Supplementary information for "Vibrational Anharmonicities and Reactivity of Tetrafluoroethylene"

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1. Observed combination and difference bands

Table S1 lists combination and difference bands, the distances of hot bands from the main Q branch, and the anharmonic and isotopic shifts of \( \text{C}_2\text{F}_4 \). Compared to the similar table 1 of the Supplementary Information of [1], it is slightly updated and supplemented with the hot bands. The bands are ordered according to combination with \( \nu_1, \nu_2 \), etc., so that each combination occurs more than once in the table. Those observed only at higher pressures or longer path lengths are listed at the end of each section. Band positions were taken from the most prominent Q branch in the case of \( b_{1u} \) and \( b_{2u} \) symmetry and from the minimum for \( b_{3u} \) symmetry. (Symmetry designations as in [1], see also main text.) The wavenumbers for the latter are less accurate.

Appended to the table are some bands, whose assignment is less clear or does not fit in this scheme.

Sometimes a combination band with sharp Q branch had to be compared with a fundamental (in particular \( \nu_9 \)) with a minimum only (\( b_{3u} \) symmetry). In this case, a comparison is also presented with the band origin found in the high-resolution work [1,2] and marked "HR", e.g. "HR \( \nu_9 \)".

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lower resolution, 0-2 cm\(^{-1}\), the apparent band origins of \(\nu_9\) and \(\nu_{11}\) were at 1338.4 and 1187.0. These values were used for combination bands without sharp Q branches.)

The harmonic sums are based on the fundamental wavenumbers given in table 1 of the main text (in which only \(\nu_{10}\) is slightly revised compared to table 1 of [1]) or use the low-resolution values of \(\nu_5\) and \(\nu_9\), as just explained.

The isotopic shifts were already reported in the Supporting Information of [1]; they are unchanged here, except the observed one of \(\nu_2+\nu_6+\nu_9\): In agreement with the analysis of the Fermi resonance of this level with \(\nu_5+\nu_9\) (see below), we now assign the peak at 2616.1 (−34.4 compared to \(^{12}\)C\(_2\)F\(_4\)) to the \(\nu_2+\nu_6+\nu_9\) band of \(^{13}\)C\(_2\)F\(_4\); the feature at −47.0 may be a substructure (hot bands) of it (Fig. S2). Also the isotopic shift of \(2\nu_7\) was revised (see Table 3 and context in the main text.) As before, the calculated isotopic shifts (versus \(^{12}\)C\(_2\)F\(_4\)) are based on observed fundamental wavenumbers of the same table 1 of [1], assuming that the shifts of each component of the combination can be added up. This was usually fulfilled within about 1 cm\(^{-1}\) (compare the calculated with the observed shifts in the table) and was useful as an assignment help. However, in some cases there were deviations. They were interpreted as indications of Fermi resonances.

Shifts (or other wavenumbers) given in parentheses refer to alternative (but less preferred) assignments, where either the combination band or a component (fundamental) showed Q branches of comparable intensity.

As discussed in [1], \(\nu_5\) and \(\nu_9\) can mix in the monosubstituted isotopologue \(^{12}\)CF\(_2\)-\(^{13}\)CF\(_2\)) due to the lower symmetry, so that both bands become IR active. Furthermore, the \(\nu_2+\nu_6\) level is in Fermi resonance with \(\nu_5\), so that a third band may emerge, and this mixture will also depend on the isotopic substitution. That is, combination bands with \(\nu_5\) or \(\nu_9\) or both will show at least two bands for the mixed isotopologue, and the shifts will be irregular. The column "observed isotopic shift" lists in these cases either no value or 2-3 values in parentheses.

The anharmonic shifts were also assumed to be additive. For binary combination bands \((i \neq j)\) and for overtones we used

\[
(\nu_i+\nu_j) = \nu_i + \nu_j + \chi_{ij}
\]

and

\[
(\nu_i\nu_j) = \nu_i\nu_j + \nu_j (\nu_i - 1) \chi_{ij}
\]

\[
(\nu_i+\nu_j) = \nu_i + \nu_j + \chi_{ij}
\]

and

\[
(\nu_i\nu_j) = \nu_i\nu_j + \nu_j (\nu_i - 1) \chi_{ij}
\]
with obvious extensions for more complicated combinations. The left hand side of these equations should be read as "wavenumber of \( \text{name} \)". The additivity again helped in a few cases to decide between different assignments, where the harmonic sums were similar to each other. The column "anharmonic shift" lists only those \( x_{ij} \) derived from the positions of the combination bands and overtones (that is, not from hot bands).

For hot bands (satellites near \( \nu_i \), that is, transitions starting from a thermally populated lower level \( \nu_j \)) we used

\[
(\nu_i + \nu_j) - \nu_j = \nu_i + x_{ij} \quad \text{(or } 2x_{ij}, \text{ if } i = j)\]

again with obvious extensions. Often one can observe sequences of equidistant Q branches, corresponding to hot bands starting from higher levels \( m\nu_j \) or combination of such sequences (from \( m\nu_i + n\nu_k \)). The last equation implies that the distance of a (first) hot band from the fundamental directly indicates the corresponding anharmonic constant. This results in more accurate \( x_{ij} \) than those derived from the other two equations, where differences of large numbers must be calculated to obtain \( x_{ij} \). But combination bands allow for a direct assignment, whereas hot bands must be identified by their intensity (Boltzmann factor, table S3). In a number of cases, the anharmonic constants resulted from both combination and difference bands. Table S2 compiles the sources for each \( x_{ij} \).

Some anharmonic "constants" such as \( x_{18} \), \( x_{26} \) or \( x_{77} \) vary, depending on the exact combination band and/or isotopologue. The variation was interpreted by Fermi resonance (sec. 4.4 in the main text and below after table S3).

Table S1. Combination and difference bands of C\(_2\)F\(_4\) (recorded with 0.2 cm\(^{-1}\) resolution, all numbers in cm\(^{-1}\)). A double arrow \((\Rightarrow)\) indicates a fundamental or a shift deduced from data of this line. An equality sign \((=)\) indicates that other data (in particular isotopic shifts) were derived from the observed data of this line. The column "hot bands" indicates the shifts from the main bands ("hb" means that hot bands were observed but are not listed). "HR" refers to the high-resolution study of [1]; sometimes the intensities relative to the main Q branch and/or the lower level of the hot band are indicated. "13C" means that the peak in the natural-abundance spectrum is due to the monosubstituted isotopologue.

| Assignment  | harmonic sum/obs. position | hot bands       | anharmonic shift (from positions) | obs. isotopic shift 12C-13C / 13C-13C | calc. isotopic shift 12C-13C / 13C-13C |
|-------------|---------------------------|-----------------|------------------------------------|--------------------------------------|----------------------------------------|
| \( \nu_1 + \nu_7, \text{b2u} \) | 2279.0/ 2274.4 | \(-0.80, -2.17, -3.2, -4.5, -5.9, \) | \( x_{17} = -4.6 \) | \(-39.96 / -79.4 \) | \(-38.71 (-39.96) / -79.29 \) |
| v1+v11−v2, b1u | 2284.7/ 2280.1 | $-1.3$, $-2.3$ | $x1,11 = -4.6$ |
|-----------------|-----------------|-----------------|-----------------|
| v1+v12, b1u     | 2429.1/ 2428.7  | $-1.24$, $-2.37$, $-3.60$, $-18.4$ | $x1,12 = -0.4$ | $-34.00$ $(36.01)$ / $-70.83$ | $-34.00$ $(35.25)$ / $-70.88$ |
| v1+v7+v8, b1u   | 2788.8/ 2764.1  | $-1.67$, $-2.9$, $-8.35$, $-20.4$, $+$.. | $x18 = -18.5$ | $-45.85$ / (covered) | $32.26+14.87=47.13$ |
| v1+v11, b1u     | 3060.8/ 3056.2  | $-1.3$, $-1.9$, $-3.1$.. $-19.6$ | $x1,11 = -4.6$ | $-46.1$ $(48.74)$ / $-94.74$ | $-46.91$ $(48.16)$ / $-95.01$ |
| v1+v9, b3u      | 3212.2/ 3208.9  | (mini-Q), hb | $x19 = -3.3$ | $(23.6, -59.6)$ / $-102.6$ | $... / -106.14$, HRv9: -102.54 |
| v1−v7, b1u      | $\Rightarrow v1 = 1873.8$ / 1468.6 | $-1.6$ | $-27.1 / -56.0$ | $25.81$ $(27.06)$ / $-55.69$ |
| v1+v8−v7, b1u   | 1978.4/1958.75  | hb | $x18 = -19.65$ | $...$ |
| v1+v10, b3u     | 2083.5/ (2077.5) 2081.4 | 2 indents similar to v10 | $x1,10 = -2.1$ | $...$ |
| v1+v2−v7, b2u   | 2244.7/ 2241.6  | $-1.6$, $-7.4$ (13C), $-19.6$ | $x12 = -3.1$ | $-29.3 / 62.4$ $(64.0)$ | $-28.4$ $(29.3)$ / $-62.06$ |
| v1+v8+v12, b2u  | 2938.9/ 2918.3  | $x18 = -20.7$ | $...$ |
| v1+3v7          | 3089.4/ 3096.3  | $-0.7$ | $x17 = -3.8$ | $...$ |
| v8+v11−v2, b2u  | $\Rightarrow v2 = 776.1$ / 920.0 | $+0.7$ | $x8,11 = -0.7$ | $...$ |
| v6+v9−v2, b1u   | 1112.3/ 1110.9  | $-2.7$, $-5.4$, $-8.0$, $-10.5$ | $\Rightarrow v2 = 776.35$ | $...$ |
| v2+v12, b1u     | 1331.4/ 1332.0  | HRv9 | $x2,12 = +0.6$ | $...$ |
| v2+v11, b1u     | 1963.1/ 1961.60 | $+0.1$, $-0.7$, $-0.8$, $-10.2$ (v7), $-17.2$ (13C) | $x2,11 = -1.5$ | $-17.22 / -33.98$ | $\Rightarrow v2$ shift |
| v2+v9, b3u      | 2114.5/ 2112.5  | $x29 = -2.0$ | $... / (-41.7, -42.6) ~ -45.6$ | $... / (-43.7) -44.9$ |
| v1+v2−v7, b2u   | 2244.7/ 2241.6  | $-1.4$, $-7.4$, $-19.6$ | $x12 = -3.1$ | $... / (44.29, 45.54)$ / $-83.26$ |
| v1+v11−v2, b1u  | 2284.7/ 2280.1  | $-1.3$, $-2.3$ | $-43.8$ / (ca. -86.2) overlapped | $-44.29$ $(45.54)$ / $-83.26$ |
| v2+v8+v11, b2u  | 2472.9/ 2469.4  | $-1.1$, $-2.2$ | $...$ | $... / (48.07) -50.27$ HRv9: -46.62 |
| v2+v6+v11, b3u  | 2513.1/ 2501.8  | $... / -35.4$ or 39.0 | $... / -39.2$ | $...$ |
| v2+v6+v9, b1u   | 2664.5/ 2650.5  | $-0.80$, $-2.25$, $-2.78$, $-3.82$, $...$ | $... / -34.4$ | $... / (48.07) -50.27$ HRv9: -46.62 |
| V & V | Frequency | Intensity | Δν | Width | Notes |
|-------|------------|-----------|-----|-------|-------|
| 2ν2+ν11, b1u | 2739.2/ 2728.6 | +1.1, +1.9, +2.5 | x2,11 = −1.5 ⇒ 2x22 = −7.6 | -19.1 (no bb) | ... |
| ν1+ν8+ν11-ν2, b1u | 2794.5/ 2770.5 | +3.1, −2.0 | x1,11 = −4.6, x8,11 = −0.7 ⇒ x18 = −18.7 | | |
| ν2+ν9-ν7, b1u | 1535.8/ 1522.4 (g) | | x26 = −10.9 | ≈5 (g) | ... |
| ν2+ν10, b3u | 983.8/ 987.5 | | x2,10 = +1.7 | | |
| ν2+ν6+ν10, b1u | 751.4/ 753.4 | | x26 = +10.9 | | |
| ν3+v7, b2u | 395.05/ 798.85 | +1.1, −1.4 | x37 = −1.4 from bb | | |
| ν3+v12, b1u | 395.05/ 951.2 | +2.7, −1.9, −4.1 | x3,12 = +0.85 from bb | | |
| ν3+ν11, b1u | 1582.1/ 1579.8 | | x3,11 = −2.3 | | |
| ν3+ν6-ν4, b2u | 751.4/ 753.4 | | x36 = +2.0 | | |
| ν5-ν4, b2u | 1144.0 | −2.4, −4.8, −8.0, −11.4 ... substructure | x45 = −3.2 from bb 2x44 = +1.6 from bb | ... / (49.7), −51.9 (54.0, −53.8) | ≈−51.9 |
| ν4+ν6+ν8, b1u | 1253.7/ 1255.7 | +2.2(50%), −3.9(90%), −9.1 | | | |
| ν4+ν5, b2u | 1531.4/ 1528.2 | +0.9, −1.5 | x45 = −3.2 2x44 = +1.6 from bb | | |
| ν3+ν6-ν4, b2u | 751.4/ 753.4 | | x36 = +2.0 | broad Q | |
| ν6+ν8-ν4, b1u | 866.1/ 861.2 | | x68 = −4.9 | | |
| ν5-ν4, b2u | 1144.0 | −2.4, −4.8, −8.0, −11.4 ... substructure | x45 = −3.2 from bb 2x44 = +1.6 from bb | ... / (49.7), −51.9 (54.0, −53.8) | ≈... / −51.9 |
| ν4+ν5, b2u | 1531.4/ 1528.2 | +0.9, −1.5 | x45 = −3.2 2x44 = +1.6 from bb | | |
| ν5+ν10, b1u | 1547.4/ 1546.2 | +1.0, −1.1, −4.5 | x5,10 = −1.2 | ... / −51.9 | ... / −52.1 |
| ν5+ν6+ν12, b1u | 2443.0/ 2444.3 | +0.6, −0.4 | | | |
| ν5+ν11, b3u | 2524.7/ 2529.6 | x5,11 = +4.9 | (−21.0, −63.2) / −80.4 (−86.5) | ... | (−51.9 (54.0), −27.6 = −79.3 (−81.6) |
| v5+v9, b1u | 2676.1/2677.9 | complicated structure | $x59 = +1.8$ (+0.2 with HRv9) | $(-10.1, -67.1) / -88.1$ (diff. structure) | $-387.7 - 51.9 = -30.6$ $35.05 - 51.9 = -87.0$ |
|----------------|----------------|---------------------|-----------------------------|------------------------------------------|------------------------------------------|
| v5+v6+v11, b1u | 3074.4/3072  | shoulder             |                             |                                          |                                          |
| v6+v11, b3u | 1737.0/1735.6 | $x6_{11} = -1.4$ | ca -16.9 / ca -32.1 | $-15.8 / -32.8$ |
| v6+v9, b1u | 1888.4/1887.25 | $-1.6, -2.0, -2.7, -3.15, -4.55 ...$ | $x69 = -1.15$ $(-2.75$ with HRv9) | $(-20.05, -30.22, -38.05) / -43.90$ | $\Rightarrow ... / 43.9$ |
| v11-v6, b3u | $\Rightarrow v6 = 549.8$ / 637.8 | $-1.0, -1.8$ |                            |                                          |                                          |
| v9-v6, b1u | $\Rightarrow v6 = 550.5$ / 789.5 | $-2.7, -5.4, -8.0, -10.5$ | $\Rightarrow v2 = 776.35$ |                                          |                                          |
| v6+v9-v2, b1u | 1112.3/1110.9 | $+2.2(50\%), -3.9(90\%), -9.1$ |                            |                                          |                                          |
| v4+v6+v8 ?, b1u | 1253.5/1255.7 | $+2.2(50\%), -3.9(90\%), -9.1$ | 2 $\Rightarrow 266$ $= -1.9$ |                                          |                                          |
| v6+v7+v8, b3u | 1465.0/1460.4 | $x67 = -0.7 \Rightarrow 2x66$ $= -1.9$ | $v7+v8 913.4$ & $x68 = -4.9 \Rightarrow x67 = -0.4$ |                                          |                                          |
| 2v6+v7, b2u | 1505.2/1501.9 | $x67 = -0.7 \Rightarrow 2x66$ $= -1.9$ | $\Rightarrow v2 = 776.35$ | $\Rightarrow ... / 43.9$ | $\Rightarrow ... / (48.07) -50.27$, HRv9: -46.62 |
| v2+v6+v9, b1u | 2664.5/2650.5 | $-0.80, -2.25, -2.78, -3.82, -4.61, -7.07 ...$ | $x26 = -10.85$ $... / -34.4$ | $... / (48.07) -50.27$, HRv9: -46.62 | $\Rightarrow ... / 43.9$ |
| v3+v6-v4, b2u | 751.4/753.4 | $x36 = +2.0$ |                            |                                          |                                          |
| v6+v8-v4, b1u | 866.1/861.2 | $x68 = -4.9$ |                            |                                          |                                          |
| v2+v6+v10, b1u | 1535.8/1522.4 | $x26 = -10.9 !$ | $=5(?) / ...$ |                                      | $-3.9 / -11.8$ |
| v5+v6+v12, b1u | 2443.0/2444.3 | $+0.6, -0.4$ |                            |                                          |                                          |
| v5+v6+v11, b1u | 3074.4/3072 | shoulder |                            |                                          |                                          |
| v7+v8, b1u | $\Rightarrow v8 = 509.8$ / 913.4 | $+0.2, -1.83, -2.6, -11.4$ | $x78 = -1.6$ from hb | $-14.87 / -29.88$ | $= $ |
| v1-v7, b2u | $\Rightarrow v1 = 1873.8$ / 1468.6 | $-1.6$ | $-27.1 / -56.0$ | $-25.81 (-27.06) / -55.69$ | $= $ |
| v7+v12+v11-v2 | 1371.4/1383.4 | $+0.6$ |                            |                                          |                                          |
| v7+2v12, b2u | 1515.8/1518.2 | $+0.7, -0.7, -3.9$ | $\Rightarrow 1514.3 ...$ | $+0.6$ | $\Rightarrow ... / 43.9$ |
| 2\(v_7\)+\(v_{11}\), b1u | 1997.4/ 2003.3 | +2.3, +1.5, -1.0, -2.5 | 2\(x_{77} = +8.2 \Rightarrow x_{7,11} = -1.15 \) | -25.0 / ca. -51 | -27.4 / -51.2 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 2\(v_7\)+\(v_{9}\), b3u | 2148.8/ 2153.0 | 2\(x_{79} + 2x_{77} = +4.2 \& 2x_{77} = +8.2 \Rightarrow x_{79} = -2.0 \) | (7.5) / -52.6 | ... / -62.3 | (HR\(v_9\): -58.65) |
| \(v_1\)+\(v_{-v_7}\), b2u | 2244.7/ 2241.6 | -1.4, -7.4, ... | \(x_{12} = -3.1 \) | -4.65 / -79.4 | -38.71 (39.96) / -79.29 |
| \(v_6\)+2\(v_7\)+\(v_{9}\), b1u | 2698.8/ 2700.0 | +0.70, -1.1, -2.5 .. | \(x_{79} = -2.0 \) | ... / -67.5 | (HR\(v_9\): -63.8) |
| \(v_1\)+\(v_{-v_7}\)+\(v_{8}\), b1u | 2788.8/ 2764.1 | -0.7, -1.7, -2.9, -8.4, -20.7, ... | \(x_{18} = -18.5 \) | -45.85 / (overlapped) | 32.26+14.87=47.13 |
| \(v_1\)+\(v_{-v_7}\)+\(v_{8}\), b1u | 880.7/ 879.38 | -0.97, -1.66, ... | \(x_{28} = -1.3 \) | -4.75 / -12.78 | -4.70 / -12.74 |
| \(3v_7\), b2u | 1215.6/ 1233.9 (1234.3) | -0.8 | \(6x_{77} = +18.3 (18.7) \) | \(x_{7,11} = -0.25 \) | \(x_{7,11} = -0.25 \) |
| \(2v_7\)+\(v_{12}\), b1u | 1365.7/ 1373.4 | +0.8 | \(2x_{77} = +8.2 \Rightarrow x_{7,12} = -0.25 \) | \(x_{7,12} = -0.25 \) | \(x_{7,12} = -0.25 \) |
| \(v_6\)+\(v_{-v_7}\)+\(v_{8}\), b3u | 1465.0/ 1460.4 | \(v_{7}+v_{8} \times 913.4 \& x_{68} = -2.3 \Rightarrow x_{67} = -0.4 \) | \(x_{67} = -0.4 \) | \(x_{67} = -0.4 \) | \(x_{67} = -0.4 \) |
| \(2v_6\)+\(v_{-v_7}\), b2u | 1505.2/ 1501.9 | \(2x_{66} + 2x_{67} = -3.3 \Rightarrow 2x_{66} = -1.9 \) | \(x_{67} = -0.4 \) | \(x_{67} = -0.4 \) | \(x_{67} = -0.4 \) |
| \(v_7\)+\(v_{-v_12}\), b2u | 1515.8/ 1518.2 (1514.3 ..) | \(hb \) | \(x_{18} = -19.65 \) | not \(hb\) of 1961.6 because of isotope shift | \(x_{18} = -19.65 \) |
| \(v_1\)+\(v_{-v_7}\), b1u | 1978.4/1958.75 (1914.3 ..) | \(hb \) | \(x_{18} = -19.65 \) | not \(hb\) of 1961.6 because of isotope shift | \(x_{18} = -19.65 \) |
| \(v_7\)+\(v_{-v_11}\), b2u | 2779.2/ 2773.7 | \(2x_{11,1} + 2x_{7,11} = -5.5 \Rightarrow 2x_{11,1} = -3.2 \) | \(x_{11,1} = -3.2 \) | \(x_{11,1} = -3.2 \) | \(x_{11,1} = -3.2 \) |
| \(v_1\)+\(3v_7\) | 3089.4/ 3096.3 | -0.7 | \(x_{17} = -3.8 \) | \(x_{17} = -3.8 \) | \(x_{17} = -3.8 \) |
| \(v_7\)+\(v_{8}\), b1u | \(\Rightarrow v_{8} = 509.8/ 913.4 \) | +0.2, -1.95, -2.6, -11.4 | \(x_{78} = -1.6 \) from \(hb\) | -14.87 / -29.88 | -14.87 / -29.88 |
| \(v_8\)+\(v_{11\hbox{-}v_{2}}\), b2u | 920.7/ 920.0 | +0.7 | \(x_{8,11} = -0.7 \) | -20.58 / -39.22 | -20.58 / -39.22 |
| \(v_8\)+\(v_{12}\), b2u | 1065.1/ 1065.6 | +1.6, +1.0, -0.8 | \(x_{8,12} = +0.5 \) (from \(hb\) \(\Rightarrow v_{8} = 509.8 \) | -10.2 / -21.45 | -10.16 / -21.47 |
| \(v_4\)+\(v_{6\hbox{-}v_{8}}\), b1u | 1233.5/ 1255.7 | +2.2(50%), -3.9(90%), -9.1 | \(v_{8} = 509.8 \) | \(v_{8} = 509.8 \) | \(v_{8} = 509.8 \) |
| $\nu_8 + \nu_{11}, \text{b}2u$ | 1696.8 / 1696.1 | -1.3 | x8,11 = -0.7 | -23.1 / -45.7 | -22.1 / -44.7 |
| $\nu_1 + \nu_8 - \nu_7, \text{b}1u$ | 1978.4 / 1958.75 | -1.0 | x18 = -19.65 | not hb of 1961.6 because of isot. |
| $\nu_2 + \nu_8 + \nu_{11}, \text{b}2u$ | 2472.9 / 2469.4 | -1.1, -2.2 | x28 + x2,11 = -2.8 (confirmed) |
| $\nu_1 + \nu_7 + \nu_8, \text{b}1u$ | 2788.4 / 2764.1 | -0.7, -1.7, -2.9, -8.4, -20.7, +... | x18 = -18.5 | -45.85 / (covered) | 32.26 - 14.87 = 47.13 |
| $2\nu_8 + \nu_{11}, \text{b}1u$ | 2206.6 / 2205.3 | 2x88 = +0.1 |
| $\nu_6 + \nu_8 - \nu_{14}, \text{b}4, \text{b}1u$ | 866.1 / 861.2 | x68 = -4.9 |
| $\nu_6 + \nu_7 - \nu_{16}, \text{b}3u$ | 1465.0 / 1460.4 | v7+8 913.4 => x67 + x68 = -3.0 confirmed |
| $\nu_1 + \nu_8 + \nu_{12}, \text{b}2u$ | 2938.9 / 2918.3 | x8,12 = +0.5, x1,12 = -0.39 => x18 = -20.7 (with origin at high waven. edge ~-19) |
| $\nu_6 + \nu_9, \text{b}1u$ | 1888.4 / 1887.25 | -1.6, -2.0, -2.7, -3.15, -4.55 ... | x69 = -2.75 (HR v9) | (-.20.05, -.30.22, -.38.05) / -43.90 | = |
| $\nu_2 + \nu_9, \text{b}3u$ | 2114.3 / 2112.5 | x29 = -2.0 | ... / (-.41.7,-.42.6) ~-.45.6 | ... / (-.43.7,-.44.9) |
| $2\nu_7 + \nu_9, \text{b}3u$ | 2148.8 / 2153.0 | 2x79 + 2x77 = +4.2 & 2x77 = +8.2 => x79 = -2.0 | (7.5) / -52.6 | ... / 62.3 (HRv9: 58.65) |
| $\nu_2 + \nu_6 + \nu_9, \text{b}1u$ | 2664.3 / 2650.5 | -0.80, -2.25, -2.78, -3.82, -4.61, -7.07 ... | v2+(v6+v9) => x26+x29 = -12.85 => x26 = -.1085 | ... / -34.4 | [... / (-.48.07,-.50.27) |
| $\nu_5 + \nu_9, \text{b}1u$ | 2676.1 / 2677.9 | hb complicated | x59 = +0.2 (HR v9) | (-10.1,-.67.1)/-.88.1 | (different structure!) 38.7+51.9=90.6 35.05+51.9 = 87.0 |
| $\nu_6 + 2\nu_7 + \nu_9, \text{b}1u$ | 2698.8 / 2700.0 | +0.70, -1.1, -2.5 ... | / -67.5 (HRv9: 63.8) |
| $\nu_1 + \nu_9, \text{b}3u$ | 3212.2 / 3208.9 (mini-Q), hb | x19 = -3.3 | -23.6, -59.6 / -102.6 | ... / -106.2 (HRv9: -102.54) |
| $\nu_9 - \nu_6, \text{b}1u$ | => $\nu_9$ = 550.5 / 789.5 | -1.0, -1.8 | with HRv9 |
| $\nu_6 + \nu_9 - \nu_{2}, \text{b}1u$ | => $\nu_2$ = 776.35 / 1110.9 | -2.7, -5.4, -8.0, -10.5 with HRv9 |

| $2\nu_{10} + \nu_{11}, \text{b}1u$ | 1606.4 / 1607.5 | +4.2, +8.2, +12.2 +3.2, ... -3.0 | 2x10,10 = +2.5, x10,11 = -0.7 (both from hb) => $\nu_{10}$ = 209.7 | isotope shift: interference by H2O |

$\nu_{10} + \nu_{2}, \text{b}3u$ | 983.8 / 987.5 | x2,10 = +1.7 |
| νl0+2ν11, b3u | 2583.7/ 2581.4 | 2x11,11 = -0.9 |
|----------------|---------------------|------------------|
| ν2+ν6+νl0, b1u | 1535.8/ 1522.4 (?) | x26 = -10.8 = x2,10 + x6,10 = -2.6 = 5 (?) / ... ... / -3.9 / -11.8 |
| ν5+νl0, b1u | 1547.4/ 1546.2 | +1.0, -1.1, -4.5 x5,10 = -1.2 ... / -51.6? ... / -52.1 |
| ν1+νl0, b3u | 2083.5/ (2077.5) 2081.4 | 2 indents similar to ν10 x1,10 = -2.1 |

| ν8+νl1–ν2, b2u | 920.7/ 920.0 | +0.7 x8,11 = -0.7 ... / -20.38 / -39.22 |
|----------------|---------------------|------------------|
| ν7+νl1+ν12–ν2, b2u | 1371.4/ 1383.4 | +0.6 |
| ν3+νl1, b1u | 1582.1/ 1579.8 | broad x3,11 = -2.3 |
| 2ν10+νl1, b1u | 1606.4/ 1607.5 | +4.2, +8.2, +12.2, +3.2, ... -3.0 2x10,10 = ±2.5, x10,11 = ±0.7 (both from hb) ⇒ ν10 = 209.7 |
| ν8+νl1, b2u | 1696.8/ 1696.1 | -1.2 x8,11 = -0.7 -23.1 / -45.7 -22.1 / -44.7 |
| ν6+νl1, b3u | 1737.0/ 1735.6 | x6,11 = -1.4 ... / -16.9 / ca. -32.1 ... / -15.8 / -32.8 |
| ν2+νl1, b1u | 1963.1/1961.60 | +1.1, -0.7, -0.8, -10.2, -17? x2,11 = -1.5 -17.22 / -33.98 = |
| 2ν7+νl1, b1u | 1997.4/ 2003.3 | +2.3, +1.5, -1.0, -2.3 2x7,11 + 2x77 (+8.2) = +5.9 ⇒ x7,11 = -1.15 -25.0 / ca. -51 27.4 / -51.2 |
| ν1+νl1–ν2, b1u | 2284.7/ 2280.1 | -1.3, -2.3 x1,11 = -4.6 -43.8 / ca. 86.2? covered -44.29 / -45.54 / -83.26 |
| ν2+ν8+νl1, b2u | 2472.9/ 2469.4 | -1.1, -2.2 x28 + x2,11 + x8,11 confirmed |
| ν2+ν6+νl1, b3u | 2513.1/ 2501.8 | x26 = -8.4 ... / -35.4 or 39.0 ... / -39.2 |
| ν5+νl1, b3u | 2524.7/ 2529.6 | x5,11 = +4.9 ... / -80.4 (86.3) ... / -79.5 |
| ν10+2νl1, b3u | 2583.7/ 2581.4 | 2x11,11 = -0.9 |
| 2ν2+νl1, b1u | 2739.2/ 2728.6 | +1.1, +1.9, +2.5 2x22 = -7.6 -19.1 (no hb!) / -19.9 / -40.3 |
| ν1+ν8+νl1–ν2, b1u | 2794.3/ 2770.5 | +3.1, -2.0 |
| ν1+νl1, b1u | 3060.8/ 3056.2 | -1.3, -1.9, -3.1 ... -19.6 x1,11 = -4.6 -46.3 / 48.3 / 94.74 (93.9) -46.91 / 48.16 / -95.01 |
| νl1–ν6, b3u | ⇒ ν6 = 549.8 / 637.8 (with HRν11) |
| 2ν8+νl1, b1u | 2206.6/ 2205.3 | -2.4 2x88 = +0.1 |
| ν5+ν6+νl1, b1u | 3074.4/ca. | shoulder |
| wavenumber | band comment |
|------------|--------------|
| 3072       |              |
| v8+v12, b2u| \( \Rightarrow v8 = 509.8 \) / 1065.6 | +1.0, 1.6, -0.8(46%v4) | \( x8,12 = +0.5 \) from hb |
| v7+v12+v11-v2, b2u | 1371.4/ 1383.4 | +0.6 | |
| v7+2v12, b2u | 1515.8/ 1518.2 (1514.3 ..) | +0.7, -0.7, -3.9 | -9.93 / -18.58 |
| 3v12 | 1665.9/ 1666.9 (1671.6 ?) | hb | 6x12,12 = +1.0 (x12,12 = +0.17) |
| v1+v12, b1u | 2429.1/2428.71 | -1.24, -2.37, -3.60, ..., -18.4 .. | x1,12 = -0.4 | -34.00 (-36.01) / -70.83 | -34.00 (-35.25) / -70.88 |
| v3+v12, b1u | 950.4/ 951.2 | +2.7, -1.9, -4.1 | x3,12 = +0.7 | |
| v2+v12, b1u | 1331.4/1332.0 (HRv9) | x2,12 = +0.6 | |
| 2v7+v12, b1u | 1365.7/ 1373.4 | +0.8 | 2x77 = +8.2 \( \Rightarrow x7,12 = -0.25 \) |
| v5+v6+v12, b1u | 2443.0/2444.3 | +0.6, -0.4 | |
| v1+v8+v12, b2u | 2938.9/2918.3 | broad Q | \( x8,12 = +0.5, x4,12 = -0.39 \Rightarrow x4,8 = -20.7 \) (with origin at high wavenumber edge --19) |

bands of uncertain assignment and others

- 411 shoulder | \( v11-v2 = 410.9 \) |
- 920.0 | \( v8+v11-v2 = 920.0 \). But the observed band is much stronger than the 411 shoulder, has a strong hb; the shifted isotopic spectra might be covered by the v7+v8 bands |
- \( \approx 1293 \) shoulder | \( v9 \) of 13C (see [1]) |
- 1255.7 | \( v4+v6+v8 = 1253.5 + x46(-1.1) + x48(-1.05) + x68(-2.3) = 1249.25 \) |

The region between 1510 and 1590 is crowded. Some bands:

- 1522.4 broad | \( v2+v6+v10 = 1535.8 + x26(-10.9..-8.4) + x2,10(+0.9) + x6,10(-0.1) = 1525.7..1528.2 \), perhaps satisfactory in view of Fermi resonance (or unusually strong R branch of v7+2v12 1518.2?) |
- 1550 broad | P + R of neighbors? |
- 1555.3, Q, hb | ? |
- 1561.7, Q, hb | \( v2+v3+v7 = 1576.4 + x23(-0.2 \text{ calc.}) + x27(-9.5) + x37(-1.4) = 1565.3 \), doubtful, because v2+v7 is covered by v11 |
- 2556.3 | \( v1+v4+v8 = 2577.3 + x14(-1.5) + x18(-18.5) + x48(-1.05) = 2556.25 \) fits, but v4+v8 (703.5 – 1.5) not found |
2. Sources of anharmonicities

*Table S2.* Values (in cm$^{-1}$) and sources of the anharmonic constants $x_{ij}$. Values were derived from (a) combination bands and (b) hot bands (hb).

In the former case, the column "source" lists the combination band with its observed wavenumber (peak of main Q branch, or if "(b$_{3u}$)" is added: a minimum), from which the harmonic sum should be subtracted. (For this sum, we use the low-resolution fundamentals, i.e. those of Table 1 of the main text except $v_9$ and $v_{11}$: for these we use the high-resolution band origins where indicated ("HR…"), if the combination band has sharp Q branches, and low-resolution values (1338.4 and 1187.0, respectively) elsewhere.

In case (b), we add "hb" after the band (with wavenumber), which is accompanied by the hot band; this is followed in parentheses by the relative intensity (which should be compared with the Boltzmann factor, Table S3) and/or the lower level of the hot band, and then the distance from the main Q branch. If the anharmonic shift consists of a sum of $x_{ij}$ it is explicitly given, with values of the other anharmonic constants added in parentheses. The column "other information" also lists some data for the isotopologues $^{13}$C$_2$F$_4$ ("$^{13}$C$_2$"), and $^{12}$C$^{13}$F$_4$ ("$^{13}$C$_1$").

Some of the constants are level dependent (for example, $x_{18}$ or $x_{17}$). In other cases, different values from different sources may indicate a numerical (or assignment) uncertainty; if there is an indication, which value to prefer, it is printed in bold face.

| $x_{ij}$ | value | source | other information |
|---------|--------|--------|-------------------|
| 2$x_{11}$ |        |        |                   |
| $x_{12}$ | −3.1   | $v_1+v_2-v_7$ 2241.6 |                 |
| $x_{13}$ |        |        |                   |
| $x_{14}$ | −1.5   | $v_1+v_{12}$ 2428.7 hb (80%) $-1.24 = x_{14} + x_{4,12}$ (+0.25) also fits to hb $v_{12}-v_7$ 1468.6 |
| $x_{15}$ |        |        |                   |
| $x_{16}$ | −5.0   | $v_1+v_{12}$ 2428.7 hb (8%) $-5.0 = x_{16} + x_{4,12}$ ($x_{4,12} \leq 0.3$) not hb($v_8$ or $v_{12}$): $x_{18} \approx -19$, $x_{1,12} = -0.4$ fits to $v_1+v_7+v_8$ 2764.1 hb (12%) $-8.0 = x_{16} + x_{6,7} + x_{6,8} (-5.0+1.9-4.9)$ |
| $x_{17}$ | −4.6   | $v_1+v_7$ 2274.4 |
|         | −3.8   | $v_1+3v_7$ 3096.3 (3$v_7$ 1233.9) |
| x_{18} | -18.5 | v_1+v_3+v_6 2764.1, v_2+v_9 913.4 \Rightarrow x_7(-4.6)+x_{18} = -23.1 |
|--------|--------|---------------------------------|
|        | -18.7 | v_1+v_3+v_4 hb (9.5%) \approx -20.4 = x_{18}+x_7(-1.6)+2x_{88}(+0.1) |
|        | -18.7 | v_1^2v_8^3v_11^{-1}v_2 2770.5 (x_{8,11} = -0.7) \Rightarrow x_{18}+x_{8,12} (+0.5) |
|        | -19.0 | v_1^2v_7 2274.4 hb (8%) \approx -19.6 = x_{18}+x_7 |
|        | -18.0 | v_1^2v_11 3056.2 hb (8%) \approx -19.6 = x_{18}+x_{8,11} (-0.7) |
|        | -18.9 | v_1^2v_8^2v_7 1958.75 |
|        | -19.65| v_1^2v_8=v_7 2918.3 (Q broad) |
|        | -20.7 | (-19 with origin at short-wavelength edge) |

x_{19} = -3.3 \quad v_1+v_9 3208.9 band shape different from v_9.!

x_{1,10} = -1.04 \quad v_1+v_{12} 2428.7 hb (80%) \approx -1.24 = x_{1,10}+x_{10,12} (-0.2) |

v_1^2v_9 2081.4 also fits to v_1=v_7 1468.6 hb (-1.6 = x_{1,10}-x_{7,10} (+0.3) = -1.4 |

x_{1,11} = -4.6 \quad v_1+v_{11} 3056.2 |

v_1+v_{11}^{-1}v_2 2280.1 |

x_{1,12} = -0.4 \quad v_1+v_{12} 2428.7 |

x_{2j}:

x_{22} = -3.8 \quad 2v_2+v_{11} 2728.6; 2x_{22}+2x_{2,11}(-3.0) = -10.6 |

x_{23}:

x_{24} = -0.7 \quad comparison of v_4+v_9 1887.25 hb \approx -2.0 and v_6+v_9=v_2 1110.9 hb \approx -2.7 |

comparison of v_4+v_9 hb \approx -2.0 and v_2+v_6+v_9 2650.5 hb \approx -2.3 |

x_{25}:

x_{26} = -10.85 | diff. of v_6+v_9 1887.25 and v_2+v_6+v_9 2650.5: -12.85 = x_{26}+x_{29}(-2.0) |
|     | -8.4 | diff. of v_6+v_{11} 1735.6 and v_2+v_6+v_{11} 2501.8: -9.9 = x_{26}+x_{2,11}(-1.5) |
|     | -8.7 | v_2^2v_11 1961.6 hb (8%) \approx -10.1 = x_{26}+x_{6,11}(-1.4) |

FR: distances 

v_5+v_9 / v_2+v_6+v_9 = 27.4 |

v_5+v_{11} / v_2+v_6+v_{11} = 27.8 |

v_5 (1337.7) / v_2+v_9 (1326.6-(8.5..10.8)) = 20.1..22.4 |

x_{26} diff. of v_6+v_9 1843.4 and v_2+v_6+v_9 2603.4 or 2616.1: -9.7 or +3.0 (instead of -12.85) = x_{26}+x_{29} \Rightarrow = -7.7 or +5.0 |

x_{27} = -9.5 \quad v_7 405.2 hb \approx -9.5 |

v_7+v_8 913.4 hb (1%) \approx -11.4 = x_{27}+x_{28}(-1.3) |

FR: distances 

v_5+v_9 / v_2+v_6+v_9 = 27.4 |

v_5+v_{11} / v_2+v_6+v_{11} = 27.8 |

v_5 (1337.7) / v_2+v_9 (1326.6-(8.5..10.8)) = 20.1..22.4 |

x_{26} diff. of v_6+v_9 1843.4 and v_2+v_6+v_9 2603.4 or 2616.1: -9.7 or +3.0 (instead of -12.85) = x_{26}+x_{29} \Rightarrow = -7.7 or +5.0 |

x_{27} = -9.5 \quad v_7 405.2 hb \approx -9.5 |

v_7+v_8 913.4 hb (1%) \approx -11.4 = x_{27}+x_{28}(-1.3) |

FR: distances 

v_5+v_9 / v_2+v_6+v_9 = 27.4 |

v_5+v_{11} / v_2+v_6+v_{11} = 27.8 |

v_5 (1337.7) / v_2+v_9 (1326.6-(8.5..10.8)) = 20.1..22.4 |

x_{26} diff. of v_6+v_9 1843.4 and v_2+v_6+v_9 2603.4 or 2616.1: -9.7 or +3.0 (instead of -12.85) = x_{26}+x_{29} \Rightarrow = -7.7 or +5.0 |

x_{27} = -9.5 \quad v_7 405.2 hb \approx -9.5 |

v_7+v_8 913.4 hb (1%) \approx -11.4 = x_{27}+x_{28}(-1.3) |

13C, v_1+v_{12} 2394.7 hb (8%) \approx -18.1 \Rightarrow x_{18} = -18.6 (hb structure different from 12C) |

13C, v_1+v_{12} 2357.8 hb (8%) \approx -16.1 \Rightarrow x_{18} = -16.6 |

13C, v_1+v_7 2195.0 hb (8%) \approx -15.7 (-17.3) (assignment?) \Rightarrow x_{18} = -14.1 (-15.7) |

13C, v_1+v_{11} 2961.3 hb (8%) \approx -17.3 \Rightarrow x_{18} = -16.6 |

x_{28} = -1.3 \quad v_2+v_8=v_7 879.38 |

13C, v_{27} = -10.9 from v_7+v_8 hb (1%) \approx -12.2 |

13C, x_{27} = -10.0 from dark state v_2+v_7 1153.13 1 [1]
| \(x_{29}\) | -2.0 | \(v_2\!+\!v_9\) (b_{3u}) 2112.5 |
| \(x_{2,10}\) | +0.9 | comparison of \(v_6\!+\!v_9\) 1887.25 hb −2.0 and \(v_2\!+\!v_9\!-\!v_2\) 1110.9 hb −2.7 |
| | +1.0 | also fits to \(v_2\!+\!v_9\) 1961.6 hb +1.1 and \(2v_2\!+\!v_{11}\) 2728.6 hb +1.1 |
| \(x_{2,11}\) | -1.5 | \(v_2\!+\!v_{11}\) 1961.6 |
| \(x_{2,12}\) | +0.6 | \(v_2\!+\!v_{12}\) 1332.0 [I] |

### \(x_3j\)

| \(x_{33}\) | +0.05 | shoulder at \(v_2\) (776.1) + 14.0 in [3] \(\Rightarrow 2x_{33}\) ≈ +0.1 |
| \(x_{34}\) | +0.9 | \(v_3\!+\!v_7\) 789.85 hb (50%) +1.2 = \(x_{34}\!+\!x_{47}\) (+0.3) |
| \(x_{35}\) | -1.5 | \(v_5\!-\!v_4\) 1144.0 hb (\(v_5\)) −2.4 = \(x_{35}\!-\!x_{34}\) (+0.9) |
| \(x_{36}\) | +2.0 | \(v_4\!+\!v_6\!-\!v_4\) 753.4 |
| \(x_{37}\) | -1.4 | \(v_5\) 405.2 hb −1.4 |
| \(x_{38}\) | +0.4 | \(v_8\!+\!v_{12}\) 1065.6 hb (18%) +1.25 = \(x_{38}\!+\!x_{3,12}\) (+0.85) |
| \(x_{39}\) | | hb cannot come from \(v_7\) because of \(x_{78}\) = −1.6 |
| \(x_{3,10}\) | -1.75 | \(v_3\!+\!v_7\) 789.85 hb (50%) −1.45 = \(x_{3,10}\!+\!x_{7,10}\) (+0.3) |
| \(x_{3,11}\) | -2.3 | \(v_3\!+\!v_{11}\) 1579.8 (broad Q) |
| \(x_{3,12}\) | +0.85 | \(v_{12}\) 555.3 hb (13%) |
| \(x_{4j}\) | | also fits to \(v_3\!+\!v_{12}\) 951.2 hb −1.9 |

| \(x_{4,10}\) | -1.75 | \(v_3\!+\!v_7\) 789.85 hb (50%) −1.45 = \(x_{3,10}\!+\!x_{7,10}\) (+0.3) |
| \(x_{4,11}\) | -2.3 | \(v_3\!+\!v_{11}\) 1579.8 (broad Q) |
| \(x_{4,12}\) | +0.85 | \(v_{12}\) 555.3 hb (13%) |
| \(x_{4,13}\) | | also fits to \(v_3\!+\!v_{12}\) 951.2 (\(\Rightarrow x_{3,12}\) = 0.7) |

| \(x_{44}\) | +0.8 | \(v_4\!+\!v_5\) 1528.2 hb −1.5 = 2\(x_{44}\!+\!x_{45}\) |
| \(x_{45}\) | -3.2 | \(v_5\!-\!v_4\) 1144.0 hb −4.8 = −2\(x_{44}\!+\!x_{45}\) |
| \(x_{4,10}\) | -1.75 | \(v_3\!+\!v_7\) 789.85 hb (50%) −1.45 = \(x_{3,10}\!+\!x_{7,10}\) (+0.3) |
| \(x_{4,11}\) | -2.3 | \(v_3\!+\!v_{11}\) 1579.8 (broad Q) |
| \(x_{4,12}\) | +0.85 | \(v_{12}\) 555.3 hb (13%) |
| \(x_{4,13}\) | | also fits to \(v_3\!+\!v_{12}\) 951.2 (\(\Rightarrow x_{3,12}\) = 0.7) |

| \(x_{44}\) | +0.8 | \(v_4\!+\!v_5\) 1528.2 hb −1.5 = 2\(x_{44}\!+\!x_{45}\) |
| \(x_{45}\) | -3.2 | \(v_5\!-\!v_4\) 1144.0 hb −4.8 = −2\(x_{44}\!+\!x_{45}\) |

solving for \(x_{44}\) and \(x_{45}\) also delivers \(v_4\) and \(v_5\) 

\(x_{45}\) also fits to \(v_5\!+\!v_{10}\) 1546.2 hb −4.5 ≈ \(x_{45}\!+\!x_{4,10}\) (−1.2) and to \(v_5\!+\!v_9\) 2677.9 hb

\(1^{11}\text{C}_2\); if \(x_{44}\) is unchanged, then \(x_{45}\) = −2.3 (from \(v_5\!-\!v_4\) 1092.1 hb −3.9)

| \(x_{46}\) | -1.1 | \(v_6\!+\!v_9\) 1887.25 hb −2.0 = \(x_{46}\!+\!x_{49}\) (−0.9) |
| \(x_{47}\) | +0.3 | \(v_7\) 405.2 hb |
| $x_{48}$  | $-1.05$ | $v_8 + v_{12} 1065.6$ hb (48\%) $-0.8 = x_{48} + x_{4,12}$  
$-0.7$ $v_7 + v_9 913.4$ hb (60\%) $-0.4 = x_{47} (+0.3)$ + $x_{48}$  |
| $x_{49}$  | $-0.9$  | $v_5 + v_9 2677.9$ hb $-4.1 = x_{45}(-3.2) + x_{49}$  
(heat bands broad, complicated)  
also fits to $v_9 - v_5$ 789.6 hb (in contour): $x_{49}$  
$-0.9 - x_{46} (-1.1) = +0.2$ |
| $x_{4,10}$ | $-1.3$  | $v_5 + v_{10} 1546.2$ hb $-4.5 = x_{45}(-3.2) + x_{4,10}$  
also fits to $v_5 - v_4$ 1144.0 hb (in contour) and to $2v_{10} + v_{11}$ 1607.4 hb $-3.0$ (broad) |
| $x_{4,11}$ | $-0.7$  | $v_{11} 1187.0$ hb $(-0.25$ would be in contour)  
$v_8 + v_{11} 1696.1$ hb (100\%) $-1.3 = x_{48}(-1.05)$ + $x_{4,11}$  
$-0.25$ also fits to $v_2 + v_{11}$ 1961.6 hb (in contour) and to $2v_8 + v_{11}$ 2205.3 hb $-2.2 = 2x_{48} (-2.1) + x_{4,11}$ |
| $x_{4,12}$ | +0.25   | $v_{12}$ 555.3 hb (31\%)  
also fits to $v_7 + 2v_{12}$ 1518.2 hb $+0.7$ |
| $x_{5j}$  |  |  |
| $x_{55}$  |  |  |
| $x_{56}$  |  |  |
| $x_{57}$  |  |  |
| $x_{58}$  |  |  |
| $x_{59}$  | $+0.2$  | $v_5 + v_9 2677.9$ (with band origin of $v_9$)  
$+1.8$ (with low-resolution value of $v_9$)  
$^{13}C_2^+$: $-1.0$ from $v_5 + v_9$ 2589.8 (with band origin of $v_9$) |
| $x_{5,10}$ | $-1.2$  | $v_5 + v_{10} 1546.2$  
$v_5 + v_{10} 1546.2$ hb $+1.0 = x_{5,10} + 2x_{10,10}$  
$+2.5$  
also fits to $v_5 - v_4$ 1144.0 hb (in contour) |
| $x_{5,11}$ | $+4.9$  | $v_5 + v_{11} 2529.6$ (b$_{3u}$)  
$^{13}C_2^+ +4.0$ from $v_5 + v_{11}$ 2449.2 (b$_{3u}$) |
| $x_{5,12}$ |  |  |
| $x_{6j}$  |  |  |
| $x_{66}$  | $-0.95$ | $2v_6 + v_7$ 1501.9: $-3.3 = 2x_{66} + 2x_{67} (-1.4)$ |
| $x_{67}$  | $-0.7$  | $v_6 + v_9$ 1887.25 hb (15\%: $v_7$, not $v_9$) $-2.7 = x_{67} + x_{79}$ $(-2.0)$  
also fits to $2v_7 + v_{11}$ 2003.3 hb (7.5\%: $v_6$, not $v_9$ or $v_{12}$) $-2.3 = 2x_{67} + x_{6,11} (-1.4)$ and to $v_6 + v_7 + v_8$ 1460.4 (with $v_7 + v_8$ 913.4 & $x_{68}$ $= -2.3$) $x_{67} = -0.4$ |
| $x_{68}$  | $-4.9$  | $v_6 + v_8 - v_4$ 861.2 (broad Q)  
$v_6 + v_7 + v_9$ 1460.4 (b$_{3u}$) & $v_7 + v_8$ 913.4: $-3.0 = x_{67} (-0.7) + x_{68}$ |
| $x_{69}$  | $-2.75$ | $v_6 + v_9$ 1887.25 (with band origin of $v_9$)  
|
| \( x_{10} \) | \(-1.15\) | (with low-resolution value of \( v_0 \)) |
| \( x_{11} \) | \(-0.1\) (calc.) fits to \( v_6 + v_9 \) \( 1887.25 \text{ hb} \ -1.6 = x_{10}^* + x_{10} \) (calc. \(-1.5\)) |
| \( x_{12} \) | \(-1.4\) | \( v_6 + v_{11} \) \( 1735.6 \) (\( b_{3u} \)) |

**\( x_j \)**

| \( x_{7} \) | \(+4.1\) +3.05 +2.48 | \( v_7 \) \( 405.2 \text{ hb} \ +8.2 = 2\nu_7 \) |
| | | \( 3\nu_7 \) \( 1233.9 = 3x\nu_7 +6x\nu_7 \) |
| | | \( v_7 \) \( 405.2 \text{ hb} \ +9.9 = 4x\nu_7 \) (only nominal \( x_{77} \), because of strong Fermi perturbations) |

**\( x_8 \)**

| \( x_{8} \) | \(-1.6\) \( \approx-1.5\) | \( v_7 + v_8 \) \( 913.4 \text{ hb} \) (5.10%) |
| | | \( v_7 \) \( 405.2 \text{ hb} \) |

**\( x_{9} \)**

| \( x_{9} \) | \(-2.0\) | \( 2v_7 + v_9 \) \( 2153.0 \) (\( b_{3u} \)): \( 2\nu_7 + (8.2) + x_79 \) |

**\( x_{10} \)**

| \( x_{10} \) | \(+0.3\) | \( v_7 \) \( 405.2 \text{ hb} \) |

**\( x_{11} \)**

| \( x_{11} \) | \(-1.15\) | \( 2v_7 + v_{11} \) \( 2003.3: +5.9 = 2\nu_7 + (8.2) + 2\nu_{7,11} \) |

**\( x_{12} \)**

| \( x_{12} \) | \(-0.25\) | \( 2v_7 + v_{12} \) \( 1373.4: +7.7 = 2\nu_7 + (8.2) + 2\nu_{7,12} \) |

**\( x_{8j} \)**

| \( x_{88} \) | \(+0.05\) | \( 2v_8 + v_{11} \) \( 2205.3: -1.3 = 2\nu_8 + 2\nu_{8,11} \) (-1.4) |

| \( x_{89} \) | | |

| \( x_{8,10} \) | \(-0.7\) | \( v_7 + v_8 \) \( 913.4 \text{ hb} \) (68%) \(-0.4 = x_{8,10} \) (\(+0.3\)) + \( x_{8,10} \) |

| \( x_{8,11} \) | \(-0.7\) | \( v_8 + v_{11} \) \( 1696.1 \) |
| | | \( v_8 + v_{11} - v_2 \) \( 920.0 \) |

| \( x_{8,12} \) | \(+0.5\) | \( v_{12} \) \( 555.3 \text{ hb} \) also fits to \( v_8 + v_{12} \) \( 1065.6 \) |

**\( x_{9j} \)**

| \( x_{99} \) | | |

| \( x_{9,10} \) | \(-1.5..-1.2\) | \( -1.5 \) (calc.) fits to \( v_6 + v_9 \) \( 1887.25 \text{ hb} \) \(-1.6 = x_{6,10} \) (calc. \(-0.1\)) + \( x_{9,10} \) |
| | | \(-1.2\) fits to \( v_9 - v_6 \) \( 789.6 \text{ hb} \) \(-1.0 = x_{9,10} - x_{9,10} \) (-0.2 calc.) |

| \( x_{9,11} \) | | |
There is a misprint in Table 1 of [1]: ν₈ of $^{13}$C₂F₄ should be 491.7 instead of 483.3 cm⁻¹.

Table S3. Boltzmann factors (B, population at 295 K relative to that of the ν = 0 level) for the lower levels νᵢ (with energies in cm⁻¹) of hot bands.

| level | energy  | B     |
|-------|---------|-------|
| ν₄    | 193.7   | 0.396 |
| ν₁₀   | 209.7   | 0.367 |
| ν₃    | 395.1   | 0.151 |
| ν₇    | 405.2   | 0.144 |
| ν₈    | 509.8   | 0.08  |
| ν₆    | 550.0   | 0.072 |
| ν₁₂   | 555.3   | 0.070 |
| ν₂    | 776.1   | 0.024 |
| ν₁₁   | 1187.6  | 0.0034|
| ν₅    | 1337.7  | 0.0017|
| ν₉    | 1340.0  | 0.0016|
| ν₁    | 1873.8  | 0.00013|
3. Fermi resonances

A pair of levels with the same symmetry can interact via a third-order potential term. Their energies \( E_1, E_2 \) result as eigenvalues of the matrix

\[
\begin{pmatrix}
E_1 & W \\
W & E_2
\end{pmatrix}
\]

where \( E_1, E_2 \) are the unperturbed level energies and \( W \) is the Fermi interaction matrix element. \( W \) still depends on quantum numbers \([4,5]\) (see the first example). Because \( W \) should be the same for different isotopologues, the parameters can sometimes be derived by comparing such data.

3.1. The \( v_2/2v_7 \) and higher level pairs

This is a strong Fermi resonance. One may suspect that the entire anharmonic shift of the \( 2v_7 \) level ("\( 2v_7 \)" = 8.2 cm\(^{-1}\)) is caused by it. One would then subtract 8.2 (we omit the unit cm\(^{-1}\) from now on) from the observed \( 2v_7 \) and add it to \( v_2 \) to get the unperturbed \( 2v_7^0 \) and \( v_2^0 \). A \( W \) of 16.8 would then result in the observed \( v_2 \) and \( 2v_7 \) as eigenvalues. However, if we use a shift of 7.7 instead of 8.2 (i.e., an unperturbed \( 2v_7^0 = +0.5 \)) and \( W_{v_2/2v_7} = 16.4 \), we can use the same \( W \) for all isotopologues. Thus for \( ^{12}\text{C}_2\text{F}_4 \) we diagonalize

\[
\begin{pmatrix}
2v_7^0 & W \\
W & v_2^0
\end{pmatrix} = \begin{pmatrix} 810.9 & 16.4 \\ 16.4 & 783.8 \end{pmatrix}
\]

and obtain

\[
\begin{pmatrix} 2v_7 \\ v_2 \end{pmatrix} = \begin{pmatrix} 818.6 \\ 776.1 \end{pmatrix}
\]

as observed. To do the corresponding calculation for \( ^{12}\text{C}^{13}\text{C}_2\text{F}_4 \) and \( ^{13}\text{C}_2\text{F}_4 \), we subtract the isotopic shifts (2×6.45 and 2×11.8, respectively) from \( 2v_7^0 \) but leave \( v_2^0 \) unchanged (i.e. assume that the small shifts of 2.6 and 6.4 are actually produced by Fermi resonance). Table S4 lists for all three isotopologues the starting values \((2v_7^0, v_2^0)\) obtained in this way, the resulting eigenvalues (calculated \( 2v_7, v_2 \)) and corresponding observed levels. (The observed \( 2v_7 \) values are from \( v_7 \) and the hot band \( v_7 \rightarrow 2v_7 \).) The agreement is excellent. Also confirmed is the assumption that the isotopic shift of \( v_2 \) (which for \( ^{13}\text{C}_2\text{F}_4 \) is more than twice that of \( ^{12}\text{C}^{13}\text{C}_2\text{F}_4 \)) is largely produced by Fermi resonance.

We can also consider the higher level pair \( v_2 + v_7/3v_7 \). For this case we should remember the dependence on the quantum numbers \([4,5]\)

\[
W \propto (v_2v_7(v_7 - 1))^{1/2}
\]
so that \( W \) increases by a factor \( \sqrt{3} \). In this relation, one should insert for \( v_2 \) and \( v_7 \) the higher of the values in the level pair. To be consistent with the lower level pair, we again assume that most of the observed anharmonic shift of \( 3v_7 \) is caused by Fermi resonance and only a small part \( (6x_{77}^0 = 1.5) \) by the unperturbed constant \( x_{77}^0 \). (In fact \( x_{77}^0 = 0 \) would even improve the agreement.) To start with, we also suppose that the relatively large \( x_{27} \) (\(-9.5, -10.9 \) and \(-10.0 \) for the three isotopologues, see Table S2) is fully due to the Fermi resonance (i.e. \( x_{27}^0 = 0 \)). Then the calculation of the unperturbed levels \( 3v_7 \) and \( (v_2+v_7)^0 \) in the table should be obvious. The observed levels in \(^{12}\text{C}_2\text{F}_4\) and \(^{13}\text{C}_2\text{F}_4\) are directly from the IR spectrum, whereas for \(^{12}\text{C}^{13}\text{F}_4\) \( v_2+v_7 = (v_2) + (v_7) + x_{27} \), the latter taken from a hot band of \( v_7+v_8 \) (Table S1). The agreement between the calculated and observed values is relatively good, and the assumption is supported that \( x_{27} \) is only due to Fermi resonance (or nearly so). The separation of interacting levels and consequently the extent of the Fermi shift differs considerably with isotopic substitution. While differing Fermi shifts in \( 2v_7 \) explain the strong variation in \( x_{77} \), the \( x_{27} \) values are similar because differing Fermi shifts in \( v_2+v_7 \) are compensated by those in \( v_2 \). This set of calculations satisfactorily accounts for both observations.

Table S4. The Fermi resonance \( v_2/2v_7 \) (values in cm\(^{-1}\))

| molecule          | unperturbed levels | interaction matrix element \( W \) | eigenvalues | observed levels |
|-------------------|--------------------|-----------------------------------|-------------|----------------|
| \(^{12}\text{C}_2\text{F}_4\) | \( 2v_7^0 = 2v_7 - 7.7 = 810.9 \) \( v_2^0 = v_2 + 7.7 = 783.8 \) | 16.4 | 818.6 776.1 | 818.6 776.1 |
| \(^{12}\text{C}^{13}\text{F}_4\) | \( 2v_7^0 = 810.9 - 2\times6.45 = 798.0 \) \( v_2^0 = 783.8 \) | 16.4 | 808.8 773.0 | 808.5 773.5 |
| \(^{13}\text{C}_2\text{F}_4\) | \( 2v_7^0 = 810.9 - 2\times11.8 = 787.3 \) \( v_2^0 = 783.8 \) | 16.4 | 802.0 769.1 | 802.8..801.3 769.7 |
| \(^{12}\text{C}_2\text{F}_4\) | \( 3v_7^0 = 3v_7 + 6x_{77}^0 = 1217.1 \) \( (v_2+v_7)^0 = v_2^0 + v_7 = 1189.0 \) | 28.4 | 1234.7 1171.4 | 1233.7 1171.8 |
| \(^{12}\text{C}^{13}\text{F}_4\) | \( 3v_7^0 = 1217.1 - 3\times6.45 = 1197.75 \) \( v_2^0 + v_7 = 1189.0 - 6.45 = 1182.55 \) | 28.4 | 1219.6 1160.8 | – 1161.3 |
| \(^{13}\text{C}_2\text{F}_4\) | \( 3v_7^0 = 1217.1 - 3\times11.8 = 1181.7 \) \( v_2^0 + v_7 = 1189.0 - 11.8 = 1177.2 \) | 28.4 | 1207.9 1151.0 | – 1153.1 |

Whereas the deviations of observed and calculated level energies seem small, it may also be that they reflect the effect of another Fermi resonance, that between \( v_2 \) and \( 2v_3 \) (FR3 in Table 3 of
the main text). It could influence the position of $\nu_2$ and its combinations. The smallness of the effect would be consistent with the fact that prominent signatures of this resonance were not observed in the spectra.

Also the intensities of (at least) some bands are consistent with such a Fermi resonance: if combination bands $2\nu_7 + \nu_x$ borrow their entire intensity from $\nu_2 + \nu_x$ due to the resonance-induced mixing, a slightly increased interaction term ($\approx 17.8 \text{ cm}^{-1}$) is required for both pairs $2\nu_7 + \nu_9/\nu_2 + \nu_9$ and $2\nu_7 + \nu_{11}/\nu_2 + \nu_{11}$ (intensity ratio $\approx 1:3$, Fig. S1a). For latter example, one has to diagonalize the matrix

$$
\begin{pmatrix}
1971.6 & 17.8 \\
17.8 & 1993.3
\end{pmatrix}
$$

and obtains the eigenvalues

- (1961.604) $\nu_2 + \nu_{11}$ (exp. 1961.6)
- (2003.296) $2\nu_7 + \nu_{11}$ (exp. 2003.3)

and the eigenvectors

$$
\begin{pmatrix}
(-0.872) & (-0.490) \\
0.490 & (-0.872)
\end{pmatrix}
$$

The square of the coefficient ratio $(0.490/0.872)^2 = 0.316$, in good agreement with the observed intensity ratio 0.31 (Fig. S1a).

The reduced value of $W_{\nu_2/2\nu_7} = 16.4 \text{ cm}^{-1}$ (instead of 17.8) implies that still the largest part of the intensity is borrowed.
**3.2. The Fermi resonances between $\nu_5$, $\nu_2 + \nu_6$ and $2\nu_7 + \nu_6$**

To find the parameter for interaction of $\nu_5$ with $\nu_2 + \nu_6$, we note that these two levels are relatively close together in $^{12}C_2F_4$ ($\nu_5 = 1337.7$ from the observed $\nu_5 - \nu_4$ and $\nu_2 + \nu_6 = 1315.3$, derived with the anharmonicity $\chi_{26} = -10.8$, see Table S2. We took the larger magnitude of $\chi_{26}$ from the table because of the small gap for Fermi resonance). The unperturbed levels will be even closer together, so that the interaction of these two levels will dominate over the perturbation by $2\nu_7 + \nu_6$ that is farther apart (Fig. 3b in the main text). We start with the assumption that the magnitude of $\chi_{26}$ is entirely caused by Fermi resonance; the unperturbed $\nu_5^0$ will then be lower by 10.8 and the unperturbed $(\nu_2 + \nu_6)^0$ higher by 10.8 than the corresponding observed or reconstructed levels. The resulting unperturbed pair is nearly degenerate, so that interaction will split them by $2W$; this implies $W = 11.2$.

In fact, with $W = 11.2$ we not only reproduced for $^{12}C_2F_4$ the energies of $\nu_5$ and $\nu_2 + \nu_6$ but also of their combinations with $\nu_9$ with high accuracy. However, the energies of the corresponding $^{13}C_2F_4$ levels were by $5 - 6$ cm$^{-1}$ too high. It can be supposed that this has to do with the fact that the isotopic substitution interchanges the positions of $\nu_5$ and $\nu_2 + \nu_6$ in $^{13}C_2F_4$, so that in the heavier isotopologue the unperturbed levels are not anymore nearly degenerate and the $\nu_5/\nu_2 + \nu_6$ interaction is therefore not so dominant. Obviously one should also take the Fermi resonance $\nu_2/2\nu_7$ (that is, $\nu_2 + \nu_6/2\nu_7 + \nu_6$) into account.

The interaction parameter for this pair should obviously be the same as derived above: $W_{\nu_2/2\nu_7} = 16.4$, also in combinations with other vibrations and for different isotopologues. With this additional level repulsion taken into account, the above $W = 11.2$ should be slightly decreased (consult Fig. 3b of the main text!). We tried with $W_{\nu_5/\nu_2 + \nu_6} = 11$ and found that this choice already reproduces many levels satisfactorily (with the energies of unperturbed levels as parameters), without further iterating the fitting procedure (see below).

To analyse this interaction of the three levels $\nu_5$, $\nu_2 + \nu_6$ and $2\nu_7 + \nu_6$ (see Fig. 3b), we fixed their energies derived from the spectra (from difference and combination bands) of $^{12}C_2F_4$, fixing also
the above (trial) values for the interaction parameters ($W_{v_2/2v_7} = 16.4$ and $W_{v_5/v_2+v_6} = 11$) and thus reconstructed the unperturbed level positions. Adding to these a $v_9$ quantum and correcting by the known anharmonic shifts and then diagonalizing the $3 \times 3$ matrix with the same nondiagonal elements ($W$) results in the energies of the combination levels $v_5+v_9$, $v_2+v_6+v_9$ and $2v_7+v_6+v_9$ (Fig. 3b) with good accuracy (maximum deviation $1.5 \text{ cm}^{-1}$); the corresponding bands are IR active and were directly observed. To calculate the unperturbed levels of $^{13}\text{C}_2\text{F}_4$, one should not use the observed isotopic shift $\Delta v_5 = -51.9$ [1], because it contains a contribution from Fermi resonance. Instead, we use the value $\Delta v_5^0 = -43.1$ from the Teller-Redlich product rule, which is valid for harmonic oscillators [4]. For the other modes, the corresponding corrections are much smaller.

The calculations involved diagonalization of $3 \times 3$ matrixes, for which we used the matrix calculator of [6]. They were done as follows:

### 3.2.1. $^{12}\text{C}_2\text{F}_4$

#### 3.2.1.1. $v_5/v_2+v_6/2v_7+v_6$

The aim is to find a parameter set that will yield

- $v_5 = 1337.7$ (from difference band $v_5-v_4$),
- $v_2+v_6 = 1315.3 = 776.1 (v_2) + 550.0 (v_6) - 10.8$
  (out of the $x_{26}$ values (-8.4, -8.7, -10.8, Table S2) we use the larger magnitude due to the small $v_5/v_2+v_6$ gap),
- $2v_7+v_6 = 1367.5 = 818.9 (2v_7) + 550.0 (v_6) + 2x(-0.7) (x_{67})$

Further fix the interaction parameters at $W_{v_2/2v_7} = 16.4$ and $W_{v_5/v_2+v_6} = 11$ (as discussed above). Then

- vary the energies of the unperturbed levels $v_5^0$, $(v_2+v_6)^0$ and $(2v_7+v_6)^0$. A preliminary estimate (start value of the variation) would be $(v_2+v_6)^0 \approx (v_2)^0 + (v_6)^0 = 783.6 + 550.0 = 1333.6$ (implying $x_{26}^0 = 0$) and a corresponding shift of $v_5$ by 10.8 to 1326.9. Similarly $(2v_7+v_6)^0 \approx 2xv_7 + v_6 + 2x_{26} = 810.9 + 550.0 + 2x(-0.7) = 1359.5$.

After variation one obtains the unperturbed levels in the diagonal of the matrix

\[
\begin{bmatrix}
1332.000 & 11.000 & 0.000 & v_5 \\
11.000 & 1328.600 & 16.400 & v_2+v_6 \\
0.000 & 16.400 & 1359.900 & 2v_7+v_6
\end{bmatrix}
\]

that on diagonalization yields the (indirectly) observed levels as the eigenvalues

$1315.315$ net Fermi shift $-13.3 \text{ cm}^{-1}$ for $v_2+v_6$
The eigenvectors $\Psi$ are

$$\Psi \begin{pmatrix} v_2 + v_6 \\ v_5 \\ 2v_7 + v_6 \end{pmatrix} = \begin{pmatrix} -0.526 \\ 0.798 \\ -0.294 \end{pmatrix}, \quad \Psi_0 \begin{pmatrix} v_5 \end{pmatrix} = \begin{pmatrix} -0.841 \end{pmatrix}, \quad \Psi_0 \begin{pmatrix} v_2 + v_6 \end{pmatrix} = \begin{pmatrix} 0.416 \end{pmatrix}, \quad \Psi_0 \begin{pmatrix} 2v_7 + v_6 \end{pmatrix} = \begin{pmatrix} 0.900 \end{pmatrix}$$

**3.2.1.2. $v_5 + v_9/v_2 + v_6/v_2 + v_6 + v_9$**

The aim is to reproduce the three observed levels of these combination bands (all three are IR active) from the corresponding unperturbed energies. As above, we use the fixed interaction parameters $W_{v_2/v_7} = 16.4$ and $W_{v_5/v_2+v_6} = 11$. But in contrast to above, the unperturbed values are not varied but directly estimated from those not containing $v_9$:

$$v_9 + v_5^0 + x59 = 1340 + 1332.0 + 1.8 \text{ (use low-resolution value)} = 2673.8$$
$$v_9 + (v_2 + v_6)^0 + x29 + x69 = 1340 + 1328.6 + (-2.0) + (-2.8) = 2663.8$$
$$v_9 + (2v_7 + v_6)^0 + 2x79 + x69 = 1340 + 1359.9 + 2(-2.8) + (-2.8) = 2691.5$$

Using these values in the matrix

$$\begin{pmatrix} 2673.800 & 11.000 & 0.000 \\ 11.000 & 2663.800 & 16.400 \\ 0.000 & 16.400 & 2691.500 \end{pmatrix}$$

yields the eigenvalues

$$\begin{pmatrix} 2651.606 \text{ (exp. 2650.5)} \\ 2677.481 \text{ (exp. 2677.9)} \\ 2700.012 \text{ (exp. 2700.0)} \end{pmatrix}$$

and eigenvectors $\Psi$

$$\Psi \begin{pmatrix} v_2 + v_6 + v_9 \\ v_5 + v_9 \\ 2v_7 + v_6 + v_9 \end{pmatrix} = \begin{pmatrix} (-0.417) \\ (0.841) \\ (-0.346) \end{pmatrix}, \quad \Psi_0 \begin{pmatrix} v_5 + v_9 \end{pmatrix} = \begin{pmatrix} -0.889 \end{pmatrix}, \quad \Psi_0 \begin{pmatrix} v_2 + v_6 + v_9 \end{pmatrix} = \begin{pmatrix} 0.452 \end{pmatrix}, \quad \Psi_0 \begin{pmatrix} 2v_7 + v_6 + v_9 \end{pmatrix} = \begin{pmatrix} 0.871 \end{pmatrix}$$

If the two other combination bands borrow their intensity from $v_5 + v_9$, it should be proportional to the square of the underlined coefficients. The intensity ratios in the spectra are consistent with this (Fig. S1b).

**3.2.2. $^{13}$C$_2$F$_4$**

**3.2.2.1. $v_5/v_2 + v_6/2v_7 + v_6$**

We use again the same interaction parameters and construct the unperturbed levels from the expected shifts.
• For $\nu_5^0$, we estimate an isotopic shift of $\Delta \nu_5^0 = -43.1$ on the basis of the Teller-Redlich product rule (which is valid for harmonic oscillators [4]) for the product $\nu_5 \times \nu_6$, using the experimental $\Delta \nu_6 = -3.0$. (Fermi resonance is expected to contribute much to the shift of the observed $\nu_5$, $\Delta \nu_5 = -51.9$; this is confirmed by the calculation.)

• For $(\nu_2+\nu_6)^0$, we use the observed $\Delta \nu_6 = -3.0$, but the computed harmonic value $\Delta \nu_2^0 = -1.4$ instead of the experimental $-6.4$. (The alternative $\Delta \nu_2^0 = 0$ does not make much difference.) This is because part of the observed shift is due to the $\nu_2/2\nu_7$ Fermi resonance, which is explicitly included in the matrix model. For $^{12}\text{C}_2\text{F}_4$, $(\nu_2+\nu_6)^0 = 1328.6$, so that the corresponding value for $^{13}\text{C}_2\text{F}_4$ will be at 1324.2.

• For $(2\nu_7+\nu_6)^0$, we use the observed $\Delta \nu_6 = -3.0$ and twice the observed $\nu_7$ shift ($2\Delta \nu_7 = 2\times(-11.8)$). Hence from the $^{12}\text{C}_2\text{F}_4$ value (1359.9) one calculates $(2\nu_7+\nu_6)^0 = 1333.3$ for $^{13}\text{C}_2\text{F}_4$.

Then diagonalization of

\[
\begin{bmatrix}
1288.9 & 11.0 & 0.0 \\
11.0 & 1324.2 & 16. \\
0.0 & 16.4 & 1333.3
\end{bmatrix}
\]

yields the eigenvalues

\[
\begin{align*}
(1285.270) & \quad \text{net Fermi shift } -3.6 \text{ cm}^{-1} \text{ for } \nu_5 \\
(1314.562) & \quad \text{net Fermi shift } -9.6 \text{ cm}^{-1} \text{ for } \nu_2+\nu_6, \\
(1346.569) & \quad \text{net Fermi shift } +13.3 \text{ cm}^{-1} \text{ for } 2\nu_7+\nu_6
\end{align*}
\]

A minor adjustment of $\nu_5^0$ by +0.6 (which is within the tolerance level of the Teller-Redlich rule) can match the observed $\nu_5$ exactly:

\[
\begin{bmatrix}
1289.5 & 11.0 & 0.0 \\
11.0 & 1324.2 & 16.4 \\
0.0 & 16.4 & 1333.3
\end{bmatrix}
\]

Eigenvalues:

\[
\begin{align*}
(1285.804) & \quad \text{net Fermi shift } -3.7 \text{ cm}^{-1} \text{ for } \nu_5 \\
(1314.619) & \quad \text{net Fermi shift } -9.6 \text{ cm}^{-1} \text{ for } \nu_2+\nu_6, \\
(1346.577) & \quad \text{net Fermi shift } +13.3 \text{ cm}^{-1} \text{ for } 2\nu_7+\nu_6
\end{align*}
\]

Eigenvectors:

\[
\begin{align*}
\Psi & \quad \nu_5 & \quad \nu_2+\nu_6 & \quad 2\nu_7+\nu_6 & \quad \Psi_0 (\nu_5) \\
(-0.942) & (-0.313) & (0.120) & & \\
(0.317) & (-0.714) & (0.625) & & \Psi_0 (\nu_2+\nu_6) \\
(-0.109) & (0.627) & (0.772) & & \Psi_0 (2\nu_7+\nu_6)
\end{align*}
\]

Notes:
The unperturbed $v_5$ shift comes out right: 1332.0 to 1289.5 is $-42.5 \text{ cm}^{-1}$ (compared to -43.1 by Teller-Redlich rule, or -41.6 cm$^{-1}$ from harmonic MP2 calculation) The overall Fermi shifts (difference of shifts for $^{13}$C$_2$F$_4$ and $^{12}$C$_2$F$_4$) contribute about $-(3.6..3.7) - 5.7= -(9.3..9.4) \text{ cm}^{-1}$ to the $v_5$ isotopic shift; adding $-9.4$ to $\Delta v_5^0 = -42.5$ perfectly agrees with the observed shift of $\Delta v_5 = -41.9$.

3.2.2.2. $v_5+v_9/v_2+v_6+v_9/2v_7+v_6+v_9$

We again use the same interaction parameters. The unperturbed wavenumbers are estimated from the $^{13}$C$_2$F$_4$ $v_5$ region (alternatively from the $^{12}$C$_2$F$_4$ $v_5+v_9$ region):

$v_9 + v_5^0 + x59 (13C value) = 1305 + 1289.5 + (-1.0) = 2593.5$
$v_9 + (v_2+v_6)^0 + x29 (12C value) + x69 (12C value) = 1305 + 1324.2 + (-2.0) + (-2.8) = 2624.4$
$v_9+(2v_7+v_6)^0 + 2x79 (12C value) + x69 (12C value) = 1305 + 1333.3 + 2x(-2.8) + (-2.8) = 2629.9$

Then diagonalizing

\[
\begin{bmatrix}
2593.5 & 11.000 & 0.000 & (v_5+v_9) \\
11.000 & 2624.4 & 16.400 & (v_2+v_6+v_9) \\
0.000 & 16.400 & 2629.9 & (2v_7+v_6+v_9)
\end{bmatrix}
\]

yields the eigenvalues

$(2589.258) \quad (\text{exp. 2589.8}) \quad v_9+v_5$, separation from $v_9+v_2+v_6$ is 24.5

$(2613.738) \quad (\text{exp. 2616.1, Fig. S2}) \quad v_9+v_2+v_6$

$(2644.804) \quad v_9+2v_7+v_6$

and eigenvectors

$\Psi' \quad v_5+v_9 \quad v_2+v_6+v_9 \quad 2v_7+v_6+v_9$

$(-0.923) \quad (-0.356) \quad (0.143) \quad \text{underlined: } \Psi_0 \quad \text{component}$

$(\frac{1}{0.356}) \quad (-0.656) \quad (0.666) \quad \Psi_0 \quad (v_2+v_6+v_9)$

$(\frac{1}{0.144}) \quad (0.665) \quad (0.732) \quad \Psi_0 \quad (2v_7+v_6+v_9)$

The deviation of the calculated $v_2+v_6+v_9$ from observation can be diminished by moving the unperturbed $(2v_7+v_6+v_9)^0$. In view of the uncertain assumption that $x_{69}$ and $x_{79}$ (also $x_{29}$) are the same for the two isotopologues, this seems more plausible than changing the interaction parameters. Using $(2v_7+v_6+v_9)^0 = 2635.5$, diagonalizing

\[
\begin{bmatrix}
2593.5 & 11.000 & 0.000 \\
11.000 & 2624.4 & 16.400 \\
0.000 & 16.400 & 2635.5
\end{bmatrix}
\]

yields the eigenvalues

$(2589.358) \quad (\text{exp. 2589.8}) \quad v_9+v_5$, separation from $v_9+v_2+v_6$ is 26.6

$(2615.992) \quad (\text{exp. 2616.1}) \quad v_9+v_2+v_6$

$(2648.050) \quad v_9+2v_7+v_6$

and eigenvectors

$(-0.929) \quad (-0.351) \quad (0.122)$
Notes:

The observed spacing of $v_5 + v_9$ (2589.8) from $v_2 + v_6 + v_9$ (2616.1) is 26.3, in good agreement with the second calculated value (26.6).

The relative intensities of the $^{13}\text{C}_2\text{F}_4$ features predicted by the matrix model is consistent with the observed spectrum (not shown).

Fig. S2, showing $v_2 + v_6 + v_9$ at 2616.1 (previously assigned to 2603.4) and $v_5 + v_9$ at 2589.8 of $^{13}\text{C}_2\text{F}_4$ (634 mbar of isotopic mixture, 10 cm). The structure around 2610 must belong to $^{12}\text{C}^{13}\text{C}_2\text{F}_4$, as demonstrated by the spectrum at high pressure (110 mbar, 1 m, upper trace) at natural abundance.

3.2.3. The $v_1/v_5 + v_6$ Fermi resonance and $\chi_{18}$

There are several indications that levels containing $v_1$ are perturbed by Fermi interaction with corresponding levels containing $v_5 + v_6$.

(1) The values of $\chi_{18}$ vary from $-18.0$ to about $-20$ cm$^{-1}$ depending on the level (8 examples in Table S2). While it can be a hint to invoke Fermi resonance, the variation is small (10%) and does not provide quantitative conclusions.

(2) For $^{13}\text{C}_2\text{F}_4$, $\chi_{18} = -16.6$ cm$^{-1}$ as derived from a hot band (starting from the $v_8$ level) of $v_1 + v_{11}$ and similarly with $v_1 + v_{12}$ (Table S2). This represents a reduction of 13% compared to $-19.0$ cm$^{-1}$ for the analogous bands of $^{12}\text{C}_2\text{F}_4$. For this symmetric $^{13}\text{C}$ substitution, the
approximate isotopic rule \( \frac{x_{18}^{13C_2}}{x_{18}^{12C_2}} = \frac{\omega_{1}^{13C_2}}{\omega_{1}^{12C_2}} \frac{\omega_{8}^{13C_2}}{\omega_{8}^{12C_2}} \) (e.g. chapter 2.6 of [4]) would lead to an expected change of 7.0 %, reducing the magnitude of \( x_{18} \) by 1.3 cm\(^{-1}\) in the absence of additional Fermi resonance effects. Thus it is possible that \( x_{18} \) of \( ^{13}C_2F_4 \) is reduced by a further 1 cm\(^{-1}\), and if so this could be attributed to a \( \nu_1/\nu_5+\nu_6 \) Fermi resonance interaction with varying separation.

(3) Whereas the hot-band structure of \( \nu_1 \) combination bands is congruent for the two monoisotopic molecules, that of \( ^{12}C^{13}C_2F_4 \) is clearly different. In this lower-symmetry isotopologue \( \nu_5 \) mixes with \( \nu_9 \) and the frequencies of both are drastically changed [1], as mentioned, so that the \( \nu_1/\nu_5+\nu_6 \) Fermi resonance is strongly altered or breaks down. Even without working out details, consequences for the hot-band structure can be expected. While we take this as a definite hint to this Fermi resonance, it is not quantitatively helpful.

(4) Assuming that this Fermi resonance is active and causes intensity borrowing, we can compare the intensity of a \( \nu_5+\nu_6 \) combination with that of a \( \nu_1 \) combination. The \( \nu_5+\nu_6+\nu_{12} \) band (2444.3 cm\(^{-1}\)) has about 1-2% the strength of the \( \nu_1+\nu_{12} \) band (2428.7 cm\(^{-1}\), Fig. 1b of the main text); similarly, the \( \nu_5+\nu_6+\nu_{11} \) shoulder (3072 cm\(^{-1}\)) is <1% as intense as \( \nu_1+\nu_{11} \) (3056.2 cm\(^{-1}\)) (barely visible in Fig. 1b of the main text). From both, one can estimate a Fermi term \( (W) \) of no more than \( \approx 2.5 \) cm\(^{-1}\), causing a shift (and change of \( x_{18} \)) of <0.5 cm\(^{-1}\). This is even an upper bound, because such weak bands can also be expected without intensity borrowing.

Points (1) to (3) represent qualitative evidence that a \( \nu_1/\nu_5+\nu_6 \) Fermi resonance is active. Its strength can be deduced from intensity borrowing (point (4)). It implies that Fermi resonance affects the magnitude of \( x_{18} \) only little (by <0.5 cm\(^{-1}\), i.e. <3%), so that we can maintain the conclusions of sec. 4.1 of the main text on the shape of the potential.

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