# $^{14}N$ Nuclear Quadrupole Hyperfine Structure in the Rotational Spectrum of Thionyl Aniline

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Nuclear quadrupole hyperfine structures have been resolved in the rotational spectrum of thionyl aniline, $C_6H_5NSO$, using pulsed molecular beam microwave Fourier transform spectroscopy. High precision nuclear quadrupole coupling constants, rotational and quartic centrifugal distortion constants have been determined from the analysis of 12 low-$J$ transitions. Coupling constants are $\chi_{aa} = +1.5730(14)$ MHz and $(\chi_{bb} - \chi_{cc}) = -5.6499(13)$ MHz, rotational constants are $A = 4026.7215(4)$ MHz, $B = 860.64732(8)$ MHz, and $C = 709.52027(7)$ MHz, and centrifugal distortion constants are $\Delta_J = 36.6(5)$ Hz, $\Delta_{JK} = -107.5(20)$ Hz, $\Delta_K = 703(68)$ Hz, $\delta_J = 8.1(5)$ Hz, and $\delta_K = 111(19)$ Hz (representation $I^r$ used).

## Introduction

Thionyl aniline is a member of the somewhat peculiar class of compounds containing the functional group $-N=S=O$. The simplest member of this class, $H-N=S=O$, has been studied in some detail by Kirchhoff [1]. According to this study, the molecule exists in the gas phase as a planar *cis*-conformer, i.e., the proton and the oxygen atom are located in a *cis*-position with respect to the $N=S$ double bond. The same conformation has been found in case of methyl thionyl amine $CH_3NSO$ [2]. In this case, no quadrupole coupling constants have ever been reported, whereas for HNSO and DNSO these constants have been determined [1]. The microwave spectrum of thionyl aniline has been assigned by Caminati et al. [3]. The conformation of this molecule has also been confirmed to be *cis*-planar, see Figure 1. However, again no quadrupole coupling constants have been determined so far. In order to shed some light on the bonding situation of the nitrogen atom in these molecules, we have now employed the very high resolution capability of pulsed molecular beam microwave Fourier transform spectroscopy (MB-MWFT) to study the hyperfine structures in the low $J$ rotational spectrum of thionyl aniline.

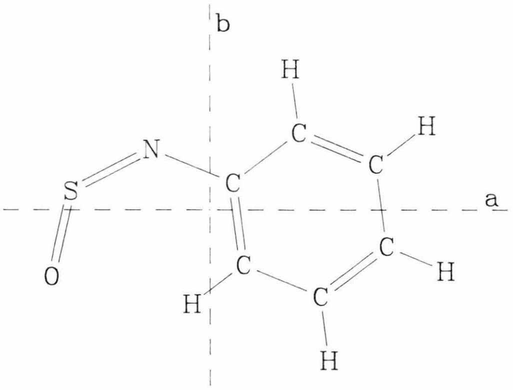

Fig. 1. Structure of thionyl aniline, *a* and *b*: principle inertia axes.

## Experimental

We used a commercial sample of thionyl aniline, supplied by Fa. Aldrich, Steinheim, Germany, without further purification. We started our work with the remeasurement of some lines already recorded by Caminati and co-workers, in order to optimize those parameters specific to beam spectroscopy, e.g., stagnation pressure and probe concentration. It soon became clear that the low volatility of the substance would present one of the major problems. We constructed a means to put a small amount of the substance directly into the nozzle housing and to heat the nozzle to about 70 °C with a hot water supply. This was only possible with the nozzle mounted in a position perpendicular to the mirror axis. This is the conventional set-up [4], but has the disadvantage of com-

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paratively less resolution and sensitivity. Accordingly, we could not resolve some of the strong *a*-type transitions, unfortunately those with some information about the coupling constant $(\chi_{bb}-\chi_{cc})$. Therefore we returned to our modified set-up with the nozzle mounted near the centre of one of the mirrors, with its axis collinear to the mirror axis. A bunch of glass-wool was then soaked with the substance and placed just upstream the nozzle. Despite the low vapour pressure of thionyl aniline, with this set-up we were able not only to detect and resolve the above mentioned *a*-type transitions, but also several weak *b*-type transitions. Because these are considerably more sensitive to the coupling constants, the statistical uncertainties could thus be reduced by more than an order of magnitude compared to the heated-nozzle results. Although only low-*J* transitions have been recorded, the precision of the measurements allowed us to calculate well determined quartic centrifugal distortion constants in addition to the rotational constants. A list of all measured lines is given in Table 1, an example for a highly resolved hyperfine structure is shown in Figure 2.

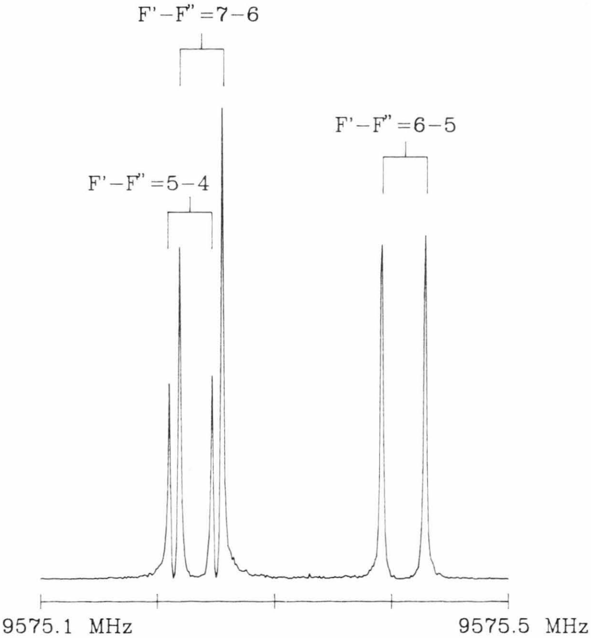

Fig. 2. Rotational transition $J'K'_aK'_c - J''K''_aK''_c = 6\,2\,4 - 5\,2\,3$ with nitrogen hyperfine structure. A collinear arrangement of beam and resonator axis was used. The Doppler splitting is 32.9 kHz. Recording conditions: polarizing pulse at 9575.3 MHz with 0.4 μs length and 0.07 mW pulse power, 100 ns sample interval, $8\,k = 8192$ data points, 1000 averaging cycles, stagnation pressure: $5 \cdot 10^4$ Pa (0.5 atm).

## Analysis

Because nitrogen hyperfine effects are much smaller than the separations of rotational energy levels, first order perturbation theory is entirely adequate for the analysis of the spectra. We chose the following two-step procedure: starting with the rotational constants of Caminati et al. [3], we first calculated angular momentum expectation values $\langle P_g^2 \rangle$, $g = a, b, c$. These were then used for the hyperfine structure analysis, centre frequencies being treated as fit parameters. The optimized line centre frequencies were then subjected to a fit of the rotational and centrifugal distortion constants. The operator used in this calculation is somewhat uncommon:

$$\begin{aligned}\mathscr{H}_{\text{rot}} = {} & \tfrac{1}{2}(B+C)\cdot \boldsymbol{P}^2 + \tfrac{1}{2}(2A-B-C)\cdot \boldsymbol{P}_z^2 \\ & + \tfrac{1}{2}(B-C)\cdot(\boldsymbol{P}_x^2-\boldsymbol{P}_y^2) - \Delta_J\cdot(\boldsymbol{P}^4-2\boldsymbol{P}^2) \\ & - \Delta_{JK}\cdot(\boldsymbol{P}^2\boldsymbol{P}_z^2-2\boldsymbol{P}_z^2) - \Delta_K\cdot(\boldsymbol{P}_z^4-\boldsymbol{P}_z^2) \\ & - 2\delta_J\cdot(\boldsymbol{P}^2-2)(\boldsymbol{P}_x^2-\boldsymbol{P}_y^2) \\ & - \delta_K\cdot\{(\boldsymbol{P}_z^2-1)((\boldsymbol{P}_x^2-\boldsymbol{P}_y^2)+(\boldsymbol{P}_x^2-\boldsymbol{P}_y^2)(\boldsymbol{P}_z^2-1)\},\end{aligned} \tag{1}$$

where

$$(B+C) = (B'+C'-4\Delta_J), \tag{1a}$$

$$(2A-B-C) = (2A'-B'-C'-4\Delta_{JK}-2\Delta_K), \tag{1b}$$

$$(B-C) = (B'-C'-8\delta_J-4\delta_K)\,. \tag{1c}$$

This is essentially the usual Watson *A*-reduction operator (representation $I^r$, i.e., $B_x = B$, $B_y = C$, $B_z = A$), however in a slightly different arrangement of terms: the quartic terms have been supplemented by appropriate quadratic operators. $A'$, $B'$, $C'$, $\Delta_J$, $\Delta_K$, $\Delta_{JK}$, $\delta_J$ and $\delta_K$ are the usual rotational and centrifugal distortion constants as defined by Watson. The corrections to the rotational constants are very small in the case of thionyl aniline but may be noticeable in other cases (especially for light molecules). The relation between these rotational constants and the moments of inertia is

$$\begin{aligned}B_\alpha = \tfrac{1}{2}\hbar^2\cdot\{(1/I_{\alpha\alpha}) + \tfrac{1}{2}\hbar^2\cdot(\tau_{\alpha\alpha\alpha\alpha}+\tau_{\alpha\alpha\beta\beta}+\tau_{\alpha\alpha\gamma\gamma} \\ +\tau_{\beta\gamma\beta\gamma}-\tau_{\beta\beta\gamma\gamma})\} \quad (\alpha, \beta, \gamma = x, y, z)\,.\end{aligned} \tag{2}$$

Correlations between rotational and centrifugal distortion constants are generally reduced with this operator, which is important as only 12 lines were used to determine eight parameters. The results of the analyses are given in Table 2. Note that the "freedom" [6] coefficients of all parameters are better than 7% and thus far from being critical. Another important feature

Table 1. Observed rotational transitions of thionyl aniline.
$\nu_0$ = centre frequencies (in MHz),
$\delta\nu_0$ = observed minus calculated values (in kHz),
$\nu_{hfs}$ = frequency offsets of hyperfine components (in kHz),
$\delta\nu_{hfs}$ = observed minus calculated values (in kHz).

| $J' K_a' K_c'$ | $J'' K_a'' K_c''$ | $F'$ | $F''$ | $\nu_0$ | $\nu_{hfs}$ | $\delta\nu_0$ | $\delta\nu_{hfs}$ |
|---|---|---|---|---|---|---|---|
| *a*-type transitions: | | | | | | | |
| 6 0 6 | 5 0 5 | | | 9242.8419 | | 0.18 | |
| | | 7 | 6 | | 33.4 | | 0.2 |
| | | 6 | 5 | | −89.6 | | −0.1 |
| | | 5 | 4 | | 61.6 | | −0.4 |
| 7 0 7 | 6 0 6 | | | 10714.4009 | | 0.04 | |
| | | 8 | 7 | | 38.6 | | 0.1 |
| | | 7 | 6 | | −95.8 | | −0.1 |
| | | 6 | 5 | | 60.3 | | −0.2 |
| 6 1 6 | 5 1 5 | | | 8928.4802 | | −0.05 | |
| | | 7 | 6 | | 10.3 | | 0.2 |
| | | 6 | 5 | | −10.4 | | −0.3 |
| | | 5 | 4 | | − 5.4 | | 0.2 |
| 6 2 4 | 5 2 3 | | | 9575.2907 | | 0.01 | |
| | | 7 | 6 | | −54.0 | | 0.3 |
| | | 6 | 5 | | 118.7 | | 0.0 |
| | | 5 | 4 | | −62.8 | | −0.7 |
| 6 2 5 | 5 2 4 | | | 9397.2329 | | 0.00 | |
| | | 7 | 6 | | −15.3 | | −0.2 |
| | | 6 | 5 | | 29.6 | | 0.3 |
| | | 5 | 4 | | −12.0 | | 0.1 |
| 5 3 2 | 4 3 1 | | | 7870.2207 | | −0.05 | |
| | | 6 | 5 | | −72.0 | | −0.1 |
| | | 5 | 4 | | 193.0 | | 0.0 |
| | | 4 | 3 | | −133.8 | | 0.1 |
| 5 3 3 | 4 3 2 | | | 7867.8020 | | 0.04 | |
| | | 6 | 5 | | −70.6 | | −0.2 |
| | | 5 | 4 | | 189.4 | | 0.2 |
| | | 4 | 3 | | −131.2 | | 0.3 |
| *b*-type transitions: | | | | | | | |
| 3 1 3 | 2 0 2 | | | 7500.7959 | | 0.00 | |
| | | 4 | 3 | | 243.3 | | 0.0 |
| | | 3 | 2 | | −781.5 | | −0.1 |
| | | 2 | 1 | | 697.7 | | 0.5 |
| 4 1 4 | 3 0 3 | | | 8779.5672 | | 0.01 | |
| | | 5 | 4 | | 248.0 | | 0.1 |
| | | 4 | 3 | | −707.6 | | −0.1 |
| | | 3 | 2 | | 532.0 | | 0.0 |
| 5 1 5 | 4 0 4 | | | 10002.4228 | | −0.11 | |
| | | 6 | 5 | | 241.4 | | −0.1 |
| | | 5 | 4 | | −641.4 | | −0.2 |
| | | 4 | 3 | | 439.4 | | 0.2 |
| 7 0 7 | 6 1 6 | | | 8773.4209 | | −0.09 | |
| | | 8 | 7 | | −154.5 | | 0.2 |
| | | 7 | 6 | | 387.1 | | −0.2 |
| | | 6 | 5 | | −246.8 | | 0.0 |
| 5 2 3 | 5 1 4 | | | 8796.7709 | | 0.00 | |
| | | 6 | 6 | | 218.8 | | 0.4 |
| | | 5 | 5 | | −567.6 | | 0.2 |
| | | 4 | 4 | | 377.2 | | −1.4 |

of the operator (1) is that for an S-reduction, only the last term has to be replaced by an appropriate term dependent on the constant $R_6'$. The rotational constants remain unchanged! They are therefore "determinable" constants.

Table 2. Spectroscopic parameters of thionyl aniline: rotational constants, quartic centrifugal distortion constants (Watson's *A*-reduction, representation $I^r$ used), and nuclear quadrupole coupling constants.

| | | Freedom |
|---|---|---|
| $A$ | = 4026.7215(4) MHz | 9.9% |
| $B$ | = 860.64732(8) MHz | 8.7% |
| $C$ | = 709.52027(7) MHz | 7.8% |
| $\Delta_J$ | = 36.6(5) Hz | 9.7% |
| $\Delta_{JK}$ | = −107.5(20) Hz | 36.3% |
| $\Delta_K$ | = 703(68) Hz | 15.5% |
| $\delta_J$ | = 8.1(5) Hz | 14.1% |
| $\delta_K$ | = 111(19) Hz | 16.3% |
| Standard deviation of the fit: | | $\sigma_{rot} = 0.13$ kHz |
| $\chi_{aa}$ | = +1.5730(14) MHz | |
| $(\chi_{bb}-\chi_{cc})$ | = −5.6499(13) MHz | $\sigma_{hfs} = 0.30$ kHz |
| $\chi_{bb}$ | = −3.6115(14) MHz | |
| $\chi_{cc}$ | = 2.0384(14) MHz | |

## Conclusion

The analysis of the rotational spectrum of thionyl aniline in its vibrational ground state confirmed that the molecule is a planar *cis*-conformer. The centrifugal distortion constants, which are rather precise despite their smallness, are comparable to those of other heavy molecules, and therefore appear reasonable.

Additionally we provide a set of very accurate nitrogen quadrupole coupling constants. Interpretation of these constants is, however, hardly possible without the help of *ab-initio* calculations. We hope that further work on this somewhat strange class of molecules, both theoretical and experimental, will give some more information about the molecular parameters.

The accuracy of all determined parameters benefits from the inherently high resolution of the MB-MWFT method as applied in our laboratory, of about 2 kHz (FWHH). The high precision enabled us to determine a complete set of accurate centrifugal distortion constants from rotational transitions with a maximum *J* and *K* of only 7 and 3, respectively.

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