High-Resolution Infrared Spectroscopy of the $\nu_1 + \nu_4$ Band of $^{14}\text{NF}_3$: Reductions of the Rovibrational Hamiltonian

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Abstract: The high-resolution Fourier transform infrared spectrum of nitrogen trifluoride NF_3 has been studied in the $\nu_1 + \nu_4$ perpendicular band region around 1523 cm^{-1} . All experimental data have been refined applying various reduction forms of the effective rovibrational Hamiltonian developed for an isolated degenerate state of a symmetric top molecule. The $\nu_1 = \nu_4 = 1$ excited state of the $^{14}\text{NF}_3$ oblate molecule was treated with models taking into account ℓ - and k -type intravibrational resonances. Parameters up to sixth order have been accurately determined and the unitary equivalence of the derived parameter sets in different reductions was demonstrated.

Keywords: Nitrogen trifluoride NF_3 , FTIR spectroscopy, Rovibration, Combination band, Reductions, Equivalences

Introduction

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

- Two totally symmetric (A_1 -type) modes: ν_1 and ν_2 ;
- Two doubly degenerate (E -type) modes: ν_3 and ν_4 .

In spite of its interest in the fluorination of organic materials, and in the manufacture of flat panel displays, thin film photovoltaic cells and microcircuits¹⁻³, NF_3 has not been much studied in the past. But recently, it has attracted new interest because of its implication in the greenhouse effects. New publications⁴⁻⁹ report indeed that the NF_3 oblate molecule is 17,000 times more potent a greenhouse gas than CO_2 and recommend to include this molecule in the basket of gases controlled by Kyoto protocol and to monitor its environmental levels.

The subject of the present study is to contribute to the experimental knowledge of the molecular potential of NF_3 which helps to test theoretical models. We extend our recent study by high-resolution Fourier transform infrared (FTIR) spectroscopy of the $\nu_1 = \nu_4 = 1$ excited state of this molecule¹⁰ by testing for this level the unitary equivalence of parameter sets obtained from different reduced forms of the rovibrational Hamiltonian H .

For symmetric tops, it is well known that because of collinearity problems, the molecular parameters of the effective rovibrational Hamiltonian cannot all be determined simultaneously by fitting experimental data. The number of parameters has to be reduced through a unitary transformation called reduction¹¹⁻¹⁷. Many studies were performed¹⁸⁻²² using this approach. The obtained results demonstrated that the procedure of reduction is an appropriate solution for the indeterminacy problems. Thus, we successfully applied reduction methods to the $\nu_3 = 1$ (E , $\nu_0 = 907.5413 \text{ cm}^{-1}$)²³, $\nu_4 = 2$ (A_1 , $\nu_0 = 983.7017 \text{ cm}^{-1}$; E , $\nu_0 = 986.6223 \text{ cm}^{-1}$)²⁴, $\nu_1 = \nu_3 = 1$ (E , $\nu_0 = 1931.5775 \text{ cm}^{-1}$) and $\nu_3 = 2$ (A_1 , $\nu_0 = 1803.1302 \text{ cm}^{-1}$; E , $\nu_0 = 1810.4239 \text{ cm}^{-1}$)²⁵ excited states of the nitrogen trifluoride $^{14}\text{NF}_3$. We also applied it more recently to the $\nu_4 = 1$ (E , $\nu_0 = 347.0861 \text{ cm}^{-1}$) degenerated state²⁶ of the phosphorus trifluoride PF_3 .

Experimental

This paper is an extension of our recent study¹⁰ of the $\nu_1 = \nu_4 = 1$ excited state of $^{14}\text{NF}_3$. The infrared spectrum analyzed was recorded at room temperature by Fourier transform spectroscopy at Wuppertal (Germany), with a Bruker 120 HR interferometer. The resolution that is equal to the inverse of the maximum optical path difference in the interferometer was adjusted to $2.3 \times 10^{-3} \text{ cm}^{-1}$. The experimental line precision was estimated to be $2 \times 10^{-4} \text{ cm}^{-1}$.

In total, 1885 rovibrational transitions up to $K_{\text{max}} = 70 = J_{\text{max}}$ were assigned. Due to the $k(\Delta\ell = 0, \Delta k = \pm 6)$ interaction ($h_3 = 2.22 \times 10^{-13} \text{ cm}^{-1}$) within the $k\ell = +4$ sublevel, A^+/A^- doublets were identified from $J = 24$ to $J = 33$. A large A^+/A^- splitting due to ℓ ($\Delta\ell = \pm 2, \Delta k = \pm 2$) rotational resonance ($q_4 = 1.730 \times 10^{-3} \text{ cm}^{-1}$) within the $k\ell = +1$ level was also observed, while the effect of the expected $\ell(\Delta\ell = \pm 2, \Delta k = \pm 4)$ interaction was not detected on the $\Delta K = -1$ transitions owing to their vanishing intensity. Assuming that the $\nu_1 + \nu_4$ perpendicular band of NF_3 is isolated, the experimental anharmonicity constant $x_{14} = -2.383\,249\,(49) \text{ cm}^{-1}$ was determined.

In this paper, we apply the concept of unitary equivalent reductions of the effective vibration-rotation Hamiltonian to the $\nu_1 = \nu_4 = 1$ state of the nitrogen trifluoride NF_3 and provide a complete set of rotational, centrifugal distortion and higher-order parameters of this level.

Theory

The diagonal and off-diagonal matrix elements of the Hamiltonian operator H that were considered for the ground and $\nu_1 = \nu_4 = 1$ states of NF_3 , which include contributions of higher order as well as K and J dependences of the interaction parameters, were taken as:

- The ground state energy:

$$E_0(J, K) = (C_0 - B_0)K^2 + B_0J(J+1) - D_J^0J^2(J+1)^2 - D_{JK}^0J(J+1)K^2 - D_K^0K^4 \\ + H_{JJ}^0J^3(J+1)^3 + H_{JK}^0J^2(J+1)^2K^2 + H_{KJ}^0J(J+1)K^4 + H_{KK}^0K^6 + \delta$$

where $K = |k|$ and $\delta = \pm h_3^0 J(J+1)[J(J+1)-2][J(J+1)-6]^{27}$.

- The excited state energy:

$$E(v, 1, J, K) = v_0 + (C - B)K^2 + BJ(J+1) - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4 + H_{JJ} J^3(J+1)^3 + H_{JK} J^2(J+1)^2 K^2 + H_{KJ} J(J+1)K^4 + H_{KK} K^6 + \left[-2C\zeta^2 + \eta_J J(J+1) + \eta_K K^2 + \eta_{JJ} J^2(J+1)^2 + \eta_{JK} J(J+1)K^2 + \eta_{KK} K^4 + \tau_{JJ} J^3(J+1)^3 + \tau_{JK} J^2(J+1)^2 K^2 + \tau_{KJ} J(J+1)K^4 + \tau_{KK} K^6 \right] kl$$

$\ell = \pm 1$ for the $\Delta K = \pm 1$ IR transitions.

- The $\ell(2, 2)$ interaction (q resonance) within the $v_1 = v_4 = 1$ state, employing the phase convention of Cartwright and Mills²⁸:

$$\langle v, \ell \mu 1, J, k | H/hc | v, \lambda \pm 1, J, k \pm 2 \rangle = -1/4 \{ q + q_J J(J+1) + q_K [k^2 + (k \pm 2)^2] + q_{JJ} J^2(J+1)^2 + q_{JK} J(J+1) [k^2 + (k \pm 2)^2] \} \times [(v \pm \lambda + 2)(v \mu \lambda)]^{1/2} F_{\pm}(J, k) F_{\pm}(J, k \pm 1) \text{ with } F_{\pm}(J, k) = [J(J+1) - k(k \pm 1)]^{1/2}.$$

- The $\lambda(2, -1)$ interaction (r resonance):

$$\langle v, \lambda \pm 1, J, k | H/hc | v, \lambda \mu 1, J, k \pm 1 \rangle = \{ (2k \pm 1) [r + r_J J(J+1)] + r_K [k^3 + (k \pm 1)^3] \} \times [(v \pm \lambda + 2)(v \mu \lambda)]^{1/2} F_{\pm}(J, k)$$

- The $\lambda(2, -4)$ interaction (t resonance):

$$\langle v, \lambda \pm 2, J, k | H/hc | v, \lambda, J, k \pm 4 \rangle = 1/2 [t + t_J J(J+1)] F_{\pm}(J, k) F_{\pm}(J, k \pm 1) F_{\pm}(J, k \pm 2) F_{\pm}(J, k \pm 3)$$

- The $k(0, 6)$ interaction (h_3 resonance):

$$\langle v, \lambda \pm 1, J, k | H/hc | v, \lambda \pm 1, J, k \pm 6 \rangle = h_3 F_{\pm}(J, k) F_{\pm}(J, k \pm 1) F_{\pm}(J, k \pm 2) F_{\pm}(J, k \pm 3) F_{\pm}(J, k \pm 4) F_{\pm}(J, k \pm 5)$$

- The $k(0, 3)$ interaction (λ -dependent d resonance):

$$\langle v, \lambda \pm 1, J, k | H/hc | v, \lambda \pm 1, J, k \pm 3 \rangle = \lambda [d + d_J J(J+1)] F_{\pm}(J, k) F_{\pm}(J, k \pm 1) F_{\pm}(J, k \pm 2)$$

- The $k(0, 3)$ interaction (λ -independent ε resonance):

$$\langle v, \lambda \pm 1, J, k | H/hc | v, \lambda \pm 1, J, k \pm 3 \rangle = (2k \pm 3) [\varepsilon + \varepsilon_J J(J+1)] F_{\pm}(J, k) F_{\pm}(J, k \pm 1) F_{\pm}(J, k \pm 2)$$

According to the theory of equivalent reductions and in order to prevent correlations in the fitting experimental data, some of the molecular parameters have to be constrained. One of the off-diagonal parameters accounting for $\Delta(k - \lambda) \neq 0$ interaction can be refined while the others are fixed, usually to zero value. In the case of an isolated $v_t = 1$ state of a symmetric top, three equivalent D -, Q - and QD -reduction schemes were proposed¹¹⁻¹³:

- In the D -reduction, the d and ε parameters of the $(0, 3)$ k -type interaction are constrained to zero, while the r parameter of the $(2, -1)$ λ -type resonance is refined.
- In the Q -reduction, the r and ε parameters are fixed to zero.
- In the QD -reduction, the ε parameter is refined.

Furthermore, the condition $r_K = 0$ and $q_K = 0$, or $\eta_{JJ} = 0$, or $\eta_{JK} = 0$, or $\eta_{KK} = 0$ has to be imposed in all reductions in order to avoid collinearity problems^{12,14}.

Results and Discussion

Since some analogy was established between the $\nu_1 + \nu_4$ combination band and the ν_4 fundamental band of $^{14}\text{NF}_3$, the present fit calculations were carried out according to the same reduction schemes of the rovibrational Hamiltonian already performed²⁰ for the $\nu_4 = 1$ state of $^{14}\text{NF}_3$ through a vibrationally isolated model. The same FULLSYM program²⁹ used for this level was adapted for the $\nu_1 = \nu_4 = 1$ state of NF_3 .

The ground state parameters were fixed to the values of Table 1. The J -dependent ones, namely B_0 , D_J^0 , D_{JK}^0 , H_{JJ}^0 , H_{JK}^0 , H_{KJ}^0 and h_3^0 are those more recently improved by G. Cazzoli *et al.*²⁷. The K -dependent ones, namely C_0 , D_K^0 and H_{KK}^0 are our values determined in using literature method²⁴.

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

Parameter	Value	Reference
C_0	0.194 992 50 (44)	[24]
B_0	0.356 282 889 1 (21)	[27]
$D_J^0 \times 10^7$	4.873 331 (27)	[27]
$D_{JK}^0 \times 10^7$	-7.596 542 (80)	[27]
$D_K^0 \times 10^7$	3.434 3 (88)	[24]
$H_{JJ}^0 \times 10^{12}$	0.613 5 (10)	[27]
$H_{JK}^0 \times 10^{12}$	-3.350 9 (76)	[27]
$H_{KJ}^0 \times 10^{12}$	4.858 (20)	[27]
$H_{KK}^0 \times 10^{12}$	-1.033 5 (481)	[24]
$h_3^0 \times 10^{13}$	1.740 5 (32)	[27]

Errors given in parentheses are one standard deviation expressed in units of the last digit quoted

The least-squares fits were started in D -reduction, the body of data being constituted of 1885 infrared transitions. A unit weight was ascribed to each pure line, while 0.1 and 0.01 weights were given to blended lines according to their profiles. Moreover, all the transition wave numbers that differed from the corresponding calculated values by more than $2 \times 10^{-3} \text{ cm}^{-1}$ were zero weighted.

According to the reduction of the rovibrational Hamiltonian, the q_K and r_K coupling-terms were fixed to zero. The best results quoted in Table 2 for the D -, Q - and QD -reduction were obtained by refining 26 parameters of the $\nu_1 + \nu_4$ combination band of $^{14}\text{NF}_3$. All the parameters not appearing in Table 2, in particular the small octic centrifugal distortion constants and the small coupling-terms r_J , t_J , d_J and ε_J are not relevant for the present work and therefore were omitted.

Table 2. Parameters (cm^{-1}) of the $v_1 = v_4 = 1$ state of $^{14}\text{NF}_3$

	<i>D</i> -Reduction	<i>Q</i> -Reduction	<i>QD</i> -Reduction
v_0	1523.040 783 (34)	1523.040 781 (34)	1523.040 763 (36)
B	0.357 413 97 (44)	0.357 413 97 (45)	0.357 414 80 (44)
C	0.193 619 11 (40)	0.193 619 17 (41)	0.193 619 15 (44)
$D_J \times 10^7$	5.834 (16)	5.833 (16)	5.875 (14)
$D_{JK} \times 10^7$	-9.693 (33)	-9.688 (34)	-9.752 (33)
$D_K \times 10^7$	6.267 (23)	6.263 (23)	6.292 (24)
$H_{JJ} \times 10^{12}$	24.5 (16)	24.5 (16)	30.1 (13)
$H_{JK} \times 10^{12}$	-243.9 (43)	-243.2 (43)	-255.9 (39)
$H_{KJ} \times 10^{12}$	72.5 (48)	71.0 (48)	79.5 (53)
$H_{KK} \times 10^{12}$	86.6 (34)	87.4 (34)	87.0 (38)
$C\zeta$	-0.170 539 3 (37)	-0.170 539 8(37)	-0.170 539 7(39)
$\eta_J \times 10^6$	-1.12 (12)	-1.16(13)	-1.00(13)
$\eta_K \times 10^6$	-4.16 (12)	-4.12(13)	-4.32 (13)
$\eta_{JJ} \times 10^8$	-1.768 (58)	-1.741 (66)	-1.847 (63)
$\eta_{JK} \times 10^8$	2.61 (11)	2.56 (12)	2.78 (11)
$\eta_{KK} \times 10^8$	-1.296 (55)	-1.278 (60)	-1.406 (72)
$\tau_{JJ} \times 10^{11}$	1.322 (68)	1.288 (80)	1.322 (68)
$\tau_{JK} \times 10^{11}$	-2.47 (19)	-2.43 (20)	-2.92 (17)
$\tau_{KK} \times 10^{11}$	0.55 (19)	0.57 (19)	1.21 (14)
$\tau_{KKK} \times 10^{11}$	0.574 (67)	0.546 (73)	0.278 (50)
$q \times 10^3$	1.730 09 (83)	1.730 20 (84)	1.728 40 (81)
$q_J \times 10^8$	4.46 (38)	4.38 (40)	5.39 (36)
$q_{JJ} \times 10^{10}$	-1.125 (43)	-1.116(44)	-1.249 (37)
$q_{JK} \times 10^{11}$	-1.25 (18)	-1.13(22)	0. ^a
$r \times 10^5$	($\pm$)1.29 (93)	0. ^c	0. ^c
$t \times 10^9$	-8.49 ^b	-8.49 ^b	-8.49 ^b
$h_3 \times 10^{13}$	2.28 (74)	2.27 (73)	1.98 (77)
$d \times 10^7$	0. ^c	($\pm$)1.57(91)	0. ^c
$\varepsilon \times 10^7$	0. ^c	0. ^c	($\pm$)1.96 (50)
No. of data	1885	1885	1885
$K_{\text{max}} / J_{\text{max}}$	70 / 70	70 / 70	70 / 70
$\sigma \times 10^3$	0.288	0.288	0.305

^aFixed to zero because not significant. ^bFixed from the $v_4 = 1$ state²⁰. ^cImposed by the reduction. Errors given in parentheses are one standard deviation expressed in units of the last digit quoted

The conditions suggested by the theoreticians for the *D*-, *Q*- and *QD*-reduction of the rovibrational Hamiltonian relative to an isolated $v_t = 1$ state of a symmetric top molecule were imposed to avoid collinearity problems.

The sign of the parameter q is assumed to be positive as in the literature²⁰. The signs of the parameters r , d and ε are arbitrary and cannot be determined from the experimental data. The sign of the h_3 excited coefficient, which cannot be determined, is assumed to be positive as for the ground state²⁷. Comparison between the different reductions can be done by checking:

- The standard deviations: Table 2 shows that the refined parameters are covered by quasi-equivalent standard deviations, their average value $\sigma = 0.293 \times 10^{-3} \text{ cm}^{-1}$ is of the same order of magnitude as the estimated experimental line precision.
- The rotational C , B constants, the $C\zeta$ term of the z -Coriolis interaction, the quartic centrifugal distortion constants, and the q ℓ -doubling terms should not be affected by the unitary transformation. Table 2 shows that these parameters have values very close to each other in the three reductions.
- Some relations demonstrating the unitary equivalence of the three reductions: The relations between parameters of the D - and Q -reductions were given by Lobodenko *et al.*¹¹ and Watson *et al.*¹². Those between the Q - and QD -reductions were proposed by Harder¹³. We assumed that these relations could be applied to $v_1 + v_4$ combination band even they were established for an isolated $v_t = 1$ excited state. As can be seen in Table 3, the relations referring to different equations are nicely fulfilled, with some reservations concerning the terms of Eqs. (1) and (3). This agreement confirms the unitary equivalence of reductions D , Q and QD for fitting the $v_1 + v_4$ perpendicular band of $^{14}\text{NF}_3$.

Table 3. Check of unitary equivalence for $^{14}\text{NF}_3$ in the $v_1 = v_4 = 1$ excited state

Equation	Quantity	Value, cm^{-1}
	r^D	1.29×10^{-5}
(1)	$\frac{d^Q F}{q}$	4.58×10^{-5}
	$\eta_J^D - \eta_J^Q$	0.04×10^{-6}
(2)	$-(\eta_K^D - \eta_K^Q)$	0.04×10^{-6}
	ϵ^{QD}	1.96×10^{-7}
(3)	$\frac{d^Q(C-B)}{2C\zeta}$	0.75×10^{-7}
	$\eta_J^D + \eta_K^D$	-5.28×10^{-6}
(4)	$\eta_J^Q + \eta_K^Q$	-5.28×10^{-6}
	$\eta_J^{QD} + \eta_K^{QD}$	-5.32×10^{-6}
	$\eta_{JJ}^D + \eta_{JK}^D + \eta_{KK}^D$	-0.45×10^{-8}
(5)	$\eta_{JJ}^Q + \eta_{JK}^Q + \eta_{KK}^Q$	-0.45×10^{-8}
	$\eta_{JJ}^{QD} + \eta_{JK}^{QD} + \eta_{KK}^{QD}$	-0.47×10^{-8}
	$F = C - B + 2C\zeta$	$-0.504\,87 \text{ cm}^{-1}$

Conclusion

In the present study, the experimental data of the $v_1 + v_4$ combination band of the symmetric top $^{14}\text{NF}_3$, near 1523 cm^{-1} , were fitted using the D -, Q - and QD -reductions of the vibration-rotation Hamiltonian. The standard deviations of the fits are comparable and the theoretical relations between parameters of different reductions are quite fulfilled.

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