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High-resolution FTIR spectroscopy of HNSO—Analysis of the highly perturbed ν_4, ν_6 and $2\nu_5$ bands

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Abstract

We report a rovibrational analysis of the ν_4 and ν_6 fundamentals and the $2\nu_5$ overtone of HNSO from high-resolution Fourier transform infrared spectra. The ν_6 band (out-of-plane bend) centred at 757.5 cm^{-1} is *c*-type. The ν_4 band (HNS bend) centred at 905.9 cm^{-1} is predominantly *a*-type with a very weak *b*-type component ($\mu_a^2/\mu_b^2 = 12.4$). Numerous global perturbations and localized avoided crossings affecting the $v_4 = 1$ rotational levels were successfully treated by inclusion of Fermi and *c*-axis Coriolis resonance terms between $v_4 = 1$ and $v_5 = 2$, and a *b*-axis Coriolis resonance term between $v_4 = 1$ and $v_6 = 1$. The latter term gives rise to an avoided crossing with an extraordinary $|\Delta K_a| = 5$ selection rule. The Fermi resonance between $v_4 = 1$ and $v_5 = 2$ gives rise to strong mixing of their rotational wavefunctions in the vicinity of $K_a = 18$. The resultant borrowing of intensity made it possible for $2\nu_5$ transitions in the range $K_a = 16$–19 to be assigned and included in a global rovibrational treatment of all three band systems.

Keywords: Thionylimide (HNSO); High-resolution IR spectroscopy; Rovibrational analysis; Spectral analysis by subtraction of simulated intensities (SASSI)

1. Introduction

N-Sulfinylamines, compounds featuring the nonlinear functional group —N=S=O, have drawn considerable interest due to their geometry. Large number of compounds of the type R-NSO have been prepared and their structure and behavior studied, [1] with the conclusion being that a planar structure with *syn* configuration is the preferred form. The simplest sulfinylimine HNSO, also known as thionylimide, was first prepared by the spontaneous gas phase reaction of ammonia and thionyl chloride at room temperature [2]. Theoretical studies using *ab initio* molecular orbital and density functional calculations have identified *cis*-HNSO as the most stable structure on the potential energy surface (PES) and predicted an additional seven structural isomers [3], four of which had already been prepared photolytically from HNSO in a low-temperature matrix and probed by spectroscopic methods [4–7]. Ultraviolet absorption spectroscopy of HNSO indicated electronic excitation centered at the S atom [8]. A planar, *cis* conformation for the HNSO molecule, in agreement with theory, was established from analysis of its microwave spectrum at room temperature [9] and quartic centrifugal distortion constants [10] and the hyperfine constants [11] were determined later. The frequencies of the six fundamental vibrations and a harmonic force field were first derived from low-resolution studies of the IR spectra of HNSO and DNSO in the gas phase [12,13] and in matrices [14]. The structure and harmonic frequencies obtained from *ab initio* calculations [15] were found to be in good agreement with experimental data [16], especially when improved larger basis sets combined with experimental mass-dependent methods were used [17]. Carlotti et al. recorded the ν_1 fundamental at medium resolution (0.04–0.06 cm^{-1}) and reported partial rotational analyses for both HNSO [18] and DNSO [19]. The S—O stretching fundamental ν_2 of thionylimide, first analyzed at low

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resolution [16], was subsequently recorded and fully analyzed by high-resolution IR spectroscopy [20]. The upper state was found to be substantially perturbed by the $v_5 = 1$, $v_6 = 1$ combination level through both *a*- and *b*-axis Coriolis coupling. Even though no $\nu_5 + \nu_6$ band transitions were identified, treatment of the perturbations and avoided crossings in ν_2 permitted Joo and Clouthier to obtain the band origin and a set of rotational constants for the dark $v_5 = 1$, $v_6 = 1$ state [20]. An analysis of the N—S stretching (ν_3) and NSO bending (ν_5) fundamentals was reported using high-resolution FTIR spectroscopy [21]. An improved set of ground state rotational constants was obtained along with excited vibrational state constants for both bands, neither of which exhibited any perturbations.

In this work, we report the full analysis of two fundamentals of HNSO, ν_4 (HNS bending) and ν_6 (out of plane bending), using high-resolution Fourier transform infrared (FTIR) spectroscopy. The $v_4 = 1$ rotational levels are found to be seriously disturbed by global perturbations and local avoided crossings. We report how a global fit to transitions from ν_4, ν_6 and $2\nu_5$ can successfully treat all of these perturbations.

2. Experimental details

The high-resolution (0.0030 cm^{-1} unapodized) Fourier transform IR spectra of HNSO were recorded on a Bruker IFS 120 HR interferometer coupled to a multi-pass sample cell. The spectrometer was equipped with a mid-infrared Globar light source, a KBr beamsplitter and a liquid nitrogen cooled mercury-cadmium-telluride (MCT) photodetector. A longwave-pass optical filter (1% transmission at 1550 cm^{-1}) was inserted prior to the detector to restrict incident radiation while the 4P (4-point) apodization function was used to minimize instrumental linewidths. To obtain the spectra the multipass White cell (~53 cm), set for an optical path length of 4.24 m (8 passes), was held at room temperature with a total pressure of ca. 0.3 mbar. A total of ~200 scans were co-added to obtain a satisfactory S/N ratio.

HNSO was a by-product generated by reaction of thiazyl chloride (NSCl) with trace moisture in the cell. A continuous flow of NSCl through the cell was used to regulate the amount of byproducts formed

$$NSCl + H_2O \rightarrow HNSO + HCl$$
$$HNSO + H_2O \rightarrow NH_3 + SO_2$$

NSCl vapour was obtained from the pyrolysis of thiodiazyl dichloride ($S_3N_2Cl_2$) at 70 °C. A half-life of a few minutes was observed for conversion of NSCl to HNSO, measured by isolating the pyrolysis products in the cell and monitoring gas composition by rapid survey scans [22].

3. Results

As first reported from the microwave study [9] HNSO has a *cis* planar near-prolate structure of C_s symmetry. Its six fundamental IR modes of vibration are characterized as either *a*/*b*-type bands of a' symmetry (ν_1–ν_5) or *c*-type bands of a'' symmetry (ν_6) as indicated in Table 1. Also shown in the table are the band origins of all six fundamentals and two other bands. Apart from ν_1 all of the other band centres have been obtained from high-resolution IR studies.

A high-resolution IR spectrum of the ν_4 and ν_6 fundamentals of HNSO is shown in Fig. 1. The contour of the HNS bending fundamental, ν_4, is narrow (~869–940 cm^{-1}), indicative of an *a*-type band, although less intense *b*-type transitions were also identified by rovibrational analysis described below. The out of plane bending fundamental ν_6 (~690–830 cm^{-1}) is a typical *c*-type band consisting of a very strong central Q-branch and much weaker structure in the wings.

Initial line assignments were performed using MacLoomis, an interactive program written for Macintosh computers that displays experimental peak positions and their intensities in a Loomis–Wood format [23]. In this format, series of peaks with regular spacing (e.g. those sharing common values of K_a or of K_c in asymmetric tops) are displayed as vertical or near vertical sets of lines on the computer screen. This allows a set of related peaks (e.g. $^qR_5$ and $^qP_5$) to be selected and the Loomis–Wood display then updated by fitting to the polynomial expression for the rovibrational transitions of a linear molecule:

$$\begin{aligned}\bar{\nu} = \overline{\nu_0} &+ (B'' + B')m - (B'' - B' - D'' + D')m^2 \\ &- (2D'' + 2D' - H'' - H')m^3 + (D'' - D' - 3H'' + 3H')m^4 \\ &+ 3(H'' + H')m^5 - (H'' - H')m^6, \qquad (1)\end{aligned}$$

where $m = J''$ for P-branch and $m = J'' + 1$ for the R-branch transition. The set of selected peaks may be saved and their assignment confirmed by generating appropriate sets of ground state combination differences (GSCD) from a known set of constants [24]. Overlapped lines or lines close to splitting in K_a series were not selected in MacLoomis and hence not included in the data sets used in the least squares fitting. The fitting was performed with the SPFIT program written by Pickett [25], using Watson's *A*

Table 1
Vibrational band centres of HNSO (in cm^{-1})

Vibration	Band centre/cm^{-1}
$\nu_1(a')$ (NH stretch)	3308.5[a]
$\nu_2(a')$ (SO stretch)	1257.5808[b]
$\nu_3(a')$ (NS stretch)	1086.8331[c]
$\nu_4(a')$ (HNS bend)	905.8792[d]
$\nu_5(a')$ (NSO bend)	447.8500 [c]
$\nu_6(a'')$ (out-of-plane bend)	757.5210[d]
$\nu_5 + \nu_6$	1206.580[b]
$2\nu_5$	896.1851[d]

[a] Estimated from low-resolution spectra, Ref. [16].
[b] Ref. [20].
[c] Ref. [21].
[d] This work.