Synthesis and Microwave Spectroscopic Study of Fluorinated Methyl Isocyanides

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Difluoromethyl isocyanide has been generated by flash vacuum pyrolysis of pentacarbonyl(difluoromethyl isocyanide)chromium at 240 °C. Spectroscopic studies revealed the presence of several major and minor impurities like HCN, HCC–CN and HCC–NC. The pyrolysis of pentacarbonyl(fluoromethyl isocyanide)chromium did not lead to the observation of free fluoromethyl isocyanide. The rotational spectrum of difluoromethyl isocyanide has been recorded with a conventional continuous wave Stark spectrometer and a molecular beam Fourier transform microwave spectrometer resulting in $A = 10.110841\,(42)$, $B = 4.550914\,(19)$, $C = 3.343550\,(19)$ GHz, $D'_J = 0.41\,(13)$, $D'_{JK} = 26.72\,(36)$, $D'_K = -21.3\,(18)$ kHz. The dipole moment components $\mu_a = 1.46\,(1)$, $\mu_c = 1.83\,(1)$ and μ_{total} 2.34 (1) D were obtained from the second order Stark effect. The ^{14}N nuclear quadrupole hyperfine structure in the rotational spectrum of CHF_2-NC has been resolved and the ^{14}N nuclear quadrupole coupling constants $\chi_{aa} = 599.0\,(10)$, $\chi_{bb} = -406.5\,(14)$, $\chi_{cc} = -192.6\,(14)$ kHz have been obtained.

Introduction

Although isocyanides are known for more than 100 years [1] the chemistry and physical properties of isocyanides are still of current interest. Some small highly reactive isocyanides like HNC [2], CN–CN [3], CN–NC [4], HCC–NC [5], and CN–CC–CN [6] have been synthesized and characterized only recently, some of them only in an argon matrix. In addition the occurrence of some small isocyanides like HNC [7], HCC–NC [8] and CH_3NC [9] have been detected in interstellar clouds by radioastronomy. The first perfluorinated derivative, CF_3NC, was reported in 1967 by Makarov et al. [10]. The chemistry and physical properties of trifluoromethyl isocyanide, however, remained unexplored until an efficient synthesis became available [11]. Trifluoromethyl isocyanide turned out to be a very reactive molecule which has very interesting ligand properties and transition metal complexes as it is one of the strongest π-accepting ligands known thus far [12]. Trifluoromethyl isocyanide was studied by UV-photoelectron spectroscopy [13] and X-ray photoelectron spectroscopy [14]. Its structure was determined by a combination of electron diffraction studies and microwave spectroscopy [15], and the microwave spectra of excited vibrational states [16] were recorded. The microwave spectroscopic studies revealed an unusually high ^{14}N quadrupole coupling constant of $\chi_{zz} = 1.06\,(3)$ MHz. Two further perfluorinated isocyanides, pentafluorophenyl isocyanide [17] and trifluorovinyl isocyanide [18] were prepared during recent years. Pentafluorophenyl isocyanide was investigated by a low temperature X-ray crystal structure determination [19] and a microwave spectroscopic study [20]. The structure of trifluorovinyl isocyanide was elucidated by low temperature X-ray crystallography [21] and ab initio calculations [22].

Herein we report on the synthesis and microwave spectroscopic studies of the partially fluorinated methyl isocyanides CH_2F-NC and CHF_2-NC in order to get information of the fluorine substitution effects on isocyanides.

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Experiment

^1H NMR and ^{19}F NMR spectra were recorded by using a Jeol FX 90Q instrument with TMS and $CFCl_3$ or solvent signals as reference standards. IR spectra were taken on a Perkin-Elmer 883 instrument. Mass spectra were obtained on a Varian 711 spectrometer (80 eV). $(CO)_5Cr(CNCH_2F)$ and $(CO)_5Cr(CNCHF_2)$ [23] were prepared by literature methods.

Preparation of Difluoromethyl Isocyanide

1.1 g (4 mmol) of $(CO)_5Cr(CNCHF_2)$ was sublimed under vacuum through a glas tube ($50 \cdot 1.4\ cm^2$) heated to 260 °C for a length of 30 cm. The tube was connectd to a vacuum line by two U-tube traps kept at −78 and −196 °C, respectively. Difluoromethyl isocyanide is collected in the trap kept at −196 °C. The product contains always HCN as major impurity.

MS $m/e = 77$ (M^+), 76 ($M^+ - H$), 58 ($M^+ - F$), 51 (CHF_2^+). IR (gaseous): 3018 w (CH), 2131 s (CN), 1377 (s), 1368 (s), 1130 (vs), 1000 (s) cm^{-1}. ^1H NMR: 6.55, $^2J_{HF} = 61$ Hz, ^{19}F NMR: −90.9, $^2J_{HF} = 61$ Hz, $^2J_{NF} = 13$ Hz. Molecular weight (MS): $m/e = 77.0077$ (found); 77.0077 (calcd.)

Attempted Preparation of Fluoromethyl Isocyanide

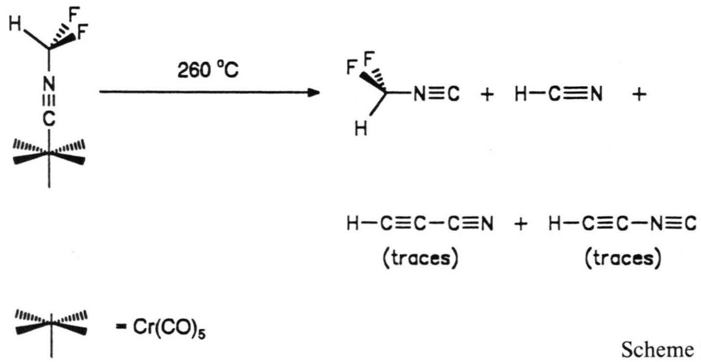
In several experiments, similar to that described above, 200 to 800 mg amounts of $(CO)_5Cr(CNCH_2F)$ were pyrolized at temperatures ranging from 180 to 260 °C. IR, ^1H, ^{19}F NMR and microwave spectroscopy of the products trapped at −196 °C and −78 °C revealed no free fluoromethyl isocyanide. Methyl isocyanide, however, was detected among the products.

Results and Discussion

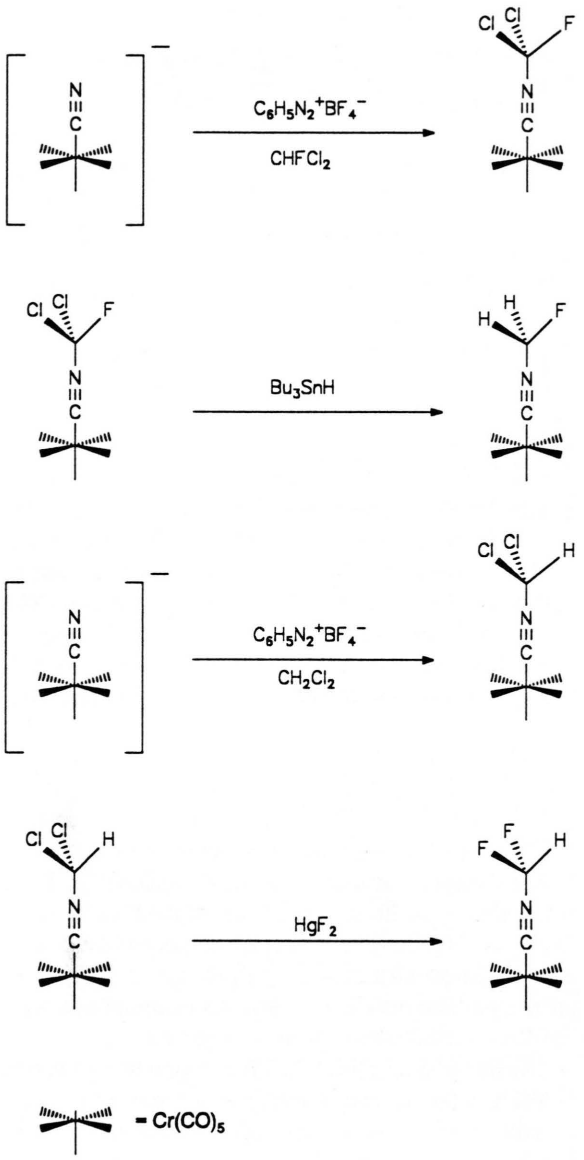
Synthesis of Fluorinated Methyl Isocyanides

The reactions of this work are summarized in Scheme 1. The synthesis methods for fluorinated isocyanides are limited to the dehalogenation of $R_f - N = CX_2$ (X = Br, F) ($R_f = CF_3, C_6F_5, SF_5, C_2F_5, C_3F_7$) by magnesium in THF [11, 17, 24] and triphenylphosphin [25], respectively. However, this method requires the availability of the corresponding dihalogene methanimines which are missing for the partially fluorinated substituents CFH_2 and CF_2H. Recently, we have shown that trifluorovinyl isocyanide can be build up on a pentacarbonyl chromium fragment. Flash vacuum pyrolysis of this organometallic precursor results in the formation of the free isocyanide [18]. The synthesis of the chromium complexes $(CO)_5Cr(CNCFH_2)$ and $(CO)_5Cr(CNCF_2H)$, outlined in Scheme 2, has been described elsewhere [23]. Flash vacuum pyrolysis of $(CO)_5Cr(CNCF_2H)$ at 260 °C yielded $CNCF_2H$. However a separation from the major impurity HCN was unsuccessful. Further minor impurities were detected by continuous wave (CW) microwave spectroscopy (see below). The characterization of difluoromethyl isocyanide is based on spectroscopic data. The ^1H NMR spectrum exhibits a triplet at 6.55 ppm with a $^2J(^1H - ^{19}F)$ of 61 Hz, whereas a doublet of a 1:1:1 triplet [$^2J(^1H - ^{19}F) = 61$ Hz, $^2J(^{14}N - ^{19}F) = 13$ Hz] can be observed in the ^{19}F NMR spectrum of a diluted solution in $CDCl_3$ at ambient temperature. In the low temperature ^{19}F NMR spectrum in CD_2Cl_2 only a broad doublet can be observed due to rapid relaxation of the ^{14}N nucleus.

Attempts to prepare the missing fluoromethyl isocyanide by similar techniques remained unsuccessful.



Scheme 1. See text.



Scheme 2. See text.

Pyrolysis experiments using different conditions all resulted in products which contain not even traces of CH_2F-NC. Interestingly, methyl isocyanide could be detected by ^1H NMR, IR and CW–MW spectroscopy.

Rotational Spectrum

After the identification of the title molecule, CHF_2-NC, by mass- and NMR-spectroscopy, the rotational spectrum was investigated. It was predicted from a plausible molecular structure, constructed from the data of the isomeric cyanide [26], methyl isocyanide [27] and trifluoromethyl isocyanide [15]. The spectrum was measured with a conventional CW Stark spectrometer equipped with a microwave (MW) synthesizer (Hewlett Packard 8341 B), thus sacrificing the frequency accuracy of modern waveguide [28, 29] or molecular beam (MB) [30, 31] Fourier transform (FT) spectrometers for a broad frequency range covered in a given time, due to the limited availability of the chromium precursor. The pyrolysis apparatus described above was placed very close to the microwave absorption cell (Stark cell) as part of a continuous flow system. The temperature of the Stark cell was kept at $-65\,°C$, the pressures were 3 and 2 Pa (25 and 15 mTorr) at the cell entrance and exit, respectively. The flow was adjusted with needle valves to give adequate line intensities with a minimum of sample throughput. The frequency range from 20 to 35 GHz was scanned with a Stark field strength of 1500 V cm^{-1}, yielding many absorption lines. The final assignment of the rotational spectrum started with the *a*-type *K*-doublet $J\,K_-\,K_+ = 4_{31}-3_{30}, 4_{32}-3_{31}$, measured with a field strength of 30 V cm^{-1}, thus suppressing most of the other lines. Both lines could be identified by their distinctive Stark effect. On the basis of this assignment five additional *a*-type $J = 4-3$ lines were found in the survey spectrum. It was also possible to identify *c*-type lines. In Table 1 39 rotational transitions of CHF_2-NC are given. The limited amount of the precursor allowed only measurements with an inferior accuracy of ± 100 kHz for dedicated scans and ± 1 MHz for survey scans.

In Table 2 the rotational and centrifugal distortion constants [32] derived from our measurements are listed together with those for difluoromethyl cyanide, CHF_2-CN [33]. The centrifugal distortion constants are, as expected, of the same order of magnitude.

The scans over the large spectral range allowed the identification of several other substances among the pyrolysis products. Hydrogen cyanide, HCN, was identified by the direct *l*-type transitions with $J = 9$ to $J = 12$, vinyl cyanide, $H_2C=CH-CN$, by five rotational *a*-type transitions with $J = 3-2$, fluoroacetonitrile, CH_2F-CN, by eight rotational transitions, and cyanoacetylene, $HC\equiv C-C\equiv N$, by two hfs-resolved transitions $J = 3-2$ and $4-3$ [34]. In addition, isocyanoacetylene, $HC\equiv C-N\equiv C$, was detected for the first time and identified [5].

Table 1. Rotational transitions of difluoromethyl isocyanide. J, K_-, K_+: Quantum numbers of the lower rotational state; ν_{obs}: measured line frequency (GHz); $\Delta\nu$: difference between calculated and measured frequency (kHz). Estimated uncertainties in parentheses, compare text.

J'	K'_-	K'_+	←	J	K_-	K_+	ν_{obs}	$\Delta\nu$
2	2	0	←	1	1	0	33.852 (1)	−98
2	2	1	←	1	1	1	34.883 (1)	158
3	1	2	←	2	0	2	33.525 45 (1)	50
3	3	0	←	3	2	2	30.937 05 (10)	58
3	3	1	←	3	2	1	30.063 7 (1)	116
4	0	4	←	3	0	3	30.003 80 (5)	40
4	1	4	←	3	1	3	28.854 12 (2)	51
4	1	3	←	3	1	2	33.587 20 (5)	124
4	3	1	←	3	3	0	31.980 77 (2)	−56
4	3	2	←	3	3	1	31.884 55 (2)	0
4	2	3	←	3	2	2	31.439 25 (5)	31
4	2	2	←	3	2	1	33.011 65 (5)	146
4	2	2	←	4	1	4	27.230 (1)	6
4	3	1	←	4	2	3	31.478 9 (2)	−358
4	3	2	←	4	2	2	28.935 8 (1)	770
5	2	3	←	5	1	5	33.230 5 (5)	344
5	2	4	←	4	2	3	39.080 5 (1)	48
5	3	3	←	4	3	2	39.923 94 (2)	0
5	3	3	←	5	2	3	27.026 86 (3)	115
5	3	2	←	5	2	4	32.649 (1)	−816
5	4	1	←	4	4	0	39.868 5 (1)	−139
5	4	2	←	4	4	1	39.858 7 (1)	−187
6	1	5	←	5	2	3	33.580 (1)	−177
6	3	3	←	6	2	5	34.830 64 (2)	−1
7	2	5	←	6	3	3	33.583 (1)	−148
9	2	7	←	9	2	8	27.906 (1)	−22
9	2	8	←	8	3	6	30.010 (1)	468
9	3	7	←	8	4	5	28.063 (1)	751
9	4	6	←	9	3	6	34.347 5 (10)	186
10	2	9	←	9	3	7	33.642 (1)	179
10	3	8	←	9	4	6	34.730 (1)	−624
10	4	6	←	9	5	4	29.122 (1)	−760
10	4	7	←	10	3	7	30.215 (1)	−437
12	3	9	←	12	3	10	30.110 3 (5)	197
12	5	8	←	11	6	6	30.901 (1)	278
13	0	13	←	12	1	11	27.120 5 (5)	−28
14	5	10	←	14	4	10	34.646 8 (10)	−1152
15	4	11	←	15	4	12	30.972 (1)	164
15	5	11	←	15	4	11	28.684 5 (10)	1193

Table 2. Rotational and centrifugal distortion constants [32] of difluoromethyl-isocyanide and difluoromethyl-cyanide [33], single standard error in parentheses; σ: standard deviation of the fit; n: number of rotational transitions; $\varkappa$: parameter of asymmetry.

		CHF_2-NC	CHF_2-CN
A	[GHz]	10.110 841 (42)	9.985 938 (51)
B	[GHz]	4.550 914 (19)	4.095 116 (30)
C	[GHz]	3.343 550 (19)	3.081 427 (34)
$\varkappa$		−0.6432	−0.7063
D'_J	[kHz]	0.41 (13)	0.36 (75)
D'_{JK}	[kHz]	26.72 (36)	17.86 (89)
D'_K	[kHz]	−21.3 (18)	−6.4 (49)
δ'_K	[kHz]	0.275 (21)	0.28 (14)
R'_6	[kHz]	−0.334 (12)	−0.20 (9)
σ	[kHz]	462	274
n		39	32

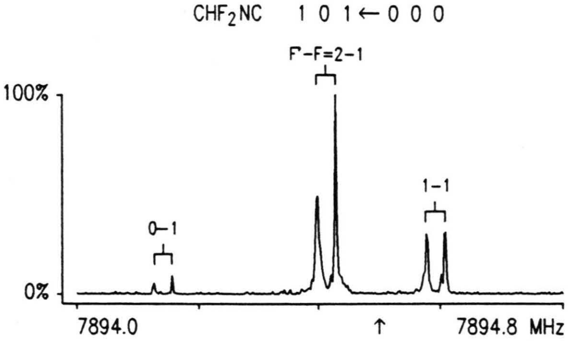


Fig. 1 High resolution MB-MWFT spectrum of the $J K_- K_+ = 101-000$ transition. The doublets arise from the Doppler effect in the cavity spectrometer.

Dipole Moment

The dipole moment was determined from the second order Stark effect [35]. In Table 3 the frequencies of the individual Stark satellites of several transitions are listed for various electric field strengths. The dipole moment resulting from the analysis is given in Table 4, in comparison to the data of $CHF_2-C^{15}N$ [26]. The dipole moments are of almost equal magnitude.

Hyperfine Structure in the Rotational Spectrum

The hyperfine structure (hfs) due to the presence of the quadrupolar nucleus ^{14}N was measured in three rotational transitions with our MB-MWFT spectrometer [30, 31]. The pyrolysis of the precursor was accomplished with argon at a pressure of 0.5 bar as carrier gas (for details, see [34]). An example of a high resolution spectrum is given in Figure 1.

The line frequencies of the hfs components are given in Table 5, the nuclear quadrupole coupling constants derived from the usual first order perturbation calculation [35] are compiled in Table 6.

Summary

The combination of a preparation via a chromium complex and different spectroscopic methods, including especially microwave spectroscopy lead to the unambiguous identification of difluoromethyl isocyanide, thus closing the gap between trifluoromethyl and methylisocyanide partially. Fluoromethyl isocyanide was not found.

As a side product of this work isocyanoacetylene (ethinylisocyanid) was detected.

Table 3. Stark-effect of difluoromethyl isocyanide. E: Electric field strength [V cm^{-1}], estimated error 1%; $\delta\nu_{obs}$: Stark shift [MHz] with estimated error; M_J: directional quantum number; $\Delta\delta\nu$: difference between calculated and observed Stark shift [kHz]. See also Table 1.

$J' K'_- K'_+ \leftarrow J K_- K_+$	ν_{obs}	E	$\|M_J\|$	$\delta\nu_{obs}$	$\Delta\delta\nu$
3 1 2 ← 2 0 2	33.525 5 (1)	212.7	2	3.1 (1)	116
		315.1	2	7.0 (1)	50
		484.9	1	3.8 (1)	110
		667.0	1	7.2 (1)	192
		1084.0	0	−1.8 (1)	22
		1412.0	0	−3.0 (1)	−2
		1870.0	0	−5.2 (1)	−38
4 2 3 ← 3 2 2	31.439 3 (1)	172.8	3	4.2 (1)	−34
			2	2.0 (1)	58
		216.6	3	6.6 (1)	−69
			2	3.2 (1)	33
		269.8	3	10.1 (2)	−4
			2	5.0 (1)	14
			1	1.9 (1)	17
		325.4	3	14.75 (20)	−126
			2	7.4 (1)	−108
			1	2.8 (1)	−10
		430.4	2	12.7 (2)	47
			1	4.85 (10)	42
			0	2.3 (1)	−76
		751.0	1	15.0 (2)	34
			0	6.6 (1)	104
5 3 3 ← 4 3 2	39.924 0 (1)	59.9	4	5.4 (1)	−239
			3	3.2 (1)	−228
		100.0	3	8.1 (2)	−249
			2	3.6 (1)	47
		118.1	4	17.7 (2)	−103
			3	10.7 (1)	−68
			2	4.9 (1)	113
		140.9	4	23.5 (3)	90
			3	14.5 (1)	30
			2	6.9 (1)	85
		195.3	2	12.8 (1)	−166
			1	3.5 (1)	−36
		258.8	2	20.5 (2)	−30
			1	6.0 (1)	−83
5 3 3 ← 5 2 3	27.027 1 (1)	105.7	5	−3.4 (1)	43
			4	−2.2 (1)	33
		138.8	5	−5.8 (1)	42
			4	−3.8 (1)	79
			3	−2.1 (1)	−27
		159.3	5	−7.7 (1)	145
			4	−4.9 (1)	10
			3	−2.8 (1)	4
		205.7	4	−8.0 (1)	−97
			3	−4.6 (1)	−43
			2	−2.1 (2)	−44
		255.0	4	−12.3 (1)	−31
			3	−6.8 (1)	−297
			2	−3.2 (2)	−86
		349.8	3	−13.2 (2)	13
			2	−6.1 (2)	47
6 3 3 ← 6 2 5	34.830 7 (1)	269.4	6	3.3 (1)	11
			5	2.3 (1)	19
		304.3	6	4.2 (1)	15
			5	3.0 (1)	−47
		346.6	6	5.5 (1)	−45
			5	3.8 (1)	26
			4	2.5 (1)	−17
		409.9	6	7.6 (1)	−1
			5	5.3 (1)	33
			4	3.4 (1)	64
			3	2.0 (2)	3
		481.0	6	10.4 (2)	7
			5	7.3 (1)	17
			4	4.7 (1)	57
			3	2.7 (1)	50
		541.0	6	13.1 (2)	19
			5	9.2 (1)	35
			4	6.1 (2)	−84
		636.0	6	18.0 (2)	−52
			5	12.7 (2)	−28
			4	8.3 (1)	−30
			3	4.8 (1)	−5
		759.0	5	17.7 (2)	164
			4	11.6 (1)	100
			3	6.7 (1)	102

Table 4. Dipole moment of difluoromethyl isocyanide and cyanide. μ_g: Components of the dipole moment along the principal axes of inertia ($g = a, c$); σ: standard deviation of the fit; n: number of evaluated Stark components; single standard error in parentheses.

CHF_2NC	$CHF_2{-}C^{15}N$ [26]
μ_a = 1.46 (1) D	μ_a = 1.634 (2) D
μ_c = 1.83 (1) D	μ_c = 1.836 (1) D
μ_{total} = 2.34 (1) D	μ_{total} = 2.458 (2) D
σ = 88.6 kHz	σ = 36 kHz
n = 77	n = 36

Table 5. Rotational transitions of difluoromethyl isocyanide with ^{14}N-hfs, measured with a MB-MWFT spectrometer. F: Quantum number of hfs level; ν_0: hypothetical center frequency [GHz]; ν_{obs}: observed frequency [GHz]; $\Delta\nu$: difference between calculated and observed frequency [kHz].

$J' K'_- K'_+ \leftarrow J K_- K_+$	ν_0	$F' \leftarrow F$	ν_{obs}	$\Delta\nu$
1 0 1 ← 0 0 0	7.894 441 7	0 ← 1	7.894 140 2	2
		1 ← 1	7.894 591 5	0
		2 ← 1	7.894 411 8	0
1 1 0 ← 0 0 0	14.661 735 5	0 ← 1	14.661 829 7	2
		1 ← 1	14.661 687 1	0
		2 ← 1	14.661 745 3	0
2 1 2 ← 1 1 1	14.581 433 4	1 ← 0	14.581 182 8	−1
		2 ← 1	14.581 582 9	0
		3 ← 2	14.581 399 4	0

Table 6. Nuclear quadrupole coupling constants χ of difluoromethyl isocyanide with single standard error in parentheses. $\chi^+ = \chi_{bb} + \chi_{cc}$; $\chi^- = \chi_{bb} - \chi_{cc}$; σ: standard deviation of the fit; n: number of hfs-components; (χ^+, χ^-): correlation coefficient.

$\chi^+ = -599.0\,(10)$ kHz	$\chi_{aa} = 599.0\,(10)$ kHz	$\sigma = 1.1$ kHz
$\chi^- = -213.9\,(26)$ kHz	$\chi_{bb} = -406.5\,(14)$ kHz	$n = 9$
	$\chi_{cc} = -192.6\,(14)$ kHz	$(\chi^+, \chi^-) = 0.25$

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