# The Vapor-Phase Infrared and Raman Spectra of $p$-Difluorobenzene ($h_4$) and ($d_4$)

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This new study of the vapor-phase infrared and Raman spectra of $p$-difluorobenzene ($h_4$) and ($d_4$) includes assignments from the high-resolution electronic spectrum, from fluorescence spectra, and one assignment from the two photon electronic spectrum. A new set of frequencies and assignments has been made for the fundamentals of this important intermediate-sized molecule. The most important changes concern the assignments previously made for the low-frequency $a_u$ mode ($\nu_8$), two members of the $b_{2u}$ class ($\nu_{19}$ and $\nu_{20}$), and one very important change for the lowest frequency fundamental of the $b_{3u}$ (out-of-plane) class ($\nu_{30}$), which has been observed directly in the far infrared. The results are all corroborated by the assignments of the perdeuterated analog where changes in previous assignments of Fermi resonance pairs have also been made. Some interesting differences between the Raman spectra of the vapor and the liquid perproto compounds have not been adequately explained in this study. © 1985 Academic Press, Inc.

## INTRODUCTION

There have been several reasonably recent studies of the $p$-dihalogenobenzenes (*1–6*), and at least one study which included some perdeuterated compounds (*6*). In most of these, the Raman spectra were obtained from solution and liquid phases and they are not, therefore, necessarily appropriate to a study of the vapor-phase electronic spectrum or direct comparison with vapor-phase infrared frequencies. Furthermore, earlier infrared studies were mostly confined to frequencies higher than ~600 cm$^{-1}$, with one important exception (*7*), and it has been necessary to both confirm and improve upon the frequencies previously quoted for the lowest energy molecular vibrations.

$p$-Difluorobenzene has recently become of some considerable interest (*8–10*) since it is a molecule which is very stable, has excellent fluorescence and absorption spectra, and has a manageable number of vibrational degrees of freedom (30). For these reasons it has been used for studies of vibrational energy redistribution processes and allied relaxation phenomena.

## EXPERIMENTAL DETAILS

The mid-infrared spectra were recorded on a Beckman IR4240 spectrometer with a resolution of ~2 cm$^{-1}$ and with a calibrated precision of ~1 cm$^{-1}$. The far-

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infrared spectra were observed with a Digilab FTIR20 with a resolution and calibrated precision of $\pm 0.5$ cm$^{-1}$ over the range 50 to 550 cm$^{-1}$. Water vapor, hydrogen chloride gas, and ammonia were used for frequency calibrations. Raman spectra were taken on a Spex Ramalog spectrometer with a 2-cm$^{-1}$ slitwidth using various argon ion and helium–neon laser lines. All spectra were taken on more than a single occasion with varying excitation wavelengths of 4880 and 6328 Å and various vapor pressures. No systematic shifts of frequency were found for different excitation frequencies.

Vapor pressures used varied from microns for the infrared spectra to $\sim 2$ atm for some of the Raman spectra. Depolarization ratios were calibrated with benzene and carbon tetrachloride to allow for grating bias.

The numbering convention is that for $D_{2h}(V_h)$ molecules recommended by Mulliken ($11$). In this scheme the number of vibrations in the various classes is $6a_g + 2\bar{a}_u + 1\bar{b}_{1g} + 5b_{1u} + 3\bar{b}_{2g} + 5b_{2u} + 5b_{3g} + 3\bar{b}_{3u}$. The superscript bar over a class indicates that the vibrations are out-of-plane. The perdeuterated compound was obtained from two sources. One sample was contributed (see Acknowledgments) and the other was synthesized by us. It analyzed to 97 atom% deuterium by mass spectroscopy with 91% $d_4$ species.

## RESULTS

These are given in Tables I($h_4$) and I($d_4$) with a summary of the fundamentals in Table II. The spectra are illustrated as Figs. 1$_{v,l}$($h_4$) and 1$_{v,l}$($d_4$). It should immediately be noted that the fundamentals have been labeled, as previously specified, in order of decreasing frequency within a class but this must not, of course, be construed to imply that the normal coordinates and vector description of the vibrations of p-$C_6H_4F_2$ ($h_4$) and ($d_4$) having the same label $i$ (in $\nu_i$) are similar, let alone nearly identical ($3$). This comment has been made because of the possibility of ambiguity arising in the discussion as to the identity of particular fundamentals. This requires us to deal specifically—and separately—with $\nu_i(h_4)$ and $\nu_i(d_4)$ rather than always simply using the same argument for both. The issue is more obvious for similar compounds such as p-$C_6H_4F_2$ and p-$C_6H_4I_2$ where, e.g., $\nu_6$ is a strongly halogen-stretching motion in the latter but not in the former ($3$). The very significant differences between the actual motions of the $h_4$ and $d_4$ "isomers" will be discussed at some length in the analysis of the high-resolution electronic spectrum ($12$).

At this stage it is also necessary to point out that there are some important differences between our results and those reported previously. The first difference applies to the frequency of the $\nu_5(a_g)$ mode of $d_4$. Specifically, we find an intense Raman band at 793 cm$^{-1}$ and not at 780 cm$^{-1}$ as reported by Gates et al. ($6$). We find it to be the strongest band in the spectrum and almost unshifted from liquid to vapor phase.

The second difference concerns the question of Fermi resonance between $\nu_5(h_4)$ and ($d_4$) with other levels in their respective manifolds ($10$). There is a peculiar reversal of intensity from vapor to liquid in the $h_4$ case and a significant change in the relative intensities of the bands in the $d_4$ spectrum which are $>70$ cm$^{-1}$ apart (see below).

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## TABLE I

## $(h_4)$

(a)  Raman Spectra

| Liquid | | | Vapour | |
|---|---|---|---|---|
| $\nu(cm^{-1})$ | Relative Intensity | Assignment | $\nu(cm^{-1})$ | Relative Intensity |
| 3231 | (2) | $[2\nu_2(a_g)]$, $A_g$ | | |
| 3199 | (2) | | | |
| 3084 | (100) | $\nu_1(a_g)$ | 3088 | (100) |
| 3080 | * | $\nu_{23}(b_{3g})$ | 3085 | (5) |
| | | $[\nu_3(a_g)+\nu_5(a_g)+2\nu_6(a_g)]$,$A_g$ | 3014 | (2) |
| 3004 | (6) | $[2\nu_{11}(b_{1u})]$, $A_g$ | | |
| 2899 | (2) | $[\nu_2(a_g) + \nu_{25}(b_{3g})]$, $B_{3g}$ | | |
| 2588 | (2) | $[\nu_{11}(b_{1u}) + \nu_{21}(b_{2u})]$, $B_{3g}$ | | |
| 2570 | (3) | $[2\nu_{25}(b_{3g})]$, $A_g$ | | |
| 1619 | (11) | $\nu_2(a_g)$ | 1615 | (3) |
| 1606 | (3) | $[2\nu_9(b_{1g})]$, $A_g$ | | |
| 1388 | (1) | $[2\nu_{16}(b_{2g})]$, $A_g$ | | |
| 1285 | (3) | $\nu_{25}(b_{3g})$ | | |
| 1244 | (42) | $\nu_3(a_g)$ | 1257 | (30) |
| 1141 | (14) | $\nu_4(a_g)$ | 1140 | (5) |
| 1019 | (2) | $[\nu_{17}(b_{2g})+\nu_{26}(b_{3g})]$, $B_{1g}$ | 1013 | (2) |
| 895 | (1) | $[2\nu_6(a_g)]$, $A_g$ | 897 | (2) |
| | | $[2\nu_{27}(b_{3g})]$, $A_g$ | 867 | (16) |
| 859 | (68) | $\nu_5(a_g)$ | 859 | (73) |
| 840 | (89) | $[2\nu_8(a_u)]$, $A_g$ | 840 | (35) |
| | | | 834 | (15) |
| 799 | (2) | $\nu_9(b_{1g})$ | | |
| 695 | (5) | $\nu_{16}(b_{2g})$ | | |
| 636 | (23) | $\nu_{26}(b_{3g})$ | 635 | (6) |
| 451 | (84) | $\nu_6(a_g)$ | 450 | (37) |
| 376 | (47) | $\nu_{17}(b_{2g})$ | 374 | (9) |

(b)  Vapour Phase Infrared

| $\bar{\nu}\ cm^{-1}$ | Intensity | Contour | Assignments |
|---|---|---|---|
| 3148 | vw | - | |
| 3126 | vw | A | $[\nu_2(a_g)+\nu_{11}(b_{1u})]$ |
| 3091 | vw | B | $\nu_{18}(b_{2u})$ |
| 3072 | m | A | $\nu_{10}(b_{1u})$ |
| 3032 | vw | - | |

TABLE I—*Continued*

(b)   Vapour Phase Infrared (continued)

| $\bar{\nu}$ cm$^{-1}$ | Intensity | Contour | Assignments |
|---|---|---|---|
| 2896 | vw | – | |
| 2768 | vw | A | $[\nu_3(a_g)+\nu_{11}(b_{1u})]$ |
| 2559 | vw | C | $[\nu_7(a_u)+\nu_{24}(b_{3g})]$ |
| 2476 | w | – | |
| 2445 | vw | | |
| 2367 | vw | A | $[\nu_4(a_g)+\nu_{12}(b_{1u})]$, $[\nu_{21}(b_{2u})+\nu_{25}(b_{39})]$ |
| 2350 | vw | – | |
| 2297 | vw | B | $[\nu_{13}(b_{1u})+\nu_{25}(b_{39})]$ |
| 2227 | vw | B | $[\nu_4(a_g)+\nu_{21}(b_{2u})]$ |
| 2074 | vw | – | |
| 1995 | w | A | $[\nu_3(a_g)+\nu_{14}(b_{1u})]$ |
| 1865 | m | B | $[\nu_{12}(b_{1u})+\nu_{26}(b_{39})]$ |
| 1762 | vw | ? | $[\nu_{15}(b_{2g})+\nu_{28}(b_{3u})]$, $[\nu_3(a_g)+\nu_{29}(b_{3u})]$ |
| 1737 | w | A | $[\nu_{20}(b_{2u})+\nu_{27}(b_{3u})]$ |
| 1633 | w | B | $\nu_{19}(b_{2u})$ |
| 1534 | m | A,B | $[\nu_{16}(b_{2g})+\nu_{28}(b_{3u})]$, $[\nu_6(a_g)+\nu_{21}(b_{2u})]$ |
| 1515 | vs | A | $\nu_{11}(b_{1u})$ |
| 1468 | vw | – | |
| 1456 | vw | – | |
| 1431 | m | A+C | $[\nu_{15}(b_{2g})+\nu_{29}(b_{3u})]$ + $[\nu_{14}(b_{1u})+\nu_{16}(b_{2g})]$ |
| 1415 | vw | C | $[\nu_3(a_g)+\nu_{30}(b_{3u})]$ |
| 1306 | vw | B | $\nu_{20}(b_{2u})$ |
| 1229 | vs | A | $\nu_{12}(b_{1u})$ |
| 1212 | m | A | $[\nu_{17}(b_{2g})+\nu_{28}(b_{3u})]$ |
| 1201 | s | C | $\{\nu_{16}(b_{2g})+\nu_{29}(b_{3u})\}$ |
| 1189 | s | A | $[\nu_6(a_g)+\nu_{14}(b_{1u})]$ |
| 1085 | m | B | $\nu_{21}(b_{2u})$ |
| 1014 | w | A | $\nu_{13}(b_{1u})$ |
| 893 | vw | – | |
| 879 | w | A | $[\nu_{17}(b_{2g})+\nu_{29}(b_{3u})]$ |
| 838 | vs | C | $\nu_{28}(b_{3u})$ |

TABLE I—*Continued*

(b)   Vapour Phase Infrared (continued)

| $\bar{\nu}$ cm$^{-1}$ | Intensity | Contour | Assignments |
|---|---|---|---|
| 769 | vw | A | $[\nu_{15}(b_{2g})-\nu_{30}(b_{3u})]B_{1u}$ |
| 742 | vs | A | $\nu_{14}(b_{1u})$ |
| 686 | vw | A | (impurity?) |
| 505 | s | C | $\nu_{29}(b_{3u})$ |
| 348 | m | B | $\nu_{22}(b_{2u})$ |
| 157.5 | w | C | $\nu_{30}(b_{3u})$ |

Table I   (d$_4$)

(a)   Raman Spectra

| Liquid | | | Vapour | |
|---|---|---|---|---|
| $\nu$(cm$^{-1}$) | Relative Intensity | Assignment | $\nu$(cm$^{-1}$) | Relative Intensity |
| 2384 | (1) | $[\nu_2(a_g)+\nu_5(a_g)]$, $A_g$ | | |
| 2367 | (2) | $[\nu_{19}(b_{2u})+\nu_{21}(b_{2u})]$, $A_g$ | | |
| 2328 | (3) | | | |
| 2307 | (51) | $\nu_{23}(b_{3g})$ and $\nu_1(a_g)$ | 2309 | (50) |
| | | | 2295 | (5) |
| 2293 | (17) | $[\nu_2(a_g)+2\nu_{22}(b_{2u}),A_g]$, $A_g$ | 2285 | (16) |
| 2278 | (11) | $[2\nu_7(a_u)$, $A_g + 2\nu_{17}(b_{2g}),A_g]$, $A_g$ | | |
| 2222 | (1) | $[\nu_2(a_g)+\nu_9(b_{1g})]$, $B_{1g}$ | | |
| 2210 | (1) | $[\nu_2(a_g)+\nu_{26}(b_{3g})]$, $B_{3g}$ | | |
| 1596 | (8) | $\nu_2(a_g)$ | 1595 | (4) |
| 1579 | (2) | $2\nu_5(a_g)$, $A_g$ | | |
| 1528 | (?) | | | |
| 1456 | (1) | $2\nu_{28}(b_{3u})$, $A_g/[\nu_5(a_g)+\nu_{25}(b_{3g})]$, $B_{3g}$ | | |
| 1242 | (9) | $2\nu_9(b_{1g})$, $A_g$ | 1248 | (33) |
| 1231 | (30) | $[\nu_5(a_g)+\nu_6(a_g)]$, $A_g$ | 1237 | (15) |
| 1202 | (1) | | | |
| 1010 | (1) | | | |
| 935 | (1) | | | |
| | | | 872 | (20) |
| 869 | (40) | $\nu_4(a_g)$ | 866 | (70) |
| 855 | (9) | $[\nu_6(a_g)+\nu_{27}(b_{3g})]$, $B_{3g}$ | 855 | (7) |

TABLE I—*Continued*

| Liquid | | | Vapour | |
|---|---|---|---|---|
| $\nu(cm^{-1})$ | Relative Intensity | Assignment | $\nu(cm^{-1})$ | Relative Intensity |
| 842 | (24) | $[2\nu_{29}(b_{3u})]$, $A_g$ | 839 | (24) |
| 839 | (18) | $[\nu_{14}(b_{1u})+\nu_{30}(b_{3u})]$, $B_{2g}$ | 830 | (13) |
| 829 | (6) | | | |
| 793 | (100) | $\nu_5(a_g)$ | 793 | (100) |
| 746 | (2) | $[2\nu_8(a_u)]$, $A_g$ | 738 | (3) |
| 622 | (12) | | | |
| 616 | (30) | $\nu_{26}(b_{3g})$ | 614 | (11) |
| 601 | (10) | | 600 | (?) |
| 448 | (50) | $\nu_6(a_g)$ | 446 | (45) |
| 363 | (25) | $\nu_{17}(b_{2g})$ | 358 | (11) |

(b)  Vapour Phase Infrared

| $\bar{\nu}\ cm^{-1}$ | Intensity | Contour | Assignments |
|---|---|---|---|
| 3156 | vw | | |
| 3096 | vw | B | $[\nu_5(a_g)+\nu_{18}(b_{2u})]$ |
| 3075 | | | |
| 3073 | vw | A | $[\nu_5(a_g)+\nu_{10}(b_{1u})]$ |
| 2925 | w | B,C,A | $[\nu_2(a_g)+\nu_{19}(b_{2u})]$, |
| 2923 | | | $[\nu_9(b_{1g})+\nu_{18}(b_{2u})]$, |
| | | | $[\nu_{18}(b_{2u})+\nu_{26}(b_{3g})]$ |
| 2875 | w | C | $[\nu_{10}(b_{1u})+\nu_{16}(b_{2g})]$ |
| 2873 | | | |
| 2718 | | | |
| 2716 | vw | A | $[\nu_{18}(b_{2u})+\nu_{27}(b_{3g})]$ |
| 2680 | | | |
| 2678 | w | B | $[\nu_{10}(b_{1u})+\nu_{27}(b_{3g})]$ |
| 2526 | vw | | |
| 2450 | | B,A | $[\nu_{11}(b_{1u})+\nu_{25}(b_{3g})]$, |
| | | | $[\nu_2(a_g)+\nu_{13}(b_{1u})]$ |
| 2426 | vw | | |
| 2380 | vw | B | $[\nu_{13}(b_{1u})+\nu_{24}(b_{3g})]$ |
| 2376 | w | A | $[\nu_3(a_g)+\nu_{12}(b_{1u})]$ |
| 2306 | w | B | $\nu_{18}(b_{2u})$ |
| 2302 | w | C | $[\nu_7(a_u)+\nu_{24}(b_{3g})]$ |
| 2276 | m | A,A | $\nu_{10}(b_{1u})$, $[\nu_{14}(b_{1u})+\nu_2(a_g)]$ |
| 2272 | | | |

TABLE I—*Continued*

(b)  Vapour Phase Infrared (continued)

| $\bar{\nu}$ cm$^{-1}$ | Intensity | Contour | Assignments |
|---|---|---|---|
| 2231 | vw | A | $[\nu_5(a_g)+\nu_{11}(b_{1u})]$ |
| 2227 | vw | | |
| 2104 | | A | $[\nu_3(a_g)+\nu_{13}(b_{1u})]$ |
| 2098 | w | | |
| 1965 | vw | | |
| 1933 | w | A | $[\nu_{14}(b_{1u})+\nu_3(a_g)]$ |
| 1927 | w | | |
| 1727 | vw | A(C?) | $[\nu_4(a_g)+\nu_{13}(b_{1u})]$, |
| | | | $[\nu_{12}(b_{1u})+\nu_{16}(b_{2g})]$ |
| 1650 | w | A | $[\nu_5(a_g)+\nu_{13}(b_{1u})]$ |
| 1585 | vw | | |
| 1570 | vw | | |
| 1557 | w | B | $[\nu_7(a_u)+\nu_{15}(b_{2g})]$ |
| 1556 | vw | A | $[\nu_{14}(b_{1u})+\nu_4(a_g)]$ |
| 1525 | vw | C | $[\nu_5(a_g)+\nu_{28}(b_{3u})]$ |
| 1496 | vw | | |
| 1479 | vw | A | $[\nu_5(a_g)+\nu_{14}(b_{1u})]$ |
| 1463 | s | C | $[\nu_{14}(b_{1u})+\nu_{15}(b_{2g})]$ |
| 1440 | vs | A | $\nu_{11}(b_{1u})$ |
| 1404 | vw | C | $[\nu_3(a_g)+\nu_{30}(b_{3u})]$ |
| 1384 | m | B | $[\nu_7(a_u)+\nu_{16}(b_{2g})]$ |
| 1369 | w | | |
| 1358 | w | | |
| 1329 | vw | B | $\nu_{19}(b_{2u})$ |
| 1284 | vw | B,C | $\nu_{20}(b_{2u})$, $[\nu_{14}(b_{1u})+\nu_{16}(b_{2g})]$ |
| 1250 | vw | B | $[\nu_6(a_g)+\nu_{21}(b_{2u})]$ |
| 1220 | w | C,C | $[\nu_5(a_g)+\nu_{29}(b_{3u})]$, |
| | | | $[\nu_{13}(b_{1u})+\nu_{17}(b_{2g})]$ |
| 1202 | m | A | $[\nu_{15}(b_{2g})+\nu_{29}(b_{3u})]$ |
| 1138 | vs | B | $[\nu_5(a_g)+\nu_{22}(b_{2u})]$ |
| 1128 | vs | A | $\nu_{12}(b_{1u})$ |
| 1104 | w | | |
| 1044 | vw | A | $[\nu_{14}(b_{1u})+\nu_{17}(b_{2g})]$ |
| 1024 | vw | C | $[\nu_4(a_g)+\nu_{30}(b_{3u})]$, |
| | | | $[\nu_{16}(b_{2g})+\nu_{29}(b_{3u})]$ |
| 891 | w | | |

TABLE I—*Continued*

(b) Vapour Phase Infrared (continued)

| $\bar{\nu}$ cm$^{-1}$ | Intensity | Contour | Assignments |
|---|---|---|---|
| 858 | s | A | $\nu_{13}(b_{1u})$ |
| 839 | vw | | |
| 800 | m | B | $\nu_{21}(b_{2u})$ |
| 787 | vw | B | $[\nu_6(a_g)+\nu_{22}(b_{2u})]$ |
| 739 | w | | |
| 730 | s | C | $\nu_{28}(b_{3u})$ |
| 684 | s | A | $\nu_{14}(b_{1u})$ |
| 444 | m | | |
| 424 | s | C | $\nu_{29}(b_{3u})$ |
| 416 | m | | |
| 343 | m | B | $\nu_{22}(b_{2u})$ |
| 156 | w | C | $\nu_{30}(b_{3u})$ |

Third, there are two major changes in the frequencies of the $b_{2u}$ fundamentals, $\nu_{19}$ and $\nu_{20}$, compared with previous studies [although Schmid *et al.* (*4*) also noted some disagreement with previous assignments].

Finally, there are systematic and widespread (but not exclusive) increases in the vapor-phase frequencies compared with those of the liquid, particularly in the Raman spectra.

TABLE II

Ground State Vibrational Fundamental Frequencies of $p$-C$_6$H$_4$F$_2$ and $p$-C$_6$D$_4$F$_2$

| | $\nu_i$ | $(h_4)^*$ | $(d_4)^*$ | $(h_4)^\dagger$ | $(d_4)^\dagger$ | | $\nu_i$ | $(h_4)^*$ | $(d_4)^*$ | $(h_4)^\dagger$ | $(d_4)^\dagger$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $a_g$ | 1 | 3088. | 2309. | 3084 | 2313 | $\overline{b_{2g}}$ | 15 | 928 | 780 | 928 | 780 |
| | 2 | 1615. | 1595 | 1617 | 1595 | | 16 | 692 | 600 | 692 | 600 |
| | 3 | 1257.3 | 1249.7 | 1245 | 1229 | | 17 | 374. | 358. | 375 | 366 |
| | 4 | 1140. | 866.9 | 1142 | 847 | | | | | | |
| | 5 | 858.6 | 793.0 | 858 | 780 | $b_{2u}$ | 18 | 3073. | 2307. | 3074 | 2310 |
| | 6 | 449.8 | 446.3 | 451 | 453 | | 19 | 1633. | 1328 | 1437 | 1328 |
| $\overline{a_u}$ | 7 | 945 | 780 | 943 | -- | | 20 | 1306. | 1286. | 1285 | 1287 |
| | 8 | 420 | 367 | 405 | -- | | 21 | 1085. | 802. | 1085 | 802 |
| $\overline{b_{1g}}$ | 9 | 800 | 614 | 800 | 614 | | 22 | 348 | 343.5 | 350 | 348 |
| $b_{1u}$ | 10 | 3073. | 2276. | 3065 | 2277 | $\overline{b_{3g}}$ | 23 | 3085. | 2304. | 3084 | 2304 |
| | 11 | 1514. | 1440. | 1511 | 1435 | | 24 | 1617 | 1523 | 1617 | 1523 |
| | 12 | 1228. | 1129. | 1225 | 1130 | | 25 | 1285 | 1008 | 1285 | 1008 |
| | 13 | 1014. | 858. | 1012 | 859 | | 26 | 635. | 614. | 635 | 614 |
| | 14 | 740. | 685. | 737 | 685 | | 27 | [434] | [406] | 430 | 406 |
| | | | | | | $\overline{b_{3u}}$ | 28 | 838. | 731. | 833 | 732 |
| | | | | | | | 29 | 505. | 424. | 509 | 422 |
| | | | | | | | 30 | 157.5 | 155.5 | 170 | 163 |

*From this study utilizing Infrared, Raman, Fluorescence and Absorption Studies. (See also ref. 12).

†Previous studies - a summary. The values in Ref. 6 are given since this was the latest previous study.

Frequencies quoted correct to 1 decimal place are from vapour phase infrared, Raman, fluorescence and electronic absorption studies. Where the accuracy is only $\pm$ 1 cm$^{-1}$ i.e., there is no precise measurement from the electronic spectrum, and the measurement is from the vapour phase, the number is followed by a period.

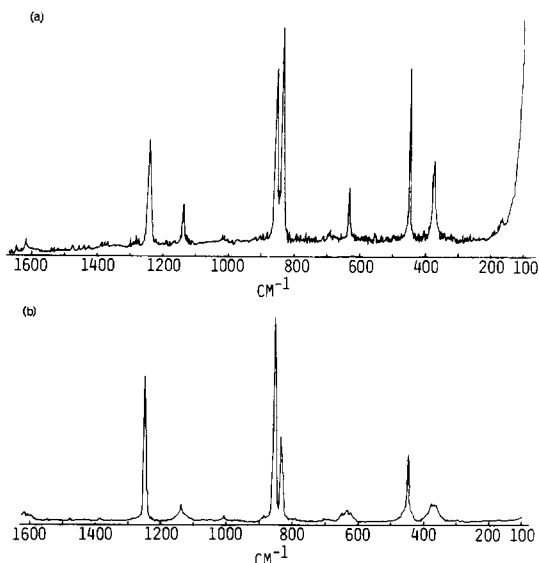Out-of-plane vibrations are indicated by a bar over the vibration class (e.g. $\bar{a}_u$).

FIG. 1. (h$_4$). The Raman spectrum of $p$-difluorobenzene(perproto); (a) liquid, (b) vapor.

## DISCUSSION

The resolution of the infrared bands is sufficient for the rotational contours to be well established and the asymmetry parameter, $\kappa$, is not so small ($-0.87$ for h$_4$, $-0.82$ for d$_4$) as to cause serious deviations from the Badger–Zumwalt $A$, $B$, and $C$ contours (13), although there are some features which indicate that the asymmetry effects are just beginning to show up. In the axis scheme which we have adopted (11), $A \equiv B_{1u}$, $B \equiv B_{2u}$, and $C \equiv B_{3u}$.

*Class a$_g$*

There are six members and all are present, to varying degrees of intensity, in the Raman spectrum. There are some changes in the frequencies from the previous, usually liquid-phase, values but the main point of interest in this group is $\nu_5$ in both h$_4$ and d$_4$ species. As mentioned above, the largest difference between our results and the earlier work is our assignment of the very strong, polarized line at 793 cm$^{-1}$ (793 cm$^{-1}$ in liquid) in d$_4$ as $\nu_5$(d$_4$). We are unable to confirm the 828/867-cm$^{-1}$ Fermi diad previously reported (6). There is a line at 869 cm$^{-1}$ which we have assigned as $\nu_4$ but we find no evidence of any strong, polarized band near 828 cm$^{-1}$. We must conclude that the line was due to an impurity or to an extraneous line of the excitation source. Our assignment is also completely confirmed from another source—electronic spectroscopic "hot" bands (12) where the frequency is 793.0 cm$^{-1}$. The assignment of the relatively strong band at 866 cm$^{-1}$ in the vapor and 869 cm$^{-1}$ in the liquid phase to $\nu_4$(d$_4$) is placed beyond doubt by its appearance in the "hot" bands of the electronic spectrum (12) as a progression, its first member being displaced from the origin by $-866.9$ cm$^{-1}$. There is a noticeable enhancement of the peak intensity of $\nu_6$ relative to $\nu_5$ in the liquid phase compared with that in the vapor and this is coupled with an apparent reduction in the absolute intensity of $\nu_6$. We have not carried out an extensive study, but it is at least clear that the
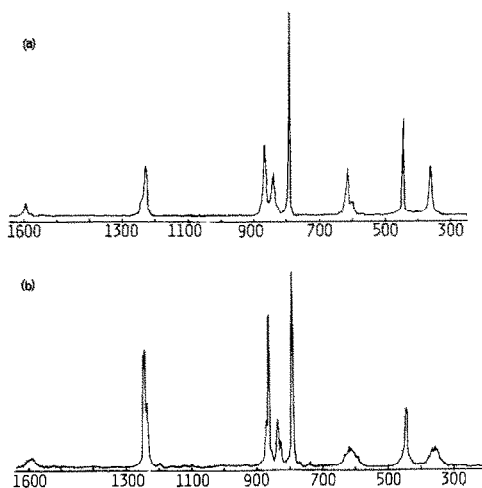
FIG. 1 (d₄). The Raman spectrum of p-difluorobenzene(perdeutero): (a) liquid, (b) vapor.

intensity reduction in $\nu_6$ is not as great as it seems to be once the integrated intensity is considered, instead of only the intensity of the $Q$-form branch maximum. It would appear, from further consideration involving $\nu_{26}$ and $\nu_{17}$, that liquid forces decidedly enhance $Q$-form intensity in the Raman spectrum, probably due to restricted rotation in the liquid, and this effect is no doubt involved in the $\nu_6$ intensity change.

Reference to the spectra of the $d_4$ species in Fig. $1_v(d_4)$ shows clearly what appear to be subsidiary maxima on the high-frequency side of $\nu_4$ and the low-frequency side of the band with a maximum of 841 cm$^{-1}$ ($2\nu_{29}$; see below). These maxima and the associated minima have very sharp profiles, and they are assumed to arise from a combination of Fermi resonance effects and, perhaps, asymmetric rotor splitting of the $Q$-form branches. This effect is noticeable in $\nu_3(d_4)$ and is also seen in the $Q$-form branches of the electronic spectrum (12). These features are not, therefore, assigned as separate fundamentals, overtones or combination bands.

The assignment of $\nu_5(h_4)$ also has some unusual aspects. From the vapor Raman spectrum, as confirmed by both the electronic "hot" bands and an electronic fluorescence spectrum (12), $\nu_5$ is the band at 859 cm$^{-1}$ (858.6 cm$^{-1}$ from the electronic spectrum (12)). It is stronger than the band at 840 cm$^{-1}$ (839.4 cm$^{-1}$ from the electronic spectrum (12)) which is assigned as $2\nu_8$. In the liquid phase, however, the 840-cm$^{-1}$ band is *stronger* than the 859-cm$^{-1}$ band, and both are very strongly polarized. It was this fact that originally led to both of them being assigned as $a_g$ fundamentals (2). This was later corrected by Stojiljkovic and Whiffen (3) who, however, incorrectly attributed the 840-cm$^{-1}$ band to $2\nu_{27}$ but correctly assigned the 858.6-cm$^{-1}$ band as $\nu_5(h_4)$.

The intensity reversal of the 859- and 840-cm$^{-1}$ bands in the liquid could be explained by invoking a change in the degree of Fermi interaction brought about by the liquid forces (leading to a rather large liquid shift of the 840-cm$^{-1}$ band) but there are some difficulties with this. A simple change in the mixing coefficients is not surprising but a *reversal* of intensity cannot occur without a reassignment of the 840-cm$^{-1}$ band of the liquid as $\nu_5(h_4)$ and the 859-cm$^{-1}$ ($h_4$) band as $2\nu_8$. This

is, of course, possible but it requires a very large liquid phase shift for the $2\nu_8$ level, followed by a very strong Fermi interaction. This is very difficult to believe when, in fact, $\nu_5(d_4)$ is almost unshifted by liquid forces.

The main problem with invoking any large degree of Fermi resonance is that, first, the combination bands of the $a_g$ class are almost *exactly* predictable using 858.6 cm$^{-1}$ as the frequency of $\nu_5(h_4)$ and, second, even though the overtone $2\nu_5(h_4)$ is anharmonic, the problem is that the level $2\nu_5(h_4)$ is significantly *higher* (by 5.5 cm$^{-1}$) than $2 \times 858.6$ cm$^{-1}$ rather than lower—as it would be if the fundamental of $\nu_5(h_4)$ had been shifted to higher energies by $2\nu_8$. The predictability is confirmed in both the electronic absorption and fluorescence spectra (*12*). This conclusion also tends to invalidate the postulate that there is a very large mixing of $\nu_5(h_4)$ and $2\nu_6(h_4)$ (*9*) and the matter will be discussed at some length in the analysis of the electronic spectrum (*12*).

There is no doubt, however, that the assignment of $\nu_5(h_4)$ in the vapor is the correct one, and the electronic spectrum confirms not only this but also the assignment of the 840-cm$^{-1}$ band (*12*) as $2\nu_8$. There is a band at 842 cm$^{-1}$ (*l*) and 839 cm$^{-1}$ (*v*) in $d_4$ which can only be assigned as $2\nu_{29}$. The overtone of $\nu_8$ for $h_4$ appears in this region but the observed frequency is far too high to be attributed to the same origin in $d_4$. The intensity of $2\nu_{29}$ is enhanced only because of mixing with $\nu_4/\nu_5$ and since $2\nu_8$ for $d_4$ has no $a_g$ modes nearby, it is seen neither in the Raman nor in the electronic spectra (*12*).

The $\nu_3$ fundamentals of both $h_4$ and $d_4$ show significant increases in frequency of 13 and 6 cm$^{-1}$, respectively, in changing from the liquid to the vapor phase, and the vapor Raman values are confirmed from "hot band" studies of the electronic spectrum (*12*). The more precise values of 1257.3 and 1249.7 cm$^{-1}$ given in Table II were obtained from the electronic spectrum. It is worth noting that $\nu_3(h_4)$ has been variously described in terms of valence field approximations as containing a great deal of C–F stretching (*1*) or else as a C–H bending mode (*3*). The assignment of $\nu_4(d_4)$ and the essentially unchanged frequency of $\nu_3(d_4)$ compared with $\nu_3(h_4)$ rules in favor of C–F stretching as the preferable "form of description" in both $h_4$ and $d_4$ species.

The above conclusion is strengthened by the assignment of $\nu_4(d_4)$ as the strongly polarized line at 869 cm$^{-1}$ (*l*) and 866 cm$^{-1}$ (*v*) [866.9 cm$^{-1}$ in the electronic spectrum (*12*)]. This mode becomes Franck–Condon active in the electronic spectrum, no doubt from "mixing" with the "ring-breathing" symmetry coordinate, to yield two modes which are hybrids of the simply expressed valence field symmetry coordinate pictures [see, e.g., Refs. (*3, 4, 14, 15*)].

There can be no doubt concerning the indentification of the 866-cm$^{-1}$ frequency as the predominantly C–D bending mode. Its activity in the electronic spectrum of the $d_4$ species, in the absence of any activity of the 1140-cm$^{-1}$ frequency in the $h_4$ species, strongly suggests this kind of mixing. In addition, the presence of $2\nu_{29}(d_4)$ at 841 cm$^{-1}$ adds a third participant in any Fermi resonance.

*Class $\bar{a}_u$*

Neither of the two members of this class has been directly observed since they are infrared and Raman inactive. On the other hand, $\nu_8$ is strongly Franck–Condon

active in the electronic spectrum both in sequences and as an overtone vibronic origin (*12*). The fundamental also appears as a single quantum in both the upper and lower states in the two-photon spectrum (*16*) of $h_4$. The two-photon spectrum was not recorded at high resolution, however, and the values of $\nu_8''$ and $\nu_8'$ are not accurate to better than $\pm 2$ cm$^{-1}$ (see below). From this source, $\nu_8''(h_4) \sim 420$ cm$^{-1}$.

The analysis of the electronic spectrum (*12*) gives a completely unambiguous assignment for the overtone $2\nu_8''$ as 839.4 cm$^{-1}$ ($h_4$) and 734.1 cm$^{-1}$ ($d_4$). The frequency of the fundamental (assumed harmonic) is therefore $\sim 420$ cm$^{-1}$ ($h_4$), $\sim 367$ cm$^{-1}$ ($d_4$), both $\pm 1$ cm$^{-1}$ unless the mode is very anharmonic.

Despite a careful search, no bands were found in either the infrared or Raman spectra which could be attributed unambiguously to combination bands of $\nu_7$ or $\nu_8$ so that the assignments rest entirely upon the two-photon and electronic overtone spectra. The overtone $2\nu_8''$ for $h_4$ is seen strongly in both the liquid- and vapor-phase Raman spectra at 840 cm$^{-1}$, and is the strongly polarized band originally assigned as a fundamental (*2*) but later reassigned (*3*) as $2\nu_{27}$. There can be no doubt that it is, as assigned here, $2\nu_8$. We note the fact that the polarized character of the 840-cm$^{-1}$ band suggests possible Fermi interaction between it and $\nu_5(h_4)$ at 859 cm$^{-1}$ but, as discussed above, it appears unlikely that any significant frequency shift occurs. This is part of the reason for the similar conclusion regarding $2\nu_{29}(d_4)$ and $\nu_4(d_4)$. There is a very weak band in the $d_4$ vapor Raman spectrum at 738 cm$^{-1}$ which we assign as $2\nu_8(d_4)$, and there is a "hot" band in the electronic spectrum $- 734.1$ cm$^{-1}$ from the origin (*12*). Its relative intensity in both spectra (Raman and electronic) is greatly reduced compared to its $h_4$ counterpart and we attribute this to the relative lack of "$\nu_5$ character" because of its much larger separation from $\nu_5$ (55 cm$^{-1}$ in $d_4$ vs 19 cm$^{-1}$ in $h_4$).

We have seen no sign of $\nu_7$ in our spectra—Raman or electronic—and the value given for $\nu_7$ is that found in the two-photon spectrum by Robey and Schlag (*16*). It is probably accurate to $\sim \pm 2$ cm$^{-1}$ (see below).

## Class $\bar{b}_{1g}$

Weak bands were found in the liquid Raman spectrum of $h_4$ at 799 cm$^{-1}$ and of $d_4$ at 622 cm$^{-1}$ which correspond closely to the assignments from previous work for $\nu_9$. Accordingly, no changes in previous assignments are proposed.

## Class $b_{1u}$

All of these fundamentals were observed directly in the infrared spectra of the vapor and were identified from their contours for both the $h_4$ and $d_4$ species. The frequencies for $h_4$ are in accord with the vapor spectra obtained by Ferguson *et al.* (*2*) as reassigned by later authors [e.g., see Ref. (*6*)]. The value of $\nu_{10}(h_4)$, which has been variously reported between 3088 cm$^{-1}$ (*5*) and 3067 cm$^{-1}$ (*6*), has been firmly established as 3073 cm$^{-1}$. The vapor-phase frequencies for $d_4$ are quite similar to the liquid-phase values of Gates *et al.* (*6*) with two exceptions. $\nu_{10}(d_4)$ is assigned to the *A*-type band at 2302 cm$^{-1}$, in preference to the ill-defined band at 2272 cm$^{-1}$. $\nu_{12}(d_4)$ is assigned to the *A*-type band at 1138 cm$^{-1}$, whereas the nearby band (also *A*-type) at 1128 cm$^{-1}$ is identified as $\nu_6 + \nu_{14}$.

*Class* $\overline{b_{2g}}$

Only $\nu_{17}$ was observed in the vapor but $\nu_{16}$ was also seen in the liquid phase for both $h_4$ and $d_4$. The contour of $\nu_{17}$ is somewhat broad [see Fig. $1_v(h_4)$] but the center of the band is well defined and has been taken as the origin. The bands in both $d_4$ and $h_4$ are very much sharper in the liquid phase and strongly suggest that liquid forces markedly affect the Raman selection rules probably due to restricted rotation.

*Class* $b_{2u}$

Our assignments for $h_4$ differ from the previous ones [e.g. Ref. (6)], for three of the five fundamentals. We identify $\nu_{18}$ with a *B*-type band at 3091 cm$^{-1}$, slightly to higher frequency of the stronger fundamental at 3072 cm$^{-1}$. Furthermore, we assign the *B*-type bands at 1633 and 1306 cm$^{-1}$ to $\nu_{19}$ and $\nu_{20}$, respectively. The 1437-cm$^{-1}$ frequency assigned previously as $\nu_{19}$ is probably the *A*-type combination band observed by us at 1431 cm$^{-1}$ ($\nu_{15} + \nu_{29}$). We find no vapor-phase band near 1285 cm$^{-1}$, which had been assigned as $\nu_{20}$. In this respect, we are in agreement with Schmidt *et al.* (4), who also preferred a frequency slightly above 1300 cm$^{-1}$ for $\nu_{20}$.

For $d_4$ we assign the B-type band at 1557 cm$^{-1}$ as $\nu_{19}$. The 1328-cm$^{-1}$ frequency quoted by Gates *et al.* (6) for $\nu_{19}$ is nearly identical with that of an *A*-type combination band observed by us at 1329 cm$^{-1}$ ($\nu_{16} + \nu_{28}$).

With these changes, the $d_4$ and $h_4$ assignments are completely consistent. In fact, the change of $\nu_{20}(h_4)$ from 1285 to 1306 cm$^{-1}$ makes sense of the $\nu_{20}(d_4)$ assignment of 1284 cm$^{-1}$.

*Class* $b_{3g}$

This class of vibrations is not very intense in the vapor Raman spectrum and, in fact, only $\nu_{26}$ appears with reasonable intensity, having frequencies of 635 cm$^{-1}$ ($h_4$) and 614 cm$^{-1}$ ($d_4$). In the absence of a separate C–D stretching mode in the spectrum, $\nu_{23}$ has been assigned as coincident with the $a_g$ mode $\nu_1$ of 2309 cm$^{-1}$ ($d_4$ vapor) and slightly resolved from $\nu_1(h_4)$ at 3085 cm$^{-1}$.

Despite a careful search, no sign of the $\nu_{27}$ fundamental in either $h_4$ or $d_4$ was found. Some information is available from a sequence study (*12*) in the electronic spectrum but not enough to obtain an explicit value for the $\nu_{27}$ fundamental. For this reason the value has been placed in square brackets in Table II. The implicit value comes from the electronic spectrum where the overtone band $27_0^2$ and the two sequences, $27_1^1$ and $27_2^2$ have been observed (*12*). This allows us to obtain a rough value for the $\nu_{27}$ fundamental.

*Class* $\overline{b_{3u}}$

This is one of the most interesting groups of fundamentals from the point of view of the electronic spectrum and it contains the lowest frequency molecular vibration, $\nu_{30}$, which is so active in sequence formation in that spectrum.

The infrared vapor spectrum gives perfect *C* contours for the bands at 838 cm$^{-1}$

($h_4$) and 731 cm$^{-1}$ ($d_4$), and these are clearly $\nu_{28}(h_4)$ and ($d_4$), respectively. The far-infrared spectrum yielded two more $C$-type contours at 505.0 cm$^{-1}$ ($h_4$), 157.5 cm$^{-1}$ ($h_4$), 424.0 cm$^{-1}$ ($d_4$), and 155.5 cm$^{-1}$ ($d_4$), and these are assignable as $\nu_{29}$ and $\nu_{30}$ for $h_4$ and $d_4$.

These assignments also allow rejection of the possible interpretation of the band at 348 cm$^{-1}$ [$\nu_{22}(h_4)$ in the infrared spectrum] as $\nu_{29} - \nu_{30}$, i.e., 505.0 − 157.5 ≡ 348.5 cm$^{-1}$, since the same difference spectrum for the $d_4$ species would give a band at 424.0 − 155.5 ≡ 268.5 cm$^{-1}$ whereas the infrared band is at 343.5 cm$^{-1}$ for $d_4$. This confirms the assignment given here. It is important to note that our frequencies for $\nu_{29}(h_4)$ and $\nu_{30}(h_4)$ are essentially identical with those obtained by Crowder and Scott (7), but they did not have the $d_4$ species to confirm this assignment.

The $\nu'_{30}$ fundamental of the $h_4$ species was also given by Robey and Schlag (16) from their two-photon study of the $h_4$ vapor as 122 cm$^{-1}$. The present study confirms that the accuracy of their measurements is more like ±2 cm$^{-1}$ for the non-totally symmetric frequencies since the correct value (12) for $\nu'_{30} = 119.7$ cm$^{-1}$.

Using these new vapor-phase frequencies, a study of the force field of the molecule is now under way and it is hoped that this will throw some light upon some of the still unresolved aspects of this problem.

The assignments given here are strengthened by a recent study (17) of the fluorescence spectrum of the matrix isolated compound in a medium at 4 K.

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