

Extended Analysis of the Rotational Spectrum of HCCF

F. Rohwer*, R. Hinze, and A. Guarnieri

Institut für Physikalische Chemie der Universität Kiel, Abteilung Chemische Physik, Kiel, West Germany

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The microwave spectrum of fluoroacetylene (HCCF) has been measured in the frequency region 35–260 GHz. Rotational constants of the ground state and rotational as well as rotation-vibrational interaction constants of several excited states of the C–C–H (ν_4) and the C–C–F (ν_5) bending vibrations have been obtained.

1. Introduction

The microwave spectrum of fluoroacetylene was first reported by Tyler and Sheridan [1]. An extended study of excited vibrational states was published in 1979 by Jones and Rudolph [2]. They investigated the states with $\nu_4 = 1, 2$; $\nu_5 = 1, 2, 3, 4$ and the combination states $\nu_4 = 1, \nu_5 = 1$ and $\nu_4 = 1, \nu_5 = 2$, where ν_4 and ν_5 designate the two degenerate bending modes of HCCF. However, for most excited states, lines were measured only up to 60 GHz, and not all the constants could be determined. In the present work, extended measurements up to the transition $J = 13 \leftarrow 12$ enabled a more detailed analysis of the ground state, the first and second excited states of the C–C–H bending vibration (ν_4), the first, second and third excited states of the C–C–F bending vibration (ν_5) and the combination states $\nu_4 = 1, \nu_5 = 1$ and $\nu_4 = 1, \nu_5 = 2$.

The notation of the various vibrational states is the same as in the publication of Jones and Rudolph [2], where states are characterized by the three quantum numbers ν_3, ν_4 and ν_5 , and the values of l_4 and l_5 are added as superscripts:

$$\nu_3, \nu_4^{l_4}, \nu_5^{l_5}$$

or, in the case of combination states,

$$\nu_3(\nu_4, \nu_5)^l,$$

where $l = l_4 + l_5$.

2. Experimental Details

Up to 80 GHz lines were recorded using a conventional Stark modulation spectrometer. Source modulation was employed at higher frequencies. The microwave sources were Oki reflex klystrons; frequencies above 80 GHz were produced by means of a harmonic generator. At lower frequencies, signal detection was achieved by a Schottky barrier type detector. Above 120 GHz, we used a liquid helium cooled InSb bolometer. Measurements have been made using a standard synthesizer Schomandl ND 800 M monitored by a 10 MHz signal derived from the 77.5 KHz signal of the broadcasting station DCF 77 (Mainflingen, West Germany) with a relative accuracy of 5×10^{-10} . The uncertainties of the measured line frequencies are believed to be ± 5 kHz.

The sample of fluoroacetylene was prepared by the method of Viehe and Franchimont [3]. The synthesis was performed in two steps, starting from pentabromoethane, via 1-fluoro-1,1,2,2-tetrabromoethane and 1-fluoro-1,2-dibromoethene to fluoroacetylene.

3. Theory

For the vibrational ground state, line frequencies were fitted to the expression

$$\nu = 2B_0(J+1) - 4D_0(J+1)^3 + H_0(J+1)^3[(J+2)^3 - J^3]. \quad (1)$$

The line frequencies of excited vibrational states were calculated using the formalism of Amat and Nielsen [4–6]. Since details of this formalism are given in their papers, and more recently in papers by Winniewisser

* Present address: Bayer AG, Leverkusen.

Reprint requests to Prof. Dr. A. Guarnieri, Institut für Physikalische Chemie, Abteilung Chemische Physik, Olshausenstraße 40, D-2300 Kiel 1.



and Winniewisser [7, 11] and by Yamada *et al.* [8, 9], only the frequency expressions are given here.

Since l_t is not a rigorous quantum number, classification of the states should be made according to their symmetry. However, spectra are most conveniently interpreted in terms of this quantum number, and both classifications will be used.

Because of l -type doubling there are two lines for each J in the first excited states. The splitting is described by the l -type doubling constant q_t :

$$\begin{aligned} v^\pm = & 2(B_v + \gamma_{l_t l_t})(J+1) \\ & - 4D_v J(J+1)(J+2) \pm q_t(J+1). \end{aligned} \quad (2)$$

$\gamma_{l_t l_t}$ is a rovibrational interaction constant. The signs + and – refer only to the signs of the last term and are not symmetry symbols. To take into account the J -dependence of the l -type doubling constant, $(q_t)_J$ may be expanded to

$$(q_t)_J = q_t^{(0)} - q_t^{(1)} J(J+1).$$

In the second excited state, l_t may have the values of 0 or ± 2 . The three frequency expressions are

$$\begin{aligned} v_a = & 2(B_v + 4\gamma_{l_t l_t} + 8D_v + \varrho_t)(J+1) \\ & - 4(D_v + 0.5\varrho_t)(J+1)^3, \\ v_s^\pm = & 2(B_v + 2\gamma_{l_t l_t} + 4D_v - 0.5\varrho_t)(J+1) \\ & - 4(D_v - 0.25\varrho_t)(J+1)^3 \\ & \pm 0.5 \{ [4(g_{l_t l_t} - 4D_v - B_v - 4\gamma_{l_t l_t}) \\ & + 4(\gamma_{l_t l_t} + 2D_v)J(J+1) \\ & + 0.5\varrho_t(J-1)J(J+1)(J+2)]^2 \\ & + 4q_t^2(J-1)J(J+1)(J+2) \}^{1/2}_{J+1} \mp 0.5 \{ \dots \}^{1/2}_J, \end{aligned} \quad (3)$$

where the contents of the second braces are identical to those of the first and the index indicates the appropriate value of the rotational quantum number J . $g_{l_t l_t}$ is a rotational constant which represents the contribution of the degenerate vibration to the rotational energy, and ϱ_t is an interaction constant arising from the off-diagonal matrix elements of the form $\langle v_t l_t | H_2 | v_t l_t \pm 4 \rangle$. Its influence is generally very small.

In the third excited state, there are four different lines according to the possible values of l , namely ± 1 and ± 3 . The frequency expressions are

$$\begin{aligned} v_s^\pm = & 2(B_v + \gamma_{l_t l_t} + 2D_v)(J+1) - 4D_v(J+1)^3 \\ & + \mathcal{A}_3^{(1)}(J+1) + q_t(J+1) \\ & \pm 0.5 \{ (\mathcal{A}_3 - W_{11})^2 + 4(W_{13}^+)^2 \}^{1/2}_{J+1} \mp 0.5 \{ \dots \}^{1/2}_J, \end{aligned} \quad (4)$$

$$\begin{aligned} v_a^\pm = & 2(B_v + \gamma_{l_t l_t} + 2D_v)(J+1) - 4D_v(J+1)^3 \\ & + \mathcal{A}_3^{(1)}(J+1) - q_t(J+1) \\ & \pm 0.5 \{ (\mathcal{A}_3 + W_{11})^2 + 4(W_{13}^-)^2 \}^{1/2}_{J+1} \mp 0.5 \{ \dots \}^{1/2}_J, \end{aligned}$$

where

$$\begin{aligned} W_{11} &= q_t J(J+1), \\ W_{13} &= (\sqrt{3}/2) q_t \{ [J(J+1)-2][J(J+1)-6] \}^{1/2}, \\ W_{-13} &= (\sqrt{3}/2) \varrho_t J(J+1) \{ [J(J+1)-2][J(J+1)-6] \}^{1/2}, \\ W_{13}^\pm &= W_{13} \pm W_{-13}, \end{aligned}$$

and

$$\begin{aligned} \mathcal{A}_3 &= \mathcal{A}_3^{(0)} + \mathcal{A}_3^{(1)} J(J+1) \\ &= 8(g_{l_t l_t} - B_v - 10D_v - 10\gamma_{l_t l_t}) \\ &\quad + (8\gamma_{l_t l_t} + 16D_v) J(J+1). \end{aligned}$$

Again, the index at the braces indicates the value of the rotational quantum number.

In the combination state of two degenerate bending modes, $v_4 = 1$, $v_5 = 1$, we have a splitting into four lines as a result of simultaneous rotational and vibrational l -type doubling:

$$\begin{aligned} v_s^\pm = & 2(B_v + 4D_v)(J+1) - 4D_v(J+1)^3 \\ & + r_{tt'}^{(1)}(J+1) + 2\varrho_{tt'} J(J+1)(J+2) \\ & \pm 0.5 \{ (\mathcal{A}_{11}^+)^2_{J+1} + (q^+)^2 J(J+1)(J+2)(J+3) \}^{1/2} \\ & \mp 0.5 \{ (\mathcal{A}_{11}^+)^2_J + (q^+)^2 (J-1)J(J+1)(J+2) \}^{1/2}, \\ v_a^\pm = & 2(B_v + 4D_v)(J+1) - 4D_v(J+1)^3 - r_{tt'}^{(1)}(J+1) \\ & - 2\varrho_{tt'} J(J+1)(J+2) \\ & \pm 0.5 \{ (\mathcal{A}_{11}^-)^2_{J+1} + (q^-)^2 J(J+1)(J+2)(J+3) \}^{1/2} \\ & \mp 0.5 \{ (\mathcal{A}_{11}^-)^2_J + (q^-)^2 (J-1)J(J+1)(J+2) \}^{1/2}. \end{aligned} \quad (5)$$

The meaning of the abbreviations is:

$$\begin{aligned} q^\pm &= q_t \pm q_{t'}, \\ (\mathcal{A}_{11}^\pm)_J &= (\mathcal{A}_{11})_J \pm \varrho_{tt'}(J-1)J(J+1)(J+2) \\ &\quad \mp [r_{tt'}^{(0)} + r_{tt'}^{(1)} J(J+1)], \\ (\mathcal{A}_{11})_J &= 2g_{l_t l_{t'}} - (4B_v + 4\gamma_{l_t l_{t'}} + 16D_v) \\ &\quad + (2\gamma_{l_t l_{t'}} + 8D_v) J(J+1). \end{aligned}$$

For the $v_t = 1$, $v_{t'} = 2$ combination states, it is not possible to give algebraic solutions of the eigenvalue equations that hold for every J . Jones and Rudolph [2] reported the matrix elements for the symmetric and the antisymmetric 3×3 matrices, neglecting elements with $\Delta l = 4$. Following this approximation and rear-

ranging the matrices, they were able to obtain formulas like (5) for the $J=2 \leftarrow 1$ transition only. We use here the complete matrices

$$\begin{pmatrix} E_3 - \varepsilon & b' + d & a' + c \\ b' + d & E_2 - \varepsilon & R + a \\ a' + c & R + a & E_1 + b - \varepsilon \end{pmatrix} \quad (6)$$

and

$$\begin{pmatrix} E_1 - b - \varepsilon & R - a & a' - c \\ R - a & E_2 - \varepsilon & b' - d \\ a' - c & b' - d & E_3 - \varepsilon \end{pmatrix}$$

where

$$\begin{aligned} a &= (1/\sqrt{2}) q_t J(J+1), \\ a' &= (1/\sqrt{2}) q_t \{[J(J+1)-2][J(J+1)-6]\}^{1/2}, \\ b &= 0.5 q_t J(J+1), \\ b' &= 0.5 q_t \{[J(J+1)-2][J(J+1)-6]\}^{1/2}, \\ c &= q_{tt'} J(J+1) \{[J(J+1)-2][J(J+1)-6]\}^{1/2}, \\ d &= q_{t't'} J(J+1) \{[J(J+1)-2][J(J+1)-6]\}^{1/2}, \\ R &= \sqrt{2} r_{tt'}, \\ E_1 &= E_v + B_v [J(J+1)-1] - D_v [J(J+1)-1]^2 + g_{l_t l_t}, \\ E_2 &= E_v + (B_v - 2\gamma_{l_t l_t}) [J(J+1)-1] \\ &\quad - D_v [J(J+1)-1]^2 + g_{l_t l_t} - 2g_{l_t l_t'} + 4g_{l_t' l_t'}, \\ E_3 &= E_v + (B_v + 2\gamma_{l_t l_t'}) [J(J+1)-9] \\ &\quad - D_v [J(J+1)-9]^2 + g_{l_t l_t} + 2g_{l_t l_t'} + 4g_{l_t' l_t'}, \end{aligned}$$

and E_v is the vibrational energy.

Eigenvalues and line frequencies have been computed in this work by numerical methods.

4. Results and Discussion

As an aid to assignment of lines to the different branches caused by l -type doubling, diagrams v^* versus J were used, where

$$v^* = 1000 \left(\frac{v_{\text{exp}}}{v_{\text{calc}, v=0}} - 1 \right)$$

(see Figs. 1 and 2). In contrast to usual diagrams of $v/2(J+1)$ vs. J , branches with the same centrifugal distortion as the ground state are represented as vertical lines. Calculated ground state frequencies – instead of observed data – were introduced for $v_{\text{calc}, v=0}$ to exclude the influence of experimental uncertainties. Line frequencies and the derived constants are given

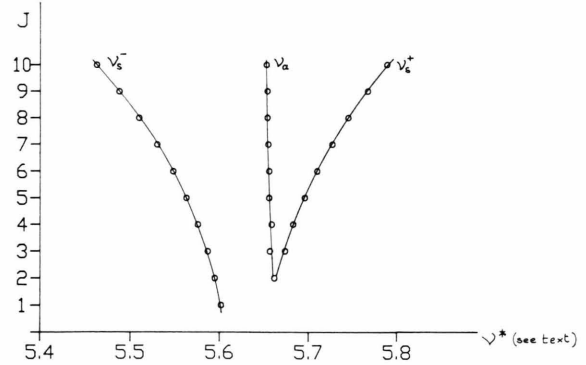


Fig. 1. Diagram v^* vs. J for $v_5=2$.

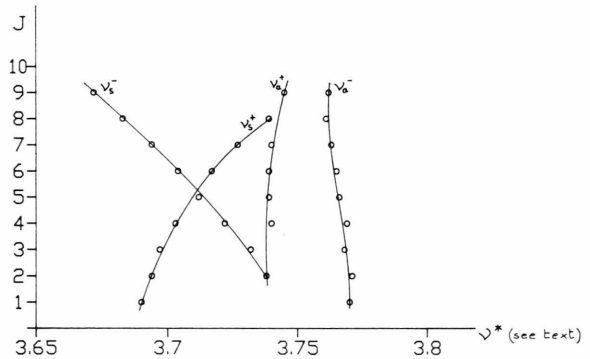


Fig. 2. Diagram v^* vs. J for $v_4=1, v_5=1$.

Table 1. Line frequencies and spectroscopic constants of HCCF in vibrational ground state.

J	Observed [MHz]	Calculated [MHz]
1	38824.63	38824.62
2	58236.72	58236.72
3	77648.58	77648.57
4	97060.08	97060.10
5	116471.20	116471.20
6	135881.80	135881.81
7	155291.83	155291.83
8	174701.19	174701.17
9	194109.73	194109.74
10	213517.55	213517.46
12	252329.94	252329.94
Standard deviation of the fit [MHz] 0.03		
B_0	9706.1815(12) MHz	
D_0	3.43(1)	kHz
H_0	-0.30(4)	Hz

Table 2. Line frequencies and spectroscopic constants of HCCF in the $v_4=1$ vibrational state.

J	Branch	Observed [MHz]	Calculated [MHz]
1	v^-	38834.28	38834.26
	v^+	38885.53	38885.54
2	v^-	58251.18	58251.18
	v^+	58328.13	58328.11
3	v^-	77667.86	77667.86
	v^+	77770.44	77770.42
4	v^-	97084.22	97084.20
	v^+	97212.40	97212.41
5	v^-	116500.11	116500.14
	v^+	116653.97	116653.97
6	v^-	135915.57	135915.56
	v^+	136095.00	136995.03
7	v^-	155330.42	155330.40
	v^+	155535.54	155535.50
8	v^-	174744.53	174744.56
	v^+	174975.23	174975.28
9	v^-	194157.96	194157.95
	v^+	194414.32	194414.28
10	v^-	213570.54	213570.47
	v^+	213852.49	213852.42
12	v^-	252392.52	252392.52
	v^+	252725.67	252725.67

Standard deviation of the fit [MHz] 0.03

B_v	9714.9956(15) MHz
D_v	3.43(2) kHz
H_v	-0.39(6) Hz
$q_4^{(0)}$	12.821(2) MHz
$q_4^{(1)}$	22.7(75) Hz

Table 3. Line frequencies and spectroscopic constants of HCCF in the $v_5=1$ vibrational state.

J	Branch	Observed [MHz]	Calculated [MHz]
1	v^-	38896.55	38896.54
	v^+	38973.93	38973.96
2	v^-	58344.63	58344.60
	v^+	58460.76	58460.72
3	v^-	77792.41	77792.40
	v^+	77947.23	77947.23
4	v^-	97239.87	97239.87
	v^+	97433.36	97433.39
5	v^-	116686.90	116686.91
	v^+	116919.11	116919.12
6	v^-	136133.43	136133.44
	v^+	136404.32	136404.33
7	v^-	155579.39	155579.37
	v^+	155888.92	155888.92
8	v^-	175024.58	175024.60
	v^+	175372.82	175372.81
9	v^-	194469.02	194469.04
	v^+	194455.93	194455.89
10	v^-	213912.75	213912.60
	v^+	214338.22	214338.07
12	v^-	252796.66	252796.65
	v^+	253299.29	253299.31

Standard deviation of the fit [MHz] 0.05

B_v	9733.8327(15) MHz
D_v	3.52(2) kHz
H_v	-0.41(6) Hz
$q_5^{(0)}$	19.355(2) MHz
$q_5^{(1)}$	65.8(74) Hz

in Tables 1–8. The symbols in the column named “branch” refer to the frequency formulas given above.

a) Ground State

Ten lines were observed, up to $J=12$. From these data, three constants, B_0 , D_0 and H_0 were fitted. Although D_0 and H_0 are highly correlated, inclusion of the latter constant gives a significantly better fit (Table 1).

b) First Excited States, $0\ 0^0\ 1^{\pm 1}$ and $0\ 1^{\pm 1}\ 0^0$

The fitted constants are in excellent agreement with those derived by Jones and Rudolph [2]. Although no direct l -type doubling transitions were measured, it

was possible to determine the constants $q_5^{(1)}$, which account for the dependence of the l -type doubling constant on the rotational quantum number J (Tables 2 and 3).

c) Second Excited States $0\ 0^0\ 2^0, \pm 2$ and $0\ 2^0, \pm 2\ 0^0$

With the second excited states, it is not possible to fit both q_l and g_{l,l_l} , as is shown by the following argument: According to (3), the splitting of the v_s^+ and v_s^- lines is

$$\Delta\nu = \{[4(g_{l,l_l} - 4D_v - B_v - 4\gamma_{l,l_l}) + 4(\gamma_{l,l_l} + 2D_v)J(J+1)]^2 + 4q_l^2(J-1)J(J+1)(J+2)\}_{J+1}^{1/2} - \{\dots\}_J^{1/2}. \quad (7)$$

The braces may be written as

$$\left| 4(g_{l,l_l} - 4D_v - B_v - 4\gamma_{l,l_l}) + 4(\gamma_{l,l_l} + 2D_v)J(J+1) \right| + \left\{ 1 + \frac{4q_l^2(J-1)J(J+1)(J+2)}{[4(g_{l,l_l} - 4D_v - B_v - 4\gamma_{l,l_l}) + 4(\gamma_{l,l_l} + 2D_v)J(J+1)]^2} \right\}^{1/2},$$

Table 4. Line frequencies and spectroscopic constants of HCCF in the $v_4=2$ vibrational state.

J	Branch	Observed [MHz]	Calculated [MHz]
1	v_s^+	38893.13 *	38893.30
2	v_s^-	58335.94 *	58336.02
	v_a^+	58335.94 *	58336.05
	v_s^+	58339.75 *	58339.72
3	v_s^-	77781.02	77780.95
	v_a^+	77781.02	77781.03
	v_s^+		77785.85
4	v_s^-	97225.44	97225.54
	v_a^+	97225.44	97225.69
	v_s^+	97231.42	97231.61
5	v_s^-	116670.77	116669.70
	v_a^+	116670.77	116669.95
	v_s^+	116677.68	116676.90
6	v_s^-	136113.65	136113.34
	v_a^+	136113.65	136113.74
	v_s^+	136121.55	136121.64
7	v_s^-	155556.64	155556.38
	v_a^+	155556.64	155556.98
	v_s^+	155565.43	155565.71
8	v_s^-		174998.72
	v_a^+		174999.58
	v_s^+	175008.91	175009.04
9	v_s^-	194440.24	194440.28
	v_a^+	194441.51	194441.47
	v_s^+	194451.35	194451.52
10	v_s^-	213881.16	213880.99
	v_a^+	213882.76	213882.56
	v_s^+		213893.07
12	v_s^-	252759.50	252759.45
	v_a^+	252762.08	252762.06
	v_s^+	252772.96	252772.99

Standard deviation of the fit [MHz] 0.33

* Lines measured by Jones and Rudolph [2].

B_v	9723.356(11) MHz	
D_v	3.60(3) kHz	
γ_{44}	-162.5(31) kHz	
q_4	12.81(55) MHz	
g_{44}	147.00 ^a GHz	^a assumed, see text

taking into account the appropriate values of J . It is clearly seen that, in the denominator of this expression, the second term may be neglected, as it is very small compared to the first one, unless by chance B_v and $g_{l_i l_i}$ are of similar magnitude. If the remaining square root is expanded and only the first term is considered, one has the expression

$$|4(g_{l_i l_i} - 4D_v - B_v - 4\gamma_{l_i l_i}) + 4(\gamma_{l_i l_i} + 2D_v)J(J+1)| \\ + \frac{q_t^2(J-1)J(J+1)(J+2)}{2(g_{l_i l_i} - 4D_v - B_v - 4\gamma_{l_i l_i})}.$$

Table 5. Line frequencies and spectroscopic constants of HCCF in the $v_5=2$ vibrational state.

J	Branch	Observed [MHz]	Calculated [MHz]
1	v_s^-	39042.10	39042.09
2	v_s^-	58562.58	58562.58
	v_a^+	58566.46	58566.19
	v_s^+	58566.46	58566.72
3	v_s^-	78082.40	78082.40
	v_a^+	78087.86	78087.83
	v_s^+	78089.15	78089.17
4	v_s^-	97601.34	97601.34
	v_a^+	97609.39	97609.13
	v_s^+	97611.70	97611.79
5	v_s^-	117119.16	117119.17
	v_a^+	117129.98	117129.98
	v_s^+	117134.63	117134.64
6	v_s^-	136635.66	136635.67
	v_a^+	136650.30	136650.30
	v_s^+	136657.73	136657.76
7	v_s^-	156150.55	156150.62
	v_a^+	156170.05	156170.00
	v_s^+	156181.14	156181.19
8	v_s^-	175663.82	175663.80
	v_a^+	175688.97	175689.00
	v_s^+	175704.90	175704.96
9	v_s^-	195174.99	195175.01
	v_a^+	195207.19	195207.20
	v_s^+	195229.19	195229.13
10	v_s^-	214684.07	214684.01
	v_a^+	214724.54	214724.51
	v_s^+	214753.68	214753.73

Standard deviation of the fit [MHz] 0.09

B_v	9760.5845(37) MHz	
D_v	3.69(2) kHz	
γ_{55}	120.8(7) kHz	
q_5	19.28 ^a MHz	
g_{55}	26.49(2) GHz	^a assumed, see text

Substitution of this expression into (7) gives the following formula for the splitting:

$$\Delta v \approx \pm 8(J+1)(\gamma_{l_i l_i} + 2D_v) \\ + 2J(J+1)(J+2) \frac{q_t^2}{g_{l_i l_i} - 4D_v - B_v - 4\gamma_{l_i l_i}}. \quad (8)$$

The sign of the first term is the same as the sign of $(g_{l_i l_i} - 4D_v - B_v - 4\gamma_{l_i l_i})$. The same approximation was obtained by Amat, Nielsen, and Tarrago [6] as a result of two contact transformations of the expanded Hamiltonian.

From (8) it is seen that it is not possible to evaluate both q_t and $g_{l_i l_i}$, because only the quotient is deter-

minable. For the C–C–H bending mode (v_5), q_t is known in the first and third excited states. Thus it seems reasonable to fix q_t at a value interpolated between these constants and then calculate g_{55} (see Table 5). Since for v_4 the value of q_t in the third excited state is not known, this procedure was not possible in the case of the state $0\ 2^0, \pm 2\ 0$. Here g_{44} was fixed at a value determined by IR measurements [10] (Table 4).

d) *Third Excited State $0\ 0^0\ 3^{\pm 1}, \pm 3$*

From the theory of *l*-type doubling and resonance we expect four lines. However, those with $l_5 = \pm 3$ are too close together to be resolved. The set of fitted constants includes B_v , D_v , γ_{55} , q_5 , g_{55} , which is, within the standard error, the value expected from IR measurements [10], and q_5 . The latter constant is not very well determined, but nevertheless improves the standard deviation of the fit (see Table 6).

e) *Combination State $0\ (11)^0, \pm 2$*

Because of rotational and vibrational *l*-type doubling, the $J+1 \leftarrow J$ transition in this combination state splits into four components, two with $l = l_t + l_v = 0$ and two with $l = +2$ and $l = -2$, respectively. Transitions were observed up to $J=9$. By a procedure similar to that described for the second excited states, or by a second contact transformation of the Hamiltonian, the following approximation formulas are obtained:

$$\begin{aligned} v_s^{\pm} &= 2B_v(J+1) - 4(J-1)(J+1)(J+3)D_v \\ &\quad + 2(J+1)\gamma_{l_t l_v} + J(J+1)(J+2)(q^+)^2/a_s, \\ v_s^{\mp} &= 2B_v(J+1) - 4(J+1)^3D_v - 2(J+1)\gamma_{l_t l_v} \\ &\quad + 2(J+1)r_{tt'}^{(1)} - J(J+1)(J+2)(q^+)^2/a_s, \\ v_a^{\pm} &= 2B_v(J+1) - 4(J-1)(J+1)(J+3)D_v \\ &\quad + 2(J+1)\gamma_{l_t l_v} + J(J+1)(J+2)(q^-)^2/a_a, \\ v_a^{\mp} &= 2B_v(J+1) - 4(J+1)^3D_v - 2(J+1)\gamma_{l_t l_v} \\ &\quad - 2(J+1)r_{tt'}^{(1)} - J(J+1)(J+2)(q^-)^2/a_a, \end{aligned} \quad (9)$$

where

$$\begin{aligned} q^{\pm} &= q_t \pm q_{t'}, \\ a_s &= 2g_{l_t l_v} - r_{tt'}^{(0)} - 4\gamma_{l_t l_v} - 4B_v - 16D_v, \\ a_a &= 2g_{l_t l_v} + r_{tt'}^{(0)} - 4\gamma_{l_t l_v} - 4B_v - 16D_v. \end{aligned}$$

Table 6. Line frequencies and spectroscopic constants of HCCF in the $v_5=3$ vibrational state.

J	Branch	Observed [MHz]	Calculated [MHz]
1	v_a^-	39070.62*	39070.72
	v_s^-	39224.38*	39224.41
2	v_a^-	58605.82*	58605.73
	v_s^-	58836.29*	58836.27
3	v_a^-	78140.23	78140.31
	v_a^+	78302.92	78303.07
	v_s^+	78302.92	78303.07
	v_s^-	78447.68	78447.69
4	v_a^-	97674.29	97674.33
	v_a^+	97877.11	97878.51
	v_s^+	97877.11	97878.51
	v_s^-	98058.71	98058.56
6	v_a^-	136740.06	136740.12
	v_a^+	137028.76	137028.71
	v_s^+	137028.76	137028.73
	v_s^-	137278.16	137278.02
7	v_a^-	156271.66	156271.61
	v_a^+	156603.51	156603.37
	v_s^+	156603.51	156603.42
	v_s^-	156886.21	156886.33
9	v_a^-	195331.03	195331.09
	v_a^+	195751.60	195751.58
	v_s^+	195751.60	195751.75
	v_s^-	196099.31	196099.39
10	v_a^-	214858.92	214858.82
	v_a^+		215325.04
	v_s^+		215325.32
	v_s^-		215703.85

Standard deviation of the fit [MHz] 0.40

* Lines measured by Jones and Rudolph [2].

B_v	9786.793(6)	MHz
D_v	3.83(3)	kHz
γ_{55}	121.7(11)	kHz
q_5	19.211(3)	MHz
g_{55}	26.66(24)	GHz
q_5	-666(482)	Hz

Again, the superscripts in (9) are not symmetry symbols but indicate the sign of a_a and a_s . In the above expressions, we have neglected $q_{tt'}$.

Apart from B_v , D_v , and γ_{55} , obviously only the coefficients $(q^+)^2/a_s$ and $(q^-)^2/a_a$ may be fitted. From these, only two of the four coefficients q_4 , q_5 , $r_{45}^{(0)}$, and g_{45} are determinable. For the constants that have to be assumed, two sets are suitable: q_4 and q_5 , which are known approximately from the first excited states, or $r_{45}^{(0)}$ and g_{45} , that have been determined by IR measurements [10]. The first set of constants yields a better

Table 7. Line frequencies and spectroscopic constants of HCCF in the $v_4=1$, $v_5=1$ vibrational state.

J	Branch	Observed [MHz]	Calculated [MHz]
1	v_s^+	38967.88	38967.88
	v_a^-	38970.99	38970.96
2	v_s^+	58451.82	58451.78
	v_s^-	58454.39	58454.07
	v_a^+	58454.39	58454.40
	v_a^-	58456.30	58456.20
3	v_s^+	77935.67	77935.66
	v_s^-	77938.32	77938.00
	v_a^+	77938.32	77938.84
	v_a^-	77941.16	77941.16
4	v_s^+	97419.52	97419.48
	v_s^-	97421.35	97421.29
	v_a^+	97423.10	97422.96
	v_a^-	97425.91	97425.73
5	v_s^+	116903.49	116903.25
	v_s^-	116903.49	116903.76
	v_a^+	116906.63	116906.69
	v_a^-	116909.84	116909.84
6	v_s^+	136385.12	136385.27
	v_s^-	136386.93	136386.94
	v_a^+	136389.90	136389.96
	v_a^-	136393.36	136393.38
7	v_s^+	155865.55	155865.65
	v_s^-	155870.57	155870.55
	v_a^+	155872.64	155872.67
	v_a^-	155876.18	155876.25
8	v_s^+	175344.73	175344.63
	v_s^-	175354.46	175354.07
	v_a^+	175354.46	175354.76
	v_a^-	175358.28	175358.37
9	v_s^+	194822.50	194822.35
	v_a^+	194836.70	194836.15
	v_s^+	194836.70	194837.48
	v_a^-	194840.00	194839.63

Standard deviation of the fit [MHz] 0.23

B_v	9742.403(5) MHz
D_v	3.61(5) kHz
γ_{45}	28.1(45) kHz
q_4	12.818 ^a MHz
q_5	19.349 ^a MHz
$r_{45}^{(0)}$	57.4(25) GHz
$r_{45}^{(1)}$	−395.5(64) kHz
g_{45}	6.7(7) GHz
Q_{45}	−17.1(690) Hz ^a assumed, see text

Table 8. Line frequencies and spectroscopic constants of HCCF in the $v_4=1$, $v_5=2$ vibrational state.

J	Observed [MHz]	Calculated [MHz]
1	39020.67 *	39020.68
	39049.24 *	39049.30
	39106.42 *	39106.59
	39129.27 *	39129.36
2	58530.94 *	58530.91
	58573.71 *	58573.66
	58659.65 *	58659.57
	58693.85 *	58693.92
3	78040.85	78041.01
	78097.66	78097.67
		78155.06
		78155.11
	78212.28	78212.19
	78258.38	78258.34
4	97550.93	97550.92
	97621.36	97621.22
	97692.91	97692.98
		97693.09
	97764.40	97764.30
	97822.66	97822.58
6	136570.10	136570.04
	136666.47	136666.46
		136767.03
		136767.34
	136866.45	136866.54
	136950.37	136950.29
7	156079.17	156079.16
	156187.92	156187.93
		156302.93
		156303.41
	156416.38	156416.41
	156513.69	156513.67
9	195096.29	195096.30
		195228.00
		195371.92
	195372.92	195372.90
	195512.85	195513.01
	195639.06	195639.24
10		214604.24
		214746.37
		214904.78
	214906.56	214906.11
	215059.63	215059.49
	215201.38	215201.32

Standard deviation of the fit [MHz] 0.12

* Lines measured by Jones and Rudolph [2].

B_v	9769.248(3) MHz
D_v	3.82(2) kHz
γ_{45}	104.3(12) kHz
q_4	12.850(6) MHz
q_5	19.41(5) MHz
$r_{45}^{(0)}$	64.05(45) GHz
$r_{45}^{(1)}$	−258.0(24) kHz
g_{45}	6.30(15) GHz
g_{55}	28.72(8) GHz
Q_{45}	−852(616) kHz
Q_{55}	344(434) kHz

fit, which may be expected since the l -type doubling constants do not change very much with the vibrational states. The second set of constants has two disadvantages: r_{45} from IR measurements gives no J -dependence and the sign of q_4 and q_5 are not determinable. The values of the q_t 's given in Table 7 are obtained from the first excited states without taking into account $q_t^{(1)}$. To reproduce the line frequencies well it was necessary to expand the vibrational l -type doubling constants r_{45} :

$$(r_{45})_J = r_{45}^{(0)} + r_{45}^{(1)} J(J+1)$$

as was proposed by Winnewisser and Winnewisser [7] (see Table 7).

f) Combination State 0 (1 2) $^{\pm 1, \pm 3}$

According to the possible combinations of the quantum numbers $l_4 = \pm 1$ and $l_5 = 0, \pm 2$, we expect six lines, four of which are associated with $|l| = 1$ and two with $|l| = 3$. The intensity of the lines of this state is very low, and not all the $|l| = 3$ -components were detected.

This combination state has been analysed before in [2]. However, at that time only the $J=2 \leftarrow 1$ and $J=3 \leftarrow 2$ transitions were measured and some constants could not be determined. With the remaining

set consisting of $(B_v - \gamma_{45})$, D_v , q_4 , q_5 , and $(g_{45} - 2g_{55})$, it was not possible to fit both measured transitions with the same value of $(g_{45} - 2g_{55})$. In the present work we use 31 measured lines instead of 8, and consequently a more detailed analysis has been possible. A first set of constants including B_v , D_v , γ_{45} , q_4 , q_5 , $r_{45}^{(0)}$, $r_{45}^{(1)}$, g_{45} and g_{55} yielded a fit with a standard deviation of 123 kHz. This result did not improve when the J -dependence of q_4 and q_5 was taken into account. Finally, a better standard deviation was achieved by inclusion of the constants q_{45} and q_{55} , which come from matrix elements with $\Delta l = \pm 4$ (see Table 8).

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