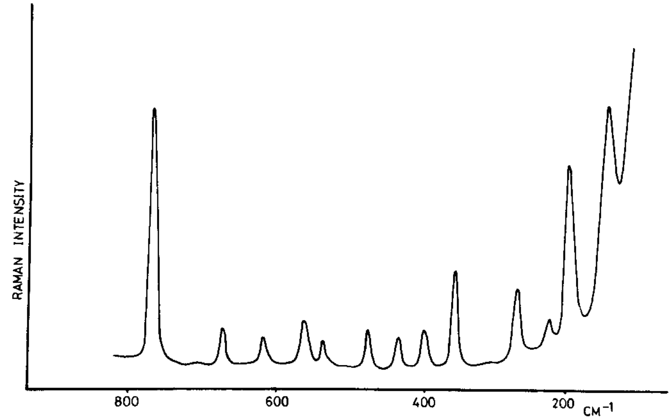

Fig. 6. The Raman spectrum of solid $C_2F_5CN$ at 77°K between 800 and 100 cm$^{-1}$.

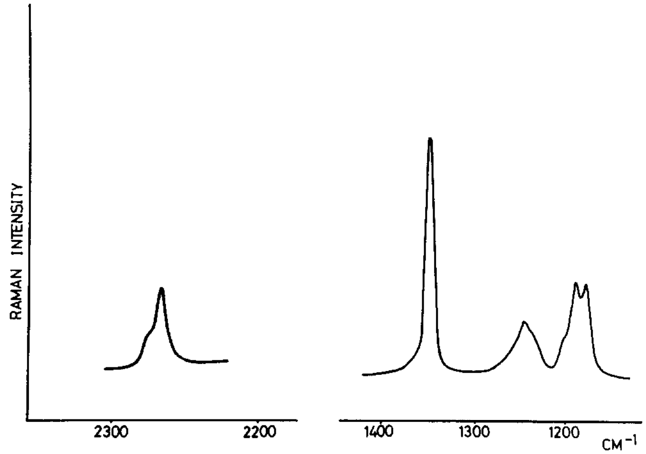

Fig. 7. The Raman spectrum of solid $C_2F_5CN$ at 77°K in the CN stretching region and between 1400 and 1000 cm$^{-1}$. Slits of 10 cm$^{-1}$ and high amplification were necessary for the 1400 to 1000 cm$^{-1}$ region.

TABLE 1

THE FUNDAMENTAL FREQUENCIES OF $C_2F_5CN$

| Symmetry | IR (gas) | | | Raman (gas) | | Raman (solid) | | Approximate description |
|---|---|---|---|---|---|---|---|---|
| | cm$^{-1}$ | I | Band type | cm$^{-1}$ | I | cm$^{-1}$ | I | |
| *a′* modes | 2272 | s | *Q* | 2276 | w | 2273 | w | C≡N str. |
| | 1344 | vs | *Q* | 1346 | w | 1343 | w | C–F str. |
| | 1246 | vs | *PR* | — | vw | 1242 | vw | |
| | 1187 | vs | *PR* | — | vw | 1186 | vw | |
| | 938 | w | *Q* | — | vw | — | vw | C–C str. and F–C–F def. |
| | 620 | vw | *Q* | — | vw | 622 | m | |
| | 570 | m | *Q* | 575 | w | 567 | m | |
| | 546 | w | *PR* | — | w | 542 | w | |
| | 482 | m | *Q* | 485 | w | 481 | m | |
| | 397 | w | *Q* | — | w | 400 | m | C–C–F def. |
| | 353 | w | *Q* | 359 | m | 359 | s | |
| | 216 | m | *Q* | — | w | 219 | w | |
| | 125 | m | *Q* | 129 | s | 137 | vs | C–C–N def. |
| *a″* modes | 1194 | vs | *PQR*? | — | vw | 1186 | vw | C–F str. |
| | 1054 | vs | *PQR*? | — | vw | — | vw | |
| | 772 | m | *PQR* | 775 | vs | 771 | vs | F–C–F def. |
| | 680 | m | *PQR* | 684 | m | 681 | m | |
| | 428 | m | *PQR* | 434 | m | 434 | m | C–C–F def. |
| | 263 | s | *PQR* | 270 | m | 267 | s | |
| | 183 | s | *PQR* | 190 | vs | 192 | vs | C–C–N def. |
| | — | — | — | 63 | vs | — | — | $CF_3$ torsion |

TABLE 2

FREQUENCIES (in cm$^{-1}$) AND ASSIGNMENTS OF SOME COMBINATION AND OVERTONE BANDS IN THE INFRARED SPECTRUM OF $C_2F_5CN$

| Frequency | Assignment |
|---|---|
| 2595 | 1246 + 1344 = 2590 |
| 2536 | 1194 + 1344 = 2538 |
| 2494 | 2 × 1246 = 2492 |
| 2375 | 2 × 1187 = 2374<br>or 1187 + 1194 = 2381 |
| 2005 | 772 + 1246 = 2018 |
| 1818 | 482 + 1344 = 1826 |
| 1778 | 428 + 1344 = 1772 |
| 1751 | 570 + 1187 = 1757 |

TABLE 2 *(Continued)*

| Frequency | Assignment |
|---|---|
| 1740 | 397 + 1344 = 1741 |
| 1597 | 353 + 1246 = 1599 |
| 1460 | 216 + 1246 = 1462 |
| 1319 | 125 + 1194 = 1319 |
| 1108 | 63 + 1054 = 1117<br>or 428 + 680 = 1108 |
| 971 | 2 × 482 = 964<br>or 216 + 772 = 988 |
| 845 | 2 × 428 = 856 |
| 722 | 2 × 353 = 706 |
| 246 | 2 × 125 = 250<br>or 63 + 183 = 246 |

Pentafluoropropionitrile belongs to the point group $C_s$ and the 21 fundamentals are divided into 13 $a'$ and 8 $a''$ modes. An approximate description of the normal modes of the $C_2F_5CN$ molecule with the frequency ranges expected for these vibrations is given in Table 3. The actual normal modes will certainly involve mixtures of internal co-ordinates, so that specific assignments can not be made for $C_2F_5CN$. However, the approximate descriptions are useful and will be retained.

TABLE 3

APPROXIMATE DESCRIPTIONS AND EXPECTED FREQUENCY RANGES (in $cm^{-1}$) FOR THE VIBRATIONS OF $C_2F_5CN$

| Vibration | Symmetry | Frequency Range |
|---|---|---|
| C≡N stretch | $a'$ | 2250–2300 |
| C–F stretch | $3a' + 2a''$ | 1000–1400 |
| C–C stretch | $2a'$ | 700–1100 |
| F–C–F deformation | $3a' + 2a''$ | 400–1000 |
| C–C–F deformation | $3a' + 2a''$ | 200–600 |
| C–C–N deformation | $a' + a''$ | 100–300 |
| $CF_3$ torsion | $a''$ | below 100 |

### *Normal co-ordinate calculations*

As a guide to the assignments of the fundamentals of $C_2F_5CN$, the Wilson *FG* matrix method[6] was used to calculate the frequencies of the fundamentals and potential energy distributions (P.E.D.). The structure assumed for the $C_2F_5CN$ molecule is shown in Figure 8. Bond lengths and angles were obtained from microwave work on the related molecules $CF_3CN$[7], $C_2F_6$[8] and $C_2H_5CN$[9], an electron diffraction study of $C_2F_6$[10] and a review of the structures of several volatile fluorine compounds[11]. The bond lengths chosen for $C_2F_5CN$ were: C–F = 1.33 Å, $C_1$–$C_2$ = 1.46 Å, $C_2$–$C_3$ = 1.50 Å and C≡N = 1.15 Å. The angles used were $\widehat{FCF} = 108.5°$, $\widehat{CCC} = 110.5°$, $\widehat{CCF} = 110.5°$ and $\widehat{NCC} = 180.0°$. Initial values of force constants were taken from the results of normal co-ordinate calculations for related molecules, especially $CF_3CN$[2].

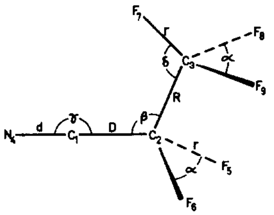

Fig. 8. The structure and internal co-ordinates of $C_2F_5CN$.

A 23 × 23 $G$ matrix including two $A'$ redundancies and based on the above structure was calculated using the methods of Decius[12]. A general valence force field (GVFF) involving 90 force constants was constructed for the sake of generality, although most of these force constants were set equal to zero. The internal co-ordinates used in setting up the $G$ and $F$ matrices are given in Table 4 while Table 5 contains the symmetry co-ordinates used to factorize the matrices in order to obtain secular equations for the $a'$ and $a''$ symmetry species. A FORTRAN IV program originally written by Schachtschneider[13] and modified by Brooks[14] was used for the calculations which were carried out on an IBM 360/50 computer.

TABLE 4

INTERNAL CO-ORDINATES FOR $C_2F_5CN$ [a]

$R_1 = \Delta r(C_1\text{–}N_4)$
$R_2 = \Delta r(C_1\text{–}C_2)$
$R_3 = \Delta r(C_2\text{–}C_3)$
$R_4 = \Delta r(C_2\text{–}F_5)$
$R_5 = \Delta r(C_2\text{–}F_6)$
$R_6 = \Delta r(C_3\text{–}F_7)$
$R_7 = \Delta r(C_3\text{–}F_8)$
$R_8 = \Delta r(C_3\text{–}F_9)$
$R_9 = \Delta \alpha(F_8\text{–}C_3\text{–}F_9)$
$R_{10} = \Delta \alpha(F_9\text{–}C_3\text{–}F_7)$
$R_{11} = \Delta \alpha(F_8\text{–}C_3\text{–}F_7)$
$R_{12} = \Delta \delta(F_8\text{–}C_3\text{–}C_2)$
$R_{13} = \Delta \delta(F_9\text{–}C_3\text{–}C_2)$
$R_{14} = \Delta \delta(F_7\text{–}C_3\text{–}C_2)$
$R_{15} = \Delta \alpha(C_3\text{–}C_2\text{–}F_5)$
$R_{16} = \Delta \alpha(C_3\text{–}C_2\text{–}F_6)$
$R_{17} = \Delta \alpha(C_3\text{–}C_2\text{–}C_1)$
$R_{18} = \Delta \alpha(C_1\text{–}C_2\text{–}F_6)$
$R_{19} = \Delta \alpha(C_1\text{–}C_2\text{–}F_5)$
$R_{20} = \Delta \alpha(F_6\text{–}C_2\text{–}F_5)$
$R_{21} = \Delta \tau(C_1\text{–}C_2\text{–}C_3\text{–}F_7)$
$R_{22} = \Delta \gamma(N_4\text{–}C_1\text{–}C_2)$
$R_{23} = \Delta \gamma(N_4\text{–}C_1\text{–}C_2)$

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[a] See Figure 8 for the numbering of the atoms.

TABLE 5

SYMMETRY CO-ORDINATES FOR $C_2F_5CN$

| $A'$ Symmetry | Description | $A''$ Symmetry | Description |
|---|---|---|---|
| $S_1 = R_1$ | C–N str. | $S_{16} = \frac{1}{\sqrt{2}}(R_4 - R_5)$ | C–F str. |
| $S_2 = R_2$ | C–C str. | $S_{17} = \frac{1}{\sqrt{2}}(R_7 - R_8)$ | C–F str. |
| $S_3 = R_3$ | C–C str. | $S_{18} = \frac{1}{\sqrt{2}}(R_{10} - R_{11})$ | F–C–F bend |
| $S_4 = R_6$ | C–F str. | $S_{19} = \frac{1}{\sqrt{2}}(R_{12} - R_{13})$ | C–C–F bend |
| $S_5 = \frac{1}{\sqrt{2}}(R_4 + R_5)$ | C–F str. | $S_{20} = \frac{1}{\sqrt{2}}(R_{15} - R_{16})$ | C–C–F bend |
| $S_6 = \frac{1}{\sqrt{2}}(R_7 + R_8)$ | C–F str. | $S_{21} = \frac{1}{\sqrt{2}}(R_{18} - R_{19})$ | C–C–F bend |
| $S_7 = R_9$ | F–C–F bend | $S_{22} = R_{21}$ | torsion |
| $S_8 = \frac{1}{\sqrt{2}}(R_{10} + R_{11})$ | F–C–F bend | $S_{23} = R_{23}$ | C–C–N bend |
| $S_9 = \frac{1}{\sqrt{2}}(R_{12} + R_{13})$ | C–C–F bend | | |
| $S_{10} = R_{14}$ | C–C–F bend | | |
| $S_{11} = \frac{1}{\sqrt{2}}(R_{15} + R_{16})$ | C–C–F bend | | |
| $S_{12} = R_{17}$ | C–C–C bend | | |
| $S_{13} = \frac{1}{\sqrt{2}}(R_{18} + R_{19})$ | C–C–F bend | | |
| $S_{14} = R_{20}$ | F–C–F bend | | |
| $S_{15} = R_{22}$ | C–C–N bend | | |

A preliminary calculation using only diagonal force constants produced an unacceptable set of frequencies. Interaction constants were added to the force field in order to produce a better set of calculated frequencies, for which a P.E.D. could be obtained. It was found that no good fit between observed and calculated frequencies could be obtained with the 10 diagonal and up to 10 interaction constants.

The fit could be improved somewhat after inspection of the Jacobian matrix relating the changes in frequencies produced by changes in force constants and assigning reasonable values to additional force constants. However, complete convergence to an exact fit between observed and calculated frequencies was not obtained with any set of force constants used in this work. It appears that normal co-ordinate calculations on perfluorinated molecules, such as $C_2F_5CN$, are not satisfactory, because a large number of interaction constants are important and there is no hope of finding a unique force field for such molecules.

In spite of the difficulties of the calculation, some useful information was obtained. A typical set of frequencies in reasonable agreement with the observed spectra are listed in Table 6. The calculation is consistent with the assignment to *a′* and *a″* modes given in Table 1 and discussed below. Furthermore, the P.E.D. calculated from the force constants of Table 6 enables us to make useful qualitative descriptions of the normal vibrations in terms of the internal coordinates. This P.E.D. is listed in Table 7. It should be pointed out, however, that since the force field is not unique, there may be some ambiguity in these descriptions of the normal modes. It will also be noted that the sums of the P.E.D.s in Table 7 are greater than 1.000. This is because several small negative contributions have been omitted from the Table in the interests of clarity.

TABLE 6

A TYPICAL SET OF CALCULATED FORCE CONSTANTS (in md/Å) AND FREQUENCIES (in $cm^{-1}$)

*Force constants*[a]

| Description | Value | Description | Value |
|---|---|---|---|
| $f_1$ $C{\equiv}N$ stretch | 18.30 | $f_{11}$ CF–CCN in-plane interaction | —0.348 |
| $f_2$ C–C stretch | 4.00 | $f_{12}$ CF–CCN out-of-plane interaction | +0.348 |
| $f_3$ C–F stretch | 4.30 | $f_{13}$ $C_3F$–$FC_3F$ interaction (no common bond) | —0.301 |
| $f_4$ F–C–F bend | 1.07 | $f_{14}$ $C_3F$–$FC_3F$ interaction (common bond) | +0.235 |
| $f_5$ $C_2$–$C_3$–F bend | 0.401 | $f_{15}$ $FC_3F$–$FC_3F$ interaction | —0.057 |
| $f_6$ $C_3$–$C_2$–F bend | 0.501 | $f_{16}$ $FC_3F$–$C_3C_2F$ interaction | —0.100 |
| $f_7$ $C_1$–$C_2$–F bend | 0.824 | $f_{17}$ $C_2C_3F$–CCN out-of-plane interaction | —0.066 |
| $f_8$ C–C–C bend | 0.413 | $f_{18}$ $C_3C_2F$–$C_3C_2F$ interaction | —0.201 |
| $f_9$ C–C–N bend | 0.268 | $f_{19}$ $C_2F$–torsion interaction | —0.143 |
| $f_{10}$ $CF_3$ torsion | 0.077 | $f_{20}$ $C_3F$–torsion interaction | —0.108 |

*Frequencies*

| | Mode | Obs. | Calc. | | Mode | Obs. | Calc. |
|---|---|---|---|---|---|---|---|
| *a′* | $\nu_1$ | 2272 | 2275 | *a″* | $\nu_1$ | 1194 | 1226 |
| | $\nu_2$ | 1344 | 1388 | | $\nu_2$ | 1054 | 1124 |
| | $\nu_3$ | 1246 | 1291 | | $\nu_3$ | 772 | 689 |
| | $\nu_4$ | 1187 | 1136 | | $\nu_4$ | 680 | 600 |
| | $\nu_5$ | 938 | 919 | | $\nu_5$ | 428 | 408 |
| | $\nu_6$ | 620 | 636 | | $\nu_6$ | 263 | 276 |
| | $\nu_7$ | 570 | 590 | | $\nu_7$ | 183 | 189 |
| | $\nu_8$ | 546 | 574 | | $\nu_8$ | 63 | 59 |
| | $\nu_9$ | 482 | 502 | | | | |
| | $\nu_{10}$ | 397 | 387 | | | | |
| | $\nu_{11}$ | 353 | 314 | | | | |
| | $\nu_{12}$ | 216 | 256 | | | | |
| | $\nu_{13}$ | 125 | 138 | | | | |

[a] The force constants involving angle bending have been divided by appropriate bond lengths, or products of bond lengths, to give consistent units of md/Å.

TABLE 7

THE POTENTIAL ENERGY DISTRIBUTION FOR THE FORCE CONSTANTS AND FREQUENCIES OF TABLE 6

a′ *Modes*

| Frequencies (cm$^{-1}$) | Potential energy distribution | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $f$C–N | $f$C–C | $f$C–F | $f$F–C–F | $f_5$C–C–F | $f_6$C–C–F | $f_7$C–C–F | $f$C–C–C | $f$C–C–N | Important interactions[a] | |
| 2275 | 0.912 | 0.086 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | none | |
| 1388 | 0.002 | 0.568 | 0.139 | 0.173 | 0.053 | 0.032 | 0.051 | 0.018 | 0.009 | none | |
| 1291 | 0.033 | 0.222 | 0.341 | 0.200 | 0.095 | 0.046 | 0.059 | 0.076 | 0.001 | none | |
| 1136 | 0.010 | 0.082 | 0.756 | 0.275 | 0.027 | 0.001 | 0.027 | 0.005 | 0.0 | $f_{13} = -0.109$ | $f_{14} = -0.085$ |
| 919 | 0.007 | 0.084 | 0.385 | 0.286 | 0.087 | 0.106 | 0.170 | 0.034 | 0.035 | $f_{14} = -0.106$ | $f_{13} = +0.067$ |
| 636 | 0.009 | 0.124 | 0.293 | 0.055 | 0.004 | 0.0 | 0.024 | 0.098 | 0.201 | $f_{11} = +0.187$ | |
| 590 | 0.0 | 0.009 | 0.174 | 0.644 | 0.003 | 0.003 | 0.0 | 0.001 | 0.002 | $f_{13} = +0.069$ | $f_{14} = +0.066$ |
| 574 | 0.0 | 0.027 | 0.598 | 0.228 | 0.064 | 0.007 | 0.024 | 0.010 | 0.029 | $f_{14} = +0.139$ | $f_{13} = -0.083$ |
| 502 | 0.010 | 0.149 | 0.170 | 0.475 | 0.002 | 0.012 | 0.183 | 0.021 | 0.076 | $f_{11} = -0.092$ | |
| 387 | 0.016 | 0.316 | 0.149 | 0.115 | 0.095 | 0.161 | 0.034 | 0.103 | 0.269 | $f_{11} = -0.150$ | $f_{18} = -0.065$ |
| 313 | 0.0 | 0.180 | 0.120 | 0.177 | 0.377 | 0.129 | 0.020 | 0.019 | 0.082 | $f_{11} = -0.059$ | $f_{18} = -0.052$ |
| 256 | 0.0 | 0.140 | 0.057 | 0.086 | 0.337 | 0.182 | 0.175 | 0.0 | 0.154 | $f_{11} = -0.058$ | $f_{18} = -0.073$ |
| 125 | 0.0 | 0.011 | 0.085 | 0.011 | 0.163 | 0.133 | 0.024 | 0.430 | 0.341 | $f_{11} = -0.138$ | $f_{18} = -0.053$ |

.../(continued)

TABLE 7 (continued)

a″ *Modes*

| Frequencies (cm$^{-1}$) | Potential energy distribution | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *f* C–F | *f* F–C–F | $f_5$ C–C–F | $f_6$ C–C–F | $f_7$ C–C–F | *f* C–C–N | Torsion | Important interactions[a] | |
| 1226 | 0.732 | 0.050 | 0.106 | 0.151 | 0.148 | 0.013 | 0.036 | $f_{19} = -0.102$ | $f_{12} = -0.071$ |
| 1124 | 0.898 | 0.230 | 0.029 | 0.005 | 0.054 | 0.006 | 0.005 | $f_{13} = -0.112$ | $f_{14} = -0.087$ |
| 689 | 0.049 | 0.020 | 0.005 | 0.005 | 0.478 | 0.294 | 0.036 | $f_{12} = 0.096$ | |
| 600 | 0.129 | 0.627 | 0.001 | 0.010 | 0.023 | 0.016 | 0.014 | $f_{13} = +0.079$ | $f_{14} = +0.062$ |
| 408 | 0.241 | 0.085 | 0.160 | 0.321 | 0.041 | 0.015 | 0.001 | $f_{18} = 0.128$ | |
| 276 | 0.116 | 0.010 | 0.215 | 0.151 | 0.141 | 0.352 | 0.0 | $f_{12} = -0.158$ | $f_{17} = +0.130$ |
| 189 | 0.223 | 0.003 | 0.540 | 0.077 | 0.104 | 0.630 | 0.018 | $f_{12} = -0.303$ | $f_{17} = -0.275$ |
| 59 | 0.225 | 0.007 | 0.018 | 0.005 | 0.012 | 0.001 | 1.179 | $f_{19} = -0.298$ | $f_{20} = -0.155$ |

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[a] Important interactions are those contributing more than ± 0.05 to the P.E.D..

It is perhaps of interest to compare some of the force constants of $C_2F_5CN$ with those obtained for $CF_3CN$. Several calculations have been made previously for $CF_3CN$[2,15,16]. The most recent of these[2] is probably the most reliable, since the coriolis constants calculated from the force field were in reasonable agreement with experimental values obtained from the gas-phase band contours[3]. The C≡N, C–F and C–C stretching constants for the two molecules are compared in Table 8. It is notable that lower C–C and C–F stretching constants were obtained for $C_2F_5CN$ than for $CF_3CN$. The C≡N stretching constant is essentially the same in the two molecules.

TABLE 8

THE STRETCHING FORCE CONSTANTS OF $CF_3CN$ AND $C_2F_5CN$ (in md/Å)

| Constant | $CF_3CN$ ref. (2) | $C_2F_5CN$ |
|---|---|---|
| $F$ C–F | 5.80 | 4.30 |
| $F$ C–C | 5.60 | 4.00 |
| $F$ C–N | 18.00 | 18.30 |

*Band contour calculations*

Another guide to the assignments to $a'$ and $a''$ modes came from the contours of the gas-phase infrared bands. $C_2F_5CN$ is an asymmetric top molecule with ground-state rotational constants $A'' = 0.07598$, $B'' = 0.05181$ and $C'' = 0.04541$ cm$^{-1}$. The asymmetry parameter $k = 0.5839$.

The principal axes of inertia for $I_a$ and $I_b$ are in the plane of symmetry of the molecule. Therefore the $a'$ modes will have $A + B$ hybrid band contours, while the $a''$ modes will have $C$-type band contours.

Calculations of $C$-type contours of $C_2F_5CN$ were carried using a computer program written by Parkin[17] and modified by Balfour[18]. Small changes in the upper state rotational constant $A'$ were made and the contour shown in Figure 9 was obtained. It is seen that the theoretical $C$-type band contour has a $PQR$ structure, with a strong $Q$ branch and a $P$–$R$ separation of approximately 11 cm$^{-1}$.

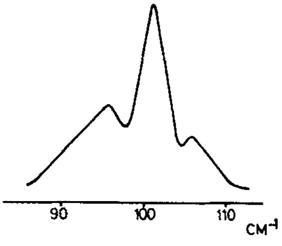

Fig. 9. The calculated contour of a $C$-type asymmetric rotor band of a molecule with $A'' = 0.07598$, $A' = 0.07218$, $B'' = B' = 0.05181$ and $C'' = C' = 0.04541$ cm$^{-1}$. An arbitrary choice of 100 cm$^{-1}$ for the band centre has been made.

### *Assignments*

#### a″ *Modes*

We have used the *C*-type band contour as a criterion in locating the *a″* modes. The infrared bands at 772, 680, 428 and 263 have well-defined *PQR* structures and these are assigned to the *a″* modes involving F–C–F and C–C–F deformations. Another band with a well-defined *PQR* structure at 183 $cm^{-1}$ is assigned to the *a″* C–C–N bending mode. All of these bands have strong *Q* branches with *P–R* separations of 12 $cm^{-1}$.

Two other *a″* fundamentals involving C–F stretching are expected somewhere between 1300 and 1000 $cm^{-1}$. These are assigned to the two very strong infrared bands at 1194 and 1054 $cm^{-1}$ respectively. Both of these bands seem to have *PQR* structures. The 1194 band has a weak *R* branch, which appears as a shoulder and the 1054 $cm^{-1}$ band has a double *Q* branch with *P* and *R* shoulders. Although the *PQR* structure is not well-defined on these two bands, the *P–R* separation is again approximately 11–12 $cm^{-1}$.

$CF_3$ torsions were observed at 64 $cm^{-1}$ in bis-(trifluoromethyl)peroxide $(CF_3)_2O_2$[19] and at 74 $cm^{-1}$ in $C_2F_5H$[20]. A value for the torsional vibration in $C_2F_6$ has been estimated[21] at 64.5 $cm^{-1}$ from the thermodynamic properties of this compound. The lowest frequency observed in the gas-phase Raman spectrum of $C_2F_5CN$ was 63 $cm^{-1}$. This is assigned to the *a″* $CF_3$ torsion in this molecule.

Examination of the P.E.D. in Table 7 for the *a″* modes enables us to say something more on the descriptions of these normal vibrations. Both the 1194 and 1054 $cm^{-1}$ frequencies (calculated as 1226 and 1124 $cm^{-1}$) are clearly C–F stretching modes. The former contains some C–C–F bending and the latter some F–C–F bending. The 772 $cm^{-1}$ mode appears to be a mixture of C–C–F and C–C–N bending motions, with little contribution from F–C–F bending contrary to the qualitative description of Table 1. The 680 $cm^{-1}$ frequency on the other hand is mainly F–C–F bending as expected. The calculated frequencies of both of these fundamentals were very low (689 and 600 $cm^{-1}$ respectively). Clearly, important interaction constants involving these modes have been omitted from the force field.

The two modes described as C–C–F deformations in Table 1 are in fact delocalized modes involving several internal co-ordinates. The frequency calculated at 189 $cm^{-1}$ involves both C–C–N and C–C–F deformations and there are large interaction constants also involved. The $CF_3$ torsion is well defined in the P.E.D., but again interaction constants are important.

#### a′ *Modes*

If we assume that the assignments of the *a″* modes are correct then the *a′* modes can be located.

The *a′* C≡N stretching vibration is obviously the 2272 $cm^{-1}$ infrared band. Three *a′* C–F stretching modes are expected in the 1000 to 1400 $cm^{-1}$ region.

However, it has been shown[22] that the qualitative assignment of C–F stretching vibrations to frequencies in this range is often at variance with the more quantitative results of normal co-ordinate calculations. The present calculation supports this view. Three very strong infrared bands were observed at 1344, 1246 and 1187 cm$^{-1}$. These frequencies were extremely weak in the Raman spectra of both the gas and solid. The P.E.D. in Table 7 indicates that the highest of these three frequencies has C–C stretching rather than C–F stretching as the largest contribution to the normal mode. A similar situation has been found in other fluorine compounds, such as $CF_3C{\equiv}CCF_3$ and $CF_3C{\equiv}CCH_3$[22]. Although the second of the three frequencies has considerable C–F stretching in the P.E.D., C–C stretching and F–C–F bending are also important. Only the lowest of the three frequencies can be called a C–F stretching mode. There are three other calculated fundamentals for which C–F stretching contributes the largest element of the P.E.D. These correspond to frequencies observed at 938, 620 and 546 cm$^{-1}$.

The two modes involving C–C stretching and three of the F–C–F bending vibrations are of species *a′*. Frequencies of 938, 620, 570, 546 and 482 cm$^{-1}$ are assigned to these fundamentals. However, no specific assignments can be made to C–C stretching and F–C–F bending modes, since these internal co-ordinates mix among themselves and with other internal co-ordinates to produce mixed vibrations rather than characteristic "group" vibrations. The location of the modes involving C–C stretching and F–C–F bending between 400 and 1000 cm$^{-1}$ is indicated by previous work on fluorinated compounds[1,23,24]. The two C–C stretching modes in $C_2H_5CN$ were located[23] at 1078 and 840 cm$^{-1}$.

The 620 cm$^{-1}$ frequency is very weak in the infrared, but is seen as a line of medium intensity in the Raman spectrum of the solid. The 938 cm$^{-1}$ infrared band was also weak. There are two other weak infrared bands in this 600–1000 cm$^{-1}$ region at 971 and 722 cm$^{-1}$, which might be assigned to fundamentals. The 938 cm$^{-1}$ and 620 cm$^{-1}$ frequencies are preferred for the following reasons. The normal co-ordinate calculation predicts frequencies considerably lower than 971 and 722 cm$^{-1}$ for these fundamentals. The 620 cm$^{-1}$ frequency also appears in the Raman spectrum. No satisfactory binary combination can account for the 938 and 620 cm$^{-1}$ frequencies, whereas the 971 and 722 cm$^{-1}$ bands can be attributed to overtones of the fundamentals at 482 and 353 cm$^{-1}$ respectively.

It is not possible to assign frequencies specifically to *a′* C–C–F deformation vibrations for the same reasons given above for the C–C stretching and F–C–F bending modes. In pentafluoroethane[24] three fundamentals were observed in the infrared spectrum between 200 and 400 cm$^{-1}$, which were associated with deformation and rocking modes. We have assigned two *a″* fundamentals in this region on the basis of their *PQR* structure and the remaining three *a′* modes are assigned to the weak infrared bands at 397 and 353 and a band of medium intensity at 216 cm$^{-1}$. Of these frequencies the second was observed as a strong line in the Raman spectrum at 359 cm$^{-1}$, while the other two lines were weak.

The degenerate C–C–N deformation was observed at 196 cm$^{-1}$ in the infrared spectrum of $CF_3CN$[1]. There should be two separate fundamentals involving C–C–N deformation in $C_2F_5CN$. The $a''$ mode is assigned to the strong infrared band at 183 cm$^{-1}$, while the $a'$ mode is associated with the lower frequency peak at 125 cm$^{-1}$. The latter fundamental is a mixed mode involving C–C–C and C–C–N deformations.

### *Thermodynamic properties*

Using the 21 fundamental frequencies together with the structural parameters, the thermodynamic properties, heat content, free energy, entropy and heat capacity have been calculated for 12 temperatures from 100 to 2000°K for the ideal gaseous state of pentafluoropropionitrile at 1 atm pressure. The rigid-rotor, harmonic oscillator approximation was used and the method of calculation was that outlined by Herzberg[25]. In Table 9 the results of the calculations are recorded for the cases with and without free internal rotation.

TABLE 9

HEAT CONTENT $H^\circ$, FREE ENERGY $G^\circ$, ENTROPY $S^\circ$ AND HEAT CAPACITY $Cp^\circ$ [a] FOR THE IDEAL GASEOUS STATE OF PENTAFLUOROPROPIONITRILE AT 1 atm PRESSURE FOR SEVERAL TEMPERATURES

| $T$°K | $(H^\circ - E^\circ)/T$ [b] | | $-(G^\circ - E_0^\circ)/T$ | | $S^\circ$ | | $Cp^\circ$ | |
|---|---|---|---|---|---|---|---|---|
| | No internal rotation | Internal rotation | No internal rotation | Internal rotation | No internal rotation | Internal rotation | No internal rotation | Internal rotation |
| 100 | 10.90 | 10.66 | 54.47 | 56.93 | 65.37 | 67.60 | 14.99 | 14.12 |
| 200 | 15.06 | 14.48 | 63.30 | 65.47 | 78.36 | 79.95 | 23.28 | 22.32 |
| 273.16 | 17.95 | 17.26 | 68.43 | 70.40 | 86.37 | 87.66 | 28.20 | 27.23 |
| 298.16 | 18.87 | 18.16 | 70.04 | 71.95 | 88.91 | 90.11 | 29.64 | 28.66 |
| 300 | 18.94 | 18.23 | 70.15 | 72.06 | 89.09 | 90.29 | 29.74 | 28.76 |
| 400 | 22.26 | 21.48 | 76.07 | 77.76 | 98.33 | 99.24 | 34.41 | 33.42 |
| 500 | 25.04 | 24.22 | 81.34 | 82.86 | 106.39 | 107.08 | 37.77 | 36.78 |
| 600 | 27.38 | 26.53 | 86.12 | 87.48 | 113.50 | 114.01 | 40.21 | 39.22 |
| 800 | 31.02 | 30.14 | 94.53 | 95.64 | 125.55 | 125.77 | 43.38 | 42.39 |
| 1000 | 33.70 | 32.79 | 101.75 | 102.66 | 135.45 | 135.45 | 45.24 | 44.25 |
| 1500 | 37.98 | 37.05 | 116.31 | 116.85 | 154.29 | 153.89 | 47.46 | 46.47 |
| 2000 | 40.48 | 39.53 | 127.60 | 127.87 | 168.09 | 167.40 | 48.37 | 47.37 |

[a] The units are calories per degree per mole.

[b] $E_0^\circ$ is the energy per mole of the perfect gas at 0°K.

## CONCLUSIONS

The 21 fundamentals of $C_2F_5CN$ have been located and assigned on the basis of a structure with $C_s$ symmetry. The shapes of the gas-phase infrared bands and a normal co-ordinate calculation were helpful in making the assignments. Qualitative descriptions based on the group vibration concept were shown by the normal co-ordinate calculation to be invalid in most cases and force constants could not be transferred from $CF_3CN$ to $C_2F_5CN$.

No evidence was found for hot bands associated with the C≡N stretching fundamental. The $CF_3$ torsion was located at 63 $cm^{-1}$, a similar frequency to that observed for other molecules containing the $CF_3$ group.

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