Internal Rotation Analysis of the Ground State Microwave Spectrum of 2-Iodopropene

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Z. Naturforsch. **49a,** 497–502 (1994); received December 10, 1993

The ground state microwave spectrum of 2-iodopropene has been reinvestigated using Fourier transform microwave spectroscopy. The barrier hindering methyl internal rotation could be obtained from narrow splittings of high-*J* lines. In addition an improved hyperfine structure and centrifugal distortion analysis resulted in refined constants and an approximate determination of the iodine spin-rotation coupling parameters.

Introduction

The microwave spectrum of 2-iodopropene, $CH_3-CI=CH_2$, was for the first time investigated by Groner and Bauder [1]. They assigned *a*-type R- and Q-branch spectra, determined rotational, centrifugal distortion and quadrupole coupling constants and obtained the barrier hindering methyl internal rotation from transitions in the first excited torsional state.

We reinvestigated the spectrum of 2-iodopropene using Fourier transform microwave (FTMW) spectroscopy. Due to the higher resolution capability of this method we were able to resolve the internal rotation splittings in the torsional ground state like in the cases of other 2-halopropenes [2–4].

In addition we present a new analysis of the ground state spectrum. We obtained refined rotational, centrifugal distortion and iodine quadrupole coupling constants using a global least squares fit procedure and could detect a small influence of the iodine spin-rotation coupling.

Experimental

23 *a*-type Q-branch transitions have been recorded with our FTMW spectrometers in the frequency range 5 to 33 GHz [5–10]. The sample of 2-iodopropene was kindly provided by Prof. A. Bauder, Zürich, and used without further purification. The measurements were carried out at pressures between 0.03 and 0.13 Pa (0.25 and 1 mTorr) and temperatures between 233 K and 293 K.

Analysis

As the constants published in [1] gave a good prediction of the microwave spectrum, our measurements could easily be extended to other transitions and frequency ranges. From the assumed structure of 2-iodopropene strong *a*-type and weak *b*-type transitions should be expected, but only *a*-type lines could be observed. The high-*J* Q-branch transitions split into six components in consequence of the iodine quadrupole coupling. Every component shows an additional splitting into a narrow doublet due to the hindered methyl internal rotation. An example is given in Figure 1. All measured frequencies, corrected by a line shape analysis [11], are given in Table 1.

The iodine hyperfine structure and centrifugal distortion analysis due to the 4th order Van Eijck/Typke Hamiltonian [12, 13] has been carried out with our program HFS [14, 15] using the A-species lines in the case of internal rotation splittings. Attempts to fit the 6th order centrifugal distortion constants failed because their contributions to the measured frequencies are very small also for high *J* lines.

The program HFS enables a direct diagonalization of the complete Hamiltonian matrix and a global least squares fit of the rotational, centrifugal distortion, iodine quadrupole and spin-rotation coupling constants to the measured frequencies. This method has the advantage that rotational and centrifugal distortion constants may be improved considering the dependence of higher order quadrupole perturbations from rotational energy level differences. For 2-iodopropene higher order contributions appear mainly from the off diagonal component χ_{ab} of the quadrupole coupling tensor.

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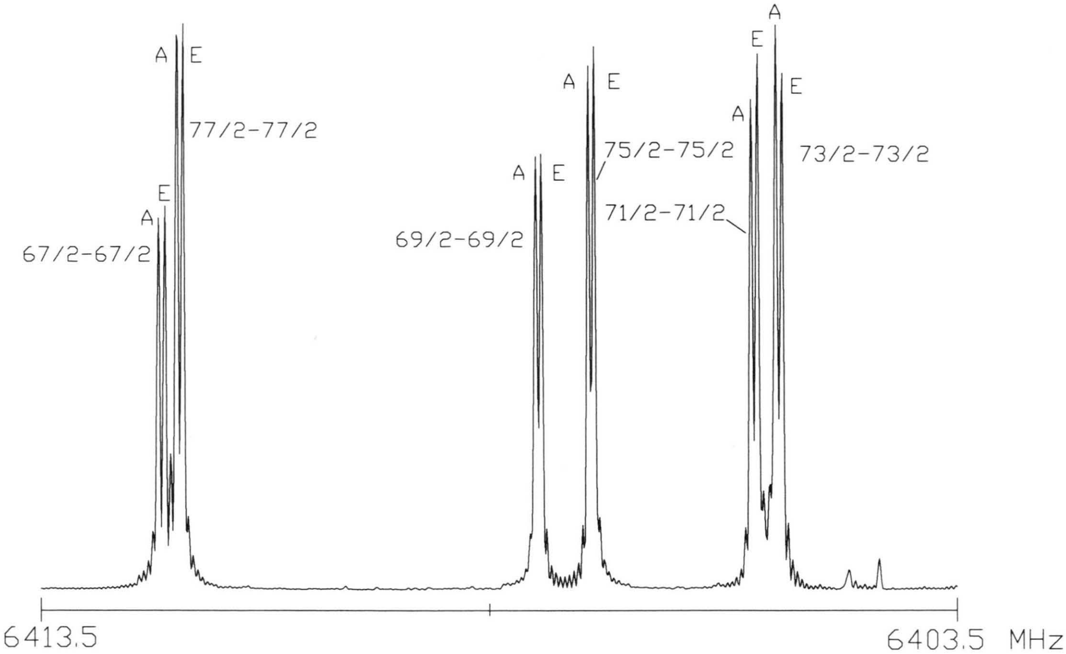

Fig. 1. The $J' K'_- K'_+ - J K_- K_+ = 36\ 7\ 29 - 36\ 7\ 30$ transition of 2-iodopropene showing iodine hyperfine structure and internal rotation splittings. A 10 MHz section out of a 25 MHz power spectrum record is displayed. The components are marked with the F quantum numbers and the internal rotation symmetry species. Experimental conditions: Temperature 243 K, pressure: 0.1 Pa, sample interval: 20 ns, polarizing frequency: 6408.5 MHz, 1024 measuring points supplemented with 3072 zeros before Fourier transformation, 250*32 k averaging cycles.

In a first attempt we used only our FTMW Q-branch measurements for the analysis. The correspondence between experimental and calculated data was excellent (total standard deviation: 4.5 kHz) but the amount of available information is limited in this case. Only two combinations of rotational constants and a restricted set of the other parameters are then determinable with high accuracy. So we decided to include some of the low J R-branch measurements given in [1] to obtain some more information. We used lines up to $J = 4$ and $K_- = 2$ with estimated contributions from the methyl internal rotation being far below our resolution limit. Due to the lower accuracy of the frequencies given in [1] compared to the FTMW measurements the total standard deviation of our fit increased to 14 kHz but all relevant parameters including the iodine spin-rotation coupling constants C_{bb} and C_{cc} could be determined with sufficient precision. Calculations excluding the spin-rotation coupling resulted in increasing errors for all other constants. So we think that an observable contribution from the spin-rotation coupling is present in the spectrum in spite of the altogether lower accuracy. The results of the fit and the components of the quadrupole coupling tensor in its own principal axes system are given in Table 2.

Because the splittings originating from the methyl internal rotation are of the same magnitude for all hyperfine components of one transition for 2-iodopropene we assumed no measurable effect from an interaction between both perturbations. So the internal rotation problem has been treated independently. We calculated hypothetical hyperfine free center frequencies using the constants of Table 2. The internal rotation splitting, averaged over all hyperfine components of one transition, had been added and the analysis carried out using Wood's IAM method [16, 17] in the high barrier approximation with our program KC3IAM [18]. The center frequencies and average internal rotation splittings are given in Table 3. The agreement between observed and calculated splittings was excellent, but like in the cases of 2-chloropropene and 2-bromopropene [2, 3] not all three possible internal rotation parameters could be determined simultaneously. A fit of the Fourier coefficient $w_1(s)$, a function of the reduced barrier s, the angle $\sphericalangle\,(a, i)$ between

Table 1. FTMW measurements of 2-iodopropene with hyperfine structure and internal rotation splittings. ν_{exp}: observed A-species frequency (MHz), $\Delta\nu_{\text{exp}}$: observed internal rotation (A−E) splitting (kHz), δ_{hfs}: observed minus calculated A-species frequencies using the constants of Table 2a (kHz), *: A−E splitting not resolved.

$J' K'_- K'_+$	$J K_- K_+$	$2F$	$2F'$	ν_{exp}	$\Delta\nu_{\text{exp}}$	δ_{hfs}
5 1 4	5 1 5	15	15	6735.462	*	5.6
		13	13	6719.768	*	−4.7
		11	11	6716.567	*	1.8
		9	9	6721.271	*	−2.2
		5	5	6741.855	*	−0.1
9 2 7	9 2 8	23	23	5892.039	*	−6.4
		21	21	5877.125	*	−2.2
		19	19	5873.393	*	−1.9
		17	17	5876.300	*	−5.4
		15	15	5883.795	*	−3.2
		13	13	5894.334	*	−2.8
12 2 10	12 2 11	29	29	14528.222	34	3.1
		27	27	14512.630	33	3.7
		21	21	14517.865	31	7.3
		19	19	14530.629	34	5.7
13 2 11	13 2 12	31	31	18280.694	40	2.5
		21	21	18282.889	36	−6.1
17 3 14	17 3 15	39	39	14824.334	42	1.9
		37	37	14810.636	43	5.5
		35	35	14805.202	44	1.3
		33	33	14806.730	43	2.3
		31	31	14814.009	41	10.0
		29	29	14825.898	41	1.6
18 3 15	18 3 16	41	41	18741.512	52	2.3
		39	39	18727.321	52	1.4
		37	37	18721.630	51	1.6
		35	35	18723.127	53	1.9
		33	33	18730.623	48	−0.7
		31	31	18743.043	52	3.7
19 3 16	19 3 17	43	43	23101.276	59	−4.6
		41	41	23086.900	60	−1.6
		39	39	23081.091	59	−1.0
		37	37	23082.535	59	−1.8
		35	35	23090.082	60	−3.1
		33	33	23102.719	59	−3.7
21 4 17	21 4 18	47	47	10628.330	41	−12.4
		45	45	10618.008	40	2.2
		43	43	10613.713	40	5.5
		41	41	10614.667	41	2.6
		39	39	10620.109	39	1.0
		37	37	10629.285	42	−11.0
22 4 18	22 4 19	49	49	13972.670	51	−1.4
		47	47	13961.188	50	3.5
		45	45	13956.372	51	4.2
		43	43	13957.383	52	2.6
		41	41	13963.415	52	2.3
		39	39	13973.697	51	0.7
24 4 20	24 4 21	53	53	22300.258	73	−0.8
		51	51	22287.217	73	6.4
		49	49	22281.676	70	−3.8
		47	47	22282.735	74	−1.4
		45	45	22289.542	73	5.0
		43	43	22301.314	73	0.4
26 4 22	26 4 23	57	57	32522.932	93	−5.3
		55	55	32508.515	93	7.9
		53	53	32503.365	102	8.6
		51	51	32504.678	95	−8.3
		49	49	32510.975	95	−6.8
		47	47	32522.246	91	3.6
25 5 20	25 5 21	55	55	6839.008	34	1.8
		53	53	6832.273	33	3.3
		51	51	6829.383	33	4.7
		49	49	6829.925	34	3.8
		47	47	6833.449	33	1.5
		45	45	6839.498	34	1.6
26 5 21	26 5 22	57	57	9347.423	42	−4.8
		55	55	9339.395	43	5.3
		53	53	9335.924	43	4.9
		51	51	9336.537	44	3.3
		49	49	9340.735	42	1.4
		47	47	9348.012	42	−2.2
27 5 22	27 5 23	57	57	12433.507	55	−0.2
		55	55	12429.476	55	3.1
		53	53	12430.154	55	1.4
		51	51	12434.994	55	−4.6
28 5 23	28 5 24	61	61	16146.520	69	−5.3
		59	59	16136.093	69	−0.4
		57	57	16131.550	69	3.2
		55	55	16132.282	69	3.1
		53	53	16137.703	71	−0.9
		51	51	16147.249	68	−4.5
29 5 24	29 5 25	63	63	20452.422	82	−8.1
		61	61	20441.046	81	1.5
		59	59	20436.068	83	−0.4
		57	57	20436.840	82	−0.4
		55	55	20442.743	82	1.4
		53	53	20453.186	81	−6.6
32 6 26	32 6 27	69	69	10605.766	58	−4.0
		67	67	10598.480	53	−0.4
		65	65	10595.243	56	0.8
		63	63	10595.702	54	−1.6
		61	61	10599.481	59	−3.3
		59	59	10606.190	56	−5.9
33 6 27	33 6 28	71	71	13964.229	70	−9.2
		69	69	13955.758	71	−1.6
		67	67	13951.983	70	0.4
		65	65	13952.499	71	−0.2
		63	63	13956.887	71	−1.6
		61	61	13964.725	69	−7.3
35 6 29	35 6 30	75	75	22629.301	103	−5.9
		73	73	22618.752	102	3.1
		71	71	22614.043	104	5.7
		69	69	22614.645	103	6.0
		67	67	22620.069	104	3.2
		65	65	22629.867	103	−3.8
36 7 29	36 7 30	77	77	6412.000	41	3.4
		75	75	6407.493	41	7.2
		73	73	6405.461	41	8.4
		71	71	6405.728	41	7.8
		69	69	6408.066	41	7.3
		67	67	6412.199	41	2.9
37 7 30	37 7 31	79	79	8732.421	53	−5.0
		77	77	8726.864	55	−4.6
		75	75	8724.353	54	−3.9
		73	73	8724.665	54	−4.7
		71	71	8727.538	54	−4.8
		69	69	8732.680	54	−3.5
38 7 31	38 7 32	81	81	11651.694	69	−16.4
		79	79	11645.043	69	4.5
		77	77	11642.024	68	6.1
		75	75	11642.384	68	6.5
		73	73	11645.821	68	2.8
		71	71	11652.008	68	−17.5
39 7 32	39 7 33	83	83	15227.933	85	−4.2
		81	81	15220.145	86	5.9
		79	79	15216.612	87	9.8
		77	77	15217.015	87	9.6
		75	75	15221.023	85	4.0
		73	73	15228.299	86	−4.5

Table 2. Results from the hyperfine structure and centrifugal distortion analysis for 2-iodopropene. In addition to our FTMW measurements, 13 transitions up to $J=4$ and $K_-=2$ given in [1] have been included. The A-species lines have been used directly for the analysis in the case of internal rotation splittings. A', B', C': rotational constants, D'_J, D'_{JK}, D'_K, δ'_J, R'_6: quartic centrifugal distortion constants of the Van Eijck/Typke Hamiltonian [12, 13], $\chi_{gg'}$: quadrupole coupling constants ($g, g'=a, b, c$, $\chi_-=\chi_{bb}-\chi_{cc}$), C_{gg}: spin-rotation coupling constants, σ: total standard deviation, n: number of rotational transitions, N: number of hyperfine components, co(X, Y): correlation coefficients between X and Y of magnitude >0.96. Standard errors are given in units of the last digits in brackets.

The components of the quadrupole coupling tensor in its own principal axis system (x', y', z') have been obtained by a rotation about the c-principal inertia axis with the angle α.

a): inclusion, b): exclusion of the iodine spin-rotation coupling.

	a)		b)		
A'	9285.200	(12)	9285.190	(18)	MHz
B'	2337.2186	(7)	2337.2150	(9)	MHz
C'	1887.5956	(6)	1887.5921	(9)	MHz
D'_J	0.32	(2)	0.27	(3)	kHz
D'_{JK}	2.55	(4)	2.52	(6)	kHz
D'_K	7.8	(11)	8.5	(16)	kHz
δ'_J	0.0815	(8)	0.0810	(11)	kHz
R'_6	−0.0192	(6)	−0.0196	(8)	kHz
χ_{aa}	−1820.829	(15)	−1820.778	(20)	MHz
χ_-	93.247	(23)	93.235	(34)	MHz
$\lvert\chi_{ab}\rvert$	147.51	(37)	147.53	(54)	MHz
C_{aa}	3.0	(16)	–		kHz
C_{bb}	8.4	(5)	–		kHz
C_{cc}	7.4	(5)	–		kHz
σ:	13.6		20.0		kHz
n:	36		36		
N:	270		270		
co (δ'_J, D'_K)	−0.996		−0.996		
co (δ'_J, D'_{JK})	0.962		0.962		
co (δ'_J, R'_6)	0.981		0.981		
co (R'_6, D'_K)	−0.984		−0.984		

$\chi_{aa} = -1820.829\ (15)$ MHz
$\chi_{bb} = 957.038\ (14)$ MHz
$\chi_{cc} = 863.791\ (14)$ MHz

$\chi_{x'x'} = 964.850\ (41)$ MHz
$\chi_{y'y'} = 863.791\ (14)$ MHz
$\chi_{z'z'} = -1828.641\ (41)$ MHz
$\alpha = 3.031\ (8)\ (^0)$

Table 3. Data used for the internal rotation analysis of 2-iodopropene. ν_A: hypothetical hyperfine free A-species transition (MHz), $\overline{\Delta\nu_{AE}}$: averaged internal rotation splitting (A–E) of the observed hyperfine components (kHz), δ_{AE}: observed minus calculated splittings using the constants of Table 4, column a (kHz), $\Delta\nu_R$: difference $\nu_A-\nu_R$ between ν_A and a hypothetical line without internal rotation splitting ν_R (kHz).

$J'\,K'_-\,K'_+$	$J\,K_-\,K_+$	ν_A	$\overline{\Delta\nu_{AE}}$	δ_{AE}	$\Delta\nu_R$
12 2 10	12 2 11	14517.424	33	1.0	22
13 2 11	13 2 12	18269.899	38	−0.8	25
17 3 14	17 3 15	14814.353	42	−0.8	28
18 3 15	18 3 16	18731.114	51	−0.4	34
19 3 16	19 3 17	23090.701	59	−1.2	40
21 4 17	21 4 18	10620.616	40	−1.0	27
22 4 18	22 4 19	13964.054	51	−0.1	34
24 4 20	24 4 21	22290.413	73	0.2	49
26 4 22	26 4 23	32512.707	95	1.1	63
25 5 20	25 5 21	6833.868	33	−0.8	22
26 5 21	26 5 22	9341.288	43	−1.1	29
27 5 22	27 5 23	12435.690	55	−0.8	37
28 5 23	28 5 24	16138.528	69	0.5	46
29 5 24	29 5 25	20443.689	82	0.3	55
32 6 26	32 6 27	10600.114	56	−0.5	38
33 6 27	33 6 28	13957.657	70	−0.7	47
35 6 29	35 6 30	22621.097	103	1.4	68
36 7 29	36 7 30	6408.452	41	0.0	27
37 7 30	37 7 31	8728.061	54	0.3	36
38 7 31	38 7 32	11646.472	68	−0.6	45
39 7 32	39 7 33	15221.813	86	0.9	57

Table 4. Internal rotation parameters for 2-iodopropene. $w_1(s)$: Fourier coefficient, $\sphericalangle(a, i)$: angle between the principal inertia axis a and the internal rotation axis, i, I_α: moment of inertia of the methyl group, co: correlation coefficient between $w_1(s)$ and $\sphericalangle(a, i)$, n: number of transitions used for the analysis, σ: standard deviation of the fit.

Derived parameters: s: reduced barrier height, V_3: internal rotation barrier, F: reduced rotational constant of the internal rotation. Standard errors are given in units of the last digits in brackets, fixed values in square brackets. Further details see text.

	a)	b)	
$w_1(s)$	$-0.376\ (12)\cdot 10^{-5}$	$-0.386\ (11)\cdot 10^{-5}$	
$\sphericalangle(a, i)$	60.18 (76)	59.96 (72)	$[^0]$
I_α	[3.167]	[3.11]	[amu Å^2]
σ	0.8	0.8	[kHz]
n	21	21	
co	0.995	0.995	
s	73.69 (29)	73.46 (28)	
V_3	2588 (12)	2626 (11)	[cal/mol]
F	163.738 (84)	166.684 (79)	[GHz]

the internal rotation axis i and the principal inertia axis a, and I_α, the moment of inertia of the methyl group, to the experimental splittings converged to unreasonable values for $w_1(s)$ and I_α. Since only a few data about the structure of 2-iodopropene are available, we fixed I_α to the value 3.167 amu Å^2 derived from the r_s-structure of 2-chloropropene [19] and fitted the remaining two parameters. This calculation resulted in reasonable values compared to the data given in [1] (Table 4, column a). Another attempt was made with $I_\alpha = 3.11$ amu Å^2 taken from the inertial defect of propylene [20]. The fitted parameters changed only inside their error limits, but a remarkable effect upon the value of the V_3 barrier height could be noticed (column b). The reason is the depen-

Table 5. Comparison of potential barriers V_3 (cal/mol) of 2-halopropenes, $CH_3-CX=CH_2$, X = F, Cl, Br, I, obtained by different methods. IR: far infrared measurements of torsional transitions, ES: microwave measurements of the first excited torsional state, GS: microwave measurements of the torsional ground state, *: no information about isotopic species given.

	F	^{35}Cl	^{37}Cl	^{79}Br	^{81}Br	I
GS	2384 (17) [2]	2568 (10) [3]	2582 (12) [3]	2571 (49) [4]	2558 (74) [4]	2588 (12) this work
ES	2432 (11) [24]	2671 [23]		2695 (30) [22]		2590.2 (5) [1]
IR	2353 [21]	2654* [21]		2654* [21]		2555 [21]

dence of the reduced barrier s not only on V_3 but also on the internal rotation constant F being a function of the molecular structure, especially I_α. Considering this uncertainty, the error of V_3 is increasing to at least 40 cal/mol.

The angle $\sphericalangle\,(a, i)$ has been estimated using again the structural parameters of 2-chloropropene and fitting the C-I bondlength and the bond angle $\sphericalangle$ CCI to the obtained rotational constants. Assuming that the internal rotation axis i is perpendicular to the plane of the three methyl hydrogen atoms, we obtained 59.65° for $\sphericalangle\,(a, i)$, being inside the error limits of our experimental value.

Finally we modified our experimental data, tentatively subtracting the internal rotation effect from each hyperfine component, and obtained therefore a hypothetical internal rotation free spectrum with hyperfine structure. An analysis of this spectrum with our program HFS resulted in constants changing their values only within the experimental errors. So we assume that in the case of 2-iodopropene the A-species lines may be analyzed like hypothetical internal rotation free lines because of the narrow splittings. The differences between the internal rotation free and the A-species lines are listed in Table 3.

Discussion

In Table 5 internal rotation barriers of all 2-halopropenes obtained by different measuring methods are given. The V_3 barrier heights from microwave measurements of excited torsional states and from new infrared measurements of torsional transitions increase from 2-fluoropropene to 2-chloropropene and 2-bromopropene but decrease slightly for 2-iodopropene. The ground state measurements do not confirm this decrement. A possible reason could be an interaction between the torsional and other vibrational states. In addition the internal rotation parameters contain structural data and the obtainable barrier height is especially sensitive to the magnitude of I_α, as has been mentioned before. In all cases, with the exception of 2-fluoropropene, I_α values had to be taken from at least partially assumed structures. So we think that the total error of the barrier height must contain these structural uncertainties and is rising then to 50–100 cal/mol. Inside this error range the barrier heights of 2-iodopropene and 2-bromopropene may be accepted as nearly equal. They confirm the general trend of barrier heights rising from fluoro to chloro compounds but remaining nearly equal for chloro, bromo, and iodo compounds inside a halide series.

Acknowledgements

We thank Prof. A. Bauder for providing a sample of the substance and the members of our group for help and discussions. The funds were provided by the Deutsche Forschungsgemeinschaft, the Fond der Chemie and the Land Schleswig-Holstein. The calculations were mainly carried out at the computer center of the University of Kiel.

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