High Resolution FTIR Study of the ν_8 Band and ab initio Calculation of the Harmonic and Anharmonic Force Field of Difluoromethanimine, CF_2NH

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Dedicated to Prof. Dr. mult. A. Haas on the occasion of his 60th birthday

The ν_8 band of CF_2NH near 830 cm^{-1} has been measured with a resolution of 0.003 cm^{-1} and rotationally analyzed. The band is unperturbed, and its rovibrational parameters are given up to fourth order. Theoretical harmonic and anharmonic force constants have been calculated at the 6-31 G** SCF level, and all vibration-rotation interaction constants α_i and anharmonicity constants x_{ij} are predicted. The theoretical results are compared with the available experimental data.

Introduction

The difluoromethanimine molecule, CF_2NH, has been synthesized only recently by the reaction of CF_3NH_2 with $N(C_2H_5)_3$ [1]. Although CF_2NH is stable at ambient temperature only in the gas phase at low pressure, its vibrational [1] and microwave spectra [2, 3] were recorded, ground state constants determined and a planar structure deduced. This planarity was confirmed by a low temperature X-ray study [4]. Accordingly, CF_2NH is an oblate asymmetric rotor near the symmetric top limit, $\varkappa = 0.89$, and its rotational energy pattern is similar to that of CF_2O and BF_3, with which its is isovalent.

A high resolution study of the vibrational spectrum of CF_2NH will therefore reveal distinctly different band types for the seven in-plane (a') and two out-of-plane (a'') vibrations. While the former have a transition moment perpendicular to the pseudo-threefold symmetry axis c, the latter are expected to be associated with parallel bands. The parallel bands ν_8 and ν_9 correspond to the NH torsion at 832 cm^{-1}, strong in the infrared, and the skeletal deformation at 695 cm^{-1}, weak in the infrared [4]. These bands are shifted to 705 and 614 cm^{-1} upon deuteration, with change of vibrational character, the ND torsion now appearing at smaller wavenumber [4]. The analysis of the ν_8 fundamental studied with a resolution of ca. 0.003 cm^{-1} is the subject of the present study.

This experimental investigation is accompanied by ab initio calculations of the harmonic and anharmonic force fields. A previous ab initio study of CF_2NH has considered the equilibrium geometry at the SCF and MP2 levels [5].

Experimental

CF_2NH was prepared as described previously [1] and handled in a standard vacuum line. A glass cell measuring 18.7 cm equipped with KBr windows was used, and the pressure adjusted to ca. 1 mbar. The spectrum was recorded at Giessen with the Bruker 120 HR interferometer [6] equipped with a Ge/KBr beamsplitter, MCT detector and a globar source; the spectral range was limited to 800–1070 cm^{-1} by means of an optical filter. A resolution of 3×10^{-3} cm^{-1} was adjusted, and the actual line width, trapezoidal apodization, was close to 3×10^{-3} cm^{-1}. Since the ν_8 band was close to the energy cut-off by the detector the signal to noise ratio was only 20 to 40 depending on the spectral range. Calibration was by comparison with ν_1 lines of N_2O [7] recorded under the same conditions; relative to these the wavenumber accuracy is $\leqq 2 \times 10^{-4}$ cm^{-1}.

Description and Analysis of the Spectrum

The ν_8 band reveals a strong and split Q branch centered at 831.65 cm^{-1} and degraded to small wave-

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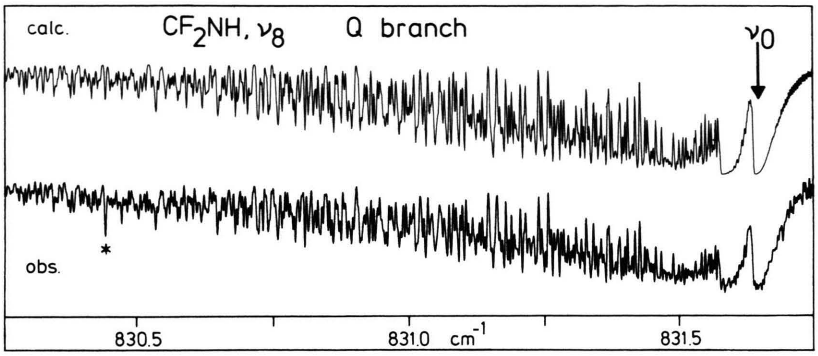

Fig. 1. IR spectrum of CF_2NH in the region of the Q branch of ν_8. *Lower trace:* Experimental spectrum, resolution 3×10^{-3} cm^{-1}, 18.7 cm^{-1} cell, 1 mbar. The asterisk identifies a line of HNCO. *Upper trace:* calculated spectrum.

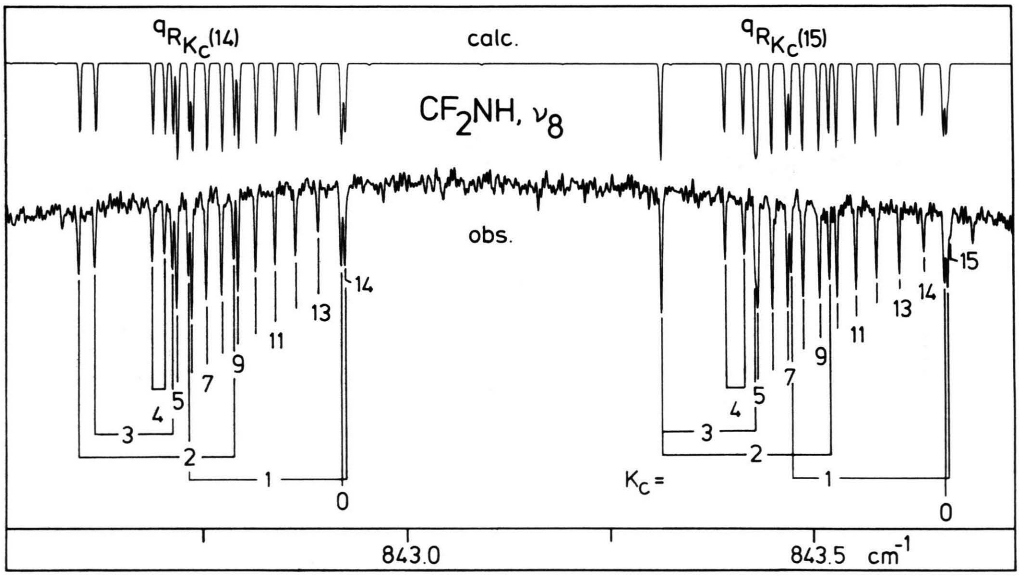

Fig. 2. Detail of the IR spectrum of CF_2NH in the R branch region showing the ${}^qR_{K_c}(14)$ and ${}^qR_{K_c}(15)$ clusters. K splitting is evident for $K_c = 1-4$. *Lower trace:* experimental spectrum. *Upper trace:* calculated spectrum.

number, Fig. 1, and P and R branches formed by J clusters. These J clusters consist of ${}^q(P, R)_{K_c}$ lines and are separated by $\sim(A+B)$, ca. 0.75 cm^{-1}, Figure 2. The lines exhibit K_c-degradation to large wavenumber because the K_c^2-dependent energy term $1/2\,(\alpha_A+\alpha_B)-\alpha_C$ is positive, $\sim 1 \times 10^{-3}$ cm^{-1}. Low-K_c lines show asymmetry splitting which was observed for $1 \leqq K_c \leqq 9$.

The Q branch could not be resolved; the gap is due to asymmetry splitting of low-K_c lines giving rise to two band heads. Some lines of the ν_4 band of the quasi-linear HNCO molecule [8], which was present as a minor contaminant, were detected, Figure 1. Lines belonging to ${}^qP$ clusters ($\Delta J = -1$, $\Delta K_a = -1$, $\Delta K_c = 0$) were assigned for $J'' \leqq 40$ and $K_c'' \leqq 32$ and ${}^qR$ lines ($\Delta J = +1$, $\Delta K_a = +1$, $\Delta K_c = 0$) for $J'' \leqq 52$ and $K_c'' \leqq 46$. Lines whose splitting was not resolved were assigned to both asymmetry components. A total of 3034 non-zero weighted data were subjected to a least squares fit to derive excited state parameters.

The model employed is Watson's A-reduced Hamiltonian in I^r representation [9]. This representation (rather than III^r) was adopted for reasons of consistency with the ground state parameters [2], which were held fixed in the refinement procedure.

The diagonal matrix elements were taken as

$$\begin{aligned}\tilde{H}^{(A)}_{rot} = {} & B^{(A)}_x J_x^2 + B^{(A)}_y J_y^2 + B^{(A)}_z J_z^2 \\ & - \Delta_J (J^2)^2 - \Delta_{JK} J^2 (J_z^2) - \Delta_K (J_z^2)^2 \\ & - 1/2\, [\delta_J J^2 + \delta_K J_z^2, J_+^2 + J_-^2]_+ \\ & + \Phi_J (J^2)^3 + \Phi_{JK} (J^2)^2 J_z^2 + \Phi_{KJ} J^2 J_z^4 + \Phi_K J_z^6 \\ & + 1/2\, [\varphi_J (J^2)^2 + \varphi_{JK} J^2 J_z^2 + \varphi_K J_z^4, J_+^2 + J_-^2]_+ \end{aligned} \qquad (1)$$

with $[x, y]_+ = xy + yx$. The axis notation for CF_2NH is $x, y, z = b, c, a$.

While ground state constants up to sixth order were used, $\nu_8 = 1$ excited state parameters were determined with significance only up to fourth order, and the sextic terms were constrained to their ground state values. The results are set out in Table 1. It is evident that changes of rotational parameters upon $\nu_8 = 1$ excitation are mostly small with regard to their absolute values, and in conjunction with the standard deviation of the fit, $\sigma = 2.6 \times 10^{-4}$ cm^{-1}, it has to be concluded that the ν_8 band is completely unperturbed.

Only C-type lines have been observed, and a search for A- and B-type lines with the assistance of predictions by means of excited state parameters was not successful. The calculated spectra illustrated in Fig. 1 and Fig. 2 are in excellent agreement with the experimental spectrum and support this assessment.

Table 1. Rovibrational parameters of CF_2NH (cm^{-1}).

	Ground state, rounded [2]	$\nu_8 = 1$
ν_0	–	831.645 447 (13) [a]
A	0.382 398 67	0.381 939 16 (6)
B	0.371 987 04	0.370 414 96 (7)
C	0.188 234 91	0.188 272 17 (4)
$\Delta_J \times 10^7$	1.753	1.729 6 (2)
$\Delta_{JK} \times 10^9$	5.8	−12.99 (11)
$\Delta_K \times 10^7$	3.196	3.423 7 (9)
$\delta_J \times 10^8$	7.276	7.148 4 (12)
$\delta_K \times 10^7$	1.698 5	1.519 2 (3)
$\Phi_J \times 10^{13}$	3	[b]
$\Phi_{JK} \times 10^{12}$	1.5	[b]
$\Phi_{KJ} \times 10^{12}$	−5.2	[b]
$\Phi_K \times 10^{12}$	4.7	[b]
$\varphi_J \times 10^{13}$	2.1	[b]
$\varphi_{JK} \times 10^{13}$	6	[b]
$\varphi_K \times 10^{12}$	1.1	[b]
No. of data		3034
$\sigma (J, K_a, K_c) \times 10^4$		2.6

[a] One standard deviation in parentheses.
[b] Fixed to ground state values.

A program [10] was used for the data fit, and lists of lines with their assignments and the correlation matrix of $\nu_8 = 1$ parameters have been deposited and are available as supplementary material [11].

Theoretical Methods

All quantum-chemical calculations were carried out at the Hartree-Fock SCF level by using the GRADSCF program system [12] and the standard 6-31 G** basis set [13, 14]. The molecular geometry was optimized within the constraint of C_s symmetry such that the largest component of the Cartesian gradient was less than 10^{-7} a.u. The quadratic force constants and the dipole moment derivatives were evaluated analytically in Cartesian coordinates, and the normal modes were obtained in the usual manner [15, 16]. The cubic and quartic normal coordinate force constants (Φ_{ijk}, Φ_{ijkk}) were then directly determined with the use of a finite difference procedure [17] which involves displacements along reduced normal coordinates (stepsize $\Delta q = 0.01$) and the calculation of analytic second derivatives (relative precision $\varepsilon < 10^{-9}$) at these displaced geometries. Spectroscopic constants were derived from the theoretical normal coordinate force constants using standard formulas based on perturbation theory [18, 19].

Theoretical Results and Discussion

Our optimized equilibrium geometry of CF_2NH at the 6-31 G** SCF level is identical to that published previously [5]. Compared with the recent solid-state X-ray structure [4], the deviations for the bond angles are below 1°, and the theoretical bond lengths between non-hydrogen atoms are too short by 0.004–0.018 Å (0.3–1.4%). Such a behaviour is quite typical for 6-31 G** SCF geometries [20]. Table 2 lists the calculated equilibrium and ground state rotational constants, the latter ones including the contributions

Table 2. Theoretical rotational constants (cm^{-1}) [a].

	Ground state	Equilibrium
A	0.3936	0.3951
B	0.3799	0.3817
C	0.1942	0.1942

[a] See Table 1 for experimental ground state values.

Table 3. Vibrational wavenumbers ω_i and ν_i (cm^{-1}) and infrared intensities A_i (km/mol),

Mode		Description [a]	CF_2NH					CF_2ND				
			calculated [b]			observed [c]		calculated [b]			observed [c]	
			ω_i	ν_i	A_i	ν_i	I_{rel}	ω_i	ν_i	A_i	ν_i	I_{rel}
a'	ν_1	N–H(D) str	3823	3382	40	3402.3	m	2805	2481	47	2519.3	m
	ν_2	C=N str	2040	1805	506	1785.2	vs	2024	1790	520	1780.0	vs
	ν_3	CF_2 a-str	1513	1338	348	1307	vs	1484	1313	355	1280	vs
	ν_4	CNH(D) bend	1174	1038	89	1031.2	s	930	832	68	836.0	s
	ν_5	CF_2 s-str	1065	942	109	947.2	s	1084	959	32	954.0	m
	ν_6	CF_2 sciss	622	550	1	572.7	vvw	618	547	2	563.7	vvw
	ν_7	CF_2 rock	594	525	32	542.0	m	539	477	35	491.8	m
a''	ν_8	NH(D) tors	948	839	128	831.6	s	685	606	24	613.9	w
	ν_9	CF_2 wag	789	698	15	695.2	w	812	719	75	705.1	m

[a] Based on the calculated potential energy distributions. In CF_2NH there is an almost even mixing of CF_2 a-str and CNH bend in ν_3 and ν_4. – [b] $\nu_i = 0.88443\ \omega_i$, see text. – [c] Reference [4], gas-phase IR values except ν_6 (matrix IR).

from the vibration-rotation interactions (see below). The theoretical ground state rotational constants are 2–3% higher than the experimental values [2, 3] which is consistent with the errors in the calculated bond lengths.

Table 3 lists the vibrational wavenumbers and infrared intensities for CF_2NH and CF_2ND. Hartree-Fock SCF calculations with medium-size basis sets are known [20] to yield harmonic wavenumbers ω_i which are usually 10–15% higher than the observed fundamental wavenumbers ν_i, and elaborate scaling procedures [21] are available to correct for these systematic deviations. However, since the vibrational assignments for CF_2NH and CF_2ND are established by now [4], we have introduced a single scale factor for both molecules, i.e. $\nu_i = 0.88443\ \omega_i$, to check the consistency between the theoretical and experimental data. The rms deviations between these calculated ν_i values and the observed ones are 17.2 and 19.9 cm^{-1} for CF_2NH and CF_2ND, respectively, which is about as good as can be expected at the chosen theoretical level. These comparisons support the recent reassignment [4] of the ν_6 vibration (572.7/563.7 cm^{-1} rather than 618/609 cm^{-1} [1]). The calculated shifts upon deuteration and the predicted intensity patterns are also in good agreement with the experimental data (see Table 3).

The theoretical vibration-rotation interaction constants α_i (see Table 4) depend on the quadratic and cubic force fields. In the case of α_6^C and α_7^C, complications may arise from the strong ν_6/ν_7 Coriolis interaction so that alternative values are given which refer to

Table 4. Vibration-rotation interaction constants α_i (10^{-3} cm^{-1}) [a].

i	α_i^A	α_i^B	α_i^C
1	0.160	0.415	0.143
2	0.941	1.408	0.505
3	0.683	1.224	0.843
4	−0.739	−0.107	0.246
5	0.759	0.496	0.447
6	0.078	−0.239	−2.524 [b]
7	0.048	−0.459	2.890 [b]
8 [c]	1.026	0.902	−0.057
9	−0.021	0.052	−0.185

[a] From perturbational formulas [19, 20].

[b] Excluding the contributions from the ν_6/ν_7 Coriolis interaction ($|\zeta_{67}| = 0.719$) yields 0.226 ($i=6$) and 0.137 ($i=7$).

[c] Experimental values for ν_8 from Table 1: 0.45951(6), 1.57208(7), −0.03726(4).

Table 5. Theoretical anharmonicity constants x_{ij} (cm^{-1}).

i	j	x_{ij}	i	j	x_{ij}	i	j	x_{ij}
1	1	−66.37	2	8	3.53	5	5	−0.78
1	2	11.54	2	9	3.82	5	6	2.99
1	3	13.95	3	3	−4.70	5	7	5.07
1	4	11.06	3	4	−13.26	5	8	4.19
1	5	13.61	3	5	−3.59	5	9	1.98
1	6	14.21	3	6	1.31	6	6	0.38
1	7	15.54	3	7	0.86	6	7	1.63
1	8	−1.56	3	8	−0.33	6	8	−5.96
1	9	13.61	3	9	0.06	6	9	−2.17
2	2	−5.92	4	4	−7.80	7	7	0.61
2	3	3.06	4	5	−4.71	7	8	−6.03
2	4	5.33	4	6	−1.80	7	9	−1.96
2	5	1.72	4	7	−2.90	8	8	−6.18
2	6	7.06	4	8	−3.74	8	9	−5.76
2	7	5.89	4	9	−3.07	9	9	−0.37

an explicit treatment of this interaction (see footnote b of Table 4). The only available experimental α_i values are those determined in this study for ν_8 (see above and Table 1). There is agreement between theory and experiment that α_8^A and α_8^B are both positive and of the order 1×10^{-3} cm^{-1}, while α_8^C is negative and very small. More quantitatively, the theoretical and experimental ν_8 values differ by factors of 1.5–2.2. These discrepancies are higher than in a previous systematic study [22] of 16 halide molecules H_3MX (M = C–Sn, X = F–I) where deviations were typically in the range 0–30%. It remains to be seen whether the discrepancies are generally larger in multiply-bonded systems such as CF_2NH.

Table 5 lists the theoretical anharmonicity constants x_{ij} which depend on the quadratic, cubic, and quartic force fields. In our calculations there is no evidence for important anharmonic resonances in CF_2NH. Accurate experimental x_{ij} values are not yet available. The predicted x_{ij} constants in Table 5 may be used to estimate the location of overtone and combination bands. It is hoped that the theoretical predictions in Tables 4 and 5 will be useful in future high resolution experimental work on CF_2NH. The ab initio cubic and quartic force constants are deposited as supplementary material [11].

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