

FTIR Study of the ν_{12} and the $\nu_{12} + \nu_{14} - \nu_{14}$ Bands of 1,3,5-Triazine Near 740 cm⁻¹

Wolfram Bodenmüller and Andreas Ruoff

Sektion Schwingungsspektroskopie, Universität Ulm, W-7900 Ulm, Germany

Laurent Manceron

Laboratoire de Spectrochimie Moléculaire, Université Pierre et Marie Curie, 4 Place Jussieu, F-75005 Paris, France

Z. Naturforsch. **47a**, 1197–1203 (1992); received October 20, 1992

Dedicated to Prof. Viliam Krivan at the occasion of his 60th birthday

The infrared spectrum of the ν_{12} fundamental and its accompanying hot band $\nu_{12} + \nu_{14} - \nu_{14}$ of triazine has been measured by means of a Fourier transform spectrometer with a resolution of about 0.0023 cm⁻¹. A total of about 2779 rovibrational transitions has been assigned. The ground state constants have been considerably improved whilst the parameters for the excited states $\nu_{12} = 1$, $\nu_{14} = 1$ and $\nu_{12} = \nu_{14} = 1$ have been obtained for the first time. The standard deviations were $2.92 \cdot 10^{-4}$ cm⁻¹ for the ground state constants and $1.53 \cdot 10^{-4}$ cm⁻¹ for the excited state parameters of ν_{12} showing the latter to be unperturbed. The upper state of the hot band $\nu_{12} + \nu_{14} - \nu_{14}$ was found to be perturbed by an accidental resonance.

Key words: 1,3,5-triazine, High resolution FTIR spectroscopy, Ground state constants, Fundamental constants, Hot band constants.

1. Introduction

1,3,5-Triazine (C₃H₃N₃, henceforth abbreviated as triazine) is a planar symmetric top molecule belonging to the molecular symmetry group D_{3h}(M)¹. Triazine has been synthesized in 1954 for the first time [1]. It has been the object of several low resolution IR and Raman investigations [2–5] which yielded the assignment of different vibrational bands. Spontaneous rotational Raman spectroscopy and band contour simulation of IR gas phase spectra (resolution $\simeq 0.2$ cm⁻¹) have been employed to obtain first estimates of B_0 [6] and of some ζ_t^z 's and $q_t^{(+)}$'s [7].

Quite recently the electron diffraction structure of the triazine molecule has been determined [8] and the intensities of the fundamentals have been derived by ab-initio methods [9].

¹ As usual the label (M) designates a molecular symmetry group.

² Lists of observed and calculated wavenumbers as well as the correlation matrices have been deposited in the "Sektion Spektren- und Strukturdokumentation", Universität Ulm, P.O. Box 4066, W-7900 Ulm (Dr. J. Vogt).

Reprint requests to Prof. Dr. A. Ruoff, Sektion Schwingungsspektroskopie, Universität Ulm, Oberer Eselsberg, W-7900 Ulm, Germany.

According to the authors' knowledge high resolution IR spectra of triazine have never been obtained. Therefore, we have started an investigation of the IR bands of triazine and its perdeuterated species using modern high resolution techniques.

In the present contribution we report on the FTIR spectrum of triazine in the 740 cm⁻¹ region covering the out-of-plane fundamental ν_{12} (A₂''') and its accompanying hot band $\nu_{12} + \nu_{14} - \nu_{14}$.

2. Experimental Details

The sample of triazine with a purity of 98% has been obtained from Merck-Schuchardt. Since no impurities could be detected in the IR spectra the substance has been used without further purification.

The spectra² have been recorded with a Bruker 120 HR instrument (Université Pierre et Marie Curie, Paris). It was equipped with a KBr beam splitter and a narrow band liquid-nitrogen-cooled HgCdTe detector, fitted with a band-pass interference filter having about 60% transmission in the 1000–600 cm⁻¹ region. The Fourier transformation was processed with a trapezoidal apodization function starting at 95% of

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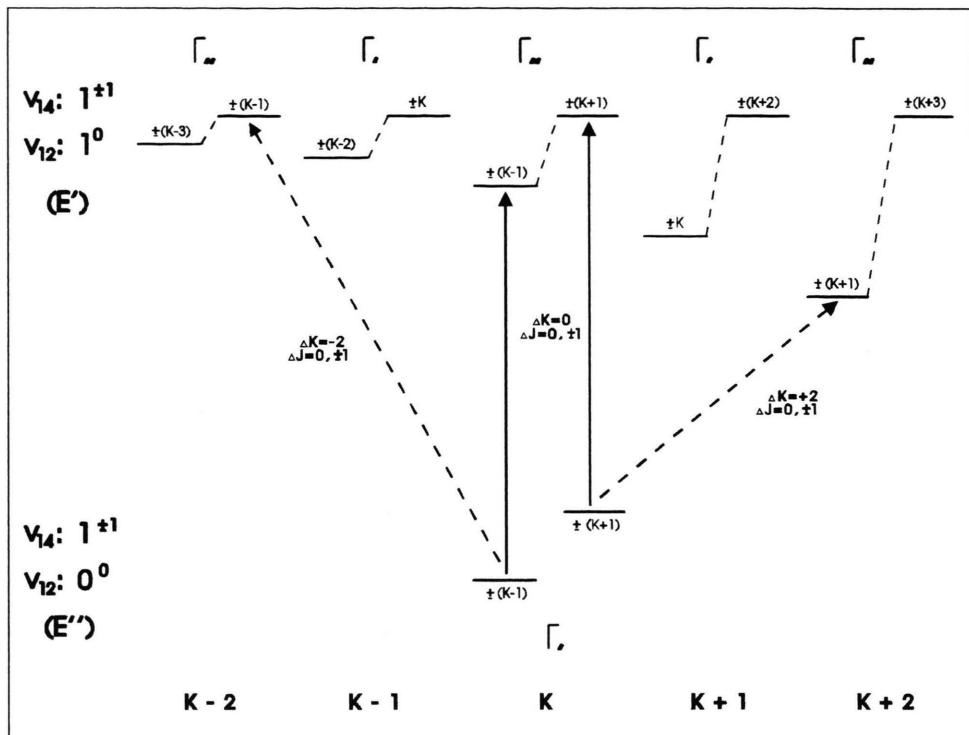


Fig. 1. Schematic transition diagram for the hot band $v_{12} + v_{14} - v_{14}$. All levels are characterized by their g quantum number. Parallel transitions (M_{11}) are given by full lines, transitions induced by \tilde{M}_{32} are given by broken lines.

Table 1. Experimental details of the infrared spectra of $C_3H_3N_3$.

Band	Cell [cm]	Range [cm ⁻¹]	Pressure [mbar]	Scans	Resolution [cm ⁻¹]	Wavenumber Standard
$v_{12}, v_{12} + v_{14} - v_{14}$	30	700–780	4.0	100	0.0023	CO_2
	300	700–780	0.38	210	0.0023	CO_2
	300	700–780	2.33	80	0.0023	CO_2

the scan length; it resulted in a 0.0023 cm^{-1} effective resolution. A 30 cm stainless steel cell and a 3 m long path cell with CsJ windows and KBr windows, respectively, have been employed. Calibration has been done with CO_2 lines [10] the absolute accuracy of which being between $1 \cdot 10^{-3}\text{ cm}^{-1}$ and $1 \cdot 10^{-4}\text{ cm}^{-1}$. The relative accuracy of the peakfinder evaluated lines is $\pm 2 \cdot 10^{-4}\text{ cm}^{-1}$. Further experimental details are given in Table 1.

3. Theory

The energy expression employed comprises the diagonal elements of the rovibrational Hamiltonian

up to third order:

$$E(v, l, J, k) = v_0 + B_v J(J+1) + (C_v - B_v) k^2 - D_J^v J^2(J+1)^2 - D_{JK}^v J(J+1) k^2 - D_K^v k^4 - l_t k [2(C \zeta_t^z)_v - \eta_t^J J(J+1) - \eta_t^K k^2 - \eta_t] + \dots, \quad (1)$$

where the quantum number l equals zero for the ground state and for the state $v_{12}=1$. As is well known, a planar symmetric top molecule is characterized by the planarity relations [11]

$$A_e = B_e = 2 C_e \quad (2)$$

and

$$2 D_J^e + 3 D_{JK}^e + 4 D_K^e = 0. \quad (3)$$

They hold strictly only in the equilibrium state but may be taken as approximations for the ground state.

For v_{12} and $v_{12} + v_{14} - v_{14}$ the selection rules and the vibration rotation line intensities are obtained from the contact transformed space-fixed dipole moment operator \tilde{M}_f [12, 13] in the form

$$\tilde{M}_f = M_{11} + \tilde{M}_{12} + \tilde{M}_{13} + \tilde{M}_{32} + \dots, \quad (4)$$

where M_{mn} is the set of terms 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}_α), and of degree 1 in the direction cosines.

For v_{12} the upper and the lower vibrational state belong to the species A_2'' and A_1' , respectively. Contrary to this, the corresponding levels of the hot band $v_{12} + v_{14} - v_{14}$ have the symmetry E' and E'' , respectively. Both degenerate levels may be perturbed by essential l -resonance ($\pm 2, \pm 2$) interactions. It seems worth mentioning that all E'' vibrational states of $D_{3h}(M)$ molecules have ζ_r^z constants vanishing at least in the small amplitude approximation.

Considering only the principal term M_{11} in (4), both v_{12} and $v_{12} + v_{14} - v_{14}$ turn out to be parallel bands with the usual selection rules $\Delta l = \Delta k = 0$, $\Delta J = \pm 1, 0$ (Figure 1). Therefore, to a first approximation the appearance of the fundamental v_{12} is very similar to that of the hot band $v_{12} + v_{14} - v_{14}$ except that in the latter case all rovibrational transitions with $K \neq 0$ split into doublets with $k l > 0$ and $k l < 0$.

From (1) this splitting for a $J \rightarrow J + \Delta J$ transition may be written as [14]

$$\Delta v = 4[(A \zeta)' - (A \zeta)''] k - 2(\eta'_K - \eta''_K) k^3 - 2[\eta'_J(J + \Delta J)(J + \Delta J + 1) - \eta''_J J(J + 1)] k. \quad (5)$$

4. Description of the Spectrum

Triazine has 14 normal vibrations, the species of which are given by

$$\Gamma_{|V\rangle} = 3A_1' \oplus 2A_2' \oplus 5E' \oplus 2A_2'' \oplus 2E''. \quad (6)$$

The currently known band centers of these fundamentals are summarized in Table 2 [5, 15], which also defines the applied numbering scheme. Only the A_2' and the E' modes are IR active.

Figure 2 shows the fundamental v_{12} near 740 cm^{-1} , which is a very intense regular parallel band. Even at medium resolution (0.03 cm^{-1}) the J structure of the P and R branch is clearly discernible and its assign-

Table 2. Fundamental vibrations of 1,3,5-triazine.

	$\Gamma_{ v\rangle}$	$v_{\text{exp}}(\text{IR})^a$	$v_{\text{exp}}(\text{Ra})^b$
v_1	A_1'	—	3042
v_2		—	1132
v_3		—	992
v_4	A_2'	—	—
v_5		—	—
v_6	E'	3056.5	3050 ^c
v_7		1555.5	1555
v_8		1409.9	1410
v_9		1172.7	1176
v_{10}		675.3	676
v_{11}	A_2''	1126.6	—
v_{12}		736.7	—
v_{13}	E''	—	1032 ^c
v_{14}		—	340

^a This work. ^b Ref. [5]. ^c Ref. [15].

Table 3. Spin weights of the rovibrational levels for 1,3,5-triazine. ^a

K	$\Gamma_{ v\rangle}$			
	A_1', A_2''	A_2', A_2''	E', E''	
0 (J even)	56	20	70	
0 (J odd)	20	56	70	
$3p \pm 1$	70	70	146	
$3p$	76	76	140	

^a Group $D_{3h}(M)$.

ment is straightforward. The K structure for $K > 5$ is resolved at high resolution (0.0023 cm^{-1}). The K assignment is more complicated because, contrary to the case of small molecules, the spin statistics of triazine (Table 3) do not give any hint on the K values. These difficulties were overcome by a stepwise trial and error procedure using the modified iterative program MILLI and the simulation program KILO [16]. A total of 2345 lines up to $J = 62$ and $K = 41$ could be unambiguously assigned. No perturbations could be detected at the present level of accuracy. The Q branch is only partly resolved and its high line density prevents any reasonable assignment.

The central part of the spectrum of v_{12} (Figure 2) shows several Q branches belonging to v_{12} and its accompanying hot bands. They may be identified using their relative intensity with respect to that of the v_{12} fundamental. The results are summarized in Table 4.

Expecting the most intense hot band $v_{12} + v_{14} - v_{14}$ to have the same appearance as the fundamental v_{12} ,

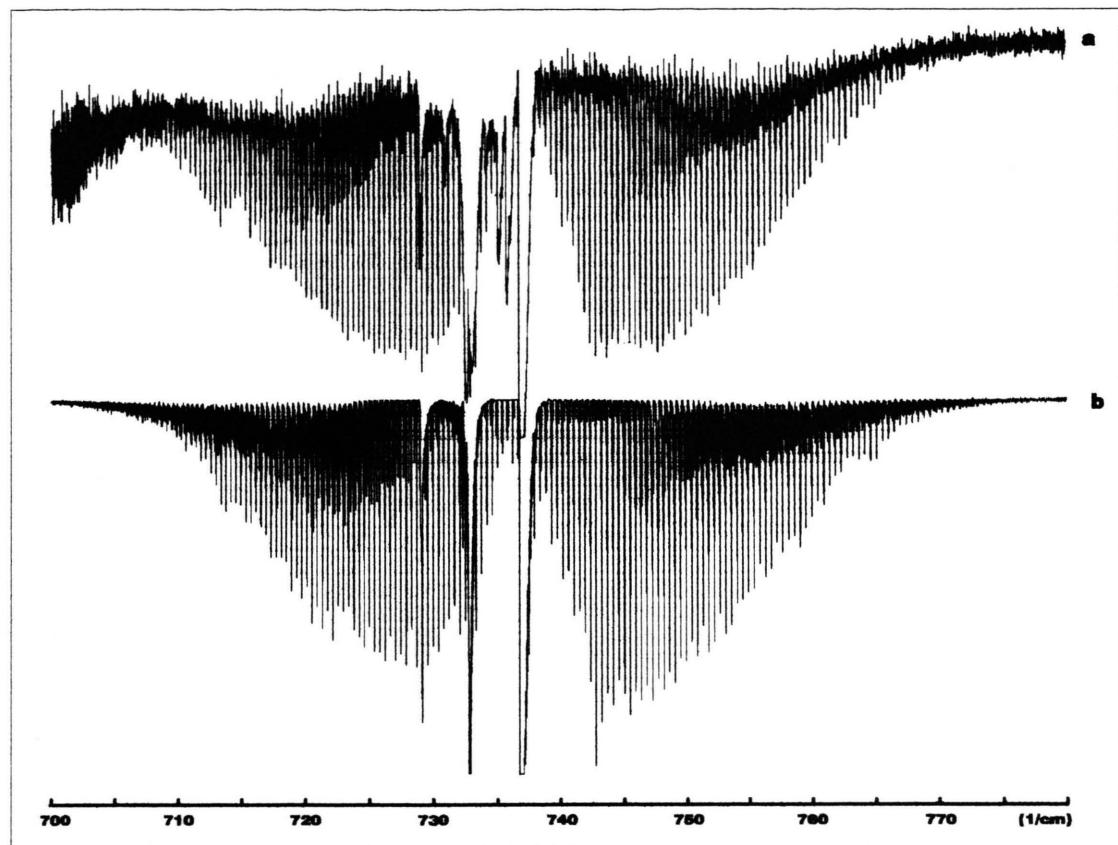


Fig. 2. Survey spectrum of the v_{12} fundamental of triazine. (a) Experimental spectrum ($p = 0.38$ mbar, 300 cm cell, resolution 0.0023 cm^{-1}). (b) Computed spectrum, the hot bands $v_{12} + v_{14} - v_{14}$ and $v_{12} + 2v_{14} - 2v_{14}$ being included.

Table 4. Relative intensities of the v_{12} band spectra at 298 K.

	v_{exp} [cm $^{-1}$]	$I_{\text{rel, calc.}}$	$I_{\text{rel, exp.}}$
v_{12}	736.739	1.0	
$v_{12} + v_{10} - v_{10}$	735.7	0.0768	0.0760
$2v_{12} - v_{12}$	735.0	0.057	0.063
$v_{12} + v_{14} - v_{14}$	732.757	0.388	0.384
$v_{12} + 2v_{14} - 2v_{14}$	728.9	0.11	0.05

Table 5. Possible perturbers of the excited state $v_{12} = v_{14} = 1^a$.

$\Gamma_{ v\rangle}$	Wavenumber ^b [cm $^{-1}$]
$v_{10} + v_{14}$	$A''_1 \oplus A''_2 \oplus E''$
$3v_{14}$	$A''_1 \oplus A''_2 \oplus E''$
v_{13}	E''
v_2	A'_1

^a $\Gamma_{|v_{12}=v_{14}=1\rangle} = E'$ at 1076 cm^{-1} . ^b Harmonic oscillator approximation.

we have identified and assigned 434 lines of the P and R branch up to $J = 40$ and $K = 21$. None of these lines are split, i.e. (5) equals zero. This has to be ascribed to the fact that $(\zeta_t^z)' \approx (\zeta_t^z)'' \approx 0$. The band in question shows a local perturbation centered at $K = 12$ causing a gap for high J values (Figure 3). Because v_{12} is by far the lowest vibrational level it seems reasonable assuming accidental resonance to occur only in the upper level of the hot band, that is in the state $v_{12} = v_{14} = 1$ which has E' symmetry. Some possible perturbers are listed in Table 5.

5. Analysis and Results

5.1. Ground State

The assigned lines of v_{12} were first processed by the program DIFNEU designed for the determination of the ground state parameters B_0 , D_J^0 , D_{JK}^0 , H_J^0 , H_{JK}^0 and

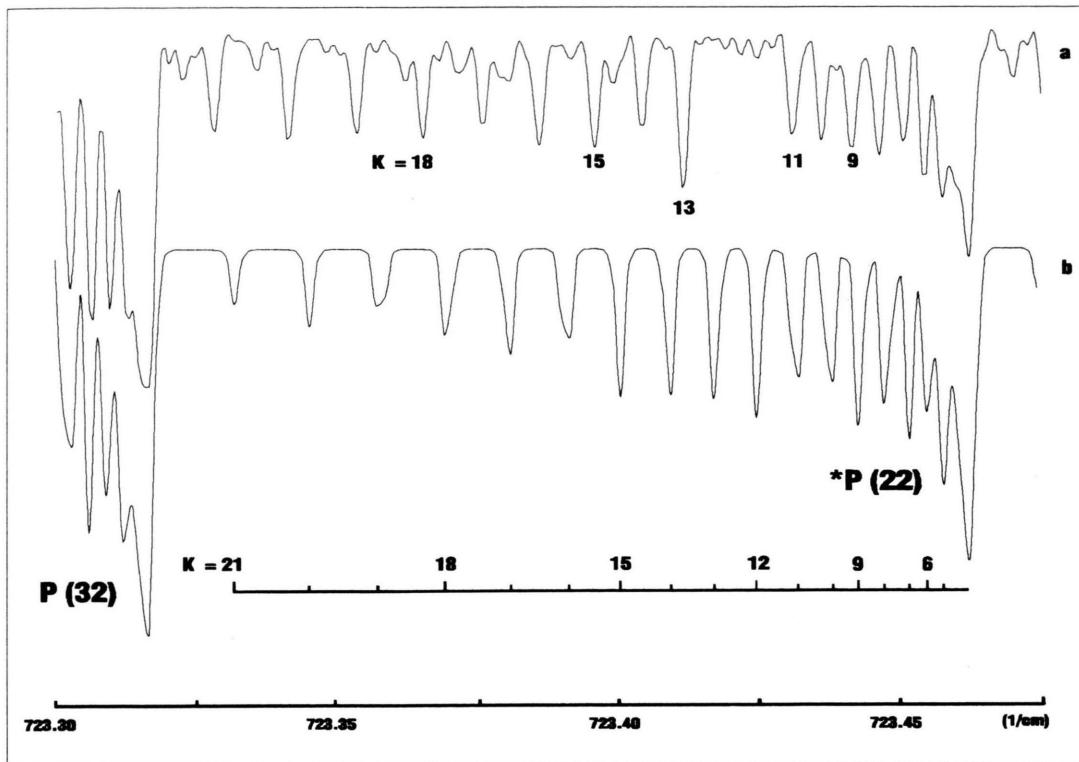


Fig. 3. A small portion of the $v_{12} + v_{14} - v_{14}$ hot band of triazine showing the local perturbation at $K=12$. (a) Experimental spectrum (resolution 0.0023 cm^{-1}). (b) Computed spectrum, cold band included. * marks the hot band.

H_{KJ}^0 . The constants B_0 , D_J^0 and D_{JK}^0 were obtained by a fit of 1026 gscd which were formed from unit-weighted lines. The results are given in Table 6, the standard deviation being $2.92 \cdot 10^{-4}\text{ cm}^{-1}$. In the course of the fit routine it became obvious that addition of the sextic constants H_J^0 , H_{JK}^0 and H_{KJ}^0 did not improve the fit. According to their high indeterminacy these parameters were constraint to zero.

5.2. The v_{12} Fundamental

The modified iterative program MILLI, which held the ground vibrational state constants fixed during the fit, was applied to adjust the upper vibrational state parameters. The constants of (1) were fitted to 1945 rovibrational lines. The refined v_{12} parameters with the ground state constants fixed to the values quoted in Table 6 are given in Table 7. The standard deviation amounts to $1.53 \cdot 10^{-4}\text{ cm}^{-1}$, indicating v_{12} to be unperturbed at the present level of resolution (Figs. 4 and 5).

Table 6. Ground state constants^a of 1,3,5-triazine (cm^{-1}).

	Ref. [6]	Ref. [8]	Ref. [17]	This work
C_0	0.1073 ^b	0.1076 ^c	0.1074 ^b	0.1074 ^b
B_0	0.214 60(8)	0.2153	0.2148	0.214 861 30(16)
D_J^0	$1.3 \cdot 10^{-8}$	—	—	$5.326 9(40) \cdot 10^{-8}$
D_{JK}^0	—	—	—	$-8.820(19) \cdot 10^{-8}$
D_K	—	—	—	$3.952 \cdot 10^{-8}$ ^b
σ	—	—	—	$2.92 \cdot 10^{-4}$

^a The numbers in parenthesis represent one standard deviation in units of the last digit.

^b From planarity conditions. — ^c From r_x^0 .

v_{12}^0	736.739 023 (11)
$C'' - C'$	$-3.371 4(30) \cdot 10^{-5}$
$B'' - B'$	$-3.291 09(16) \cdot 10^{-4}$
$D_J'' - D_J'$	$-2.704 9(56) \cdot 10^{-9}$
$D_{JK}'' - D_{JK}'$	$4.771(18) \cdot 10^{-9}$
$D_K'' - D_K'$	$-2.067(25) \cdot 10^{-9}$
σ	$1.53 \cdot 10^{-4}$

Table 7. Molecular constants^a for v_{12} of 1,3,5-triazine (cm^{-1}).

^a The numbers in parenthesis represent one standard deviation in units of the last digit.

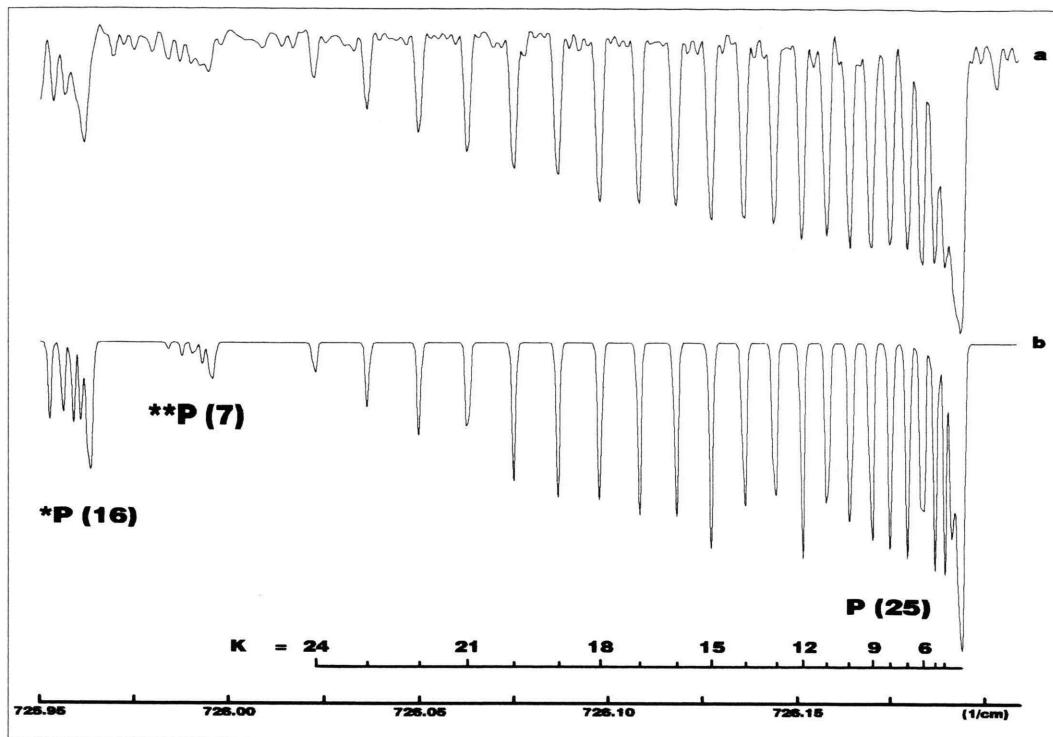


Fig. 4. Detail of the v_{12} band of triazine. (a) Experimental spectrum (resolution 0.0023 cm^{-1}). (b) Computed spectrum, hot bands included. * marks $v_{12} + v_{14} - v_{14}$, while ** designates $v_{12} + 2v_{14} - 2v_{14}$.

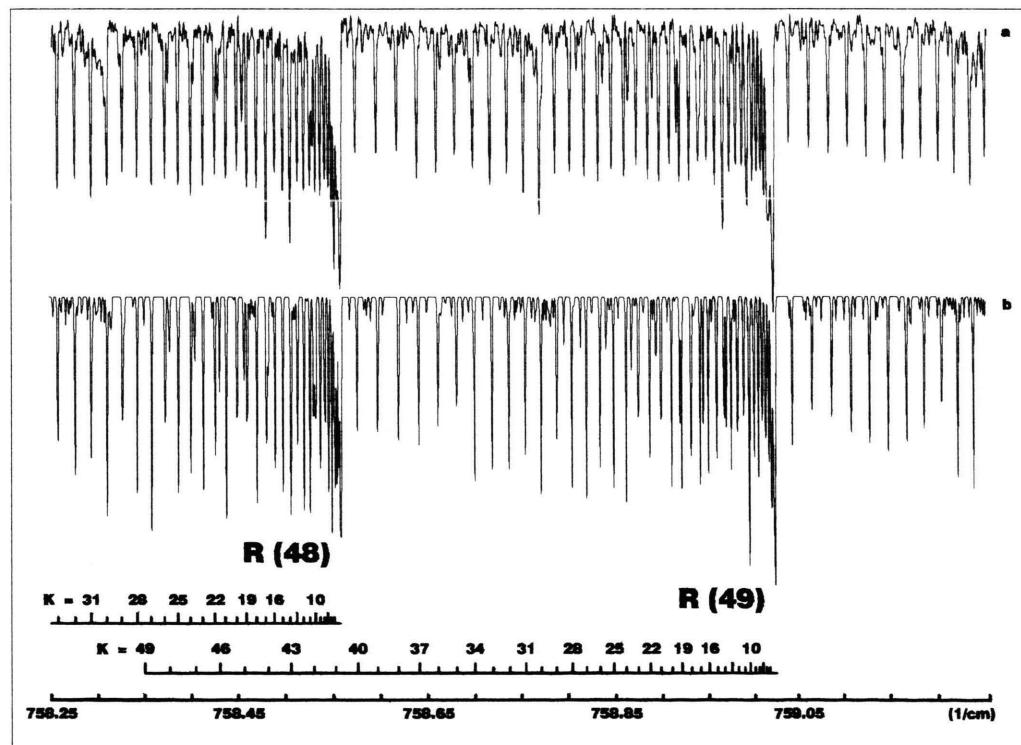


Fig. 5. A small part of the R branch of the v_{12} band to triazine. (a) Experimental spectrum (resolution 0.0023 cm^{-1}). (b) Computed spectrum, hot band included.

C'' ^b	0.1074
B'' ^c	0.214 7713 (15)
D''_J ^c	$5.21 (23) \cdot 10^{-8}$
D''_{JK} ^c	$-3.11 (50) \cdot 10^{-8}$
D''_K ^b	$-2.68 \cdot 10^{-9}$
σ ^c	$5.14 \cdot 10^{-4}$
$\nu_{12+14-14}^0$	732.757 071 (92)
$C'' - C'$ ^d	$-3.552 (34) \cdot 10^{-5}$
$B'' - B'$ ^d	$-3.418 1 (30) \cdot 10^{-4}$
$D''_J - D'_J$ ^d	$-0.78 (21) \cdot 10^{-9}$
$D''_{JK} - D'_{JK}$ ^d	$-2.79 (38) \cdot 10^{-9}$
$D''_K - D'_K$ ^d	$-7.16 (37) \cdot 10^{-9}$
σ ^d	$3.71 \cdot 10^{-4}$

Table 8. Estimated molecular constants^a for the hot band $\nu_{12} + \nu_{14} - \nu_{14}$ of 1,3,5-triazine (cm⁻¹).

^a The numbers in parenthesis represent one standard deviation in units of the last digit.

^b From planarity rules.

^c Program DIFNEU.

^d Program MILLI.

5.3. The Hot Band $\nu_{12} + \nu_{14} - \nu_{14}$

A determination of the upper and lower state constants of the hot band $\nu_{12} + \nu_{14} - \nu_{14}$ has been made with the aid of the programs DIFNEU and MILLI. Omitting 119 lines exhibiting noticeable perturbations, the remainder of 319 lines yielded 117 gscd which served to fit the constants B'' , D''_J and D''_{JK} , where " stands for $\nu_{14} = 1$. The results are set out in Table 8, the standard deviation being $\sigma = 5.14 \cdot 10^{-4}$ cm⁻¹. The refined constants of the $\nu_{12} = \nu_{14} = 1$ state are summarized in Table 8 reproducing the data with $\sigma = 3.71 \cdot 10^{-4}$ cm⁻¹. It should be pointed out that we have not included the essential $q_t^{(+)}$ -resonance in our fit. Comparing the standard deviations of $\nu_{12} + \nu_{14} - \nu_{14}$ with those of the fundamental ν_{12} our model seems to be satisfactory.

Attempts to include accidental resonances with some possible perturbers of the upper state (Table 5) proved to be unsuccessful.

6. Conclusion

In the present study the high resolution FTIR spectrum of ν_{12} and $\nu_{12} + \nu_{14} - \nu_{14}$ of triazine has been investigated for the first time.

2345 rovibrational transitions of the fundamental ν_{12} and 434 of its hot band $\nu_{12} + \nu_{14} - \nu_{14}$ have been measured and assigned.

The ground state constants and the constants for the $\nu_{12} = 1$ state have been determined accurately. No indications of perturbations of these states have been found at the present level of accuracy.

For the analysis of the hot band $\nu_{12} + \nu_{14} - \nu_{14}$ a simple parallel band model has been chosen zero weighting all perturbed lines. It explains satisfactorily the main features of this band. Therefore, the resulting parameters for the states $\nu_{12} = \nu_{14} = 1$, though preliminary, seem satisfying.

The spectra of all other IR active fundamentals of triazine have been recorded. Their analysis will be reported elsewhere.

Acknowledgements

The authors thank Miss E. Kaltenegger for technical assistance and Mrs. E. Cloppenburg for some stylistic corrections. One of us (W.B.) expresses his gratitude to the Physikalisch-Chemisches Institut der Universität Giessen, for hospitality extended to him during his work in Giessen.

All calculations were carried out at the Rechenzentrum der Universität Ulm, a service that is gratefully acknowledged. The programs MILLI and KILO were made available to us through the courtesy of Dr. G. Graner of the Université de Paris-Sud, Orsay, France.

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