Rotational Spectra of Symmetric Top Molecules in Ground and Different Vibrational Excited States, and Phenomenon of Resonance – Applying in CF$_3$CCH

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Abstract: This paper deals with review of exploration of resonance in symmetric top molecules in different vibrational excited states, $v_t = n$ ($n = 1, 2, 3, 4$). Calculations for CF$_3$CCH shows that resonance take place at $k = \frac{x_{\ell \ell} + (A - B) - 2A\zeta}{A\zeta - (A - B)}$ and $k = \frac{x_{\ell \ell} + (A - B) - 2A\zeta}{A\zeta - (A - B)}$ for $v_{10} = 2$ and $v_{10} = 3$ respectively. In order to account for splitting about 3 MHz for the - 2 series in $v_{10} = 4$ is necessary to introduce the element $\langle J, k, \ell | f_{32} | J, k + 2, \ell - 4 \rangle$ in fitting program.

Keywords: excited states, resonance, CF$_3$CCH, symmetric top molecules

1. Introduction

The vibrational spectrum of CF$_3$CCH was assigned by Berney et al [1]. The energy level of its lowest lying degenerate vibration is only $E = 171$ cm$^{-1}$, consequently according to the Boltzman distribution law it has a population of 58% (29%×2 for vibrational degeneracy) of the ground state at dry ice temperature (200 K). Therefore the rotational spectrum in the $v_{10} = 1$ state is also strong and it is not complicated by interactions with nearby vibrational states. Whereas it is a prolate top, its rotational constants $A \approx 5.7$ and $B \approx 2.9$ GHz are not large. So, it is a possible candidate for the
observation of the A₁-A₂ splitting in the ground state. The qᵣ⁺ is rather large and A – B – Aζ is small and it is possible to observe direct ℓ-type resonance transitions in the microwave range [2]. These situation have been previously observed only for PF₃, v₄ = 1 [3], for CF₃H and CF₃D, v₆ = 1 [4], CF₃Cl, v₆ = 1 [5] and CH₃CF₃, v₁₂ = 1 [6]. The rotational spectra of CF₃CCD, the isotopomer of this molecule in the ground, v₁₀ = 1 and v₁₀ = 2 states have been measured and studied by several authors [7-11].

Three identical fluorine atoms (I = 1/2) in CF₃CCH have important consequences in the determination of relative intensities of signals. The symmetry operations like exchange of nuclei, have symmetric effect on the total wavefunction for nuclei with integral or zero spin (Bose particles). But for nuclei with half integral spin (Fermi particles) the total wavefunction is antisymmetric. The rotation about the C₃ axis through 2π/3 or 4π/3 rotation is equal to two exchanges of nuclei. Therefore it is symmetric (A) for Fermi particles as well as Bose particles. A rotation of 2π/3 about top axis will not change ψ旋转 states with k = 3n (n = integer, including n = 0) since ψ旋转 ∝ e^ikψ. For the symmetric state, the species are A and in antisymmetric state (k ≠ 3n ) the species are E. There are eight different possibilities for combinations of three fluorine atoms with spin 1/2. Two of them can occur when three spins are the same 1/2 or -1/2, these are totally symmetric because they remain unchanged by any permutation of nuclei which are equivalent to a rotation. But this situation can not take place for the remaining 6 arrangements, which are 2A₁ + 2E. So the 8 spin functions are 4A₁ + 2E. The statistical weight depends on the ratio between the spin function of symmetry A and the spin function of symmetry E. Consequently:

The intensity of A rotational states = 2 (intensity of E rotational states)

For symmetric top molecules like CF₃CCH, the ground vibrational state rotational energies are given up to sextic terms by equation (1) and by application of selection rules ΔJ = + 1 and Δk = 0, the frequencies are given by equation (2).

\[
E_{J,k} = BJ(J + 1) + (A - B)k^2 - D_JJ^2(J + 1)^2 - D_{Jk}(J + 1)k^2 - D_kk^4
\]

\[
+ H_JJ(J + 1)^3 + H_{Jk}J^2(J + 1)^2k^2 + H_{kJ}J(J + 1)k^4 + H_kk^6
\]

\[
ν = 2B(J + 1) - 4D_J(J + 1)^3 - 2D_{Jk}(J + 1)k^2 + H_J(J + 1)^3[(J + 2)^3 - J^3]
\]

\[
+ 4H_{Jk}(J + 1)^3k^2 + 2H_{kJ}(J + 1)k^4
\]

The spectra in this state are simple, so the different k values (k = 0,1,2,3,4...) for each J transition are assigned easily. This is illustrated in Figure 1, which shows part of the observed transition J = 24 → 25, and compares it with the calculated spectrum.

The centrifugal distortion produces a band head to high frequency at k = 0, with a spread to lower frequency with higher k Figure 2. Due to negative value of D_{Jk} for CH₃Cl, this situation is different Figure 3.
Figure 1. Part of the $J = 24 \rightarrow 25$ spectrum of CF$_3$CCH in ground state. The top trace (A) is the observed spectrum, the lower (B) is a computer simulation.

If $|k|$ values are plotted against frequency for this state, the Fortrat diagrams are produced which are shown in Figures 2,3. In these diagrams the splitting increase as $k$ increases and this is due to the $D_{Jk}$ parameter. $D_{Jk}$ is 6.27 and -2.517 kHz for CF$_3$CCH and CHCl$_3$ respectively [2, 12].

The sextic centrifugal distortion constants were accurately determined for the first time for the ground state, and result shows that $H_{Jk} > |H_{kJ}|$ and $H_{kJ} < 0$. For this molecule the sextic splitting constant $h_3$ is very small [2]. Cazzoli et al. [13] have found amount of this value, which is $h_3 = 2.3 \times 10^{-21} \frac{B^4}{A-B}$. The predicted value of $h_3$ for CF$_3$CCH, $2.6 \times 10^{-11}$ MHz, gives a splitting about 12 MHz for the highest - J transition ($J = 112$) [2].

Figure 2. Fortrat diagram of CF$_3$CCH in ground state $J = 21 \rightarrow 22$. 
2. Rotation Spectrum in Excited State $v_{10} = 1$

Because $v_{10}$ state of this molecule has a high population, the rotational spectra in this state are also strong. It is isolated in frequency from other vibrational states, so is not complicated by interactions with nearby states.

Rotational frequencies for transitions $J \rightarrow J + 1$ in the excited degenerate vibrational state $v_1 = 1$, $\ell_1 = \pm 1$ of molecules with axial symmetry were calculated by Nielsen [14]. Although the Nielsen theory was fairly satisfactory for the rotation spectrum of these type of molecules, some of the calculated frequencies by this method were different from the observed frequencies. This formula was extended to the case of higher J value by Gordy et al. [7]. They also interpreted the transitions $J = 4 \rightarrow 5$ and $J = 8 \rightarrow 9$ of CF$_3$CCH in the excited state $v_{10} = 1$. Then the frequencies of lines for transition $J \rightarrow J + 1$ were investigated and calculated for $v_1 = 1$ and $v_1 = 2$ states [15, 16].

The frequency of transition $J \rightarrow J + 1$ for molecules belonging to the point group $C_{3v}$ in singly excited vibrational state $v_1 = 1$, is given by the approximate perturbation expression, equation (3).

$$\nu = 2B(J + 1) - 4D_J(J + 1)^3 - 2D_{Jk}(J + 1)k^2 + 2\eta_J(J + 1)k\ell + \Delta \nu$$

where $\Delta \nu$ has the value $\pm q_i^+(J + 1)$ if $(k\ell - 1) = 0$ ($\ell$ - type doubling) or

$$\Delta \nu = -\frac{(q_i^+)^2(J + 1)^3}{4(B - A + A\zeta)(k\ell - 1)}$$

if $(k\ell - 1) \neq 0$ ($\ell$ - type resonance) (4)

Where is the $\ell$-type doubling constant, $B$ and $A$ are rotational constants, and $\zeta$ is the z-coriolis constant for the vibrational state $v_i$. The degree of $\ell$-resonance thus largely depends on the ratio of $q_i^+$ to the resonance denominator $(B - A + A\zeta)$. With low to moderate values of this denominator, the spectrum usually found consists of two extreme outer lines for $(k\ell - 1) = 0$ (the $\ell$- doublets) and a center group of lines for $(k\ell - 1) \neq 0$ whose structure depends very strongly on other parameters such as the centrifugal distortion constants. As the strength of the resonance increase, the lines of the center group
spread out until the low $|k_l-1|$ transitions approach the positions of the $\ell$-doublets. So for large $q_t^+$ and small $(A - B - A_\zeta = -458$ MHz value it is possible to observe direct $\ell$-resonance transitions in the microwave range. This is a typical pattern for $C_3v$ doubly degenerate states and is predominantly due to the combinations of the splitting of the positive and negative $(k\ell - 1)$ series by $\ell$-type resonance [which is inversely proportional to $(k\ell -1)$] and the shift to low frequency due to $D_{jk}$ [which is proportional to $(k\ell -1)^2$]. Thus one series goes from high frequency at low k to low frequency at high k, while the other is at low frequency both for high and low k, with a head at some intermediate value.

In order to obtain more accuracy than can be obtained from perturbation theory in rotational energies for singly excited vibrational states it is necessary to set up the rotational Hamiltonian as a matrix $(H)$ in equation $H\psi = E\psi$ and diagonalise to obtain the energy (2,10,11,17,18,21,22). This is particularly necessary when $\zeta$ is small in the above equation; the diagonalization avoids the errors implicit in perturbation theory or the need to go to higher orders of perturbation.

The Hamiltonian is set up for a symmetric top molecule like CF$_3$CCH [2, 11]. This rotation-vibrational Hamiltonian has two different blocks belong to the different $\ell = +1$ and $\ell = -1$ series. $k$ and $\ell$ are no longer good quantum numbers but $(k - \ell)$ or $(k\ell - 1)$ may be used to distinguish between the symmetry species; those levels with $(k\ell - 1) = 3n$, where $n$ is an integer, are of species $A_1$ or $A_2$. If $(k\ell - 1) \neq 3n$ the species are $E$. The $q_t^+$ produces a first order splitting of the $(k\ell - 1) = 0$, $A_1A_2$ pair which are the familiar $\ell$ - doublets, as shown by Grenier-Besson and Amat and others [2, 10, 11, 15, 19]. The main difference from the ground state spectra is the splitting of the $|k - \ell| = 0$ into two widely separate $\ell$ - doublets and the splitting, due to $\ell$ - resonance. Where $\ell$ is the vibration angular momentum quantum number and $\zeta$ is the Coriolis coupling coefficient. Hence $k$ and $\ell$ are not good quantum numbers, though $k\ell - 1$ may be used as a satisfactory label.

The diagonal elements of the Hamiltonian used were:

\[<v_t, \ell_t, J, k | H/h | v_t, \ell_t, J, k> = BJ(J + 1) + (A - B)k^2 \times 2A_\zeta k\ell - D_JJ^2(J + 1)^2 - D_{jk}(J + 1)^2 - H_JJ^3(J + 1)^3 + H_{jk}J^2(J + 1)^2k^2 + H_{k}J(J + 1)k^4 + H_kk^6 + \eta_J(J + 1)k\ell + \eta_kk^3\ell\] (5)

In addition there are off-diagonal elements given by:

\[<v_t, \ell, J, k | H/h | v_t, \ell \pm 2, J, k \pm 2> = -\frac{1}{4}q_t^+\{(v_t \mp \ell)(v_t \pm \ell + 2)[J(J + 1) - k(k \pm 1)] \times [J(J + 1) - (k \pm 1)(k \pm 2)]\}^{1/2}\] (6)

and $<v_t, \ell, J, k | H/h | v_t, \ell \pm 2, J, k \mp 1>$

\[= r_{t1}[(v_t + 1)^2 - (\ell \pm 1)^2]^{1/2}[J(J + 1) - k(k \mp 1)]^{1/2}(2k \mp 1).\]
In equation 5, the $D_J$, $D_{Jk}$, $D_k$ are quartic, $H_J$, $H_{Jk}$, $H_{kJ}$ are sextic centrifugal distortion terms respectively. $\zeta$ is the Coriolis coupling coefficient between the two components of the degenerate state and $\eta_J$ represents the centrifugal distortion of $(A\zeta)$. The general effect of the additional parameters to complicate the spectrum relative to that of a non-degenerate state.

If $|k\ell - 1|$ values are plotted against frequency for this state, the Fortrat-diagram is produced which is shown for CH$_3$CCH in Figure 4. This diagram shows the 'l' doublet and two different series $\ell = \pm 1$. So the spectrum is more complex compared with ground state [2].

![Figure 4. Fortrat diagram of CF$_3$CCH in v$_{10}$ = 1 state. J = 20 → 21.](image)

In the present example the rotational Hamiltonian was diagonalised to give exact $\ell$-resonance shifts. The spectrum in the millimetre-wave should consist of two widely spaced lines, the $\ell$-doublets, whose separation is given by equation (4), and a central group of transitions with $|k\ell - 1| > 0$, whose frequencies are determined by equation (3). In the latter set the transitions with low values of $|k\ell - 1|$ will tend to lie towards the outside of the group since their $\ell$-resonance shifts as predicted by equation (3) will be large. Two series should thus be observed depending on the sign of $k\ell - 1$. There are two different series in spectrum, making it more difficult to assign than the ground state Figure 4.

3. Rotational Spectra in Excited States, v$_{10}$ = 2, 3, 4

The vibrational level v$_{10}$ = 2 is located at 342 cm$^{-1}$. The vibrational levels closest to v$_{10}$ = 2 are v$_5$ = 1 and v$_9$ = 1 at 536 and 452 cm$^{-1}$, respectively [2, 9, 20-22]. As the analysis will show, the level can be considered as being isolated and an effective Hamiltonian for a v$_l$ = 2 level is suitable for the analysis of the data. The general features of the direct $\ell$-resonance transitions in the v$_l$ = 2 level have been discussed by Harder et al. [21]. There is a good agreement for the obtained rotational constants B and the $\ell$-dependence $\gamma_{\ell l} = (B_2 - B_0)/4$. Because the main information is obtained from the data of Carpenter et al [20]. The fact that the direct $\ell$-type resonance transitions provide further information on [21]. Excellent agreement is obtained for the values of $g_{\ell l} = E_{\ell} - E_0^l/4$, because the parameter A constrained in its value [20]. The B and other spectroscopic constants determined accurately up to v$_{10}$ = 4 and show a regular dependence on the vibrational quantum number Figure 5 [2, 20, 22, 23].
Figure 5. Plot of B against $v_t$ for CF$_3$CCH.

These spectra show no obvious regularity from the point of view of frequencies as well as intensities, because there are three series for each J since the vibrational angular momentum quantum number $l$ can have values 0 and $\pm$ 2. Therefore it is difficult to identify the quantum numbers k and $\ell$ associated with each absorption in these spectra. However from the point of view of experimental work, correspondence between the lines of different J value should be observed with respect to their relative position as well as their intensities.

In order to obtain more accuracy in rotational energies for excited vibrational state $v_t = 2$ it is necessary to set up the rotational Hamiltonian as a matrix (H) in eigenvalue equation, $H\psi = E\psi$, and diagonalise to obtain the energy [20-22]. The diagonal matrix elements are given by equation (7). This Hamiltonian can set up for a symmetric top molecule such as CF$_3$CCH, CF$_3$CCD, CF$_3$CN, and OPF$_3$ [10, 20-30]. It has three different vibrational blocks related to $l = 2, 0$ and -2 Figure 6. The vibrational anharmonicity $x_\ell l^2$ separates the $l = \pm 2$ and $l = 0$ blocks and they are coupled by the matrix elements $q_\ell$ and $r_\ell$.

In order to explain the form of the spectra we need to consider the energy levels in $v_t = 2$ as given by the Hamiltonian matrix. The diagonal elements are:

$$<v, \ell, J, k|H|v, \ell, J, k> = v_0 + x_\ell \ell^2 + B[J(J + 1) - k^2] + A_k^2 - 2A_\ell k \ell$$

$$-D_{J2}(J + 1)^2 - D_{Jk}(J + 1)k^2 - D_k k^4 + \eta_J J(J + 1) k \ell + H_2 J^3(J + 1)^3 + H_{k2}(J + 1)k^2$$

$$+ H_4 (J + 1)k^4 + H_6 k^6 + \eta_J J^2(J + 1)^2 k \ell + \eta_k k^3 \eta_\ell + .......$$

(7)

Where $v_0$ = pure vibrational frequency which is independent of J, k, $\ell$ and $x_\ell$ is the anharmonicity factor in $\ell$. The main off-diagonal elements are the $\ell$-doubling elements equation (6).
Figure 6. The Hamiltonian matrix for $v_{10} = 2$ state, $J = 2$.

4. Plot of Beff

Plotting of $\frac{v}{2(J+1)}$ against $(J + 1)^2$ can help us to analysis of signals in excited states. Which is described below?

From the theoretical point the frequency expression for transition $J \rightarrow J + 1$ may be put in following effective form:

$$v = (J + 1) A(J, k, \ell) + (J + 1)^3 B(J, k, \ell)$$

where $A(J, k, \ell)$ and $B(J, k, \ell)$ are complicated functions of $J$, $k$ and $\ell$.

Therefore:

$$\frac{v}{(J+1)} = A(J, k, \ell) + (J + 1)^2 B(J, k, \ell)$$

For analysis and investigation of signals, equation (7) can be changed after some abbreviation and alteration to the following form:

$$v = 2B(J + 1) - 4D_J(J + 1)^3 - 2D_k(J + 1)k^2$$

$$\pm (q_{\ell}^+)(J + 1) \quad \text{for } k\ell - 1 = 0$$
or \(-\frac{(q^+_i)^2(J+1)^3}{4(B-A+A\zeta)(k\ell-1)}\) for \(|k\ell-1| \neq 0\)

If both sides of Eq (13) are divided by \(2(J+1)\), then:

\[
\frac{v}{2(J+1)} = B - D_{jk}k^2 \pm \frac{1}{2}q^+_i - 2D_J(J+1)^2 \quad \text{for} \ k\ell - 1 = 0
\]

(11)

and

\[
\frac{v}{2(J+1)} = B - D_{jk}k^2 \pm 2D_J(J+1)^2 - \frac{(q^+_i)^2(J+1)^2}{8(B-A+A\zeta)(k\ell-1)} \quad \text{for} \ (k\ell - 1) \neq 0
\]

(12)

Hence plotting \(\frac{v}{2(J+1)}\) as a function of \((J+1)^2\) will produce a series of lines; two of them relate to \(k\ell - 1 = 0\) with slope \(-2D_J\) and intercept \(B - D_{jk}k^2 \pm \frac{1}{2}q^+_i\).

The \(k\ell - 1 \neq 0\) states will produce a series of lines with slope

\[-2D_J - \frac{(q^+_i)^2}{8(B-A+A\zeta)(k\ell-1)}\]

(13)

and intercept \(B - D_{jk}k^2\). Some of them are nearly parallel to each other and some of them show curvature due to strong \(\ell\) resonance. Equation (10) can be further simplified by taking the term in \(D_j\) to the right hand side. This is then an effective \(B\) value for the given transition; hence termed BPlot. Any slope or curvature is then due to the effect of \(\ell\)-resonance.

\[v = 2B_{\text{eff}}(J + 1) - 4D_J(J + 1)^3\]

(14)

\[\therefore B_{\text{eff}} = \frac{v}{2(J+1)} + 2D_J(J+1)^2\]

(15)

Plotting of \(B_{\text{eff}}\) as a function of \((J+1)^2\) will produce a series of lines, each of which belongs to a different \((k\ell - 1)\) value. Correlation of observed lines in different \(J\) can then be used to help with the assignment.

In \(v_t = 2\) state the Hamiltonian blocks off into factors which for a \(C_{3v}\) molecule are of symmetry species \(A_1, A_2\) and \(E\). \(k\) and \(\ell\) are no longer good quantum numbers but \((k - \ell) \times s\) remains a good symmetry label. In this label \(s\) is sign of \(\ell\), \(s = +1\) for \(\ell \geq 0\) and \(s = -1\) for \(\ell < 0\). The spectra are labeled by \((k-\ell)^{\prime}\) such as 0\(^2\), -1\(^2\) and 0\(^3\) in the spectrum of \(J = 19\) Figure 7.

Accidental resonances can occur when the \(\ell = 0\) series are coupled via the \(q^+_i\) term with \(\ell = 2\) series. This resonance will affect the frequencies of the \(|J, k, \ell\rangle \rightarrow |J + 1, k, \ell\rangle\) transitions. The maximum resonance will occur when the energy of state \(\ell = 2, k + 2\) equals that of \(\ell = 0, k\) i.e.

\[E(|J, k, \ell = 0\rangle) = E(|J, k + 2, \ell = 2\rangle)\]

(16)

After omitting terms which are the same from both sides of equation (8) this gives:
\[(A - B)k^2 = 4x_{\ell\ell} + (A - B)(k + 2) - 4A\zeta(k + 2)\]  

(17)

Hence \[k = \frac{x_{\ell\ell} + (A - B) - 2A\zeta}{A\zeta - (A - B)}\]  

(18)

Figure 7. Part of the J = 19 → 20 spectrum of CF₃CCH in ν₁₀ = 2 state. The top trace (A) is the observed spectrum, the lower (B) is a computer simulation.

If the rotational constants of CF₃CCH from Table 1 are put in equation (18) then k is found to be 9.7. Experimentally the resonance is indeed observed between k = 9 and k = 10 for this molecule and is independent of J, as expected from equation (18). The calculated spectrum of CF₃CCH in J = 20 → 21 show this resonance Figure 8. Like this resonance take places in different k values for different molecules which depends on their parameters Table 2.

Figure 9 shows the energy levels as \(\ell = 2, 0, -2\) stacks. The lines between states in adjacent stacks represent the \(\ell\)-type interaction; for example k = 4 in \(\ell = -2\) is linked to k = 6, \(\ell = 0\) and this also interacts with k = (6 + 2) = 8, \(\ell = +2\). The interaction results in the energy levels being pushed apart; for example k = 4 is shifted up and k = 6 is shifted down. The extent of this shift depends on how nearly equal are the energy levels. When they are close, a large shift is obtained. The maximum shift...
will occur when the energies are almost equal, see equation (18) and is found in the region of \( k = 9 \). This phenomenon can occur at \( k \approx 16 \) value for CF\(_3\)CCD, Table 2.

**Figure 8.** Calculated Spectrum of CF\(_3\)CCH in \( v_{10} = 2 \) State. \( J = 20 \rightarrow 21 \).

**Figure 9.** Diagram of energy levels for CF\(_3\)CCH in \( v_{10} = 2 \) State.
Table 1. Comparison of the Parameters for the Excited States
\( v_{10} = n \) (n = 0, 1, 2, 3, 4) of CF$_3$CCH.

| Parameter       | \( v_{10} = 0 \) [2] | \( v_{10} = 1 \) [2] | \( v_{10} = 2 \) [20] | \( v_{10} = 3 \) [22] | \( v_{10} = 4 \) [22] |
|-----------------|-----------------------|-----------------------|------------------------|------------------------|------------------------|
| A/MHz           | 5718.8436*            | 5718.8436*            | 5718.8436*             | 5718.8436*             | 5718.8436*             |
| B/MHz           | 2877.9535(78)         | 2883.4613(1)          | 2888.9678(3)           | 2894.3884(75)          | 2899.7481(14)          |
| \( A\zeta \)/MHz| -                     | 3293.5541(71)         | 3293.064(9)            | 3289.833(162)          | 3285.999(334)          |
| \( q_1^+ \)/MHz | -                     | 3.6206334(72)         | 3.6206334*             | 3.6154(4)              | 3.6169(8)              |
| \( r_1^+ \)/MHz | -                     | 0.0*                  | 0.203(24)              | 0.165(12)              | 0.197(9)               |
| \( D_f \)/kHz   | 0.2684784(190)        | 0.275890(33)          | 0.2817(2)              | 0.2888(8)              | 0.2954(16)             |
| \( D_{Jf} \)/kHz| 6.276962(20)          | 6.239328(46)          | 6.2073(15)             | 6.1628(8)              | 6.1351(17)             |
| \( D_g \)/kHz   | -5.23*                | -5.23*                | -5.23*                 | -5.23*                 | -5.23*                 |
| \( \eta_f \)/kHz| -                     | 25.50129(89)          | 25.025(13)             | 24.977(6)              | 24.847(8)              |
| \( \eta_k \)/kHz| -                     | -19.1916(42)          | -19.1916*              | -15.38(71)             | -28.86(177)            |
| \( D_{fJ} \)/Hz | -                     | -                     | -0.3950(62)            | -0.395*                | -0.395*                |
| \( D_{fJ} \)/Hz | -                     | -                     | -0.967(280)            | -0.967*                | -0.967*                |
| \( H_f \)/mHz   | 0.03195(110)          | 0.0348(33)            | 0.0*                   | 0.0*                   | 0.0*                   |
| \( H_{fJ} \)/mHz| 18.0092(170)          | -17.824(43)           | 15.15(96)              | 15.15*                 | 15.15*                 |
| \( H_{kJ} \)/mHz| -11.5756(170)         | -12.19(66)            | 0.0*                   | 0.0*                   | 0.0*                   |
| \( H_k \)/mHz   | -                     | 0.0*                  | 0.0*                   | 0.0*                   | 0.0*                   |
| \( q_f \)/Hz    | -                     | 4.29834(36)           | 0.0*                   | 0.0*                   | 0.0*                   |
| \( \gamma_f \)/kHz| -                     | -                     | -27.189(86)            | -27.030(36)            | -28.193(32)            |
| \( x_f \)/MHz   | -                     | -                     | 8260.443(85)           | 8135.83(2.1)           | 8056.1(3.1)            |
| \( \eta_{JJ} \)/Hz| -                     | 0.0*                  | -72.2(67)              | -72.2*                 | -72.2*                 |
| \( f_{24} \)/kHz| -                     | -                     | 0.0*                   | 0.0*                   | -1.039(23)             |

* Constrained at this value.
Table 2. Resonance phenomena and k value for some different symmetric top molecules.

| compound          | CF3CCH [20] | CF3CCD [10] | CF3CN [23] | CH3CN [29] | CD3CN[29] |
|-------------------|-------------|-------------|-------------|-------------|-----------|
| Resonance take place at | k = 9 → 10 | k = 16 → 17 | k = 21 → 22 | k = 3 → 4  | k = 3 → 4 |

The Hamiltonian for \( v_{10} = 3 \) has four vibrational blocks correspond to the \( \ell = +3, +1, -1, -3 \). Figure 10. The \( \ell = \pm 3 \) and \( \ell = \pm 1 \) blocks are separated in vibrational energy by the anharmonic term. There are, however, couplings between +3 and +1, -1 and -3, due to the off-diagonal matrix elements \( q_\ell \) and \( r_\ell \) (abbreviated as \( q \) and \( r \), respectively, in Figures. 6, 10). The labelling of the eigenvalues of this Hamiltonian by \( (k-\ell)s \) where \( s \) is 1 for \( \ell = +3 \) and +1, and -1 for \( \ell = -3 \) and -1; the symmetry of a given transition can then be easily deduced from the fact that

- \( A_1A_2 \) symmetry \( (k - \ell)s = 3n \), \( n = 0, 1, 2, \ldots \)
- \( E \) symmetry \( (k - \ell)s \neq 3n \), \( n = 0,1,2,\ldots \)

\[ |v,\ell,J,k> \]

\[
\begin{array}{cccccccccc}
  & 1 = +3 & 1 = +1 & 1 = -1 & 1 = -3 \\
 k & 2 & 1 & 0 & -1 & -2 & 2 & 1 & 0 & -1 & -2 & 2 & 1 & 0 & -1 & -2 \\
 2 & E_2^2 & E_1^3 & E_0^3 & E_1^3 & r & q & r & q \\
 1 & E_2^1 & E_1^2 & E_0^2 & E_1^2 & r & q & r & q \\
 0 & r & q & E_2^1 & E_1^0 & E_0^1 & E_1^0 & r & q & r \\
 -1 & r & q & r & E_2^1 & E_1^0 & E_0^1 & E_1^0 & r & q & r \\
 -2 & r & q & r & r & E_2^1 & E_1^0 & E_0^1 & E_1^0 & r & q & r \\
\end{array}
\]

Figure 10. The Hamiltonian matrix for \( v_{10} = 3, J = 2 \).

The extension to the \( v_{10} = 4 \) is straightforward. The possible values are +4, +2, 0, -2, and -4, so that Hamiltonian consists of five blocks and five series are apparent in the spectra. It is worth noting that, to the order of magnitude that was included in the Hamiltonian.

For \( v_{10} = 2 \), there are no new parameters in either of the above extension of this Hamiltonian to the cases of \( v_{10} = 3 \) and \( v_{10} = 4 \).
5. Results and Discussion

For the CF$_3$CCH some of the lines belonging to the $\ell = 0$, $\ell = 2$ and $\ell = -2$ are shown separately in different plots, (Figures 11, 12, 13).

1. In the $\ell = -2$ series, the lines are nearly parallel to each other, and the distances between these lines become less as $|k - \ell|^s$ becomes smaller.

2. The two lines 0$^{-2}$ and 0$^{2}$, which are expected to have the same frequency but observed to be are separated, the line 0$^{-2}$ is parallel with $(J + 1)^2$ axis whereas 0$^{2}$ line is not Figure 14.

3. The $\ell = 0$ series are located between line 9$^{0}$ to line 10$^{0}$ but most of them are on the lower frequency side of the spectrum Figure 11.

4. The lines 1$^{2}$ to 9$^{2}$ are above the 0$^{2}$ line whereas the other observed lines related to 10$^{2}$ and greater are hidden under the 0$^{2}$ lines Figures. 11,13.

5. Line 10$^{0}$ is above line 0$^{-2}$ and lines 11$^{0}$,12$^{0}$,13$^{0}$,14$^{0}$ cross line 0$^{-2}$ but other observed lines belong to the $\ell = 0$ are under the 0$^{2}$ line Figures. 11,13.

Comparing of Fortrat diagrams of v$_{10} = 3$ and v$_{10} = 4$ with corresponding for v$_{10} = 1$ Figure. 4 and v$_{10} = 3$ [22] is instructive. The $\ell \pm$ series of v$_{10} = 3$ are qualitatively similar to those of v$_{10} = 1$, with $\ell$-doublets and strong $\ell$-resonance. In the same way the $\ell = 0$ and $+2$ series of v$_{10} = 4$ show a similar resonance to the corresponding series in v$_{10} = 2$ while the $\ell = -2$ series is relatively unperturbed.

In the case of v$_{10} = 2$ [20], as k increase, the $\ell = 0$ energies come into accidental resonance with those of the positive $(k - \ell)$ s series. These two series of energies are coupled via the $q_{ij}$. $\ell$-resonance matrix element, giving an avoided crossing. Such a resonance is also present for v$_{10} = 3$, but in this case, because the vibrational separation due to the $x_{ij}$ term is so much larger, this resonance only starts to become obvious at high k [22]. The maximum resonance can occur when

\[ E[J, k + 2, \ell = 3] = E[J, k, \ell = 1] \]  

(19)

Omitting all centrifugal distortion and higher terms and terms which are the same for both states this gives: equation (20).

\[ k = \frac{x_{\ell \ell} + (A - B) - 2A\zeta}{A\zeta - (A - B)} \]  

(20)

If appropriate values input in equation 20 then solving this equation yields a value of k between 19 and 20. There is a slight kink in this diagram which is caused by the accidental degeneracy of the $|J, k, \ell = -1\rangle$ and $|J, k + 4, \ell = +3\rangle$ states which are not directly connected by a matrix element but are coupled in second order by the interaction of both of them with $|J, k = +2, \ell = +1\rangle$. Applying the equation 21 yields a value for the k = 8.4 which is indeed where the perturbation is observed.

\[ k = \frac{x_{\ell \ell} + 2(A - B) - 3A\zeta}{A\zeta + (A - B)} \]  

(21)
The $\ell = 0$ and $\ell = \pm 2$ series have separation in $v_{10} = 4$ which are close found in the $v_{10} = 2$ vibrational state. Consequently, this resonance arises in the same position found for $v_{10} = 2$, namely between $k = 9$ and 10. The $\ell = \pm 4$ series are further away in the energy due to the $x_{ij} \ell^2$ term. In the $v_{10} = 4$ spectrum Figure.15, the transition with $(k - \ell) s = -3$ for the -2 series is split by about 3 MHz in the $J = 20$ spectrum. This splitting is not reproduced by the parameters obtained by extrapolation of the $v_{10} = 2$ and $v_{10} = 3$ values. In order to account for this, it is necessary to introduce the element $\langle J,k,\ell|f_{24}|J,k+2,\ell-4 \rangle$. This provides a first-order coupling between the otherwise degenerate energies of the $k = +1$, $\ell = +2$, and $k = -1$, $\ell = +2$ states which comprise the -3 pair of levels and leads to a splitting of this transition.

Figure 11. Plot of $B_{\text{eff}}$ against $(J + 1)^2$ for $v_{10} = 2$, $\ell = +0$ of CF$_3$CCH.

Figure 12. Plot of $B_{\text{eff}}$ against $(J + 1)^2$ for $v_{10} = 2$, $\ell = 2$ of CF$_3$CCH.
**Figure 13.** Blot of $B_{\text{eff}}$ against $(J + 1)^2$ for $v_{10} = 2$, $\ell = -2$ of CF$_3$CCH.

**Figure 14.** Plot of $B_{\text{eff}}$ against $(J + 1)^2$ for selected values of $(k-\ell)$s of CF$_3$CCH.
Figure 15. The splitting \( k - \ell \)s = -3 for -2 series state in part of the \( J = 20 \rightarrow 21 \) spectrum of CF\(_3\)CCH in the \( v_{10} = 4 \). The top trace is the observed spectrum, the lower is a computer simulation.

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