Centrifugal Distortion Constants of Methylhypochlorite and [D_3]-Methylhypochlorite from the Microwave and Millimeterwave Rotational Spectra

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The microwave and millimeterwave spectra of CH_3OCl and CD_3OCl have been investigated up to 200 GHz and centrifugal distortion constants up to the sixth order have been calculated using both Watson's *s*-reduction and van Eijck-Typke operators. Watson's determinable parameters have been obtained starting from both sets of constants.

Introduction

The microwave spectrum of Methylhypochlorite (CH_3OCl) has been measured by Rigden and Butcher [1] who determined the molecular structure and the barrier to internal rotation from the first excited torsional state.

From the rotational Zeeman spectrum the magnetical parameters as well as the value and orientation of the electric dipole moment and the barrier to internal rotation in the ground state have been determined [2]. During this last investigation we observed appreciable centrifugal distortion contributions for some lines measured in the high frequency range which have been found useful for the determination of the torsional barrier. In the present paper we report the investigation of the millimeter wave spectrum of both isotopic species $CH_3O^{35}Cl$ and $CD_3O^{35}Cl$ with the purpose of performing an accurate centrifugal distortion analysis. Methylhypochlorite is an asymmetric top molecule with an asymmetry parameter $\varkappa = -0.96$, hence a nearly prolate top suitable to be used as further check of the Hamiltonians [3, 4, 5] developed for this type of problems.

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Experimental

CH_3OCl was prepared following the method of Sandmeyer [6] and purified at 0 °C by vacuum distillation.

In the used cell it decomposes immediately even at −75 °C and for this reason the gas was flowed continuously through the cell during the measurements at a pressure of about 0.5 Pa (7 mTorr). The millimeterwave video spectrometer with frequency multiplication is the same as described in [7]. A block scheme is reported in Fig. 1, giving a picture of two modes of use besides video; mode 1: source modulation, mode 2: millimeterwave-radio frequency-double resonance (MMW-RF-DR). A special X-Band cell with a septum allowing a "coaxial"-type transmission mode for the radiofrequency up to 4500 MHz was used [7]. The transmission for the millimeterwaves was satisfactory up to 200 GHz, higher frequencies seemed to be strongly absorbed. The frequency measurements were carried out by means of a synthesized signal generator Schomandl ND 800 M continuously monitored by a 5 MHz-Signal derived from the 77.5 KHz-Signal of the broadcasting station DCF 77 (Mainflingen, Germany) with a relative accuracy of 5×10^{-13}. The measurements are believed to be accurate to 1×10^{-7}.

Spectrum and Rotational Parameters

We started with the record of the spectrum of $CD_3O^{35}Cl$ for two reasons: first because the *b*-type

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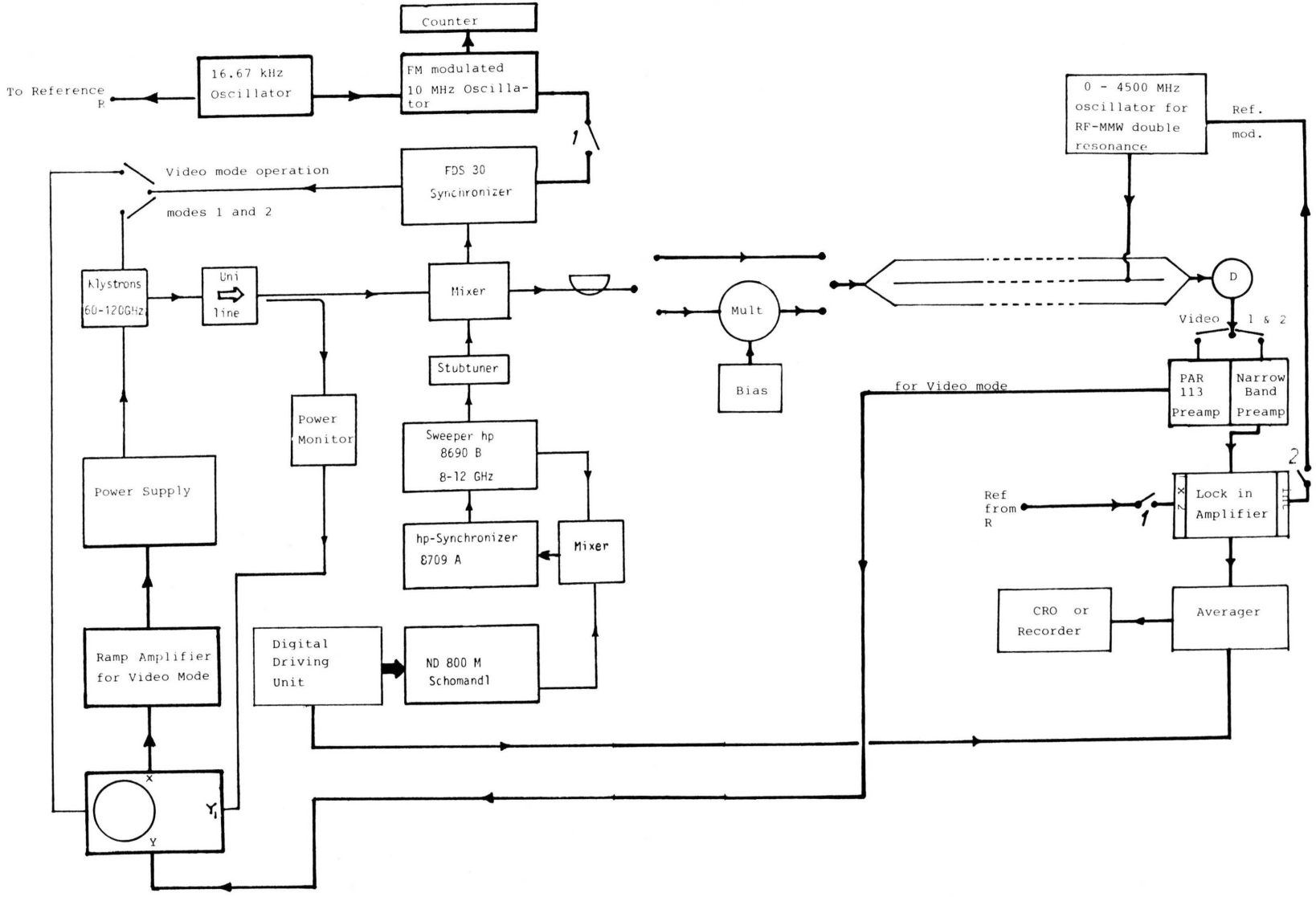

Fig. 1. Block Diagram of the Millimeterwave Spectrometer. – In the operation mode 'Video' the Klystron is free running and switches 1 and 2 are open. The correction signal from the FDS 30 Synchronizer is used as frequency for positioning the convenient stabilisation frequency. – In operation mode '1' the Klystron is stabilized with a two loops stabilisation circuit driven by an ND 800 M Schomandl standard oscillator, where switch 1 is closed and switch 2 is open. The system works with source modulation. – In operation mode '2' the Klystron remains further stabilized but switch 1 is open and switch 2 is closed. The system works with millimeterwave-radio frequency-double resonance.

Table 1a. Rotational and Centrifugal Distortion Constants of $CH_3O^{35}Cl$ after van Eijck-Typke and Watson's *s*-reduction operators. The errors are standard from the least squares fitting procedure and are given in units of the last figure.

$CH_3O^{35}Cl$ (118 Lines)				
by van Eijck-Typke		by Watson's s-reduction		
A'	42.064925(10)	$A^{(s)}$	42.064925(10)	GHz
B'	6.296878(1)	$B^{(s)}$	6.296878(1)	GHz
C'	6.670610(1)	$C^{(s)}$	5.670610(1)	GHz
D_J'	4.260(2)	D_J	4.260(2)	KHz
D_{JK}'	− 24.57(4)	D_{JK}	− 24.57(4)	KHz
D_K'	693.22(26)	D_K	693.22(26)	KHz
δ_J'	0.653(1)	d_1	− 0.653(1)	KHz
R_6'	− 0.0172(3)	d_2	− 0.0172(3)	KHz
H_J'	0.0002(16)	H_J	0.0002(16)	Hz
H_{JK}'	− 0.09(5)	H_{JK}	− 0.09(5)	Hz
H_{KJ}'	− 3.4(3)	H_{KJ}	− 3.4(3)	Hz
H_K'	53(6)	H_K	53(6)	Hz
H_5'	0.0003(8)	h_1	0.0003(9)	Hz
H_6'	0.0019(22)	h_2	0.0005(6)	Hz
H_{10}'	− 0.00003(84)	h_3	0.000004(105)	Hz
standard deviation:				
68 KHz		68 KHz		

lines show no internal rotation splitting, second because, due to the smaller rotational constants, a larger number of lines were supposed to be present in the frequency range limited by the power absorption of the used cell. The identification of the lines was made using the chlorine quadrupole hyperfine structure of the MMW-RF-DR technique [7]. A total of 223 lines** was measured following different branches up to 200 GHz.

The record of the spectrum of $CH_3O^{35}Cl$ had to be limited to 118 lines** because the other lines measured in the frequency range limited by the power absorption of the cell gave no better information. The determined constants using the van Eijck-Typke Hamiltonian [5] are given in Tables 1a and

** Requests for tables of measured lines to Prof. Dr. A. Guarnieri, Institut für Physikalische Chemie, Universität Kiel, Olshausenstr. 40 or under the number TNA4 to Universitätsbibliothek, Westring 400, 2300 Kiel, Germany.

Table 1b. Correlation coefficients among the van Eijck-Typke constants of $CH_3O^{35}Cl$.

	A'	B'	C'	D_J'	D_{JK}'	D_K'	δ_J'	R_6'	H_J'	H_{JK}'	H_{KJ}'	H_K'	H_5'	H_6'
B'	0.73													
C'	0.53	0.61												
D_J'	0.62	0.80	0.76											
D_{JK}'	0.69	0.82	0.57	0.86										
D_K'	0.03	−0.22	−0.06	−0.13	−0.51									
δ_J'	0.30	0.55	−0.23	0.20	0.46	−0.30								
R_6'	0.23	0.39	−0.24	0.10	0.31	−0.19	0.91							
H_J'	0.46	0.63	0.67	0.90	0.87	−0.39	0.14	0.02						
H_{JK}'	0.40	0.59	0.50	0.75	0.83	−0.51	0.34	0.26	0.92					
H_{KJ}'	0.63	0.65	0.38	0.69	0.84	−0.43	0.39	0.24	0.68	0.55				
H_K'	−0.46	−0.59	−0.30	−0.59	−0.86	0.73	−0.51	−0.39	−0.72	−0.75	−0.88			
H_5'	0.26	0.46	−0.15	0.20	0.45	−0.34	−0.92	0.88	0.21	0.48	0.32	−0.53		
H_6'	−0.20	−0.31	0.05	−0.21	−0.37	0.24	−0.68	−0.82	−0.29	−0.58	−0.17	0.45	−0.81	
H_{10}'	0.13	0.17	0.15	0.29	0.31	−0.17	−0.23	0.39	0.45	0.64	0.09	−0.34	0.35	−0.82

Table 1c. Correlation coefficients among Watson's s-reduction constants of $CH_3O^{35}Cl$.

	$A^{(s)}$	$B^{(s)}$	$C^{(s)}$	D_J	D_{JK}	D_K	d_1	d_2	H_J	H_{JK}	H_{KJ}	H_K	h_1	h_2
$B^{(s)}$	0.73													
$C^{(s)}$	0.53	0.61												
D_J	0.62	0.80	0.76											
D_{JK}	0.69	0.82	0.57	0.86										
D_K	0.03	−0.22	−0.06	−0.13	−0.51									
d_1	−0.30	−0.55	0.24	−0.20	−0.46	0.30								
d_2	0.23	0.39	−0.24	0.09	0.31	−0.19	−0.91							
H_J	0.46	0.63	0.67	0.90	0.87	−0.39	−0.14	0.02						
H_{JK}	0.40	0.59	0.50	0.75	0.83	−0.51	−0.35	0.26	0.92					
H_{KJ}	0.63	0.65	0.38	0.69	0.84	−0.43	−0.39	0.24	0.68	0.56				
H_K	−0.46	−0.59	−0.30	−0.59	−0.86	0.73	0.51	−0.39	−0.72	−0.75	−0.88			
h_1	0.26	0.44	−0.08	0.26	0.48	−0.34	−0.85	0.87	0.33	0.61	0.30	−0.55		
h_2	−0.20	−0.31	0.05	−0.21	−0.37	0.24	0.68	−0.82	−0.29	−0.58	−0.17	0.45	−0.95	
h_3	0.13	0.17	0.15	0.29	0.31	−0.17	−0.23	0.39	0.45	0.64	0.09	−0.34	0.63	−0.82

Table 2a. Rotational and Centrifugal Distortion Constants of $CD_3O^{35}Cl$ after van Eijck-Typke and Watson's s-reduction operators. The errors are standard errors from the least squares fitting procedure and are given in units of the last figure.

$CD_3O^{35}Cl$ (223 Lines)				
by van Eijck-Typke		by Watson's s-reduction		
A'	32.539201(4)	$A^{(s)}$	32.539201(4)	GHz
B'	5.465252(1)	$B^{(s)}$	5.465252(1)	GHz
C'	4.974985(1)	$C^{(s)}$	4.974985(1)	GHz
D'_J	3.219(2)	D_J	3.219(2)	KHz
D'_{JK}	− 5.710(11)	D_{JK}	− 5.710(11)	KHz
D'_K	273.1(3)	D_K	273.1(3)	KHz
δ'_J	0.4534(2)	d_1	− 0.4534(2)	KHz
R'_6	0.0100(1)	d_2	0.0100(1)	KHz
H'_J	− 0.003(1)	H_J	− 0.003(1)	Hz
H'_{JK}	− 0.006(8)	H_{JK}	− 0.006(7)	Hz
H'_{KJ}	− 0.54(9)	H_{KJ}	− 0.54(8)	Hz
H'_K	9.8(64)	H_K	9.8(64)	Hz
H'_5	0.0009(1)	h_1	0.0010(2)	Hz
H'_6	− 0.00010(43)	h_2	− 0.00003(11)	Hz
H'_{10}	0.00028(17)	h_3	0.00004(2)	Hz
standard deviation:				
53 KHz		53 KHz		

2a, respectively. For comparison we give in the same tables the constants determined using the Watson's s-reduction Hamiltonian [12].

The correlation coefficients among the 15 constants of $CH_3O^{35}Cl$ obtained from a least squares procedure using the van Eijck-Typke and Watson's reduction formulae are given in the Tables 1b and 1c, respectively. Those for $CD_3O^{35}Cl$ are listed in Tables 2b and 2c.

The rotational constants and the fourth and sextic centrifugal distortion constants, obtained by the two kinds of Hamiltonians, are equal in the limits of their standard errors. It seems, however, that the convergences of the H'_6 and H'_{10} terms in the van Eijck-Typke are worse than those of the h_1 and h_2 terms in Watson's s-reduction.

Table 2b. Correlation coefficients among the van Eijck-Typke constants of $CD_3O^{35}Cl$.

	A'	B'	C'	D'_J	D'_{JK}	D'_K	δ'_J	R'_6	H'_J	H'_{JK}	H'_{KJ}	H'_K	H'_5	H'_6
B'	0.73													
C'	0.66	0.86												
D'_J	0.73	0.90	0.87											
D'_{JK}	0.52	0.45	0.34	0.30										
D'_K	0.76	0.66	0.63	0.82	−0.01									
δ'_J	0.41	0.59	0.15	0.40	0.49	0.26								
R'_6	0.35	0.42	0.20	0.31	0.49	0.18	0.76							
H'_J	0.65	0.80	0.79	0.96	0.18	0.81	0.33	0.23						
H'_{JK}	0.43	0.43	0.31	0.30	0.88	0.03	0.60	0.65	0.21					
H'_{KJ}	0.44	0.30	0.19	0.25	0.81	0.02	0.36	0.34	0.17	0.62				
H'_K	0.59	0.64	0.66	0.84	−0.14	0.91	0.17	0.07	0.91	−0.08	−0.14			
H'_5	0.38	0.53	0.16	0.37	0.50	0.23	0.96	0.77	0.32	0.69	0.34	0.15		
H'_6	−0.26	−0.31	−0.18	−0.24	−0.49	−0.09	−0.63	−0.90	−0.20	−0.76	−0.32	−0.03	−0.73	
H'_{10}	0.14	0.15	0.16	0.12	0.43	−0.02	−0.34	0.71	0.12	0.68	0.27	−0.05	0.44	−0.92

Table 2c. Correlation coefficients among Watson's s-reduction constants of $CD_3O^{35}Cl$.

	$A^{(s)}$	$B^{(s)}$	$C^{(s)}$	D_J	D_{JK}	D_K	d_1	d_2	H_J	H_{JK}	H_{KJ}	H_K	h_1	h_2
$B^{(s)}$	0.73													
$C^{(s)}$	0.66	0.86												
D_J	0.73	0.90	0.87											
D_{JK}	0.52	0.45	0.34	0.30										
D_K	0.76	0.66	0.63	0.82	−0.01									
d_1	−0.41	−0.59	−0.15	−0.40	−0.49	−0.26								
d_2	0.35	0.42	0.20	0.31	0.49	0.18	−0.76							
H_J	0.65	0.80	0.79	0.96	0.18	0.81	−0.33	0.23						
H_{JK}	0.43	0.43	0.31	0.30	0.88	0.03	−0.60	0.65	0.21					
H_{KJ}	0.44	0.30	0.19	0.25	0.81	0.02	−0.36	0.34	0.17	0.62				
H_K	0.59	0.64	0.66	0.84	−0.14	0.91	−0.17	0.07	0.91	−0.08	−0.14			
h_1	0.35	0.47	0.18	0.33	0.55	0.17	−0.88	0.87	0.29	0.79	0.36	0.10		
h_2	−0.26	−0.31	−0.18	−0.24	−0.49	−0.09	0.63	−0.90	−0.20	−0.76	−0.32	−0.03	−0.91	
h_3	0.14	0.15	0.16	0.12	0.43	−0.02	−0.35	0.71	0.12	0.68	0.27	−0.05	0.71	−0.92

Discussion

CH_3OCl is a nearly symmetric top molecule with a negative asymmetry parameter $\varkappa = 2B-A-C/(A-C) = -0.96$. For this type of molecules it turned out to be useful, for the centrifugal distortion analysis, to apply the operator in the "symmetric top reduction" [3]. Watson [11] has given a form for this operator and van Eijck-Typke [4, 5] have proposed a similar one with another choice of the s_{111}, s_{311}, s_{131}, s_{113} coefficients for the transformations.

Theoretically there are many possibilities of transforming the Watson standard form [11, 12] into an operator with 15 constants. The result shows so many different sets of centrifugal distortion constants as given possibilities. Thus it is worth to obtain constants which are independent of the used transformation and consequently of the used Operator. Watson [12] has shown that this happens for the following 15 combinations of standard constants:

$$
\begin{aligned}
&1.\ B_x &&= h_{200} - 2h_{022} = \tilde{h}_{200} - 2\tilde{h}_{022}\\
&2.\ B_y &&= h_{020} - 2h_{202}\\
&3.\ B_z &&= h_{002} - 2h_{220}\\
&4.\ T_{xx} &&= h_{400} = 1/4\,\tau'_{xxxx}\\
&5.\ T_{yy} &&= h_{040} = 1/4\,\tau'_{yyyy}\\
&6.\ T_{zz} &&= h_{004} = 1/4\,\tau'_{zzzz}\\
&7.\ T_1 &&= h_{022} + h_{202} + h_{220}\\
&8.\ T_2 &&= h_{200}h_{022} + h_{020}h_{202} + h_{002}h_{220}\\
&9.\ \Phi_{xxx} &&= h_{600}
\end{aligned}
$$

Table 3. Relations among the $\tilde{h}_{pqr}$'s and the constants of the Typke Operator.

$$
\begin{aligned}
\tilde{h}_{200} &= B'_x - 8H'_J - 4H'_{JK} + 4H'_5 + 4H'_{10}\\
\tilde{h}_{020} &= B'_y + 16H'_J + 4H'_{JK} - 4H'_5 - 12H'_6 + 4H'_{10}\\
\tilde{h}_{002} &= B'_z - 8H'_J + 12H'_6 - 8H'_{10}\\
\tilde{h}_{400} &= -D'_J - 2\delta'_J + 2R'_6\\
\tilde{h}_{040} &= -D'_J + 2\delta'_J + 2R'_6\\
\tilde{h}_{004} &= -D'_J - D'_{JK} - D'_K\\
\tilde{h}_{220} &= -D'_J - 6R'_6 - 4H'_J + 6H'_6 - 4H'_{10}\\
\tilde{h}_{202} &= -D'_J - 1/2\,D'_{JK} - \delta'_J + 8H'_J + 2H'_{JK} - 2H'_5 - H'_6 + 2H'_{10}\\
\tilde{h}_{022} &= -D'_J - 1/2\,D'_{JK} + \delta'_J - 4H'_J - 2H'_{JK} + 2H'_5 + 2H'_{10}\\
\tilde{h}_{600} &= H'_J + H'_5 + 1/2\,H'_6 + H'_{10}\\
\tilde{h}_{060} &= H'_J - H'_5 + 1/2\,H'_6 - H'_{10}\\
\tilde{h}_{006} &= H'_J + H'_{JK} + H'_{KJ} + H'_K\\
\tilde{h}_{420} &= 3/2\,H'_J + 1/2\,H'_5 - 5/4\,H'_6 - 3/2\,H'_{10}\\
\tilde{h}_{240} &= 3/2\,H'_J - 1/2\,H'_5 - 5/4\,H'_6 + 3/2\,H'_{10}\\
\tilde{h}_{402} &= 3/2\,H'_J + 1/2\,H'_{JK} + H'_5 + 1/4\,H'_6\\
\tilde{h}_{042} &= 3/2\,H'_J + 1/2\,H'_{JK} - H'_5 + 1/4\,H'_6\\
\tilde{h}_{204} &= 3/2\,H'_J + H'_{JK} + 1/2\,H'_{KJ} + 1/2\,H'_5\\
\tilde{h}_{024} &= 3/2\,H'_J + H'_{JK} + 1/2\,H'_{KJ} - 1/2\,H'_5\\
\tilde{h}_{222} &= 3H'_J + H'_{JK} - 3/2\,H'_6
\end{aligned}
$$

Table 4. Relations between Watson's determinable constants and the constants of the Typke Operator.

$$
\begin{aligned}
B_x &= B'_x + 2D'_J + D'_{JK} - 2\delta'_J\\
B_y &= B'_y + 2D'_J + D'_{JK} + 2\delta'_J\\
B_z &= B'_z + 2D'_J + 12R'_6
\end{aligned}
$$

$$
\begin{aligned}
T_{xx} &= -D'_J - 2\delta'_J + 2R'_6\\
T_{yy} &= -D'_J + 2\delta'_J + 2R'_6\\
T_{zz} &= -D'_J - D'_{JK} - D'_K\\
T_1 &= -3D'_J - D'_{JK} - 6R'_6\\
T_2 &= -D'_J(B'_x + B'_y + B'_z) - 1/2\,D'_{JK}(B'_x + B'_y) + \delta'_J(B'_x - B'_y) - 6R'_6B'_z
\end{aligned}
$$

$$
\begin{aligned}
\Phi_{xxx} &= H'_J + H'_5 + 1/2\,H'_6 + H'_{10}\\
\Phi_{yyy} &= H'_J - H'_5 + 1/2\,H'_6 - H'_{10}\\
\Phi_{zzz} &= H'_J + H'_{JK} + H'_{KJ} + H'_K\\
\Phi_1 &= 30H'_J + 10H'_{JK} + 3H'_{KJ} - 15/2\,H'_6\\
\Phi_2 &= B'_x(3H'_J + 1/2\,H'_{JK} + 3/2\,H'_5 - H'_6 - 3/2\,H'_{10}) - B'_y(3/2\,H'_J + 1/2\,H'_{JK} + H'_5 + 1/4\,H'_6) - B'_z(3/2\,H'_J + 1/2\,H'_5 - 5/4\,H'_6 - 3/2\,H'_{10}) + 2\delta'_J(D'_{JK} - 2\delta'_J) - 8R'_6(D'_{JK} - 3\delta'_J + 4R'_6)\\
\Phi_3 &= B'_x(-3/2\,H'_J - 1/2\,H'_{JK} + H'_5 - 1/4\,H'_6) + B'_y(3H'_J + 1/2\,H'_{JK} - 3/2\,H'_5 - H'_6 + 3/2\,H'_{10}) + B'_z(-3/2\,H'_J + 1/2\,H'_5 + 5/4\,H'_6 - 3/2\,H'_{10}) - 2\delta'(D'_{JK} + 2\delta'_J) - 8R'_6(D'_{JK} + 3\delta'_J + 4R'_6)\\
\Phi_4 &= (3H'_J + 2H'_{JK} + H'_{KJ})(B'_z - 1/2\,B'_x - 1/2\,B'_y) + 1/2\,H'_5(B'_x - B'_y) - 1/2\,D'^2_{JK} - 2D'_{JK}D'_K - 2D'^2_K + 2\delta'^2_J.
\end{aligned}
$$

$$
\begin{aligned}
&10.\ \Phi_{yyy} &&= h_{060}\\
&11.\ \Phi_{zzz} &&= h_{006}\\
&12.\ \Phi_1 &&= 3(h_{420} + h_{402} + h_{240} + h_{042} + h_{204} + h_{024}) + h_{222}\\
&13.\ \Phi_2 &&= (h_{200} - h_{002})h_{420} + (h_{200} - h_{020})h_{402} - 2(h_{400} - h_{220})(h_{400} - h_{202})\\
&14.\ \Phi_3 &&= (h_{020} - h_{200})h_{042} + (h_{020} - h_{002})h_{240} - 2(h_{040} - h_{022})(h_{040} - h_{220})\\
&15.\ \Phi_4 &&= (h_{002} - h_{020})h_{204} + (h_{002} - h_{200})h_{024} - 2(h_{004} - h_{202})(h_{004} - h_{022}).
\end{aligned}
$$

Since these quantities are independent of the used transformation [12], they can be expressed as functions either of the original h_{pqr} or of the transformed $\tilde{h}_{pqr}$ without any change in the value of the B-, T- and Φ-constants.

We put, for comparison, the van Eijck-Typke Operator also in the (transformed) Watson standard form [11]. This can be made by mathematical rearrangement with use of the commutation rules. After some calculations one gets the relations between the 19 constants of the transformed Watson standard form and the 15 constants of the suitable operator used in form of a matrix equation. These

Table 5. Watson's determinable constants for Methylhypochlorite up to the sixth order obtained from van Eijck-Typke and Watson's s-reduction constants. – The errors are standard errors from the least squares fitting procedure and are given in units of the last figure. – The symbol M indicates the value of $A + B + C$.

	$CH_3O^{35}Cl$		$CD_3O^{35}Cl$		
	from van Eijck-Typke	from Watson's s-reduction	from van Eijck-Typke	from Watson's s-reduction	
A	42.0649336(97)	42.0649336(97)	32.5392076(45)	32.5392076(45)	GHz
B	6.29686060(116)	6.29686060(116)	5.46525189(73)	5.46525189(73)	GHz
C	5.67059500(102)	5.67059499(100)	4.97498694(60)	4.97498694(60)	GHz
τ_{aa}	−2691.6(12)	−2691.6(10)	−1082.2(12)	−1082.2(12)	KHz
τ_{bb}	− 22.401(14)	− 22.401(12)	− 16.426(9)	− 16.426(9)	KHz
τ_{cc}	− 11.952(12)	− 11.952(12)	− 9.171(8)	− 9.171(8)	KHz
τ_1	47.574(202)	47.574(193)	− 16.032(57)	− 16.032(57)	KHz
τ_2/M	− 5.804(30)	− 5.804(29)	− 10.26(1)	− 10.26(1)	KHz
Φ_{aaa}	49.9(52)	49.9(52)	9.3(64)	9.3(64)	Hz
Φ_{bbb}	0.0015(14)	0.0018(22)	0.0043(14)	0.0052(15)	Hz
Φ_{ccc}	0.0008(28)	0.0004(30)	0.0019(15)	0.0010(14)	Hz
Φ_1	− 11.02(107)	− 11.02(133)	− 1.59(27)	− 1.59(32)	Hz
$\Phi_2 + \Phi_3/M$	0.0027(62)	0.0027(55)	− 0.0062(26)	− 0.0061(30)	Hz
$\Phi_2 - \Phi_3/M$	− 0.0024(62)	− 0.0026(20)	− 0.0002(26)	− 0.0007(34)	Hz
Φ_4/M	− 19.5(2)	− 19.5(3)	− 3.74(6)	− 3.74(6)	Hz

relations are listed in Table 3 for the van Eijck-Typke Operator. From this matrix equation it follows that there should exist four different relations between the $\bar{h}_{pqr}$ constants which can be obtained by solution of the equations system. One relation connects the fourth order contants, the others the sixth order constants together. If one considers only the terms up to the fourth order, one gets for the Watson and the van Eijck-Typke Operators the same relation:

$$\bar{h}_{400} - \bar{h}_{040} = 2\,(\bar{h}_{202} - \bar{h}_{022})$$

which means that both Operators are equal up to the fourth order. We can see that this relation agrees with the results given in Tables 1a and 3a. The further consideration of the sixth order terms gives different relations for both operators, i.e. for the van Eijck-Typke Operator

$$\begin{aligned} &3\,(\bar{h}_{600} - \bar{h}_{060}) + 2\,(\bar{h}_{420} - \bar{h}_{240}) \\ &= 4\,(\bar{h}_{402} - \bar{h}_{042}) = 8\,(\bar{h}_{204} - \bar{h}_{024}) \\ &3\,\bar{h}_{600} + 2\,\bar{h}_{222} = 4\,\bar{h}_{402} + 2\,\bar{h}_{240} \end{aligned}$$

and for the Watson Operator

$$\begin{aligned} &15\,(\tilde{\bar{h}}_{600} - \tilde{\bar{h}}_{060}) + 2\,(\tilde{\bar{h}}_{420} - \tilde{\bar{h}}_{240}) \\ &= 16\,(\tilde{\bar{h}}_{402} - \tilde{\bar{h}}_{042}) = 32\,(\tilde{\bar{h}}_{204} - \tilde{\bar{h}}_{024}); \\ &27\,\tilde{\bar{h}}_{600} + 16\,\tilde{\bar{h}}_{222} = 3\,\tilde{\bar{h}}_{060} + 6\,\tilde{\bar{h}}_{420} + \\ &+ 32\,\tilde{\bar{h}}_{402} + 10\,\tilde{\bar{h}}_{240}, \end{aligned}$$

were the $\tilde{\bar{h}}_{pqr}$'s indicate that in this case another transformation is needed. Because of these different relations among the sixth order terms, both Operators are different and the constants obtained cannot be directly compared.

The transformation of the constants obtained by the van Eijck-Typke Operator in one set of "determinable parameters" according to Watson, can be performed through the constants h_{pqr} of Table 3 and leads to a representation which is independent of the chosen form of the operator [11]. In Table 4, Watson's "determinable parameters" are listed as functions of the van Eijck-Typke constants, and this procedure is applied to $CH_3O^{35}Cl$ and $CD_3O^{35}Cl$. The results are shown in Table 5. A comparison among Watson's determinable parameters obtained using the constants of the two operators (Table 8) shows a large agreement within the given standard errors for both molecules, as expected.

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