Nitrogen Quadrupole Coupling in the Microwave Spectra of Phenyl Isocyanate and Phenyl Isothiocyanate

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The microwave spectra of phenyl isocyanate, C_6H_5NCO, and phenyl isothiocyanate, C_6H_5NCS, have been measured by microwave Fourier transform spectroscopy between 4.7 and 8.0 GHz and analysed for nuclear quadrupole hyperfine splitting due to ^{14}N.

1. Introduction

Some years ago the microwave spectra of phenyl isocyanate, C_6H_5NCO, and phenyl isothiocyanate, C_6H_5NCS, were measured and assigned by Bouchy and Roussy [1] and Onda et al. [2], respectively.

They determined the rotational constants, proved that these molecules are planar and that the NCO and NCS group, respectively, is tilted with respect to the C_2 phenyl axis. Furthermore for phenyl isocyanate a partial centrifugal distortion analysis was given and the dipole moment was determined [1]. So far the nuclear quadrupole hyperfine structure (hfs) due to ^{14}N for these molecules was not reported.

We investigated the rotational spectra in the region 4.7 to 8.0 GHz with the high resolution of microwave Fourier transform (MWFT) spectroscopy to resolve the nitrogen hfs.

2. Experimental

Phenyl isocyanate and isothiocyanate were purchased from Merck-Schuchardt, Hohenbronn bei München, and used after vacuum destillation.

The spectra were recorded in the range 4.7 to 8.0 GHz by use of a microwave Fourier transform spectrometer which was modified in comparison to that described in [3]. Details of this schema will be published [4].

By a fault of the travelling wave tube (TWT) amplifier, see part 17 in Fig. 1 of [3], we were forced to work with the signal source alone, which delivers approximately 100 mW in some ranges. This resulted in a remarkable decrease of sensitivity and of the range of polarization. Because the ^aQ type transitions of phenyl isothiocyanate are of low intensity and, as lines of this type were not measured until now, the frequency prediction was inaccurate, it was not possible to observe these lines without the TWT

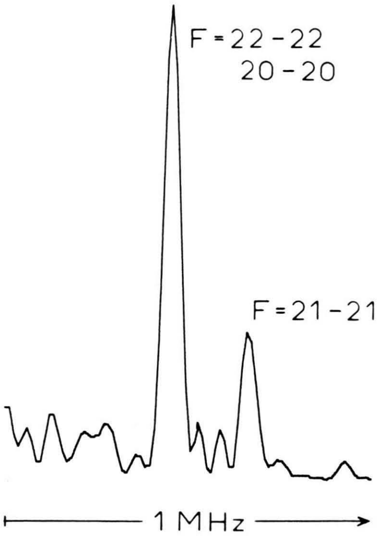

Fig. 1. $J_{K_- K_+} = 21_{2\,19} - 21_{2\,20}$ transition of phenyl isothiocyanate, $C_6H_5{-}NCS$, with nitrogen quadrupole hyperfine structure. A section of 1 MHz out of 25 MHz range of the power spectrum is given. Sample interval 20 ns, 32 000 k cycles, 1024 data points supplemented bei 3072 zeros, pressure 0.07 Pa (0.5 mTorr), temperature – 18 °C.

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Table 1a. Measured frequencies ν_{obs} of phenyl isocyanate, C_6H_5NCO, refined by line contour analysis of overlapping hfs components. $\nu_{unsplit}$: hypothetical frequency without hfs-splitting. Frequencies in MHz.

$J'\,K'_-\,K'_+ - J\,K_-\,K_+$	$F' - F$	ν_{obs}	$\nu_{unsplit}$
3 0 3 − 2 0 2	4−3; 3−2 2−1	5 360.591 5 360.762	5 360.619
3 1 2 − 2 1 1	4−3; 2−1 3−2	5 603.845 5 604.079	5 603.914
3 1 3 − 2 1 2	4−3; 2−1 3−2	5 144.746 5 144.986	5 144.818
3 2 1 − 2 2 0	2−1 4−3 3−2	5 392.550 5 393.027 5 393.895	5 393.221
3 2 2 − 2 2 1	2−1 4−3 3−2	5 376.257 5 376.728 5 377.610	5 376.929
4 0 4 − 3 0 3	5−4; 4−3 3−2	7 128.575 7 128.654	7 128.592
4 1 3 − 3 1 2	5−4 3−2 4−3	7 466.913 7 466.955 7 467.024	7 466.956
4 1 4 − 3 1 3	5−4 3−2 4−3	6 855.113 6 855.151 6 855.223	6 855.155
4 2 2 − 3 2 1	3−2 5−4 4−3	7 206.459 7 206.572 7 206.943	7 206.665
4 2 3 − 3 2 2	3−2 5−4 4−3	7 165.852 7 165.951 7 166.300	7 166.041
4 3 1 − 3 3 0	5−4 4−3	7 177.398 7 178.201	7 177.594
4 3 2 − 3 3 1	5−4 4−3	7 176.983 7 177.791	7 177.181
8 1 7 − 8 1 8	9−9; 7−7 8−8	5 478.599 5 478.667	5 478.622
14 2 12 − 14 2 13	15−15; 13−13 14−14	5 722.632 5 722.687	5 722.651
15 2 13 − 15 2 14	16−16; 14−14 15−15	7 092.185 7 092.236	7 092.201

Table 1b. Measured frequencies ν_{obs} of phenyl isothiocyanate refined by line contour analysis. $\nu_{unsplit}$ hypothetical frequency without ^{14}N hfs-splitting. – Frequencies in MHz. (* Not used for centrifugal distortion analysis.)

$J'\,K'_-\,K'_+ - J\,K_-\,K_+$	$F' - F$	ν_{obs}	$\nu_{unsplit}$
4 0 4 − 3 0 3	5−4; 4−3 3−2	4 792.718 4 792.775	4 792.722
4 1 3 − 3 1 2	5−4 4−3	4 936.494 4 936.580	4 936.528
4 2 2 − 3 2 1	3−2 5−4 4−3	4 807.360 4 807.440 4 807.689	4 807.501
4 3 1 − 3 3 0 4 3 2 − 3 3 1	3−2 5−4 4−3	4 801.587 4 801.812 4 802.392	4 801 953 *
5 0 5 − 4 0 4		5 985.143	5 985.143
5 1 4 − 4 1 3		6 169.174	6 169.174
5 1 5 − 4 1 4		5 825.109	5 825.109
5 2 3 − 4 2 2	6−5; 4−3 5−4	6 014.113 6 014.256	6 014.158
5 2 4 − 4 2 3	6−5; 4−3 5−4	5 998.749 5 998.900	5 998.799
5 3 2 − 4 3 1	4−3 6−5 5−4	6 003.073 6 003.145 6 003.433	6 003.222
5 3 3 − 4 3 2	4−3 6−5	6 002.944 6 003.024	6 003.101
5 4 1 − 4 4 0 5 4 2 − 4 4 1	4−3 6−5 5−4	6 001.957 6 002.098 6 002.624	6 002.239
6 0 6 − 5 0 5		7 173.773	7 173.773
6 1 5 − 5 1 4		7 400.795	7 400.795
6 1 6 − 5 1 5		6 988.077	6 988.077
6 2 4 − 5 2 3	7−6; 5−4 6−5	7 223.928 7 224.019	7 223.959
6 2 5 − 5 2 4	7−6; 5−4 6−5	7 197.109 7 197.192	7 197.136
6 3 3 − 5 3 2	7−6; 5−4 6−5	7 204.927 7 205.114	7 204.988
6 3 4 − 5 3 3	7−6; 5−4 6−5	7 204.607 7 204.792	7 204.667 *
6 4 2 − 5 4 1 6 4 3 − 5 4 2	5−4 7−6 6−5	7 203.073 7 203.152 7 203.452	7 203.230
6 5 1 − 5 5 0 6 5 2 − 5 5 1	5−4 7−6 6−5	7 202.308 7 202.437 7 202.901	7 202.556
21 2 19 − 21 2 20	22−22; 20−20 21−21	5 403.350 5 403.551	5 403.417
22 2 20 − 22 2 21	23−23; 21−21 22−22	6 274.181 6 274.395	6 274.252
23 2 21 − 23 2 22	24−24; 22−22 23−23	7 215.616 7 215.831	7 215.687

amplifier. After its repair we were able to measure these lines, see Table 1 b.

The sample pressure was around 0.1 Pa (0.8 mTorr) and the cell temperature was around −20 °C for both substances.

3. Spectra and Analysis

The measured frequencies and their assignments are listed in Table 1 a and 1 b for phenyl isocyanate and phenyl isothiocyanate, respectively. Figure 1 gives an example of the recordings. The measurements are refined by line contour analyses [5].

The ^{14}N hyperfine structure was analysed by first order perturbation theory to provide the quadrupole coupling constants (program HT1NQ and DH14KS). We proved that no line of the two molecules in the range of our spectrometer is sensitive enough to the off diagonal elements χ_{ab} of the quadrupole coupling tensors. The results for the hfs analyses are given in Table 2. The standard deviation of the fits are 9 kHz for mean experimental splittings of 303 kHz and 210 kHz for phenyl isocyanate and isothiocyanate, respectively.

Table 2. Quadrupole coupling constants of phenyl isocyanate, C_6H_5NCO, and phenyl isothiocyanate, C_6H_5NCS. For the hfs analyses rotational constants of Table 3a and 3b were taken. Standard deviations in brackets in units of the last digit. σ = standard deviation of the fit, $\overline{\Delta\nu}$ = mean experimental hfs-splitting, $|(\chi_+, \chi_-)|$ = correlation coefficient.

	C_6H_5NCO	C_6H_5NCS
χ_+ [MHz]	− 2.701 (12)	− 1.925 (14)
χ_- [MHz]	− 0.186 (18)	− 0.942 (23)
χ_{aa} [MHz]	2.701 (12)	1.925 (14)
χ_{bb} [MHz]	− 1.444 (15)	− 1.434 (18)
χ_{cc} [MHz]	− 1.258 (15)	− 0.491 (18)
$\overline{\Delta\nu}$ (kHz)	303	201
σ [kHz]	9	9
$\|(\chi_+, \chi_-)\|$	0.024	0.018

The deviations from the hypothetical rigid rotor lines were added to the observed frequencies ν_{obs} of the hfs components. The hypothetical hfs unsplit line was then calculated as a mean value, see Table 1a and 1b.

For phenyl isocyanate we included the frequencies $\nu_{unsplit}$ of Table 1a and the lines of Table I of [1], and for phenyl isothiocyanate those of Table 1b and Table 1 of [2], respectively, to perform centrifugal distortion analyses to fourth order with the Hamiltonian of Watsons A reduction [6] (program ZFAP4 [7]).

Because in [1] and [2] only $^aR_{01}$ type transitions $(J_{K_-K_+} - (J+1)_{K_-(K_++1)})$ were observed and also in this work the measured lines were mostly of this type, it was not possible to determine Δ_K and δ_K.

When we take $v = \left(\sum_i (\nu_{i,\,obs} - \nu_{i,\,calc})^2/n\right)^{1/2}$ as a measure of precision, we get for phenyl isocyanate 16 kHz for the 15 lines measured by MWFT spectroscopy and 75 kHz for those of Table 1 of [1], and for phenyl isothiocyanate 32 kHz for the 22 lines measured by us and 212 kHz for those of Table 1 of [2].

To take into account the higher precision of the frequencies measured by MWFT spectroscopy we

Table 3a. Rotational and centrifugal distortion constants of phenylisocyanate, C_6H_5NCO. Standard deviations in brackets in units of the last digit. Assumptions in square brackets. $\varkappa$ = asymmetry parameter.

		Correlation coefficient matrix					
A [MHz]	5 202.103 (46)	1.00					
B [MHz]	972.68072 (62)	0.04	1.00				
C [MHz]	819.62766 (61)	−0.07	0.67	1.00			
Δ_J [kHz]	0.0689 (11)	−0.14	0.75	0.70	1.00		
Δ_{JK} [kHz]	−0.209 (16)	0.19	0.07	0.16	−0.27	1.00	
δ_J [kHz]	0.01210 (77)	−0.69	0.28	−0.20	0.16	−0.17	1.00
Δ_K [kHz]	[0.0]						
δ_K [kHz]	[0.0]						
$\varkappa$	−0.930152						

Table 3b. Rotational and centrifugal distortion constants of phenyl isothiocyanate, C_5H_5NCS, see Table 3a.

		Correlation coefficient matrix					
A [MHz]	5 219.03 (38)	1.00					
B [MHz]	634.4716 (16)	0.87	1.00				
C [MHz]	565.6340 (17)	−0.87	−0.68	1.00			
Δ_J [kHz]	0.0489 (52)	−0.03	0.24	0.29	1.00		
Δ_{JK} [kHz]	−0.134 (53)	−0.02	0.19	0.24	0.07	1.00	
δ_J [kHz]	0.00918 (54)	0.56	0.74	−0.70	−0.03	0.09	1.00
Δ_K [kHz]	[0.0]						
δ_K [kHz]	[0.0]						
$\varkappa$	−0.970414						

Table 4a. Quadrupole coupling constants [MHz] of some isocyanates.

	χ_{aa}	χ_{bb}	χ_{cc}	
H−NCO	2.056 (11)	−0.473 (10)	−1.583 (10)	[8]
CH_3−NCO	2.836 (8)	−1.288 (21)	−1.548 (21)	[9]
C_2H_5−NCO	2.529 (16)	−1.137 (20)	−1.392 (20)	[10]
C_6H_5−NCO	2.701 (12)	−1.444 (15)	−1.258 (15)	this work
trans-CH_2=CH−NCO	2.52 (2)	−1.56 (1)	−0.96 (2)	[11]
cis-CH_2=CH−NCO	2.76 (2)	−1.88 (1)	−0.88 (1)	[11]

Table 4b. Quadrupole coupling constants [MHz] of some isothiocyanates.

	χ_{aa}	χ_{bb}	χ_{cc}	
H−NCS	1.114 (26)	−0.530 (71)	−0.585 (71)	[12]
CH_3−NCS	1.866 (7)	−1.112 (18)	−0.754 (18)	[9]
C_2H_5−NCS	1.873 (18)	−1.264 (26)	−0.609 (26)	[13]
C_6H_5−NCS	1.925 (14)	−1.434 (18)	−0.491 (18)	this work

performed analyses, where we weighted our measurements by a factor five with respect to those measured by [1] and by a factor ten with respect to those measured by [2], respectively.

The results are given in Table 3a and 3b.

As only few measurements of the hfs in rotational spectra of isocyanates and isothiocyanates have been reported we give in Table 4a and 4b a comparison of the coupling constants.

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