

Research Article

Rovibrational Interaction and Vibrational Constants of the Symmetric Top Molecule $^{14}\text{NF}_3$

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Several accurate experimental values of the α^C and α^B rotation-vibration interaction parameters and ω_i , x_{ij} , and g_{ij} vibrational constants have been extracted from the most recent high-resolution Fourier transform infrared, millimeter wave, and centimeter wave investigations in the spectra of the oblate symmetric top molecule $^{14}\text{NF}_3$. The band-centres used are those of the four fundamental, the overtones, the combination, and hot bands identified in the region between 400 cm^{-1} and 2000 cm^{-1} . Comparison of our constants with the ones measured previously, by infrared spectroscopy at low resolution, reveals orders of magnitude higher accuracy of the new values. The agreement between our values and those determined by *ab initio* calculations employing the TZ2Pf basis is excellent.

1. Introduction

Nitrogen trifluoride NF_3 is a pyramidal symmetric top molecule belonging to C_{3v} point group. It has four vibrational normal modes:

- (i) two totally symmetric (A_1 type): ν_1 and ν_2 ;
- (ii) two doubly degenerate (E type): ν_3 and ν_4 .

Today, NF_3 is employed in the cleaning of the PECVD chambers in the high volume production of liquid crystal displays and silicon-based thin film solar cells. It has been considered as an environmentally preferable substitute for sulphur hexafluoride or perfluorocarbons such as hexafluoroethane [1]. But, recent publications [2–7] reported that NF_3 is 17,000 times more potent a greenhouse gas than CO_2 and recommended to include it in the basket of gases controlled by Kyoto protocol and to monitor its environmental levels.

Nitrogen trifluoride is also used in hydrogen fluoride and deuterium fluoride lasers, which are types of chemical lasers.

In spite of these interesting properties and important applications, the spectra of this molecule have not yet been much studied in the past, because of difficulties to obtain high

quality spectra and to interpret its perturbed bands. Many of these difficulties have now been overcome through the advent of high-resolution spectrometers and the development of computers.

This is within the framework of this research orientation and the Moroccan/European collaboration that several bands of NF_3 gas were recently analysed [8–14]. We used independent and complementary methods, Fourier transform infrared (FTIR), millimetre wave (MMW), and centimetre wave (CMW) spectroscopies. All studied IR spectra were recorded at Wuppertal (Germany) with the Bruker 120 HR interferometer, except for the region around 1032 cm^{-1} , which was recorded at the University of Giessen (Germany). The rotational spectra were measured in Lille (France) with a computer-controlled MMW spectrometer. The measurements in the CMW range were performed at Kiel (Germany) by means of wave-guide microwave Fourier transform spectroscopy.

The subject of this work is to extract accurate experimental rotation-vibration interaction parameters and anharmonicity constants of the potential function of $^{14}\text{NF}_3$ from

our recent studies by high-resolution spectroscopy and the latest results available in the literature.

2. Relationships Linking Vibrational Constants

More recently, we have established the following relationships linking band-centres, harmonic wavenumbers, and anharmonicity constants of a symmetric top molecule [15].

2.1. Fundamental Bands $\nu_i = 1$

$$(\nu_i^{\ell_i}) = \omega_i^0 + x_{ii} + g_{ii}\ell_i \quad (1)$$

ω_i is the normal wavenumber of the i th mode; ν_i is its vibrational quantum number; i refers to a totally symmetric or to a degenerate vibration; x_{ii} and g_{ii} are the anharmonicity constants; and ℓ_i is the vibrational angular momentum: $|\ell_i| = \nu_i, \nu_i - 2, \dots, 1$, or 0 only exists for a doubly degenerate vibration.

2.2. Harmonic Bands $\nu_i = n$ (Integer > 1)

$$(n\nu_i^{\ell_i}) = n(\nu_i^{\pm 1})^0 + (n^2 - n)x_{ii} + (\ell_i^2 - n)g_{ii}. \quad (2)$$

2.3. Combination Bands $\nu_i = n$ and $\nu_{i'} = m$ (Integer), $i \neq i'$

$$(n\nu_i^{\ell_i} + m\nu_{i'}^{\ell_{i'}})^0 = (n\nu_i^{\ell_i})^0 + (m\nu_{i'}^{\ell_{i'}})^0 + nm x_{ii'} + g_{ii'} \ell_i \ell_{i'}. \quad (3)$$

For the oblate symmetric top NF_3 , we count $4\omega_i^0$, $10x_{ij}$, and $3g_{ij}$; $i \leq j$.

3. The Ground State Constants of $^{14}\text{NF}_3$

The experimental ground state (GS) axial rotational parameters for the symmetric top molecule $^{14}\text{NF}_3$ employed in the present study and reported in Table 1 come from different sources.

For the C_0 K -dependent constant, we used in our high-resolution studies the following values:

- (i) $C_0 = 0.1949980$ (10): a preliminary value obtained in the course of our work on the $2\nu_4$ overtone band of $^{14}\text{NF}_3$,
- (ii) $C_0 = 0.19499250$ (44): the definitive value adopted in the study of the $\nu_4 = 2$ state of $^{14}\text{NF}_3$. In the two cases, we used the “loop method” as described in [16].

For the B_0 J -dependent constant, the values adopted were determined by Höhe et al. [17], Breidung et al. [18], and Cazzoli and Puzzarini [19].

TABLE 1: Ground state constants (cm^{-1}) of $^{14}\text{NF}_3$.

Parameter	Value [12, 17]	Value [11, 18]	Value [11, 19]
C_0	0.1949980 (10)	0.19499250 (44)	0.19499250 (44)
B_0	0.3562828965 (40)	0.3562827950 (15)	0.3562828891 (21)

Numbers in parentheses represent one standard deviation in units of the last digit quoted.

4. The Rovibrational Bands of $^{14}\text{NF}_3$ Observed below 2000 cm^{-1}

4.1. The ν_1 Fundamental Band [17]. The $\nu_1 = 1$ excited state of $^{14}\text{NF}_3$ was investigated by FTIR spectroscopy and with saturation technique using CO_2 side bands as a tunable infrared source. This level was considered unperturbed, and the fit gave the band-centre: $(\nu_1)^0 = 1032.00123750$ (47) cm^{-1} . For the excited rotational constants, the values were determined relative to the GS.

4.2. The ν_4 Fundamental Band [14]. The lowest fundamental band ν_4 of the nitrogen trifluoride $^{14}\text{NF}_3$ was studied by high-resolution FTIR, MMW, and CMW spectroscopies near 493 cm^{-1} . The analysis of the $\nu_4 = 1$ state included $\ell(2, 2)$, $\ell(2, -1)$, $\ell(2, -4)$, and $k(0, 6)$ intravibrational interactions and gave the band-centre: $(\nu_4)^0 = 493.4227759$ (89) cm^{-1} .

4.3. The ν_2 Fundamental, $2\nu_2 - \nu_2$ Hot, $2\nu_2$ Overtone, and $\nu_2 + \nu_4$ Combination Bands [13]. They were analysed by FTIR and MMW spectroscopies. The corresponding excited states were treated as isolated levels, and the following band-centres were determined:

$$\begin{aligned} (\nu_2)^0 &= 647.1340617 \text{ (73) } \text{cm}^{-1}, \\ (2\nu_2 - \nu_2)^0 &= 645.121943 \text{ (14) } \text{cm}^{-1}, \\ (\nu_2 + \nu_4)^0 &= 1138.276629 \text{ (10) } \text{cm}^{-1}. \end{aligned} \quad (4)$$

Because of the low intensity of the $2\nu_2$ overtone, the $\nu_2 = 2$ state constants were determined from the $2\nu_2 - \nu_2$ hot and ν_2 fundamental bands.

We point out that any explanation was offered for a severe intensity perturbation observed in the spectra of ν_2 and $2\nu_2$ bands (see [13]).

4.4. The ν_3 Fundamental Band [12]. The perpendicular band ν_3 of the symmetric top $^{14}\text{NF}_3$ was analysed by high-resolution FTIR and MMW spectroscopies. The $\nu_3 = 1$ excited state was considered vibrationally isolated, but several intravibrational interactions were included in the final fit. The band-centre obtained is $(\nu_3)^0 = 907.5413300$ (72) cm^{-1} .

4.5. The $2\nu_4$ Overtone Band [11]. The $\nu_4 = 2$ excited state of the oblate molecule $^{14}\text{NF}_3$, lying near 985 cm^{-1} , was successfully studied by high-resolution FTIR and MMW spectroscopies. Assumed to be isolated, the treatment of this level gave the

TABLE 2: Band-centres and rovibrational interaction constants of $^{14}\text{NF}_3$ molecule (in cm^{-1}).

Band or component	Experimental band-centre, this work	Experimental $\alpha^C \times 10^3$, this work	<i>Ab initio</i> $\alpha^B \times 10^3$, [18]	Experimental $\alpha^B \times 10^3$, this work	<i>Ab initio</i> $\alpha^B \times 10^3$, [18]
ν_1	1032.00123750 (47)	0.593526 (40)	0.643	-1.4496825 (43)	-1.227
ν_2	647.1340617 (73)	0.4346 (10)	0.404	1.289844 (18)	1.300
ν_3	907.5413300 (72)	0.7374 (11)	0.857	2.628451 (22)	2.758
ν_4	493.4227759 (89)	0.5566 (10)	0.544	0.150021 (23)	0.164
$2\nu_2 - \nu_2$	645.121943 (14)	0.8777 (10)	—	2.592650 (37)	—
$2\nu_2$	1292.25004 (21) ^a	0.8777 (10)	—	2.592650 (37)	—
$\nu_2 + \nu_4$	1138.276629 (10)	0.9922 (10)	—	1.447060 (43)	—
$2\nu_4^0$	983.701767 (34)	1.10135 (63)	—	0.192090 (23)	—
$2\nu_4^{\pm 2}$	986.622364 (18)	1.10101 (56)	—	0.302179 (50)	—
$2\nu_3^0$	1803.130213 (57)	1.47497 (80)	—	4.84308 (22)	—
$2\nu_3^{\pm 2}$	1810.423993 (21)	1.49747 (50)	—	5.24715 (12)	—
$\nu_1 + \nu_3$	1931.577516 (19)	1.30958 (56)	—	1.460127 (78)	—
$\nu_1 + \nu_4$	1523.040783 (34)	1.37339 (84)	—	-1.13109 (44)	—
$\nu_2 + \nu_3$	1546.30 ^b	—	—	—	—

Numbers in parentheses represent one standard deviation in units of the last digit quoted.

^aValue extracted from the values of $(\nu_2)^0$ and x_{22} (Tables 2 and 3). ^bValue estimated from our FTIR spectrum which is in course of study.

following band-centres for the parallel and perpendicular components:

$$\begin{aligned} (2\nu_4^0)^0 &= 983.701767 \text{ (34) cm}^{-1}, \\ (2\nu_4^{\pm 2})^0 &= 986.622364 \text{ (18) cm}^{-1}. \end{aligned} \quad (5)$$

4.6. *The $2\nu_3$ Overtone and $\nu_1 + \nu_3$ Combination Bands [10].* In the analysis of these bands, we used spectra recorded by Fourier transform spectrometer. The same models applied to the $\nu_4 = 2$ and $\nu_3 = 1$ excited states were applied to treat the $2\nu_3$ and $\nu_1 + \nu_3$ bands. We obtained the following results:

$$\begin{aligned} (2\nu_3^0)^0 &= 1803.130213 \text{ (57) cm}^{-1}, \\ (2\nu_3^{\pm 2})^0 &= 1810.423993 \text{ (21) cm}^{-1}, \\ (\nu_1 + \nu_3)^0 &= 1931.577516 \text{ (19) cm}^{-1}. \end{aligned} \quad (6)$$

4.7. *The $\nu_1 + \nu_4$ Combination Band [8, 9].* The $\nu_1 + \nu_4$ perpendicular band of $^{14}\text{NF}_3$ was studied by high-resolution infrared spectroscopy. It was treated by a model taking into account ℓ - and k -type intervibrational interactions. The band-centre obtained in the D -reduction of the rovibrational Hamiltonian is $(\nu_1 + \nu_4)^0 = 1523.040783 \text{ (34) cm}^{-1}$.

5. Results and Discussion

In Table 2, we gather the recent measurements, at high-resolution, of the centres of the all studied bands between 400 cm^{-1} and 2000 cm^{-1} and the corresponding experimental rotation-vibration interaction constants: $\alpha^C = C_0 - C'$ and

$\alpha^B = B_0 - B'$ and C' and B' being the constants of the upper level.

The values of the rovibrational interaction constants were determined by *ab initio* calculations (Table 2) for only the fundamental bands. The agreement with our values is excellent.

Equation (2) leads to $x_{24} = (\nu_2 + \nu_4)^0 - (\nu_2)^0 - (\nu_4)^0 = -2.280208 \text{ (11) cm}^{-1}$.

For the $2\nu_4$ harmonic band, we obtain the system of equations:

$$\begin{aligned} (2\nu_4^0)^0 &= 2(\nu_4^{\pm 1})^0 + 2x_{44} - 2g_{44}, \\ (2\nu_4^{\pm 2})^0 &= 2(\nu_4^{\pm 1})^0 + 2x_{44} + 2g_{44}. \end{aligned} \quad (7)$$

We derive $x_{44} = -0.841743 \text{ (22) cm}^{-1}$ and $g_{44} = 0.730149 \text{ (21) cm}^{-1}$.

As for $2\nu_4$, we deduce $x_{33} = -4.15278 \text{ (18) cm}^{-1}$ and $g_{33} = 1.82344 \text{ (18) cm}^{-1}$.

Using the band-centres of ν_1 and ν_4 , we obtain $x_{14} = -2.383248 \text{ (49) cm}^{-1}$. We can also derive, from the band-centres of ν_1 and ν_3 , the anharmonic constant: $x_{13} = -7.965051 \text{ (26) cm}^{-1}$.

All experimental anharmonicity constants determined in this work for the nitrogen trifluoride $^{14}\text{NF}_3$ are given in Table 3.

The experimental centre of the $2\nu_2$ band was estimated from the $^{\text{Q}}\text{Q}$ branches edge at 1292.26 cm^{-1} . But a precise value can be obtained combining the values of the experimental centres of ν_2 and $2\nu_2 - \nu_2$ (Table 2). From the relationships:

$$\begin{aligned} (2\nu_2)^0 &= 2(\nu_2)^0 + 2x_{22}, \\ (2\nu_2 - \nu_2)^0 &= (\nu_2)^0 + 2x_{22}, \end{aligned} \quad (8)$$

TABLE 3: Anharmonicity constants of $^{14}\text{NF}_3$ (in cm^{-1}).

Anharmonicity constant	Experimental value, this work	<i>Ab initio</i> TZ2Pf [18]	Experimental value [20, 21]
x_{11}	—	-3.15	-2.9
x_{12}	—	-3.56	-4
x_{13}	-7.965051 (26)	-8.14	-9.9
x_{14}	-2.383248 (49)	-2.08	-1.5
x_{22}	-1.006059 (11)	-0.88	—
x_{23}	-8.53 ^a	-6.46	-7.6
x_{24}	-2.280208 (11)	-1.98	-2.5
x_{33}	-4.15278 (18)	-4.19	—
x_{34}	—	-5.12	—
x_{44}	-0.841743 (22)	-0.79	-0.820
g_{33}	1.82344 (18)	1.96	—
g_{34}	—	-0.10	—
g_{44}	0.730149 (22)	0.72	0.729
$x_{34} + g_{34}$	—	—	-1

Numbers in parentheses are one standard deviation in units of the last digit quoted.

^aValue deduced from the $(\nu_2 + \nu_3)^0$ given in Table 2.

TABLE 4: Harmonic wavenumber constants of $^{14}\text{NF}_3$ (in cm^{-1}).

Harmonic wavenumber	Experimental value, this work	<i>Ab initio</i> unscaled value, [22]	<i>Ab initio</i> value TZ2Pf, [18]
ω_1^0	—	1042.8	1053.8
ω_2^0	648.140120 (18)	659.3	660.7
ω_3^0	909.84264 (43)	905.0	935.7
ω_4^0	493.534359 (52)	500.6	502.8

Numbers in parentheses represent one standard deviation in units of the last digit quoted.

we can indeed deduce that $(2\nu_2)^0 = 1292.25004$ (21) cm^{-1} and $x_{22} = -1.006059$ (11).

The values obtained for x_{22} , x_{44} , and g_{44} are small suggesting that the corresponding levels $\nu_2 = 2$ and $\nu_4 = 2$ are not significantly affected by the anharmonic perturbations, whereas the vibrational dependence is extremely important for the $\nu_1 = \nu_3 = 1$ and $\nu_2 = \nu_3 = 1$ levels.

It is worth noting that our values of the anharmonicity constants of $^{14}\text{NF}_3$ are in good agreement with previous medium experimental studies (column 4 of Table 3), but significantly more accurate by at least three orders of magnitude.

One can notice the fair agreement between our values and those obtained by *ab initio* methods [18] employing the TZ2Pf basis.

We can also extract accurate values of the harmonic wavenumbers of the oblate symmetric top molecule $^{14}\text{NF}_3$. The results are gathered in Table 4.

The agreement between our values and those determined by the theoretical *ab initio* calculations is significantly worse. We think that it is necessary to give much more credibility to our ω_i^0 values which were deduced from experimental constants.

6. Conclusion

Using the recent accurate results obtained for the bands below 2000 cm^{-1} , of the symmetric top molecule $^{14}\text{NF}_3$, several

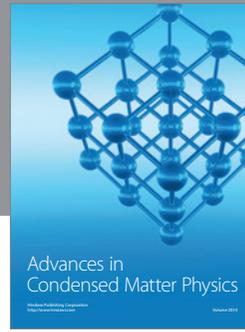
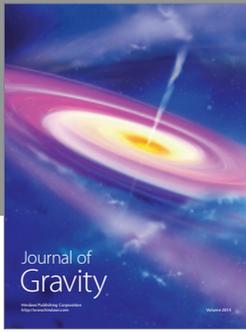
rovibrational interaction and anharmonicity constants have been deduced.

Our results contribute incontestably to the experimental knowledge of the molecular potential of this molecule which helps to test and improve theoretical models.

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