High Resolution FTIR Spectroscopy of 1,3,5-Triazine*: The Parallel Bands ν_{11} and ν_{12} of $^{12}C_3{}^{14}N_3H_3$, $^{13}C_3{}^{14}N_3H_3$, $^{12}C_3{}^{15}N_3H_3$, $^{13}C_3{}^{15}N_3H_3$ and $^{12}C_3{}^{14}N_3D_3$

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The present contribution reports on the analysis of the high resolution FTIR spectra of the only two IR-active parallel fundamentals ν_{11} and ν_{12} of the isotopomers $^{12}C_3{}^{14}N_3H_3$, $^{13}C_3{}^{14}N_3H_3$, $^{12}C_3{}^{15}N_3H_3$, $^{13}C_3{}^{15}N_3H_3$ and $^{12}C_3{}^{14}N_3D_3$, respectively, of 1,3,5-triazine. The molecular constants of the ground state and the upper states $v_{11}=1$ and $v_{12}=1$, respectively, for all molecules under consideration are listed. The enhancement of the P- and the depletion of the R-banches, observed in the ν_{11} bands of all non-deuterated isotopomers, is discussed, and the Herman-Wallis constants obtained are given.

Key words: High Resolution FTIR Spectroscopy, 1,3,5-Triazine, Parallel Band, Herman-Wallis Constants.

1. Introduction

1,3,5-Triazine ($C_3N_3H_3$, henceforth abbreviated as triazine) is a planar symmetric top molecule belonging to the molecular symmetry group $D_{3h}(M)$. Triazine and its derivates are of importance as starting materials for the syntheses of a large number of N-containing organic compounds. Following its first successful preparation in 1954 [1], structure determinations have been supplied by X-ray diffraction [2], low resolution rotational Raman spectroscopy [3] and, more recently, electron diffraction [4, 5].

Up to now, the r_0-, r_z- and r_e-structures are unknown, since no MW spectrum exists because of the symmetry forbidden dipolmoment $\mu_e(=M_{01})$. Therefore, high resolution IR investigations of triazine and its isotopomers are urgently required to get a r_0- or even r_S-structure and a general harmonic force field.

In two previous papers [6, 7] we have investigated the high resolution FTIR spectra of the fundamental ν_{12}, its accompanying hot band $\nu_{12}+\nu_{14}-\nu_{14}$ and of the combination band $\nu_{12}+\nu_{14}$ of $^{12}C_3{}^{14}N_3H_3$. From the latter bands we could determine the parameters of the IR-inactive fundamental ν_{14}.

In the present contribution we shall report on the analysis of the high resolution FTIR spectra of the only two IR-active parallel fundamentals ν_{11} and ν_{12} of $^{13}C_3{}^{14}N_3H_3$, $^{12}C_3{}^{15}N_3H_3$, $^{13}C_3{}^{15}N_3H_3$, $^{12}C_3{}^{14}N_3D_3$, and of ν_{11} of $^{12}C_3{}^{14}N_3H_3$*. We have obtained the molecular constants of the ground state and the upper states $v_{11}=1$ and $v_{12}=1$, respectively, for all molecules under consideration. The enhancement of the P- and the depletion of the R-banches of ν_{11} observed will be discussed and the Herman-Wallis constants obtained will be given additionally.

The r_0- and r_S-structures as well as a harmonic force field will be the subject of a forthcoming paper [5].

2. Experimental

The sample of $^{12}C_3{}^{14}N_3H_3$ with a purity of 98% has been obtained from Merck-Schuchardt. Since no impurities could be detected in the IR spectra, the material was used without further purification. We tested several methods of preparation for the isotopomers of triazine with regard to the isotopic labelled starting materials available ($KC^{15}N$, $K^{13}CN$, D_2O, $H(^{13}CO)^{15}NH_2$). The following routes proved successful. In each case, the raw product was purified by sublimation.

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* Lists of observed and calculated wavenumbers as well as the correlation matrices have been deposited in the "Sektion Spektren- und Strukturdokumentation", Universität Ulm, 89069 Ulm (Dr. J. Vogt).

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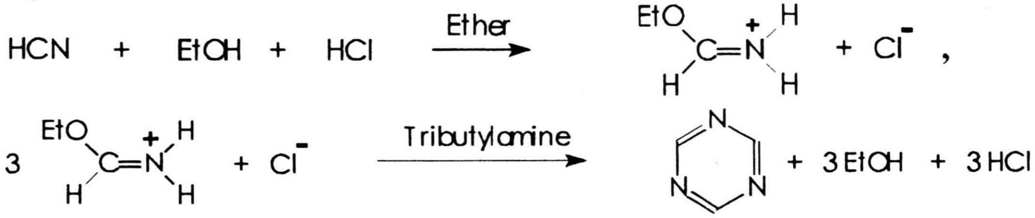
A) $^{13}C_3{}^{14}N_3H_3$, $^{12}C_3{}^{15}N_3H_3$ and $^{12}C_3{}^{14}N_3H_3$

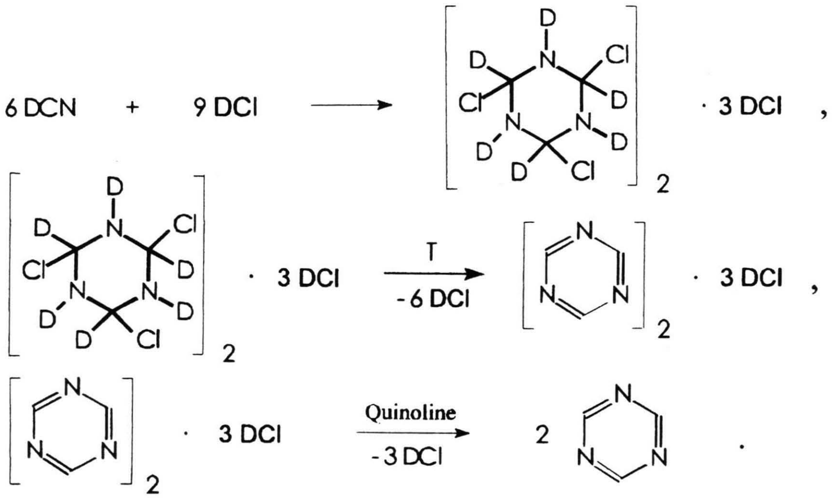
Using $KC^{15}N$ and $K^{13}CN$, respectively, triazine was synthesized in a two step method developed by Schaefer and Peters [8]. In a first step HCN is obtained by reaction of KCN with 85% – H_3PO_4. HCN is then trimerized according to



The yield was about 69%.

B) $^{12}C_3{}^{14}N_3D_3$

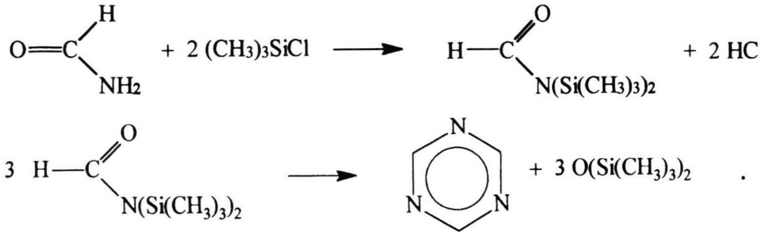
The synthesis of $^{12}C_3{}^{14}N_3D_3$ follows a modified three step method given by Grundmann et al. [9]. DCN and DCl needed as precursor have been obtained by the reaction of $KCN/D_2O/P_2O_5$ and $D_2O/SOCl_2$, respectively. DCN is then trimerized according to



The yield was 24%.

C) $^{13}C_3{}^{15}N_3H_3$

Following a two step method given by Kantlehner et al. [10] formamide, $H(^{13}CO)^{15}NH_2$, is reductively trimerized according to



The yield was 51%.

All the spectra have been recorded at room temperature with the Bruker IFS 120 HR instruments at the University of Gießen and at the University of Oulu, respectively. Stainless steel cells with CsI and KBr windows, respectively, have been employed. The maximum optical path difference was between 417 cm and 542 cm. A Ge : Cu detector was used operating at 4 K. All other experimental details are summarized in Table 1.

Boxcar apodization has been applied to the interferograms. Calibration has been done by comparison with CO_2 and H_2O lines, the wavenumbers of which were taken from [11].

The absolute accuracy of the calibration lines was between $1 \cdot 10^{-3}$ cm^{-1} and $1 \cdot 10^{-4}$ cm^{-1}. The relative accuracy of the peakfinder evaluated lines of the triazines is about $\pm 2 \cdot 10^{-4}$ cm^{-1}.

3. Theory

The energy expression employed comprises the usual diagonal elements of the rovibrational Hamiltonian up to $\widehat{h}_4^{\dagger}$:

$$\begin{aligned} E(v, J, k) = {} & v_0 + B_v J(J+1) + (C_v - B_v) k^2 \\ & - D_J^v J^2 (J+1)^2 - D_{JK}^v J(J+1) k^2 - D_K^v k^4 \\ & + H_J^v J^3 (J+1)^3 - H_{JK}^v J^2 (J+1)^2 k^2 \\ & + H_{KJ}^v J(J+1) k^4 + H_K^v k^6 , \end{aligned} \tag{1}$$

where v_0 equals zero for the ground state.

As is well known, a planar symmetric top molecule in its equilibrium configuration is characterized by the planarity relations [12]

$$\begin{aligned} & B_e = 2 C_e \\ & 2 D_J^e + 3 D_{JK}^e + 4 D_K^e = 0 \\ & 3 H_J^e + 4 H_{JK}^e + 5 H_{KJ}^e + 6 H_K^e = 0 . \end{aligned} \tag{2}$$

These relations hold also approximately for the ground state.

Generally speaking, the selection rules and the rovibrational line intensities are obtained from the contact transformed space-fixed dipole moment operator $\tilde{M}_f$ [13, 14] having the form

$$\tilde{M}_f = M_{11} + \tilde{M}_{12} + \cdots + \tilde{M}_{mn} , \tag{3}$$

where $\tilde{M}_{mn}$ is a term of degree m in the vibrational operators ($\hat{q}_k$ and/or $\hat{p}_k$), of degree $(n-1)$ in the rotational operators ($\hat{J}_\alpha$) and the degree 1 in the direction cosines.

Rovibrational IR-transitions of the fundamentals are governed by the terms $M_{11}, \tilde{M}_{12}, \ldots, \tilde{M}_{1n}$ of (3). Here M_{11} describes the unperturbed case, whilst the higher order moments, $\tilde{M}_{1n}$, reflect the different types of perturbations; e.g. the influence of Coriolis interaction is modelled by $\tilde{M}_{12}$, which is given [14] as

$$\tilde{M}_{12} = i [S_{12}, M_{01}] + i [S_{21}, M_{11}] . \tag{4}$$

In the case of $D_{3h}(M)$ symmetry, (4) reduces to

$$\tilde{M}_{12} = i [S_{21}, M_{11}] . \tag{5}$$

As is well known [14], the line strength for an electric dipole transition $A \rightarrow B$ is expressed as

$$S_{AB} = \sum_f |\langle A | \tilde{M}_f | B \rangle|^2 , \tag{6}$$

where A and B, respectively, stand for all quantum numbers of the states involved.

To a first approximation, i.e. taking only M_{11} and $\tilde{M}_{12}$ into account, (6) may be simplified as

$$S_{AB} = S_v \cdot R_{AB} \cdot F_{HW} , \tag{7}$$

where S_v and R_{AB} are the (unperturbed) vibrational and rotational line strength, respectively, and F_{HW} is

Table 1. Experimental details of the IR-spectra of the isotopomers of triazine.

Isotopomer	Fundamental	Range [cm^{-1}]	Pressure [mbar]	Scans	Resolution [cm^{-1}]	Cell length [cm]
$C_3N_3H_3$	ν_{11}	890–960	2.40	200	0.0024	1440
	ν_{12}	705–775	0.38	210	0.0018	328
$C_3{}^{15}N_3H_3$	ν_{11}	885–965	0.53	82	0.0021	1060
	ν_{12}	695–760	0.50	350	0.0018	328
${}^{13}C_3N_3H_3$	ν_{11}	885–940	1.51	300	0.0018	1312
	ν_{12}	700–765	0.42	300	0.0018	328
${}^{13}C_3{}^{15}N_3H_3$	ν_{11}	880–940	1.46	300	0.0019	1640
	ν_{12}	690–760	0.15	300	0.0018	984
$C_3N_3D_3$	ν_{11}	830–895	1.00	240	0.0019	530
	ν_{12}	545–604	1.00	240	0.0019	530

the Herman-Wallis correction factor. S_v and R_{AB} are the vibrational and rotational components of M_{11}, being well known in the literature [15]. F_{HW} yields the influence of $\tilde{M}_{12}$ on S_{AB} and is given in the case of a parallel band by [16]

$$F_{HW} = \{1 + A_n^J m_J + A_n^{JJ\,(Q)} [\overline{J(J+1)} - m_J^2] + A_n^{JJ\,(PR)} m_J^2 + A_n^{KK} k^2\}^2, \tag{8}$$

where

$$m_J = \begin{cases} J+1 & \text{R} \\ 0 & \text{for the Q branch} \\ -J & \text{P} \end{cases}$$

and

$$\overline{[J(J+1)]} = \tfrac{1}{2}[J'(J'+1) + J''(J''+1)].$$

Following [17], the intensity ratio of the transitions originating in the same lower state amounts to

$$\frac{F_{HW}(J+1)}{F_{HW}(-J)} = \frac{S_A^B(J+1)\, S_{KJ}(-J)\, \nu(-J)}{S_A^B(-J)\, S_{KJ}(J+1)\, \nu(J+1)} = \frac{\{1 + A_n^J (J+1) + A_n^{KK} k^2\}^2}{\{1 - A_n^J J + A_n^{KK} k^2\}^2}, \tag{9}$$

neglecting the quartic terms of (8).

4. Spectra and their Analysis

Triazine is a planar molecule belonging to $D_{3h}(M)$ symmetry under which the 21 normal modes distribute as $3\,A_1' \oplus 2\,A_2' \oplus 5\,E' \oplus 2\,A_2'' \oplus 2\,E''$. The double primed species are out-of-plane vibrations, while the single primed are in-plane vibrations. Only the A_2'' and the E' modes are IR active.

The ν_{12} and ν_{11} vibrations of species A_2'' are typical parallel bands. The ν_{12} bands of all isotopomers and ν_{11} of $C_3N_3D_3$ are of medium intensity. Contrary to this, the ν_{11} bands of $^{12}C_3{}^{14}N_3H_3$, $^{13}C_3{}^{14}N_3H_3$, $^{12}C_3{}^{15}N_3H_3$, and $^{13}C_3{}^{15}N_3H_3$ are very weak. This weakness has caused some problems in the past [18]. As typical examples, ν_{11} and ν_{12} of $^{13}C_3{}^{14}N_3H_3$ are shown in Figures 1 and 2.

Even at medium resolution the J-structure of the P- and R-branches is clearly discernible and its assignment is straightforward. The K-structure is resolved for $K > 5$. The K assignment is more complicated because the spin statistics of triazine [6] do not give any hint on the K values. These difficulties were overcome by a stepwise trial and error procedure using the modified least squares fit program MILLI [19] and the

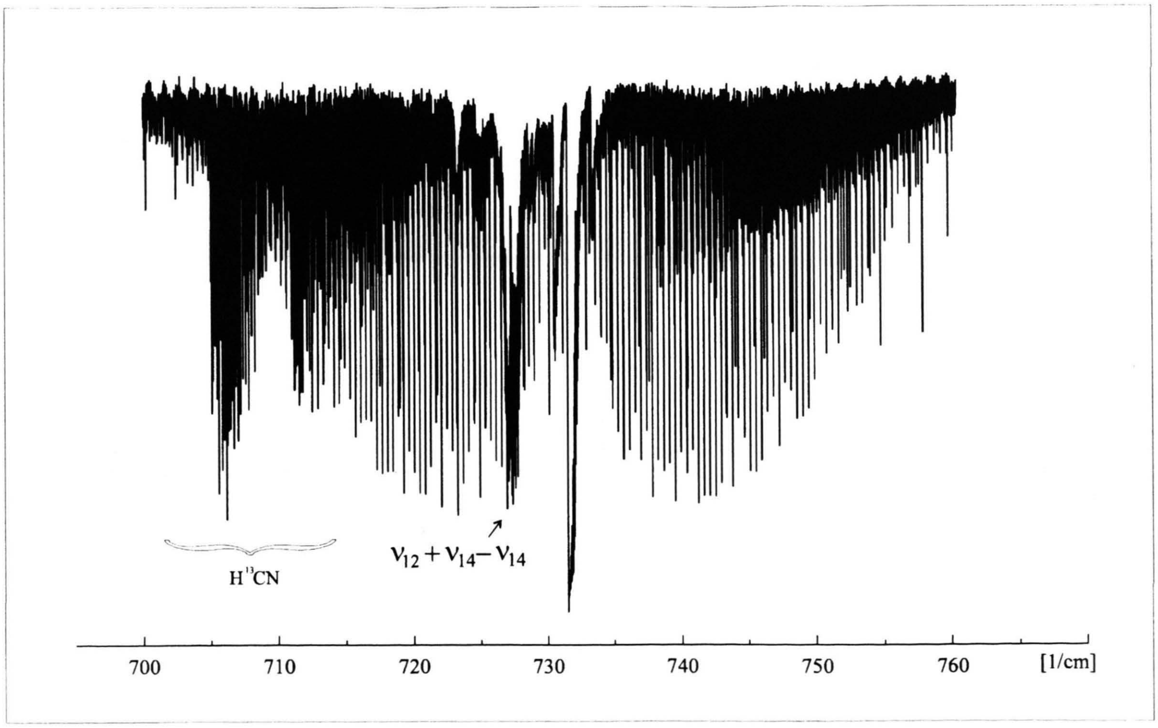


Fig. 1. The fundamental band ν_{12} of $^{13}C_3{}^{14}N_3H_3$.

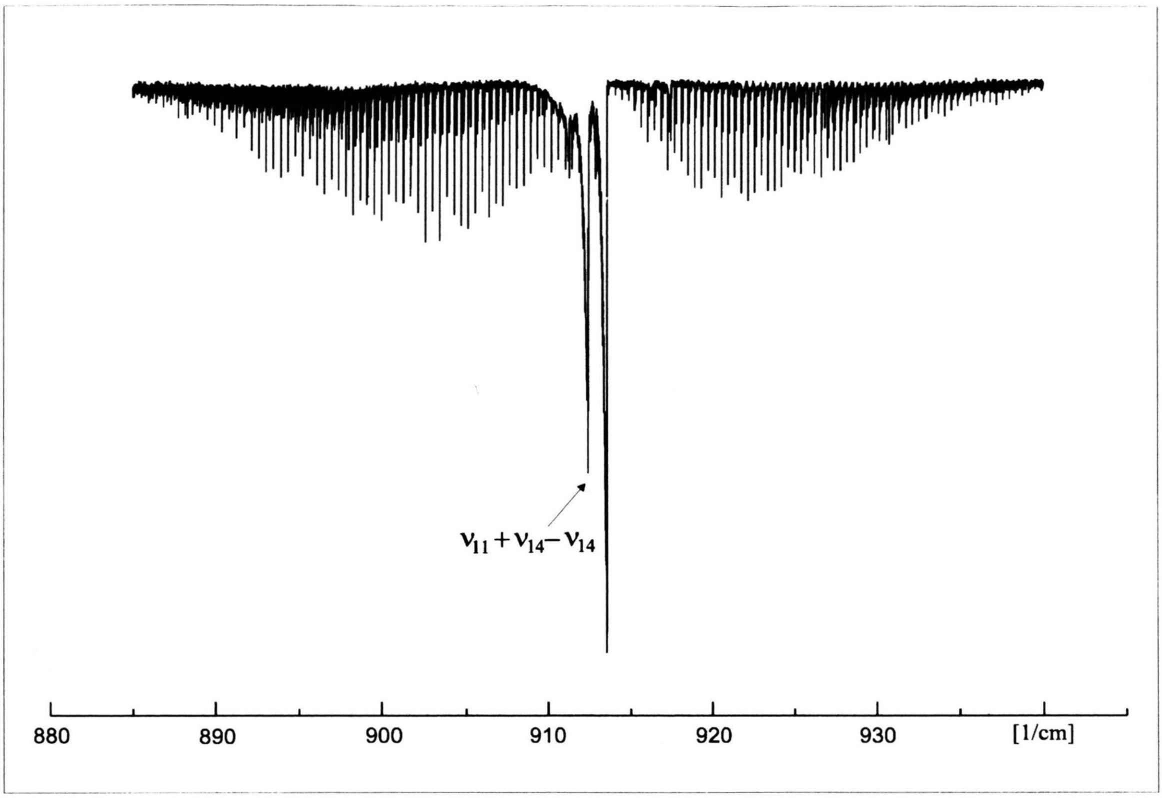


Fig. 2. The fundamental band ν_{11} of $^{13}C_3{}^{14}N_3H_3$.

Table 2. Ground state constants [cm^{-1}] of triazine isotopomers (numbers in parentheses are one standard deviation in units of the last significant digit).

	$^{12}C_3{}^{14}N_3H_3$	$^{13}C_3{}^{14}N_3H_3$	$^{12}C_3{}^{15}N_3H_3$	$^{13}C_3{}^{15}N_3H_3$	$^{12}C_3{}^{14}N_3D_3$
C_0*	0.1074	0.1041	0.1037	0.1006	0.0969
B_0	0.21486152 (10)	0.20819716 (6)	0.20741116 (8)	0.20119592 (9)	0.19377014 (83)
D_J^0	$5.3419\ (56) \cdot 10^{-8}$	$5.0191\ (29) \cdot 10^{-8}$	$5.0196\ (36) \cdot 10^{-8}$	$4.7131\ (39) \cdot 10^{-8}$	$3.96743\ (40) \cdot 10^{-8}$
D_{JK}^0	$-8.861\ (16) \cdot 10^{-8}$	$-8.3267\ (83) \cdot 10^{-8}$	$-8.330\ (10) \cdot 10^{-8}$	$-7.8178\ (91) \cdot 10^{-8}$	$-6.5400\ (12) \cdot 10^{-8}$
D_K^0*	$3.98 \cdot 10^{-8}$	$3.74 \cdot 10^{-8}$	$3.74 \cdot 10^{-8}$	$3.51 \cdot 10^{-8}$	$2.92 \cdot 10^{-8}$
H_J^0	$2.7\ (11) \cdot 10^{-14}$	$1.84\ (42) \cdot 10^{-14}$	$2.05\ (52) \cdot 10^{-14}$	$1.41\ (52) \cdot 10^{-14}$	$1.73\ (59) \cdot 10^{-14}$
H_{JK}^0	$-1.52\ (40) \cdot 10^{-13}$	$-8.9\ (15) \cdot 10^{-14}$	$-3.5\ (20) \cdot 10^{-14}$	$-9.9\ (15) \cdot 10^{-14}$	$-5.8\ (23) \cdot 10^{-14}$
H_{KJ}^0	$2.93\ (69) \cdot 10^{-13}$	$1.70\ (25) \cdot 10^{-13}$	$-3.5\ (35) \cdot 10^{-14}$	$2.21\ (23) \cdot 10^{-13}$	$1.26\ (48) \cdot 10^{-13}$
H_K^0*	$-1.6 \cdot 10^{-13}$	$-9.2 \cdot 10^{-14}$	$4.2 \cdot 10^{-14}$	$-1.2 \cdot 10^{-13}$	$-7.5 \cdot 10^{-14}$
σ	$88 \cdot 10^{-6}$	$119 \cdot 10^{-6}$	$85 \cdot 10^{-6}$	$120 \cdot 10^{-6}$	$197 \cdot 10^{-6}$
GSCD's	937	2535	1005	1562	5223

* from planarity conditions.

simulation program KILO [19]. KILO calculates the rovibrational line intensity in zeroth order approximation, i.e. takes only M_{11} into account. The analysis has been done using only unblended lines which were equally weighted. The ground state constants were fitted with the GSCD program DIFNEU [20], the results being listed in Table 2. The upper state constants were fitted with the programs MILLI and KILO and are given in the Tables 3, 4, 5, and 6.

The ground state constants have been derived from a combined analysis of the data of ν_8, ν_9, ν_{10}, ν_{11}, ν_{12} for $^{12}C_3{}^{14}N_3D_3$ and of ν_{11} and ν_{12} for all other isoto-

Table 3. Molecular constants [cm^{-1}] of the ν_{11} (A_2'') band of triazine isotopomers, Model 1 (numbers in parentheses are one standard deviation in units of the last significant digit). $\Delta JJ_{\max} = \Delta J \cdot J_{\max}$, $\Delta JK_{\max} = \Delta J \cdot K_{\max}$.

	$^{12}C_3{}^{14}N_3H_3$	$^{13}C_3{}^{14}N_3H_3$	$^{12}C_3{}^{15}N_3H_3$	$^{13}C_3{}^{15}N_3H_3$	$^{12}C_3{}^{14}N_3D_3$
ν_0	926.5939264 (89)	913.5465418 (74)	922.042194 (15)	909.430654 (21)	860.637966 (12)
$C''-C'$	$-3.028\,(13) \cdot 10^{-6}$	$-2.20\,(14) \cdot 10^{-7}$	$-2.703\,(24) \cdot 10^{-6}$	$2.4937\,(46) \cdot 10^{-5}$	$-1.1339\,(45) \cdot 10^{-5}$
$B''-B'$	$2.517423\,(94) \cdot 10^{-4}$	$2.45537\,(10) \cdot 10^{-4}$	$2.36729\,(18) \cdot 10^{-4}$	$2.30709\,(25) \cdot 10^{-4}$	$2.16205\,(13) \cdot 10^{-4}$
$D_J''-D_J'$	$1.304\,(21) \cdot 10^{-10}$	$1.2357\,(27) \cdot 10^{-10}$	$1.778\,(51) \cdot 10^{-10}$	$8.91\,(65) \cdot 10^{-11}$	$1.8538\,(33) \cdot 10^{-9}$
$D_{JK}''-D_{JK}'$	$-4.119\,(54) \cdot 10^{-10}$	$-4.954\,(72) \cdot 10^{-10}$	$-5.14\,(13) \cdot 10^{-10}$	$-5.77\,(18) \cdot 10^{-10}$	$-4.795\,(15) \cdot 10^{-9}$
$D_K''-D_K'$	$2.783\,(44) \cdot 10^{-10}$	$3.361\,(68) \cdot 10^{-10}$	$3.26\,(11) \cdot 10^{-10}$	$1.77346\,(16) \cdot 10^{-8}$	$4.125\,(32) \cdot 10^{-9}$
σ	$151 \cdot 10^{-6}$	$143 \cdot 10^{-6}$	$205 \cdot 10^{-6}$	$341 \cdot 10^{-6}$	$200 \cdot 10^{-6}$
Number of lines	2903	3292	2297	2383	2543
$\Delta JJ_{\max}$	−71/54	−63/58	−66/63	−58/56	−58/56
$\Delta JK_{\max}$	−69/52	−60/53	−63/60	−48/48	−48/48

Table 4. Molecular constants [cm^{-1}] of the ν_{11} (A_2'') band of triazine isotopomers, Model 2 (numbers in parentheses are one standard deviation in units of the last significant digit).

	$^{12}C_3{}^{14}N_3H_3$	$^{13}C_3{}^{14}N_3H_3$	$^{12}C_3{}^{15}N_3H_3$	$^{13}C_3{}^{15}N_3H_3$	$^{12}C_3{}^{14}N_3D_3$
ν_0	–	913.546541 (11)	–	–	860.637653 (98)
$C''-C'$	–	$-2.85\,(35) \cdot 10^{-7}$	–	–	$-1.4594\,(55) \cdot 10^{-5}$
$B''-B'$	–	$2.45567\,(25) \cdot 10^{-4}$	–	–	$2.15947\,(20) \cdot 10^{-4}$
$D_J''-D_J'$	–	$1.49\,(15) \cdot 10^{-10}$	–	–	$1.811\,(12) \cdot 10^{-9}$
$D_{JK}''-D_{JK}'$	–	$-5.65\,(37) \cdot 10^{-10}$	–	–	$-8.270\,(42) \cdot 10^{-9}$
$D_K''-D_K'$	–	$3.12\,(35) \cdot 10^{-10}$	–	–	$3.412\,(72) \cdot 10^{-9}$
$H_J''-H_J'$	–	$8.3\,(2.6) \cdot 10^{-15}$	–	–	$4.17\,(21) \cdot 10^{-14}$
$H_{JK}''-H_{JK}'$	–	$-6.96\,(94) \cdot 10^{-14}$	–	–	$-7.922\,(98) \cdot 10^{-13}$
$H_{KJ}''-H_{KJ}'$	–	$8.80\,(14) \cdot 10^{-14}$	–	–	$-6.40\,(32) \cdot 10^{-13}$
$H_K''-H_K'$	–	$-4.94\,(84) \cdot 10^{-14}$	–	–	$-2.78\,(21) \cdot 10^{-13}$
σ	–	$143 \cdot 10^{-6}$	–	–	$124 \cdot 10^{-6}$
Number of lines	–	3292	–	–	2543

Table 5. Molecular constants [cm^{-1}] of the ν_{12} (A_2'') band of triazine isotopomers, Model 1 (numbers in parentheses are one standard deviation in units of the last significant digit). $\Delta JJ_{\max} = \Delta J \cdot J_{\max}$, $\Delta JK_{\max} = \Delta J \cdot K_{\max}$.

	$^{12}C_3{}^{14}N_3H_3$	$^{13}C_3{}^{14}N_3H_3$	$^{12}C_3{}^{15}N_3H_3$	$^{13}C_3{}^{15}N_3H_3$	$^{12}C_3{}^{14}N_3D_3$
ν_0	736.7389672 (50)	731.483804 (37)	728.5030313 (60)	722.5580817 (61)	574.6229012 (47)
$C''-C'$	$-3.3740\,(10) \cdot 10^{-5}$	$-3.28625\,(55) \cdot 10^{-5}$	$-3.0640\,(15) \cdot 10^{-5}$	$-2.98613\,(77) \cdot 10^{-5}$	$-4.19200\,(90) \cdot 10^{-5}$
$B''-B'$	$-3.291105\,(70) \cdot 10^{-4}$	$-2.783681\,(33) \cdot 10^{-4}$	$-2.596787\,(11) \cdot 10^{-4}$	$-2.304937\,(61) \cdot 10^{-4}$	$4.39283\,(49) \cdot 10^{-4}$
$D_J''-D_J'$	$-2.7025\,(23) \cdot 10^{-9}$	$-2.07017\,(62) \cdot 10^{-9}$	$-1.7597\,(56) \cdot 10^{-9}$	$-1.3885\,(13) \cdot 10^{-9}$	$2.12039\,(11) \cdot 10^{-9}$
$D_{JK}''-D_{JK}'$	$4.7662\,(61) \cdot 10^{-9}$	$3.5516\,(18) \cdot 10^{-9}$	$2.989\,(14) \cdot 10^{-9}$	$2.2886\,(30) \cdot 10^{-9}$	$-5.3786\,(35) \cdot 10^{-9}$
$D_K''-D_K'$	$-2.0578\,(54) \cdot 10^{-9}$	$-1.5455\,(16) \cdot 10^{-9}$	$-1.240\,(12) \cdot 10^{-9}$	$-9.074\,(23) \cdot 10^{-10}$	$3.2095\,(49) \cdot 10^{-9}$
σ	$69 \cdot 10^{-6}$	$74 \cdot 10^{-6}$	$65 \cdot 10^{-6}$	$119 \cdot 10^{-6}$	$106 \cdot 10^{-6}$
Number of lines	2313	3994	2993	4006	3711
$\Delta JJ_{\max}$	−61/61	−81/78	−70/69	−72/71	−68/72
$\Delta JK_{\max}$	−59/61	−68/63	−68/66	−69/70	−67/71

pomers. They are listed up to the H constants in Table 2. As can be seen, the B_0, C_0 and D^0 values decrease very regularly with increasing molecular mass. Contrary to this, the H constants show a more irregular behaviour. Therefore, the latter constants may be taken as effective ones. The excited state parameters up to the D constants (Model 1) are given in Tables 3 and 5, respectively. For all ν_{12} bands (Table 6) and for the ν_{11} bands of $^{13}C_3{}^{14}N_3H_3$ and $^{12}C_3{}^{14}N_3D_3$ (Table 4) the data allowed to fit also the H constants (Model 2). The low intensity of the ν_{11} bands of $^{12}C_3{}^{14}N_3H_3$, $^{12}C_3{}^{15}N_3H_3$ and $^{13}C_3{}^{15}N_3H_3$, respectively, prevented the determinations of the H parameters for the latter molecules.

As the Tables 3, 4, 5, and 6 reveal, the σ's give no hint on a perturbation of $v_{11}=1$ and $v_{12}=1$, respec-

Table 6. Molecular constants [cm^{-1}] of the ν_{12} (A_2'') band of triazine isotopomers, Model 2 (numbers in parentheses are one standard deviation in units of the last significant digit).

	$^{12}C_3{}^{14}N_3H_3$	$^{13}C_3{}^{14}N_3H_3$	$^{12}C_3{}^{15}N_3H_3$	$^{13}C_3{}^{15}N_3H_3$	$^{12}C_3{}^{14}N_3D_3$
ν_0	736.738915 (73)	731.4838424 (52)	728.5030633 (44)	722.5580843 (73)	574.6229846 (71)
$C''-C'$	$-3.3843\ (25)\cdot 10^{-5}$	$-3.2859\ (38)\cdot 10^{-5}$	$-3.06771\ (61)\cdot 10^{-5}$	$-2.9793\ (17)\cdot 10^{-5}$	$-4.1649\ (19)\cdot 10^{-5}$
$B''-B'$	$-3.29276\ (17)\cdot 10^{-4}$	$-2.783639\ (81)\cdot 10^{-4}$	$-2.595552\ (42)\cdot 10^{-4}$	$-2.30542\ (30)\cdot 10^{-4}$	$4.394640\ (12)\cdot 10^{-4}$
$D_J''-D_J'$	$-2.843\ (12)\cdot 10^{-9}$	$-2.06848\ (33)\cdot 10^{-9}$	$-1.67635\ (98)\cdot 10^{-9}$	$-1.4278\ (62)\cdot 10^{-9}$	$2.2398\ (58)\cdot 10^{-9}$
$D_{JK}''-D_{JK}'$	$5.044\ (30)\cdot 10^{-9}$	$3.54894\ (96)\cdot 10^{-9}$	$2.7933\ (27)\cdot 10^{-9}$	$2.382\ (14)\cdot 10^{-9}$	$-5.668\ (15)\cdot 10^{-9}$
$D_K''-D_K'$	$-2.356\ (27)\cdot 10^{-9}$	$-1.54134\ (85)\cdot 10^{-9}$	$-1.1362\ (24)\cdot 10^{-9}$	$-0.914\ (11)\cdot 10^{-9}$	$3.787\ (12)\cdot 10^{-9}$
$H_J''-H_J'$	$-2.98\ (25)\cdot 10^{-14}$	$-1.780\ (39)\cdot 10^{-14}$	$-1.418\ (83)\cdot 10^{-14}$	$-0.778\ (82)\cdot 10^{-14}$	$1.9366\ (77)\cdot 10^{-14}$
$H_{JK}''-H_{JK}'$	$7.75\ (92)\cdot 10^{-14}$	$4.48\ (17)\cdot 10^{-14}$	$4.91\ (30)\cdot 10^{-14}$	$2.25\ (27)\cdot 10^{-14}$	$-7.24\ (27)\cdot 10^{-15}$
$H_{KJ}''-H_{KJ}'$	$-5.9\ (12)\cdot 10^{-14}$	$-4.10\ (23)\cdot 10^{-14}$	$-5.76\ (41)\cdot 10^{-14}$	$-1.86\ (34)\cdot 10^{-14}$	$1.020\ (39)\cdot 10^{-13}$
$H_K''-H_K'$	$-4.38\ (83)\cdot 10^{-14}$	$2.58\ (1.53)\cdot 10^{-15}$	$2.53\ (21)\cdot 10^{-14}$	$1.22\ (18)\cdot 10^{-14}$	$6.58\ (23)\cdot 10^{-14}$
σ	$68\cdot 10^{-6}$	$75\cdot 10^{-6}$	$66\cdot 10^{-6}$	$99\cdot 10^{-6}$	$113\cdot 10^{-6}$
Number of lines	2313	3994	2993	4006	3711

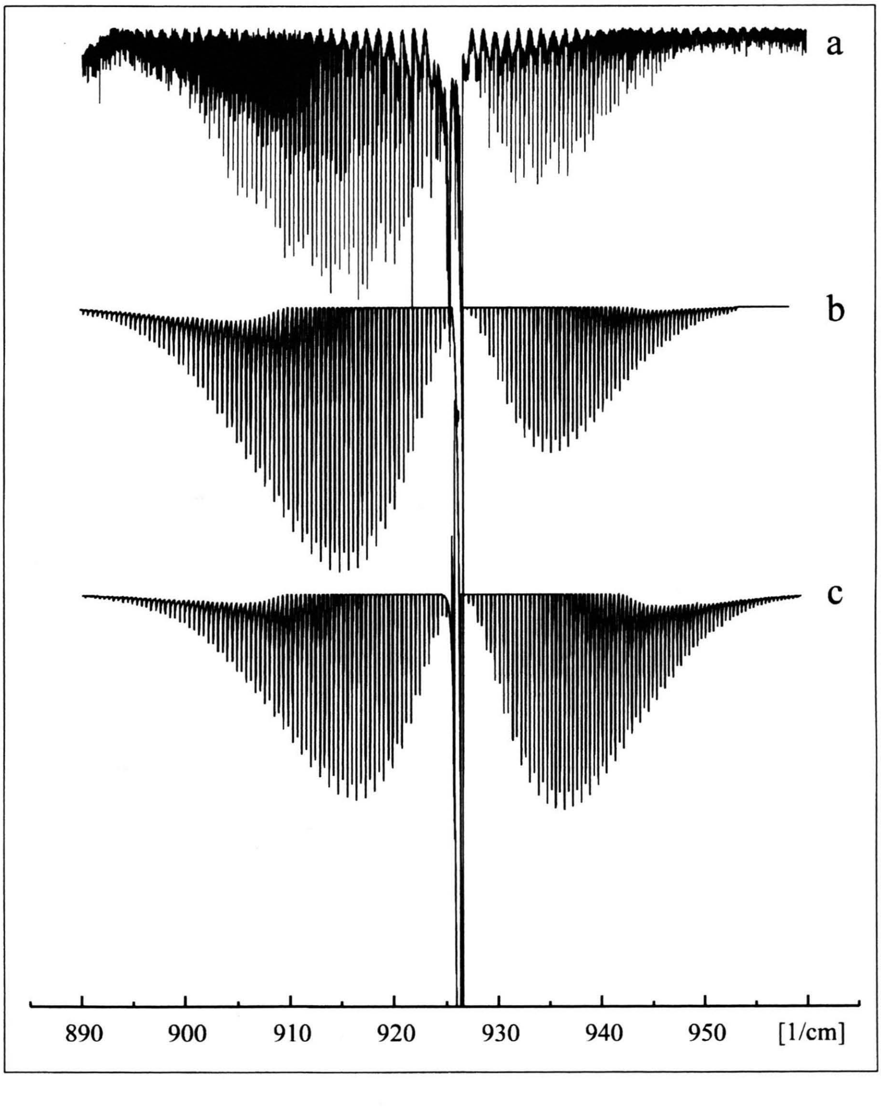


Fig. 3. The ν_{11} band of $^{12}C_3{}^{14}N_3H_3$;
a) observed;
b) calculated with F_{HW} of Table 7;
c) calculated without F_{HW}.

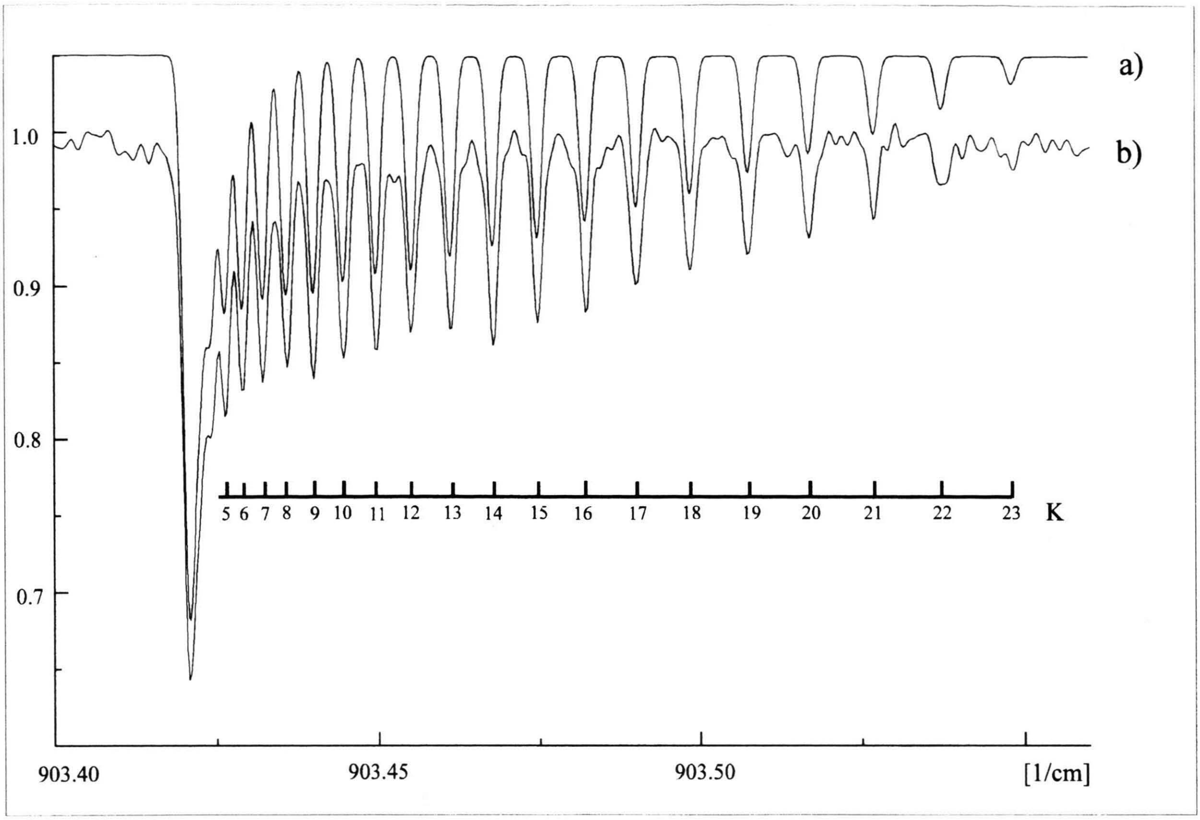


Fig. 4. $P_Q(24)$ of the ν_{11} band of the isotopomer $^{13}C_3{}^{14}N_3H_3$, a) calculated spectrum; b) experimental spectrum.

Table 7. Herman-Wallis factors of ν_{11} of some triazine isotopomers.

ν_{11}	$^{12}C_3{}^{14}N_3H_3$	$^{13}C_3{}^{14}N_3H_3$	$^{12}C_3{}^{15}N_3H_3$	$^{13}C_3{}^{15}N_3H_3$
$A^J_{11} \cdot 10^2$	-0.9154	-0.4001	-0.4938	-0.2678
$A^{KK}_{11} \cdot 10^2$	-0.0047	-0.0128	-0.0029	-0.0157
Number of data	958	1016	908	852

tively. However, upon simulation with KILO the ν_{11} and ν_{12} bands show a different behaviour. While all ν_{12} bands could be reproduced very nicely, all ν_{11} bands, except the one of $^{12}C_3{}^{14}N_3D_3$, show an enhancement of the P-branch and a depletion of the R-branch, compared to the unperturbed case. As an example the ν_{11} band of $^{12}C_3{}^{14}N_3H_3$ is given in Figure 3. This type of intensity perturbation is indicative for a global Coriolis resonance, i.e. is caused by $\tilde{M}_{12}$.

In order to settle this problem, the intensity ratios of P- and R-lines originating in the same lower level have been derived from the observed spectra yielding Herman-Wallis A^J_n and A^{KK}_n constants via a least-squares procedure based on (9). These latter coefficients have been incorporated in the program KILO. The results are given in Table 7 and in Fig. 3 b for the band ν_{11} of $^{12}C_3{}^{14}N_3H_3$. It can be seen that the Herman-Wallis coefficients found reproduce the observed intensity distribution well.

Summarizing it may be stated that the ν_{12} bands of all isotopomers are unperturbed at the present level of resolution. Contrary to this, the ν_{11} bands of the H-containing triazines reveal an intensity perturbation originating in $\tilde{M}_{12}$, i.e. in a global Coriolis perturbation which is not reflected in the frequencies observed and the excited state parameters derived thereof.

5. Conclusions

In the present study the ground state constants of natural triazine and its $^{13}C_3{}^{14}N_3H_3$, $^{12}C_3{}^{15}N_3H_3$, $^{13}C_3{}^{15}N_3H_3$, and $^{12}C_3{}^{14}N_3D_3$ isotopomers have been determined with high precision by analyzing the high resolution FTIR spectra of the parallel bands ν_{11} and ν_{12}, respectively.

The structural parameters of triazine, extracted from the five experimental B_0-constants by using the r_0- and r_S-method will be reported in an forthcoming publication [5]. The ground state constants found in the present work have been of essential value for the assignment and analysis of the five perpendicular bands ν_6, ν_7, ν_8, ν_9, and ν_{10} of triazine, which will be reported on in two forthcoming papers [21].

The synthesis of the three missing isotopomers of triazine with D_{3h} symmetry is in progress and will be reported later.

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