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High-resolution infrared and theoretical study of the fundamental bands ν_2, ν_4 and ν_9 and the *c*-Coriolis interacting dyad ν_5, ν_{14} of 1,3,4-thiadiazole

F. Hegelund [a,*], R. Wugt Larsen [b], R.A. Aitken [c], M.H. Palmer [d]

[a] *Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark*
[b] *Institut für Physikalische Chemie, Universität Göttingen, Tammanstrasse 6, D-37077 Göttingen, Germany*
[c] *School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, KY16 9ST Scotland, UK*
[d] *School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ Scotland, UK*

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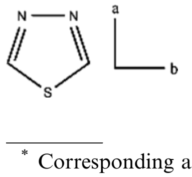
Abstract

The Fourier transform gas-phase IR spectrum of 1,3,4-thiadiazole, $C_2H_2N_2S$, has been recorded with a resolution of ca. 0.003 cm^{-1} in the 800–1500 cm^{-1} spectral region. Five fundamental bands $\nu_2(A_1;\ 1391.9\ cm^{-1})$, $\nu_4(A_1;\ 964.4\ cm^{-1})$, $\nu_5(A_1;\ 894.6\ cm^{-1})$, $\nu_9(B_1;\ 821.5\ cm^{-1})$, and $\nu_{14}(B_2;\ 898.4\ cm^{-1})$ have been analysed using the Watson model. Ground state rotational and quartic centrifugal distortion constants as well as upper state spectroscopic constants have been obtained from fits. The ν_4 and ν_9 bands are unperturbed while a strong *c*-Coriolis resonance perturbs the close-lying ν_5 and ν_{14} bands. This dyad system has been analysed by a model including first and second order *c*-Coriolis resonance using the theoretically predicted Coriolis coupling constant $\zeta^c_{14,5}$. The ν_2 band is strongly perturbed by a local resonance, and we obtain a set of spectroscopic parameters using a model including second order *a*-Coriolis resonance with the inactive $\nu_{10} + \nu_{14}$ band. Ground state rotational and quartic centrifugal distortion constants, anharmonic frequencies, and vibration-rotational α-constants predicted by quantum chemical calculations using a cc-pVTZ basis and B3LYP methodology, have been compared with the present experimental data, where there is generally good agreement.

Keywords: 1,3,4-Thiadiazole; High-resolution infrared spectrum; Rotational constants; Coriolis resonance; Vibrational frequencies; Vibration-rotational constants; Anharmonic frequencies; DFT study

1. Introduction

In recent papers, we studied the unsaturated five-membered heterocyclic sulphur-containing compounds 1,2,5-thiadiazole, $C_2H_2N_2S$ [1] and the parent ring system thiophene, C_4H_4S, [2]. The present Note deals with 1,3,4-thiadiazole, (1).



(1)

Our motivation for investigating this molecule by high-resolution infrared spectroscopy is to obtain precise spectroscopic constants for comparison with our recent predictions of anharmonic frequencies of five-membered heterocycles [3], and for our ongoing theoretical study of ground state rotational and quartic centrifugal distortion constants and vibration-rotational constants of this class of molecules [4]. Four fundamental bands in the ring- and CH-deformation region 800–1000 cm^{-1} and one band near 1400 cm^{-1} of 1,3,4-thiadiazole are dealt with in the present work. The appearance of these bands is very similar to those analysed previously in [1,2].

1,3,4-Thiadiazole is a planar asymmetric top ($\kappa = -0.218$) with point group C_{2v}. The *a*-inertial axis coincides

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[*] Corresponding author. Fax: +45 8619 6199.
E-mail address: heg@chem.au.dk (F. Hegelund).

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with the C_2-axis, as in Eq. (1). The 15 normal vibrations of the molecule are classified by symmetry as: ν_1–ν_6(A_1), ν_7–ν_8(A_2), ν_9–ν_{10}(B_1), ν_{11}–ν_{15}(B_2). The six totally symmetric modes give rise to *a*-type bands in the infrared, while the five in-plane B_2-modes are of *b*-type. The two B_1-modes describe out-of-plane deformations giving rise to *c*-type bands, while the two A_2-modes are infrared forbidden. In Ref. [3] the earlier experimental low-resolution infrared and Raman data [5,6] for the lowest A_1-bands were reassigned, now locating ν_4 and ν_5 in the 800–1000 cm^{-1} region. The assignment [5,6] of the remaining bands, ν_9 and ν_{14}, in this region as well as ν_2 near 1400 cm^{-1} was confirmed in [3].

To our knowledge no high-resolution infrared study of 1,3,4-thiadiazole has been published previously. We have described in detail [1,2,7] our methods of both assigning and fitting of *a*-, *b*-, and *c*-type bands of asymmetric tops, with the same range of asymmetry as 1,3,4-thiadiazole, and where κ is numerically small. The Reader is therefore referred to these papers for these details. The survey spectrum of the 800–1000 cm^{-1} region (Fig. 1) illustrates the overall appearance of four of the bands studied, while the region around 1400 cm^{-1} (Fig. 2) shows the ν_2 band. A summary of the most important information concerning the assignments is given in Table 1. Lists of observed line positions for assigned transitions are available from one of the Authors (F.H.).

2. Experimental

A sample of 1,3,4-thiadiazole was synthesized from *N*,*N*′-diformylhydrazine with Lawesson's reagent [8]. The infrared gas-phase absorption spectrum of this sample was recorded in the spectral region 800–1500 cm^{-1} with a resolution of ca. 0.0030 cm^{-1}; we used the Bruker IFS 120 HR Fourier transform spectrometer located on the infrared beam-line at MAX-lab (Lund University, Sweden). MAX-I is a 550 MeV electron storage ring with a 300 mA maximum ring current and a mean lifetime of 4 h [9,10]. The high-brightness source of synchrotron radiation (SR) from the MAX-I storage ring was used. The room temperature sample, with a pressure of 0.4 Torr, resided in a 0.5 L White absorption cell, with a total absorption path length of 184 cm. The instrumental settings are listed in Table 2. The absolute wavenumber scale of the resulting absorbance spectra was calibrated against highly accurate reference water line positions reported by Guelachvili [11], and scaled according to Brown and Toth [12]. The precision of the fitted line positions is estimated to better than 0.00100 cm^{-1}.

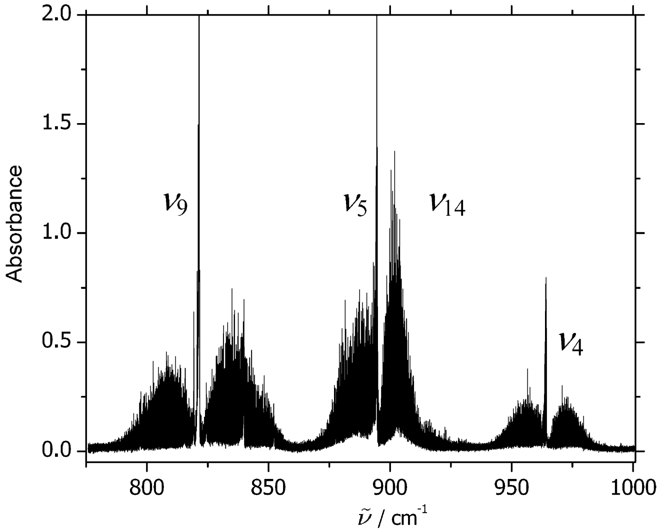

Fig. 1. A survey spectrum of the 775–1000 cm^{-1} region of the infrared spectrum of gaseous 1,3,4-thiadiazole. The fundamental bands ν_9 and ν_4 are observed at 821.5 cm^{-1} and 964.4 cm^{-1}, respectively. In between the strongly *c*-Coriolis interacting dyad ν_5, ν_{14} is observed. The absorption from small traces of the by product 1,3,4-oxadiazole from the sample synthesis has been subtracted based on Ref. [16]. Path length = 184 cm. Sample pressure = 0.4 Torr.

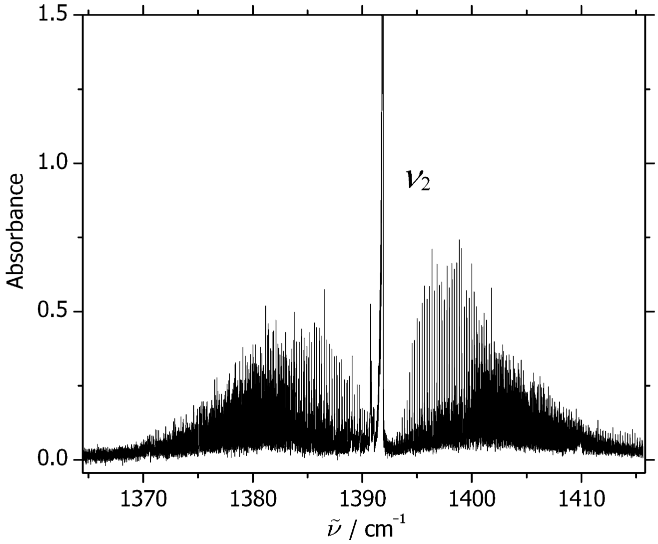

Fig. 2. A survey spectrum of the 1365–1415 cm^{-1} region of the infrared spectrum of gaseous 1,3,4-thiadiazole. The ν_2 band is observed. Path length = 184 cm. Sample pressure = 0.4 Torr.

3. Experimental results

Each of the five bands studied were initially analysed by the Watson Hamiltonian model [13], using A-reduction and III^r-representation. The ground state fit was selected from 1542 ground state combination differences (GSCDs) of the type $R(J-1)-P(J+1)$ originating from mainly unblended lines; we used the *a*-type band ν_4 and the *c*-type band ν_9. We decided to discard additional GSCD data from both ν_5 and ν_{14} since the *c*-Coriolis interaction between these close-lying bands depletes the intensity in one of their wings. Hence, GSCDs originating from this dyad are of somewhat lower quality. Similarly ν_2 was excluded, since extended clustering in both P- and R-wing lowers significantly the quality of GSCDs. Our ground state fit was slightly improved by including the 12 micro-