Nitrogen Quadrupole Coupling of Nitrosobenzene
An Application of Microwave Fourier Transform Spectroscopy

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The microwave spectrum of nitrosobenzene, C_6H_5NO, was first investigated by Hanyu et al. in its ground state [1] and excited torsional and vibrational states [2].
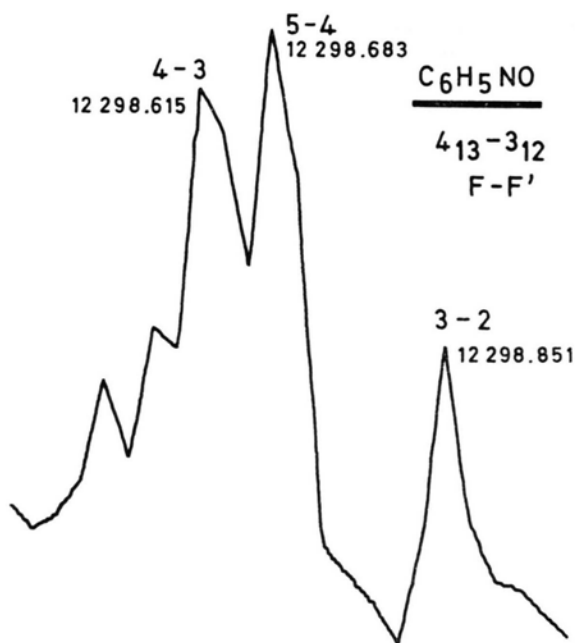

Fig. 1. A range out of a 25 MHz scan of the nitrosobenzene rotational spectrum. $J_{K-K+} - J'_{K-'K+'} = 4_{13} - 3_{12}$. Measuring time 47 min. (7×10^6 average cycles) Sample interval 20 ns in the time domain, 1024 data points incremented by 1024 zeros before Fourier transformation. Pressure = 0.4 mTorr, temperature = 233 K. Frequencies in MHz. The recording of the transitions of nitrosobenzene was more difficult than that of other substances. So the splitting pattern is of minor quality compared to other substances. It is limited by the spectral point width of approx. 25nHz.

* The lines of Table I marked with "a" and $5_{42}-6_{43}$, $5_{41}-6_{42}$, $6_{42}-7_{43}$ have been omitted.

By use of Microwave Fourier transform Spectroscopy [3, 4] we were able to resolve the nitrogen hyperfinestructure (hfs).

Nitrosobenzene with a purity of 97% was purchased from Ega Chemie, Steinheim, and sublimated into the cell. The spectra were taken at pressures in the range of 0.3 to 1.5 mTorr and at a temperature of 233 K.

To check our measurements and assignments we carried out a centrifugal distortion analysis [5, 6] with the lines of Table 1 together with those measured by Hanyu et al. (Table I) *.

Table 1. Measured lines (MHz) of nitrosobenzene with hfs splitting. The intensity weighted mean frequency $\bar{\nu}$ [8] was used for the centrifugal distortion analysis. $\Delta\nu_{calc}$ was calculated with the constants of Table 2. Accuracy of ν_{exp} 20 kHz. Mean square deviation of $\Delta\nu_{calc}$ 20 kHz.

$J_{K-K+} - J'_{K-'K+'}$	$F - F'$	ν_{exp}	$\bar{\nu}$	$\Delta\nu_{exp}$	$\Delta\nu_{calc}$
$3_{03} - 2_{02}$	4 — 3	8566.408	8566.301	0.335	0.272
	2 — 1				
	3 — 2	8566.073			
$3_{13} - 2_{12}$	4 — 3	8080.709	8080.601	0.125	0.113
	3 — 2	8080.584		0.191	0.178
	2 — 1	8080.393			
$3_{22} - 2_{21}$	4 — 3		8685.733	—	0.012
	3 — 2	8685.733			
	2 — 1				
$4_{03} - 3_{03}$	5 — 4	11289.824	11289.709	0.352	0.343
	3 — 2				
	4 — 3	11289.472			
$4_{13} - 3_{12}$	3 — 2	12298.851	12298.703	0.168	0.163
	5 — 4	12298.683			
	4 — 3	12298.615		0.068	0.058
$4_{14} - 3_{13}$	5 — 4	10742.294	10742.217	0.134	0.121
	4 — 3				
	3 — 2	10742.160			
$4_{22} - 3_{21}$	4 — 3	11848.927	11848.719	0.309	0.292
	5 — 4				
	3 — 2	11848.618			
$6_{15} - 6_{16}$	6 — 6	8099.791	8097.387	3.343	3.340
	7 — 7	8096.448		0.558	0.564
	5 — 5	8095.890			
$7_{16} - 7_{17}$	7 — 7	10664.569	10662.265	3.233	3.245
	8 — 8	10661.336		0.472	0.468
	6 — 6	10660.864			

Table 2. Rotational and centrifugal distortion constants of nitrosobenzene. Highest correlation coefficient was $|(\Delta K, \delta K)| = 0.91$. — Quadrupole coupling constants. Correlation 0.02. Standard errors are given.

A		5248.87	$\pm$ 0.5	MHz
B		1643.261	$\pm$ 0.02	MHz
C		1252.002	$\pm$ 0.01	MHz
$\varkappa$		$-\ 0.804216$		
Δ_J		0.007	$\pm$ 0.1	kHz
Δ_{JK}		0.36	$\pm$ 0.5	kHz
Δ_K		$-\ 262.0$	± 200.0	kHz
δ_J		0.03	$\pm$ 0.05	kHz
δ_K		$-\ 9.4$	$\pm$ 7.0	kHz
$\chi^+ = \chi_{bb} + \chi_{cc}$		0.037	$\pm$ 0.06	MHz
$\chi^- = \chi_{bb} - \chi_{cc}$	$-$	9.997	$\pm$ 0.05	MHz
	χ_{aa}	$-\ 0.037$	$\pm$ 0.06	MHz
	χ_{bb}	$-\ 4.968$	$\pm$ 0.06	MHz
	χ_{cc}	$+\ 5.005$	$\pm$ 0.06	MHz

The results are given in Table 2. Due to the limited number of lines and the large errors, we take this analysis only as a kind of interpolation to check the assignment. The standard deviation was 115 kHz. An example of a hfs splitted line is given in Figure 1.

An analysis of the hfs by first order perturbation theory results in the coupling constants given in Table 2. The hfs analysis was checked by a program using direct diagonalisation [7]. No difference was found. A mean splitting of 775 kHz was fitted with 20 kHz mean square deviation. These calculations also showed that no line splitting in the range of the MWFT-Spectrometer is sensitive to χ_{ab}.

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