The Iodine Hyperfine Structure in the Microwave Spectrum of Ethyl Iodide: Nuclear Quadrupole and Spin Rotation Coupling

Joachim Gripp and Helmut Dreizler
Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

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Some rotational transitions of ethyl iodide, CH_3CH_2I, have been reinvestigated by microwave Fourier transform (MWFT) spectroscopy. The iodine hyperfine structure splittings were first analyzed using a direct diagonalization procedure of the complete quadrupole Hamiltonian matrix. The results of this analysis showed deviations from our measurements up to 60 kHz. A new analysis using additional spin rotation coupling matrix elements reproduces our measurements within the experimental error limit and decreases the standard deviation of the least squares fit from 28 kHz to only 4 kHz.

Introduction

The microwave spectra of molecules containing an iodine atom are rather complex because the quadrupole coupling of iodine leads to wide and overlapping hyperfine structure splittings. First order perturbation calculation methods are no longer sufficient to obtain the quadrupole coupling parameters. The best way of analyzing is the direct diagonalization of the complete quadrupole interaction Hamiltonian matrix. In the case of linear and symmetric top molecules also additional influences of the iodine spin rotation coupling were detected [1–3] but no report about iodine containing asymmetric top molecules is given yet. This effect, based on the coupling of the magnetic moment of the iodine nucleus to the magnetic field induced by the molecular rotation is about 4 to 5 magnitudes smaller than the quadrupole coupling and causes a small frequency shift of the hyperfine splitting components. In the case of asymmetric top molecules the spin rotation coupling depends on three independent parameters in a first order approximation.

The first investigation of the microwave spectrum of ethyl iodide is reported in 1959 [4]. Ethyl iodide is a near prolate asymmetric top molecule containing a plane of symmetry. A detailed analysis of the iodine quadrupole coupling in the ground state is given by Boucher et al. [5]. In a new publication by Inagusa et al. the r_s-structure, dipole moment and the iodine quadrupole coupling constants of seven isotopic species of ethyl iodide is reported [6]. We reinvestigated a part of the spectrum using MWFT spectroscopy. The accuracy of the frequency measurements can then be assumed to be at least better than 10 kHz. The analysis of the iodine hyperfine structure considering only the quadrupole coupling yielded differences between the observed and calculated spectra up to about 60 kHz being out of the range of our measuring accuracy. So we performed a new analysis of the spectra introducing a simultaneous least squares fit of the quadrupole and spin rotation coupling parameters. Going this way spin rotation matrix elements had to be evaluated which could directly be added to the quadrupole interaction matrix. This method allowed the determination of the three spin rotation coupling constants and improved the values of the quadrupole coupling parameters.

Experimental

The spectra were recorded with our MWFT spectrometers between 5 and 18 GHz [7–9]. The sample of ethyl iodide was obtained commercially and used without further purification. The measurements were carried out at pressures between 0.1 and 0.5 mTorr (0.01 and 0.07 Pa) and temperatures between $-30\,°C$ and $-40\,°C$.

Hamiltonian

The Hamiltonian for a near prolate asymmetric top molecule containing one coupling nucleus may be

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Reprint request to Prof. Dr. H. Dreizler, Abteilung Chemische Physik im Institut für Physikalische Chemie Kiel, Olshausenstr. 40, D-2300 Kiel, FRG.

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Table 1. Observed and calculated hyperfine splittings of CH_3CH_2I. ν: measured frequency of the reference component, $\Delta\nu$: difference between the frequencies of the reference component and a second component (splitting), δ_{NQ}: difference between observed and calculated splittings using only the quadrupole coupling constants of Table 2a, δ_{tot}: difference between observed and calculated splittings using the quadrupole- and spin rotation coupling constants of Table 2b. Frequencies and splittings in MHz, deviations in kHz.

J'	K'_-	K'_+	F'	J	K_-	K_+	F	ν	$\Delta\nu$	δ_{NQ}	δ_{tot}
1	0	1	7/2	0	0	0	5/2	5 852.284			
			5/2				5/2		310.250	2	1
			3/2				5/2		−134.505	62	−3
2	1	2	9/2	1	1	1	7/2	11 467.919			
			7/2				5/2		294.112	−14	2
			5/2				3/2		77.942	20	11
			5/2				5/2		249.100	14	−4
			5/2				7/2		126.945	59	4
			3/2				5/2		115.594	55	−6
			7/2				7/2		171.956	30	9
2	0	2	9/2	1	0	1	7/2	11 583.739			
			7/2				5/2		−23.875	16	3
			7/2				7/2		286.377	20	6
			5/2				3/2		341.173	−20	−5
			5/2				5/2		−103.574	47	−1
			3/2				3/2		135.456	32	0
2	1	1	9/2	1	1	0	7/2	11 824.365			
			7/2				5/2		299.455	−16	2
			5/2				3/2		−4.066	18	−5
			5/2				5/2		271.120	7	2
			3/2				3/2		−90.561	38	−8
2	1	2	9/2	3	0	3	11/2	8 570.137			
			7/2				9/2		−101.796	−2	5
			5/2				7/2		−138.096	12	0
			3/2				5/2		−136.382	−4	−4
3	0	3	11/2	2	0	2	9/2	17 342.329			
			9/2				7/2		−12.621	15	2
			7/2				7/2		−21.336	27	−1
			7/2				5/2		58.361	−6	1
			5/2				3/2		128.862	2	2
3	1	3	11/2	2	1	2	9/2	17 095.830			
			9/2				7/2		61.991	5	2
			7/2				7/2		60.743	41	0
			7/2				5/2		105.756	14	7
			5/2				3/2		119.037	12	1
3	1	2	11/2	2	1	1	9/2	17 643.789			
			7/2				5/2		93.865	16	−1
3	2	1	11/2	2	2	0	9/2	17 438.788			
			9/2				7/2		283.235	−27	−6
			7/2				7/2		286.663	15	−5
			7/2				5/2		210.189	−13	−2
3	2	2	11/2	2	2	1	9/2	17 435.127			
			9/2				7/2		283.549	−22	0
			7/2				7/2		286.994	17	−3
			7/2				5/2		210.564	−7	3
6	0	6	17/2	5	1	5	15/2	9 743.917			
			15/2				13/2		−10.589	−4	1
			13/2				11/2		3.045	15	3
			11/2				9/2		17.131	15	2
			9/2				7/2		22.673	11	3
			7/2				5/2		15.535	12	1
7	1	6	19/2	7	1	7	19/2	5 088.796			
			17/2				17/2		−59.840	8	7
			15/2				15/2		−73.001	9	1
			13/2				13/2		−56.345	11	5
			11/2				11/2		−22.953	−7	4
			9/2				9/2		18.155	−37	3
8	1	7	21/2	8	1	8	21/2	6 551.896			
			19/2				19/2		−58.840	0	−1
			17/2				17/2		−75.550	−2	0

Table 1 (Continued).

J'	K'_-	K'_+	F'	J	K_-	K_+	F	ν	$\Delta\nu$	δ_{NQ}	δ_{tot}
			15/2				15/2		−62.300	−11	−1
			13/2				13/2		−29.293	−26	0
			11/2				11/2		14.855	−49	1
9	1	8	23/2	9	1	9	23/2	8 197.318			
			21/2				21/2		−58.017	4	3
			19/2				19/2		−76.335	−1	3
			17/2				17/2		−64.674	−13	1
			15/2				15/2		−32.112	−29	1
			13/2				13/2		13.266	−55	−2
10	1	9	25/2	10	1	10	25/2	10 024.640			
			23/2				23/2		−57.249	4	4
			21/2				21/2		−76.592	1	7
			19/2				19/2		−66.135	−13	5
			17/2				17/2		−34.015	−33	1
			15/2				15/2		12.187	−58	−1

written in the form

$$\hat{H} = \hat{H}_{\text{R}} + \hat{H}_{\text{CD}} + \hat{H}_{\text{Q}} + \hat{H}_{\text{M}} \tag{1}$$

with the rotational part

$$\hat{H}_{\text{R}} = A'\,\hat{J}_a^2 + B'\,\hat{J}_b^2 + C'\,\hat{J}_c^2 \tag{2}$$

and the centrifugal distortion contribution

$$\begin{aligned}\hat{H}_{\text{CD}} = &- D'_J\,\hat{J}^4 - D'_{JK}\,\hat{J}^2\,\hat{J}_a^2 - D'_K\,\hat{J}_a^4 - 2\,\delta'_J\,\hat{J}^2(\hat{J}_b^2 - \hat{J}_c^2) \\ &+ 2\,R'_6\,[\hat{J}_b^4 + \hat{J}_c^4 - 3(\hat{J}_b^2\,\hat{J}_c^2 + \hat{J}_c^2\,\hat{J}_b^2)],\end{aligned} \tag{3}$$

written in the I^r representation and using the fourth order centrifugal distortion constants from van Eijck [10]. Matrix elements in the symmetric top basis are given in [11].

The quadrupole- and the spin rotation coupling contributions $\hat{H}_{\text{Q}}$ and $\hat{H}_{\text{M}}$ are written as Cartesian tensor operators in space fixed axes according to Gordy [12]:

$$\hat{H}_{\text{Q}} = 1/6\,(\hat{V} : \hat{Q}), \tag{4}$$

$$\hat{H}_{\text{M}} = \mathbf{\hat{I}} \cdot \mathbf{\hat{C}} \cdot \mathbf{\hat{J}}. \tag{5}$$

The components of these tensors are transformed to a space fixed spherical basis where they constitute tensors with transformation properties due to the irreducible representations of the rotation group. $\hat{H}_{\text{Q}}$ can then be written as the scalar product of two irreducible tensors with a rank of 2:

$$\hat{H}_{\text{Q}} = \hat{V}^{(2)} \cdot \hat{Q}^{(2)}. \tag{6}$$

Application of methods to evaluate the matrix elements of irreducible tensor operators based on the Wigner Eckart theorem allows to express the matrix elements of $\hat{H}_{\text{Q}}$ in the following way:

$$\begin{aligned}\langle J', K', I, F\,|\hat{H}_{\text{Q}}|\,J, K, I, F\rangle = &(-1)^{I+F-K-q'} \\ &\cdot [(2J+1)(2J'+1)]^{1/2} \cdot \begin{Bmatrix} F & I & J' \\ 2 & J & I \end{Bmatrix} \cdot \frac{\begin{pmatrix} J & 2 & J' \\ K & q' & -K' \end{pmatrix}}{\begin{pmatrix} I & 2 & I \\ -I & 0 & I \end{pmatrix}} \\ &\cdot \tfrac{1}{2}\,e\,Q\,V_{q'}^{\prime(2)}.\end{aligned} \tag{7}$$

The symbols in brackets are $3j$ symbols being related to the Clebsch-Gordan coefficients. The symbol in braces is the $6j$ symbol being related to the Racah functions. The coupling scheme $\hat{J} + \hat{I} = \hat{F}$ has been used. The matrix is diagonal in the quantum numbers I and F and independent of the quantum number M_F. There are off diagonal elements in J and K. The irreducible components of the field gradient tensor $V'^{(2)}$ in a body fixed spherical basis are transformed to the molecular principal axes system in the following way using the I^r representation:

$$\begin{aligned} 2\,V_0^{\prime(2)} &= V_{aa}, \\ 2\,V_{\pm 1}^{\prime(2)} &= \mp\,(2/3)^{1/2} \cdot (V_{ab} \pm i\,V_{ac}), \\ 2\,V_{\pm 2}^{\prime(2)} &= (1/6)^{1/2} \cdot (V_{bb} - V_{cc} \pm i\,V_{bc}). \end{aligned} \tag{8}$$

Explicit formulas for all matrix elements are given in [13]. For ethyl iodide, V_{ac} and V_{bc} vanish by symmetry. So $\hat{H}_{\text{Q}}$ is formulated as a real symmetric matrix with a rank of $(2I+1) \cdot (2F+1)$. $\hat{H}_{\text{M}}$ is transformed from the space fixed Cartesian axes to a spherical basis decomposing it to a sum of scalar products of irreducible tensors according to Gordy [14]:

$$\hat{H}_{\mathrm{M}} = \sum_{L=0}^{2} N_L [\hat{C}^{(L)} \times \hat{J}^{(1)}]^{(1)} \cdot \hat{I}^{(1)}. \tag{9}$$

The N_L are normalization factors. They can be obtained using the rules for the direct and the scalar products of irreducible tensors by a relative long calculation.

$$N_0 = -(1/3)^{1/2}, \quad N_1 = -1, \quad N_2 = -(5/3)^{1/2}. \tag{10}$$

In a first order approximation, only the matrix elements diagonal in J and the diagonal elements of the spin rotation coupling tensor are considered. The matrix elements are evaluated applying again the irreducible tensor method:

$$\langle J, K', I, F \,|\hat{H}_{\mathrm{M}}|\, J, K, I, F \rangle = (-1)^{J+I+F} \cdot [I(I+1)(2I+1)]^{1/2} \cdot [J(J+1)(2J+1)]^{1/2} \cdot \begin{Bmatrix} F & I & J \\ 1 & J & I \end{Bmatrix} \cdot C_J \tag{11}$$

with

$$C_J = -3^{1/2} \cdot (2J+1) \sum_{L=0}^{2} (-1)^{J+L-K-q'} \cdot \begin{Bmatrix} L & 1 & 1 \\ J & J & J \end{Bmatrix} \cdot \begin{pmatrix} J & L & J \\ K & q' & -K' \end{pmatrix} \cdot (N_L C'^{(L)}_{q'}).$$

The $C'^{(L)}_{q'}$ are the components of the spin rotation coupling tensor in a body fixed spherical basis. Following the explanations of Gordy, the $C'^{(L)}_{q'}$ can be transformed to the molecular principal axes system and be expressed in the I^{r} representation considering only diagonal elements:

$$\begin{aligned} C'^{(0)}_{0} &= -(1/3)^{1/2} \cdot (C_{aa} + C_{bb} + C_{cc}), \\ C'^{(2)}_{0} &= (1/6)^{1/2} \cdot [3\,C_{aa} - (C_{aa} + C_{bb} + C_{cc})], \\ C'^{(2)}_{\pm 2} &= (1/2) \cdot (C_{bb} - C_{cc}). \end{aligned} \tag{12}$$

The evaluation of (11) leads finally to the following matrix elements considering only elements diagonal in J:

$$\langle J, K, I, F \,|\hat{H}_{\mathrm{M}}|\, J, K, I, F \rangle = \{\tfrac{1}{2}(C_{bb} + C_{cc}) + [C_{aa} - \tfrac{1}{2}(C_{bb} + C_{cc})] \cdot K^2/[J(J+1)]\} \cdot (G/2), \tag{13a}$$

$$\langle J, K \pm 2, I, F |\hat{H}_{\mathrm{M}}|\, J, K, I, F \rangle = \{[(J \mp K - 1)(J \mp K)(J \pm K + 1)(J \pm K + 2)]^{1/2} \cdot (C_{bb} - C_{cc})/[4J(J+1)]\} \cdot (G/2), \tag{13b}$$

$$G = F(F+1) - J(J+1) - I(I+1). \tag{13c}$$

The matrix elements of $\hat{H}_{\mathrm{R}}$, $\hat{H}_{\mathrm{CD}}$, $\hat{H}_{\mathrm{Q}}$ and $\hat{H}_{\mathrm{M}}$ can be added because those of $\hat{H}_{\mathrm{R}}$ and $\hat{H}_{\mathrm{CD}}$ do not change their values when they are transformed from the symmetric top basis to the coupled basis. This is reasonable because the components of the rotational angular momentum in space fixed Cartesian coordinates and the components in the molecular principal axes system commute. The phase factors are chosen according to Condon and Shortley [15].

A FORTRAN program which performs the calculation and direct diagonalization of the Hamiltonian matrix [16] has been extended to consider supplementary the elements of $\hat{H}_{\mathrm{M}}$ given in (13). The consistency of the results for the spin rotation coupling has been checked with those obtained from the formula given by Gordy [17]

$$E_{\mathrm{M}} = \{\sum_{g} C_g \langle \hat{J}_g^2 \rangle / [J(J+1)]\} \cdot (G/2), \qquad (g = \mathrm{a, b, c}). \tag{14}$$

The $\langle \hat{J}_g^2 \rangle$ are average values of the squares of the angular momentum components.

Also his sign convention for the spin rotation coupling constants has been used. The opposite sign is used in [18].

Analysis and Results

The major part of the measurements could be directly used for the hfs analysis. In the case of narrow splittings a line shape analysis was necessary [19].

Only lines with $J \leq 10$ not showing additional splitting due to the internal rotation of the methyl group has been taken for the investigation because the computer time and storage size needed increases rapidly with the rank of the matrices. So we were not able to determine the centrifugal distortion constants and the analysis was carried out by taking the components with the highest values of quantum number F as references and the differences to the other components as splittings. The rotational and centrifugal distortion constants were taken from [5] and are given in Table 2c. Due to the plane of symmetry and the position of the molecular principal axes a and b type transitions could be observed.

In Table 1 the observed splittings, quantum numbers and deviations from the calculated splittings are given. Table 2a contains the determined parameters from a least squares fit considering only the quadru-

Table 2. Results from the hfs analysis. The quadrupole coupling constants eQV'_{gg} have been abbreviated to χ_{gg}. Because the quadrupole coupling tensor is traceless only the independent constants $\chi_{+} = \chi_{bb} + \chi_{cc}$, $\chi_{-} = \chi_{bb} - \chi_{cc}$ and χ_{ab} could be obtained directly from the least squares fit. χ_{aa}, χ_{bb} and χ_{cc} have been calculated afterwards. From this values and χ_{ab} the tensor components in its own principal aces system are determined by a rotation about the c-axis with the angle α. The errors have been calculated using the Gauss formula [20].

a) Parameters obtained by fitting only the quadrupol coupling constants.

		Correlation matrix		
χ_{+} =	1478.202(34) MHz	1.000		
χ_{-} =	−349.321(35) MHz	0.020	1.000	
χ_{ab} =	894.53 (89) MHz	0.073	−0.060	1.000

χ_{aa} =	−1478.202(34) MHz	χ_{zz} =	−1814.56 (59) MHz
χ_{bb} =	564.440(24) MHz	χ_{xx} =	900.79 (59) MHz
χ_{cc} =	913.762(24) MHz	χ_{yy} =	913.762(24) MHz

Rotation angle $\alpha = 20.61\,(1)^0$
Number of splittings: 60. Standard deviation of the fit: 25.8 kHz.

b) Parameters obtained by fitting the quadrupole- and spin rotation coupling constants simultaneously.

		Correlation matrix					
χ_{+} =	1478.058 (7) MHz	1.000					
χ_{-} =	−349.231 (6) MHz	−0.016	1.000				
χ_{ab} =	896.31 (14) MHz	0.200	−0.028	1.000			
C_{aa} =	11.8 (8) kHz	−0.191	0.083	0.103	1.000		
C_{bb} =	7.5 (2) kHz	0.538	−0.080	0.275	0.282	1.000	
C_{cc} =	9.5 (2) kHz	0.543	0.073	0.287	0.278	0.955	1.000

χ_{aa} =	−1478.058 (7) MHz	χ_{zz} =	−1814.61 (9) MHz
χ_{bb} =	564.413 (5) MHz	χ_{xx} =	901.96 (9) MHz
χ_{cc} =	913.644 (5) MHz	χ_{yy} =	913.644 (5) MHz

Rotation angle $\alpha = 20.638\,(2)^0$
Standard deviation of the fit: 3.9 kHz.

c) Rotational and centrifugal distortion constants given by Boucher et al. [5] used for the calculations.

A' =	29116.321 (8) MHz	D'_{JK} =	−11.952 (8) kHz
B' =	2979.5639(8) MHz	D'_{K} =	260.3 (8) kHz
C' =	2796.4521(9) MHz	δ'_{J} =	0.1133(2) kHz
D'_{J} =	1.165 (2) kHz	R'_{6} =	−0.0041(2) kHz

pole coupling constants and Table 2b those including the spin rotation coupling constants of iodine which have been simultaneously fitted. The standard errors of all quadrupole coupling constants of Table 2b are about five times smaller than those of Table 2a. The difference between the constants from Table 2a and Table 2b are larger than the standard errors. The spin rotation coupling constants are well determined within a few percent error.

Additional the elements of the quadrupole coupling tensor rotated to its own principal axes system are given. The tensor can be transformed directly because the off diagonal element $eQV'_{ab} = \chi_{ab}$ is well determined. The column δ_{NQ} in Table 1 gives deviations between the observed and the calculated splittings up to about 60 kHz. In the column δ_{tot} the agreement is better and reproduces approximately the accuracy of our measurements.

The spin rotation coupling constants C_{bb} and C_{cc} are highly correlated (0.955, see Table 2) because their numerical values are very similar. If they were equal, the off diagonal elements in K of $\hat{H}_{\text{M}}$ vanish and only the sum $C_{bb} + C_{cc}$ is determinable. Nevertheless the contribution of the spin rotation coupling has to be considered for further investigations of the hyperfine structure of iodine and probably bromine containing molecules using highly accurate methods like MWFT spectroscopy*.

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* *Erratum*: In our publication given in Z. Naturforsch. **43a**, 133–137 (1987) we have found a misprint on page 134: The sign of $\hat{H}_{\text{M1}}$ has to be taken positive.

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