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Anharmonic Force Field and Vibrational Spectra of Perfluoromethanimine CF_2NF

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Accurate quartic anharmonic force field for perfluoromethanimine CF_2NF has been calculated from the MP_2 method using a triple ζ basis set. The vibrational wavenumbers calculated using a variation-perturbation algorithm agree for the fundamental bands very well with the experimental data. Our results predict a new interpretation of some overtone bands observed in the medium infrared region between 250 and 3500 cm^{-1}.

I. Introduction

The compounds containing the link C═N play an important role in organic chemistry. It is well-known that their structures and their reactivities are particularly affected by the nature of the substituent on the nitrogen atom. Methylenimine CH_2═NH, the simplest imine prototype molecule, has been the subject of considerable chemical[1] and theoretical[2,3] interest despite its instability. Perfluoromethanimine CF_2═NF, on the other hand, is a very stable compound, reactive toward nucleophiles and strong electrophiles,[4−7] much more amenable to experimental study, but the difficulty of its synthesis has for a long time limited its structural characterization. A new preparative method proposed by Sekiya and DesMarteau[4] allowed a detailed investigation of the spectroscopic properties and structure of perfluoromethanimine[8−10] by means of microwave, infrared, and Raman spectroscopy. These experimental investigations are accompanied by some theoretical works,[9,11,12] but none of them is dedicated to the knowledge of the complete vibrational spectra of the perfluoromethanimine. Following our investigations on the anharmonic vibrational spectra of X_2CNX (X = H, F) compounds,[2,3,13] we propose in this study an accurate ab initio quartic force field for perfluoromethanimine in order to analyze and to complement the assignment of all the fundamental and combinations bands observed in the medium IR region between 250 and 3500 cm^{-1}.

This paper is organized as follows: In Section II, we briefly summarize the computational details, and we present in Section III the quartic force field calculated by means of a Moller−Plesset approach, as well as the theoretical anharmonic vibrational spectra, and discuss the results obtained by comparison with the observed data.

II. Method and Computational Considerations

The complete quartic force field of perfluoromethanimine was determined using a least-squares fit performed on a grid of 730 molecular energies corresponding to displacements described in terms of curvilinear coordinates S_k (see Figure 1). For all distorted structures generated by several displacements of 0.01 Å and 0.01 rad for bond and angular coordinates, the corresponding energies were calculated at the MP2 level of theory using the 6−311 G* basis set of Pople and co-workers.[14] All the molecular electronic wave function calculations were performed with the *Gaussian 98* package.[15]

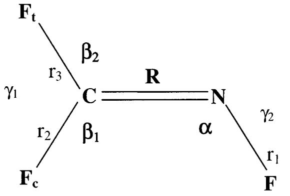

Figure 1. Internal coordinates for perfluorothanimine CF_2NF. γ_1 is the CF_2 wagging and γ_2 the NF torsion.

On the basis of curvilinear coordinates S_k and their conjugate moment P_{S_k} the vibrational Hamiltonian is written as follows:

$$H_v = \frac{1}{2}\sum_{i,j} g_{ij}(s)P_{s_i}P_{s_j} + V_{(s)}$$

where g_{ij} are the elements of the G matrix described by Wilson et al.[16] and $V_{(S)}$ is the potential function. In our approach, the potential and the kinetic part of the Hamiltonian are expressed as a Taylor expansion in terms of curvilinear coordinates:

$$V_{(S)} = \frac{1}{2}\sum_{i,j} f_{ij}S_iS_j + \frac{1}{3!}\sum_{i,j,k} f_{ijk}S_iS_jS_k + \frac{1}{4!}\sum_{i,j,k,l} f_{ijkl}S_iS_jS_kS_l$$

where f_{ij}, f_{ijk}, and f_{ilkl} are the quadratic, cubic, and quartic force constants determined from the fit

$$T = \frac{1}{2}\sum_{i,j} g_{ij}(o)P_{S_i}P_{S_j} + \frac{1}{2}\sum_{i,j,k} g_{ijk}P_{S_i}S_kP_{S_j}$$

with $g_{ijk} = (\partial g_{ij}/\partial S_k)_0$ and where $g_{ij}(o)$ are the elements of the Wilson matrix for the equilibrium geometry.

The anharmonic energy levels are calculated from a configuration interaction treatment according to a previously published variation-perturbation algorithm,[3,17,18] in which a primary subspace S built interatively and containing the major configurations is treated by a variational procedure. The multireference vibrational function is then corrected to first order by a secondary subspace M containing configurations which interact weakly with those of the subspace S. This latter contribution to vibrational energy levels is estimated by the second-order perturbation theory. In our problem, the primary and the secondary subspaces contain, respectively, about 3000 and 8000

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TABLE 1: Optimized MP2/6-311G* Geometry (in angstroms and degrees) and Calculated Rotational Constants (MHz) for CF_2NF[a]

	$F_2C{=}NF$			
coordinates	ab initio (r_e) MP2/6-311G*	exptl data (r_α^0)	MP2/ 6-31G*[b]	B3LYP/ 6-31G*[c]
C=N	1.272	1.274 (6)	1.279	1.271
CF_c	1.300	1.300 (3)	1.312	1.309
CF_t	1.302	1.300 (3)	1.314	1.309
NF	1.388	1.389 (2)	1.409	1.404
$N{=}CF_c$	128.1	127.2 (2)		127.9
$N{=}CF_t$	119.4	119.8 (2)	106.8	119.6
C=NF	108.3	107.9 (2)		107.7
A	11174.73	11235.412 (8)		
B	4303.62	4316.781 (3)		
C	3107.04	3115.288 (2)		

[a] Standard errors in parentheses in units of last digit. [b] From Mack et al.[11] [c] From Gristan et al.[12]

TABLE 2: Quadratic Force Constants Calculated at MP2/6-311G Level of Theory for CF_2NF[a]**

quadratic force constants	ab initio	exptl. values[9]	quadratic force constants	ab initio	exptl. values[9]
f_{RR}	10.716	9.055	$f_{r2\alpha}$	−0.242	
f_{Rr1}	0.198		$f_{r2\beta1}$	−0.076	−0.010
f_{Rr2}	0.333		$f_{r2\beta2}$	−0.640	−0.765
f_{Rr3}	0.486		f_{r3r3}	7.816	7.492
$f_{R\alpha}$	0.665	0.316	$f_{r3\alpha}$	0.122	
$f_{R\beta1}$	0.455	0.367	$f_{r3\beta1}$	−0.621	−0.765
$f_{R\beta2}$	0.478	0.367	$f_{r3\beta2}$	0.085	−0.010
f_{r1r1}	5.490	4.388	$f_{\alpha\alpha}$	1.628	2.054
f_{r1r2}	0.150		$f_{\alpha\beta1}$	0.023	0.004
f_{r1r3}	0.151		$f_{\alpha\beta2}$	0.115	
$f_{r1\alpha}$	0.905	0.705	$f_{\beta1\beta1}$	2.330	2.081
$f_{r1\beta1}$	−0.163		$f_{\beta1\beta2}$	1.323	1.374
$f_{r1\beta2}$	0.139		$f_{\beta2\beta2}$	2.356	2.539
f_{r2r2}	7.619	7.526	$f_{\gamma1\gamma1}$	0.359	0.439
f_{r2r3}	0.701	0.773	$f_{\gamma1\gamma2}$	−0.176	0.007
			$f_{\gamma2\gamma2}$	0.487	0.521

[a] Units are consistent with energy measured in aJ.

configurations; harmonic functions are used as expansion functions in this treatment.

III. Results and Discussion

Our perfluoromethanimine-optimized structure is given in Table 1 and is compared to the data deduced from a joint analysis of microwave and electron diffraction data.[9] Results previously obtained from MP2/6-31G* and B3LYP/6-31G* approaches (see Christen et al.[9] and Gristan et al.,[12] respectively) are also reported for comparison.

All calculated bond lengths obtained at the MP2/6-311G* level are quite close to those of experimental data: the deviations are less than 0.002 and 0.001 Å for CN and NF, respectively. Calculated values for bond angles do not deviate more than 0.9° by comparison with those from experiment. These results confirm the well-known tendency of MP2/TZP calculations to give very accurate geometrical parameters. For comparison, MP2/DZP- and B3LYP/DZP-optimized geometries[9,12] give for CF and NF bond lengths overestimated by about 0.01 and 0.02 Å respectively. In the case of the rotational constants, our MP2/6-311G* values are only 0.5% higher than the experimental data[9] for A and about 0.3% smaller for B and C. The quadratic, cubic, and quartic force field obtained from a fourth-order polynomial fit is expressed in terms of curvilinear coordinates, which are then given in terms of reduced normal coordinates. Table 2 reports and compares our quadratic force field expressed in curvilinear coordinates with the empirical force field published by Christen et al.[9] As expected, our theoretical quadratic force constants are generally larger than the adjusted experimental parameters mainly because these latter are not composed of quadratic elements but came directly from the experimentally observed anharmonic frequencies. It should be noted that the computed difference between F_{CF_t} (7.816 aJ $Å^{-2}$) and F_{CF_c} (7.619 aJ $Å^{-2}$) is consistent with the different CF bond lengths found in our calculations.

Turning our attention to the interaction force constants we find, as experimentally expected, large positive values between CN and all bending coordinates ($F_{CN/CNF} = 0.665$ aJ $Å^{-1}$; $F_{CN/NCF_c} = 0.455$ aJ $Å^{-1}$; $F_{CN/NCF_t} = 0.478$ aJ $Å^{-1}$) and between NF and the CNF bending ($F_{NF/CNF} = 0.905$ aJ $Å^{-1}$). In the same way, large negative values are found between CF and the nonadjacent bending coordinate β FCN ($F_{CF_c/NCF_t} = -0.640$ aJ $Å^{-1}$; $F_{CF_t/NCF_c} = -0.621$ aJ $Å^{-1}$). The study of the others off-diagonal terms reveals also the large coupling $F_{CN/CF}$ (0.333 and 0.486 aJ $Å^{-2}$) and $F_{CN/NF}$ (0.198 aJ $Å^{-2}$) values neglected in the empirical adjusted potential. The harmonic, cubic, and quartic force constants reported in Table 3 show the anharmonicity of the surface along some directions. Some cubic terms involving the CN stretch (ϕ_{111}) and its coupling with the CF_2 asymmetric and symmetric stretching (ϕ_{122}, ϕ_{114}) appear relatively large. In the same way, the diagonal cubic values concerning ν_{NF} (ϕ_{333}) and the two CF_2 stretching modes (ϕ_{222}, ϕ_{444}) are found to be quite significant. For the CNF bending mode and the two CF_2 scissoring and rocking vibrations, the weakness of the cubic terms reveals a lower anharmonicity.

A rough analysis of the quartic data shows the great importance of the terms involving the CF_2 wagging mode (ϕ_{8888}) and its coupling with the NF stretching (ϕ_{1188}).

The nine harmonic ($\bar{\omega}$) and anharmonic ($\bar{\nu}$) fundamental vibrations deduced from the force field previously discussed are reported in Table 4. Our calculated values are compared to the IR spectra recorded at room temperature in the gas phase by Christen et al.[9]

At the harmonic level approximation, the absolute intensities of the fundamental bands are in good agreement with the qualitative experimental data. The very small intensity values calculated for the bands expected around 640 cm^{-1} (CF_2 scissoring and wagging modes) and around 300 cm^{-1} (CNF bending and torsion) explain the difficulty of the experimental assignment. The CF_2 scissoring mode hidden in the IR band assigned at the CF_2 wagging vibration appears at about 644 cm^{-1} in the Raman spectra recorded in the liquid phase.[9]

The anharmonicity effect appears to be quite significant for fundamental frequencies corresponding to the stretching modes. The CN, NF, and the CF_2 asymmetric and symmetric frequencies are lowered by 51, 31, 38, and 20 cm^{-1}, respectively.

For the bending vibrations, the anharmonicity effects are smaller: the harmonic values are lowered in the range between 17 cm^{-1} for ν_8 (CF_2 wagging) and 4 cm^{-1} for ν_7 (CNF bending).

In Table 5, we report for CF_2NF the results obtained for fundamental and some overtone bands that might be found in the same medium IR region between 250 and 3500 cm^{-1}. For all fundamental bands, our calculated anharmonic results are in very good agreement with the experiments confirming the predicted sequence, particularly in the region where the scissoring band is hidden by the peak relative to the wagging vibration. We found in our calculations the CF_2 wagging (648 cm^{-1}) at higher frequency than the CF_2 scissoring (645 cm^{-1}) by about 3 cm^{-1} as expected in Raman where the observed difference is 5 cm^{-1} (644 vs 649 cm^{-1}). For all fundamental bands the mean deviation between the calculated values and

TABLE 3: Quadratic (ω_i), Cubic (ϕ_{ijk}), and Quartic (ϕ_{ijkl}) Force Constants (in cm^{-1}) Calculated at the MP2/6.311G* Level of Theory for F_2CNF[a]

parameter	value (cm^{-1})	parameter	value (cm^{-1})	parameter	value (cm^{-1})	parameter	value (cm^{-1})
ω_1	1792.4	ϕ_{335}	−69.1	ϕ_{599}	20.1	ϕ_{267}	19.6
ω_2	1417.7	ϕ_{336}	46.0	ϕ_{699}	−11.0	ϕ_{345}	−13.3
ω_3	1068.8	ϕ_{337}	21.8	ϕ_{444}	−116.8	ϕ_{346}	30.2
ω_4	956.4	ϕ_{144}	−39.4	ϕ_{445}	−17.2	ϕ_{389}	13.9
ω_5	654.5	ϕ_{244}	48.4	ϕ_{446}	10.0	ϕ_{356}	16.0
ω_6	525.9	ϕ_{455}	−39.8	ϕ_{447}	−16.7	ϕ_{589}	−15.8
ω_7	284.0	ϕ_{555}	−21.1	ϕ_{155}	−28.1	ϕ_{1111}	43.8
ω_8	664.5	ϕ_{166}	11.8	ϕ_{255}	−16.4	ϕ_{1122}	−23.4
ω_9	308.1	ϕ_{466}	−12.7	ϕ_{123}	−60.4	ϕ_{1188}	−56.8
ϕ_{111}	415.3	ϕ_{566}	−32.9	ϕ_{125}	−10.9	ϕ_{1199}	−30.9
ϕ_{112}	24.0	ϕ_{666}	−12.2	ϕ_{127}	−11.6	ϕ_{2222}	86.2
ϕ_{113}	114.2	ϕ_{177}	29.8	ϕ_{134}	−37.5	ϕ_{2277}	−10.1
ϕ_{114}	−192.4	ϕ_{277}	−13.1	ϕ_{135}	35.1	ϕ_{2288}	−24.2
ϕ_{115}	−57.8	ϕ_{377}	23.9	ϕ_{136}	16.7	ϕ_{2299}	−29.2
ϕ_{116}	25.7	ϕ_{477}	33.4	ϕ_{137}	23.6	ϕ_{3333}	10.3
ϕ_{122}	−234.3	ϕ_{577}	14.4	ϕ_{145}	12.0	ϕ_{3344}	25.8
ϕ_{222}	−137.8	ϕ_{677}	12.3	ϕ_{146}	−32.1	ϕ_{3377}	−16.8
ϕ_{223}	156.1	ϕ_{777}	−59.5	ϕ_{189}	−76.9	ϕ_{3399}	−47.4
ϕ_{224}	−172.3	ϕ_{188}	−14.4	ϕ_{234}	−27.0	ϕ_{4444}	−15.5
ϕ_{225}	−66.9	ϕ_{388}	−15.8	ϕ_{235}	49.4	ϕ_{4488}	−13.2
ϕ_{227}	−13.8	ϕ_{488}	50.4	ϕ_{236}	−26.5	ϕ_{8888}	−90.7
ϕ_{133}	−92.3	ϕ_{688}	−10.8	ϕ_{245}	−27.1	ϕ_{4499}	−25.7
ϕ_{233}	28.6	ϕ_{299}	39.4	ϕ_{247}	18.6	ϕ_{8899}	32.2
ϕ_{333}	−155.0	ϕ_{399}	49.7	ϕ_{289}	−10.8	ϕ_{5588}	−11.2
ϕ_{334}	−170.2	ϕ_{499}	59.1	ϕ_{257}	12.4	ϕ_{5599}	−19.6
						ϕ_{9999}	46.1

[a] All terms are calculated but only values over 10 cm^{-1} are reported for the cubic and quartic terms.

TABLE 4: Harmonic $\bar{\omega}$ and Anharmonic $\bar{\nu}$ Wavenumbers Calculated for the Fundamental Vibrations of CF_2NF from the Quartic MP2/6-311G Potential**

assigment	$\bar{\omega}$ (cm^{-1})	A_i (km/mole)	$\bar{\nu}_{calc}$ (cm^{-1})	$\bar{\nu}_{obs}$ (cm^{-1})[8]	I_{obs}
A′					
ν_1 CN_{str}	1792	177.67	1741	1740.3	s
ν_2 $CF_{2asym\text{-}str}$	1418	267.85	1380	1385.5	s
ν_3 NF_{str}	1069	97.00	1038	1021.2	s
ν_4 $CF_{2sym\text{-}str}$	956	11.66	936	932.9	m
ν_5 $CF_{2scissor}$	655	2.10	645	644 (Raman)	
ν_6 CF_{2rock}	526	3.19	521	520	w
ν_7 CNF_{bend}	284	4.58	280	285.7	w
A″					
ν_8 CF_{2wag}	665	15.46	648	643.2 649 (Raman)	
ν_9 torsion	308	0.08	301	302.5	w

TABLE 5: Anharmonic $\bar{\nu}$ Wavenumbers (in cm^{-1}) Calculated for Fundamental and Some Overtone Bands of CF_2NF

assignment	$\bar{\nu}_{calc}$ (cm^{-1})	$\bar{\nu}_{obs}$ (cm^{-1})	assignment	$\bar{\nu}_{calc}$ (cm^{-1})	$\bar{\nu}_{obs}$ (cm^{-1})
ν_7	280	285.7	ν_2	1380	1385.5
ν_9	301	302.5	$\nu_3 + \nu_6$	1557	1541
ν_6	521	520	$\nu_3 + \nu_5$	1677	1659
ν_5	645	644	ν_1	1741	1740
ν_8	648	643	$2\nu_4$	1868	1859
$\nu_6 + \nu_7$	801	800	$\nu_2 + \nu_6$	1898	1897
ν_4	936	932.9	$2\nu_3$	2062	2025
ν_3	1038	1021.2	$\nu_2 + \nu_4$	2308	2318
$\nu_5 + \nu_6$	1164	1098	$\nu_1 + \nu_5$	2385	2370
$\nu_4 + \nu_7$	1216	1210	$\nu_2 + \nu_3$	2405	2405
$2\nu_5$	1288	1252	$\nu_1 + \nu_4$	2669	2660
$2\nu_8$	1283	1281	$2\nu_2$	2749	2750
$\nu_3 + \nu_7$	1318	1309	$\nu_1 + \nu_2$	3107	3120
			$2\nu_1$	3454	3475

the observed data is about 0.6% (≈5 cm^{-1}). The largest deviation is found to be 16.8 cm^{-1} for the NF stretching mode, whereas deviations in other fundamentals are no more than 5 cm^{-1}. When overtone are taken into consideration, the root-mean-square deviation becomes higher (≈10 cm^{-1}). Except for the $\nu_5 + \nu_6$ mode for which the experimental assignment is doubtful for us, the largest deviation is still observed for the NF stretching overtone $2\nu_3$ (≈37 cm^{-1}). If for $2\nu_3$ most of this deviation is accounted for by error in the predicted value of ν_3, this not the case for the overtone $\nu_5 + \nu_6$. Indeed ν_5 and ν_6 are calculated at, respectively, 645 and 521 cm^{-1} in perfect agreement with the observed bands situated around 644 and 520 cm^{-1} for which both the anharmonicity is found to be weak and the coupling force constants ϕ_{i56} is not very important. We conclude that the band observed at 1098 cm^{-1} is not assignable to the $\nu_5 + \nu_6$ combination as predicted experimentally but corresponds to the ternary combination $\nu_6 + 2\nu_9$ or $\nu_6 + \nu_7 + \nu_9$.

In summary, our proposed potential function, calculated at the MP2/6-311G* level of theory, leads for the fundamental vibrations of CF_2NF to results in very good agreement with the most reliable experimental data, rising some doubt in the assignment of very weak bands, and allows a new interpretation of some overtone bands in the medium infrared region.

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