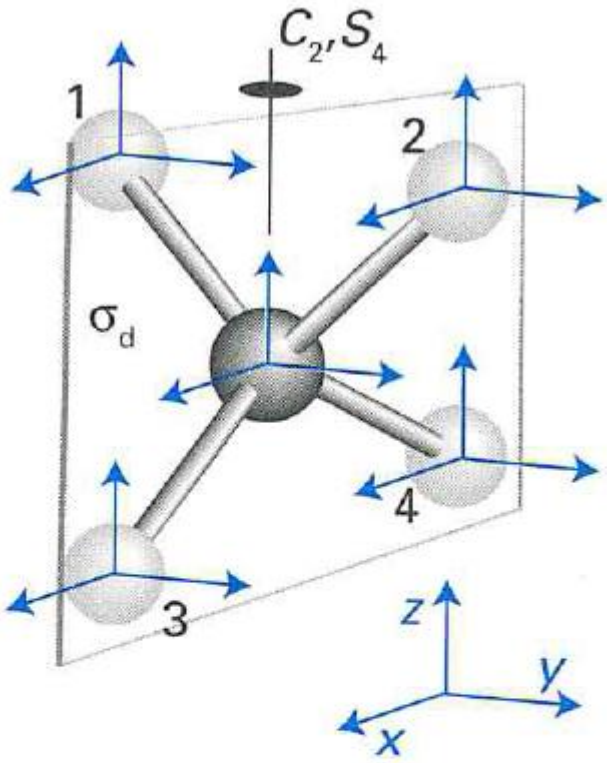
Schwingungsmoden von CH_4



$T_d, \bar{4}3m$	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	$h = 24$
A_1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_2	1	1	1	−1	−1	
E	2	−1	2	0	0	$(3z^2 - r^2, x^2 - y^2)$
T_1	3	0	−1	−1	1	(R_x, R_y, R_z)
T_2	3	0	−1	1	−1	(x,y,z), (xy,xz,yz)

5 Symmetrieklassen
5 Symmetrierassen
24 Symmetrieoperationen (=h)

Fig. 10.27 The displacements used in the discussion of the normal modes of a tetrahedral methane molecule.

S_4 = Molekülachse (damit auch C_2)
Bei Transformation (x,y,z) alle drei C_2 beachten!

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Schwingungsmoden von CH_4

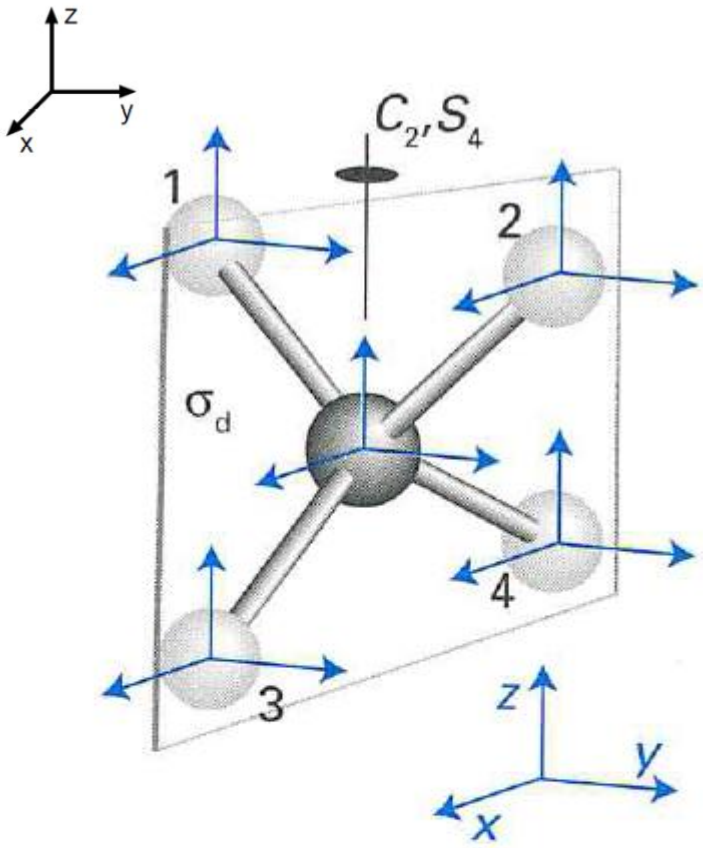

Fig. 10.27 The displacements used in the discussion of the normal modes of a tetrahedral methane molecule.

Charaktere der Symmetrieoperationen

$$\chi_E = 15$$

$$\chi_{C_2} = (-1-1+1) = -1$$

$$\chi_{\sigma_d} = (1-1+1)+(1-1+1)+(1-1+1) = 3$$

$$\chi_{S_4} = (0+0-1) = -1$$

$$\chi_{C_3} = ?$$

S_4 = Molekülachse (damit auch C_2)
Bei Transformation (x,y,z) alle drei C_2 beachten!

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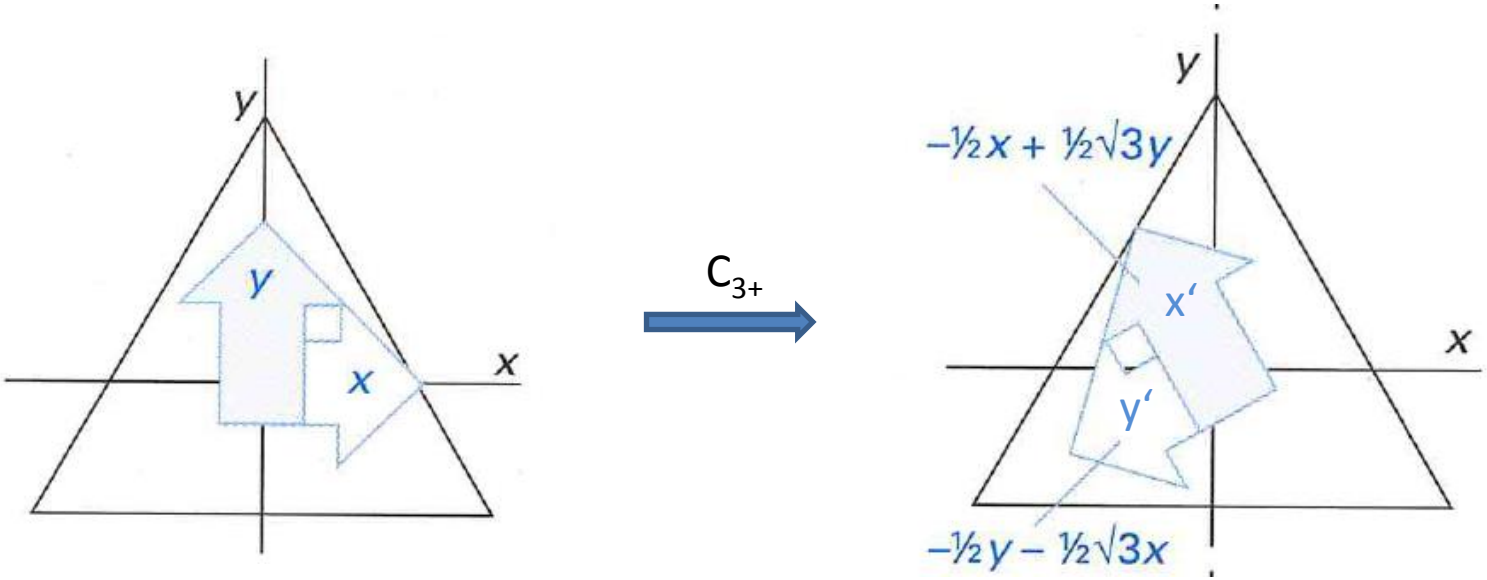
Zur Symmetrieoperation C_3



$$\vec{q}_x = \begin{pmatrix}1\\0\\0\end{pmatrix}, \vec{q}_y = \begin{pmatrix}0\\1\\0\end{pmatrix}, \vec{q}_z = \begin{pmatrix}0\\0\\1\end{pmatrix}$$

$$\vec{q}_x' = \begin{pmatrix}-\cos(60°)\\+\sin(60°)\\0\end{pmatrix}, \vec{q}_y = \begin{pmatrix}-\sin(60°)\\-\cos(60°)\\0\end{pmatrix}, \vec{q}_z = \begin{pmatrix}0\\0\\1\end{pmatrix}$$

$$\Gamma_{C_{3+}} = \begin{pmatrix}-1/2 & \sqrt{3}/2 & 0\\ -\sqrt{3}/2 & -1/2 & 0\\ 0 & 0 & 1\end{pmatrix}$$

$$\chi_{C_{3+}} = 0$$

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Schwingungsmoden von CH_4

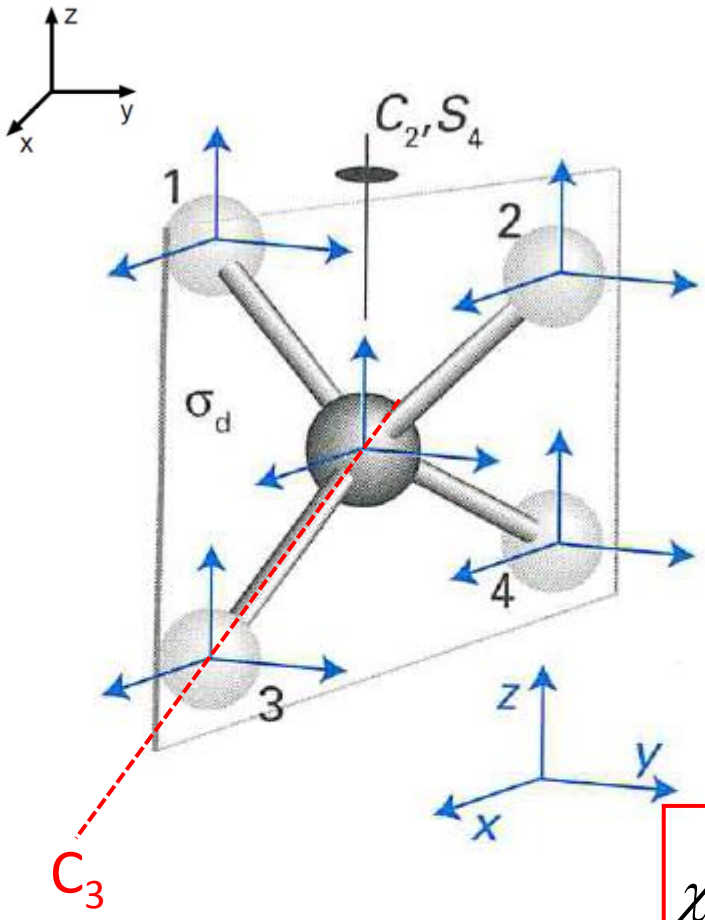

Fig. 10.27 The displacements used in the discussion of the normal modes of a tetrahedral methane molecule.

Charaktere der Symmetrieoperationen

$$\chi_E = (1+1+1)+(1+1+1)+(1+1+1)+$$
$$(1+1+1)+(1+1+1)=15$$

$$\chi_{C_2} = (-1-1+1)=-1$$

$$\chi_{\sigma_d} = (1-1+1)+(1-1+1)+(1-1+1)=3$$

$$\chi_{S_4} = (0+0-1)=-1$$

$$\chi_{C_3} = \left(\left(-\frac{1}{2}\right)+\left(-\frac{1}{2}\right)+1\right)+\left(\left(-\frac{1}{2}\right)+\left(-\frac{1}{2}\right)+1\right)=0$$

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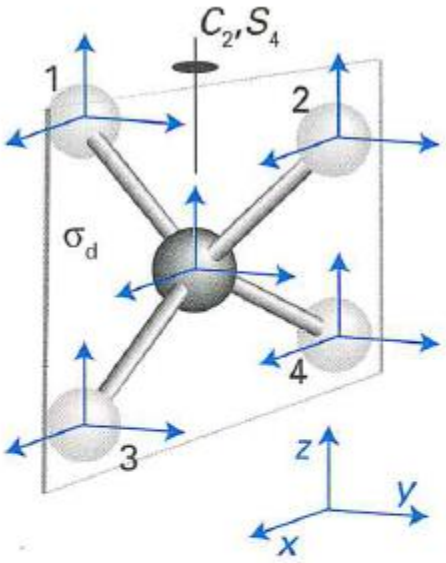

Fig. 10.27 The displacements used in the discussion of the normal modes of a tetrahedral methane molecule.

Reduzible Darstellung von CH_4

$$\Gamma_{ges} = c_1 A_1 + c_2 A_2 + c_3 E + c_4 T_1 + c_5 T_2$$

$$c_1(A_1) = \frac{1}{h}\sum_{i=1}^{5}[n(R_i)\chi(R_i, A_1)\chi(R_i, CH_4)]$$

$T_d, \bar{4}3m$	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	$h=24$	
A_1	1	1	1	1	1	$x^2+y^2+z^2$	
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0	$(3z^2-r^2, x^2-y^2)$	
T_1	3	0	−1	−1	1		(R_x, R_y, R_z)
T_2	3	0	−1	1	−1	$(x, y, z), (xy, xz, yz)$	

	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
$\chi_{R_i}(CH_4)$	15	0	-1	3	-1

Schwingungsmoden von CH_4

$T_d, \bar{4}3m$	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	$h = 24$
A_1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_2	1	1	1	−1	−1	
E	2	−1	2	0	0	$(3z^2 - r^2, x^2 - y^2)$
T_1	3	0	−1	−1	1	(R_x, R_y, R_z)
T_2	3	0	−1	1	−1	(x,y,z), (xy,xz,yz)

Reduzible Darstellung (3N x 3N Matrix):

$$\Gamma_{ges} = A_1 + E + T_1 + 3T_2$$ ***(3N Freiheitsgrade)***

Translation: $\Gamma_{trans} = T_2$ ***(3 FGs Translation)***

Rotation: $\Gamma_{rot} = T_1$ ***(3 FGs Rotation)***

Schwingung: $\Gamma_{vib} = A_1 + E + 2T_2$ ***(3N-6 Schwingungen)***

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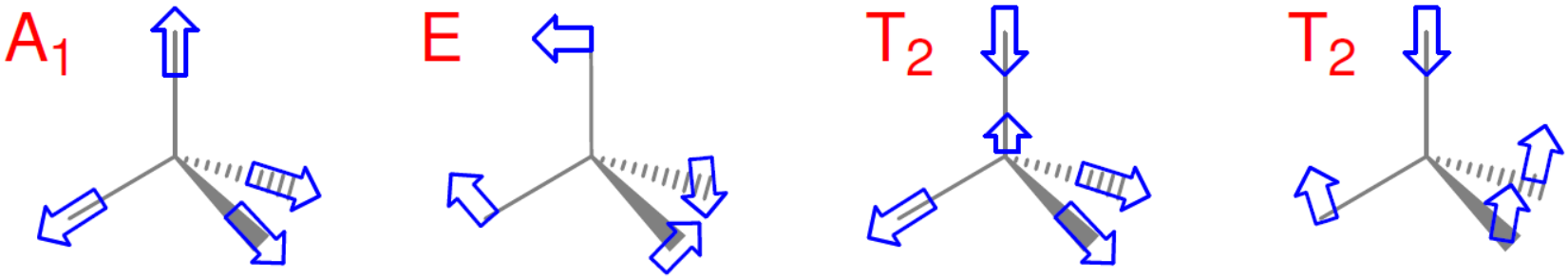
Schwingungsmoden von CH_4

$$\Gamma_{vib} = A_1 + E + 2T_2$$



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$T_d, \bar{4}3m$	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	$h=24$	
A_1	1	1	1	1	1	$x^2+y^2+z^2$	
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0	$(3z^2-r^2, x^2-y^2)$	
T_1	3	0	−1	−1	1		(R_x, R_y, R_z)
T_2	3	0	−1	1	−1	$(x, y, z), (xy, xz, yz)$	

Schwingungsmoden von CH_4

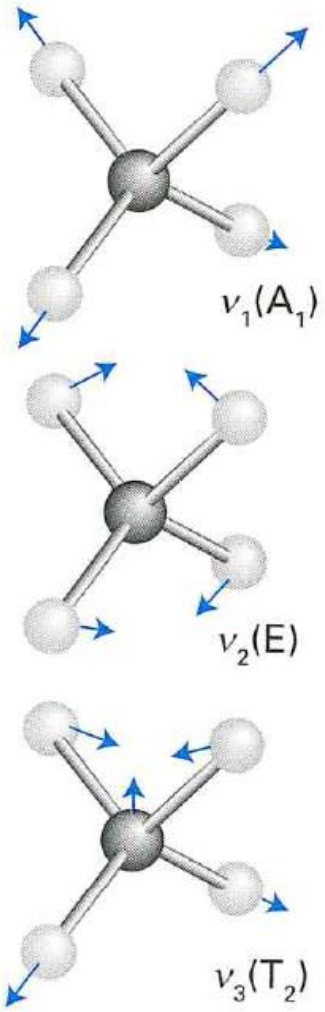

Fig. 10.28 Three representative normal modes of a tetrahedral molecule.

$T_d, \bar{4}3m$	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	$h = 24$
A_1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_2	1	1	1	−1	−1	
E	2	−1	2	0	0	$(3z^2 - r^2, x^2 - y^2)$
T_1	3	0	−1	−1	1	(R_x, R_y, R_z)
T_2	3	0	−1	1	−1	(x,y,z), (xy,xz,yz)

$$\Gamma_{vib} = A_1 + E + 2T_2$$

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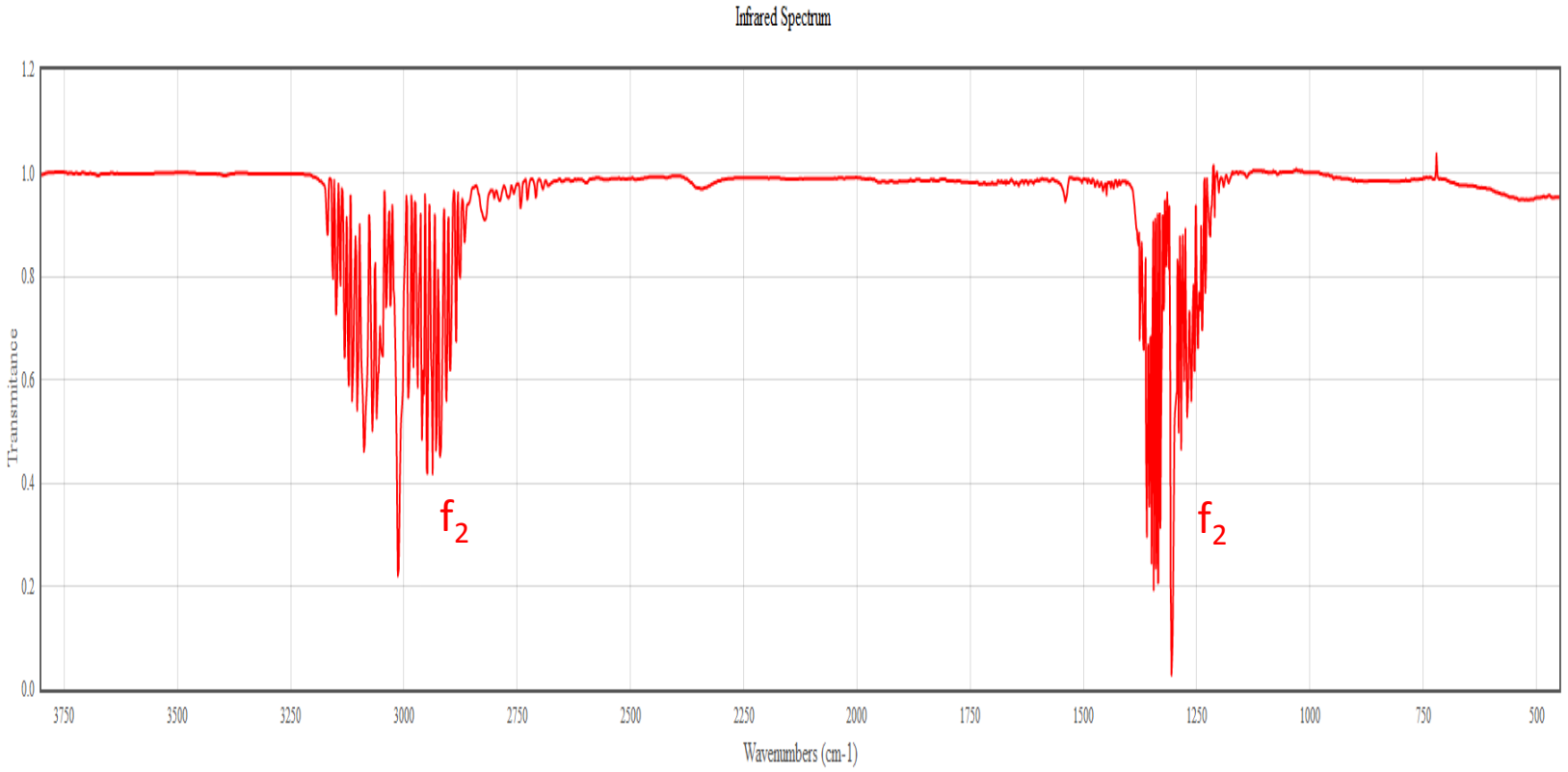
Schwingungsmoden von CH_4



a_1	1	Sym str	2917 cm-1
e	2	Deg deform	1534 cm-1
f_2	3	Deg str	3019 cm-1
f_2	4	Deg deform	1306 cm-1

Schwingungsmoden von SF_6

O_h ($m3m$)	E	$8C_3$	$6C_2$	$6C_2$	$3C_2 (=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$h=48$	
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xy, yz, xy)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

Reduzible Darstellung (3N x 3N Matrix):

$$\Gamma_{ges} = A_{1g} + E_g + T_{1g} + T_{2g} + 3T_{1u} + T_{2u}$$ ***(3N Freiheitsgrade)***

Translation: $\Gamma_{trans} = T_{1u}$ ***(3 FGs Translation)***

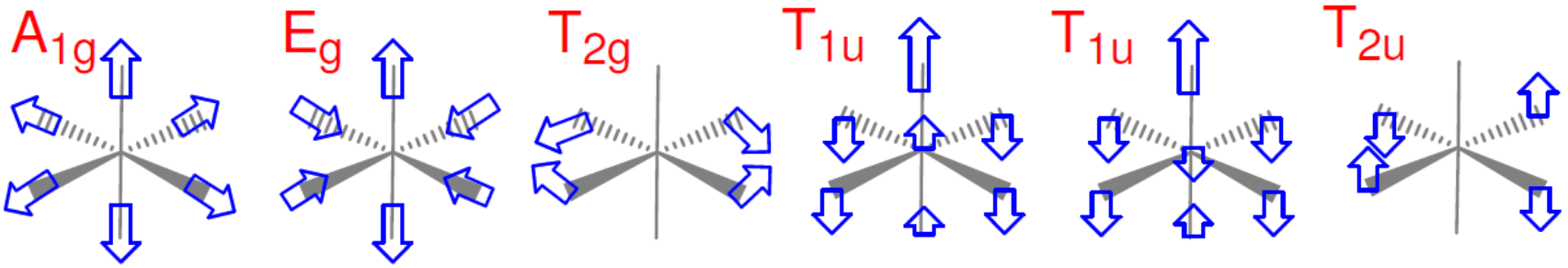
Rotation: $\Gamma_{rot} = T_{1g}$ ***(3 FGs Rotation)***

Schwingung: $\Gamma_{vib} = A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u}$ ***(3N-6 Schwingungen)***

Schwingungsmoden von SF_6

O_h ($m3m$)	E	$8C_3$	$6C_2$	$6C_2$	$3C_2 (=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$h=48$	
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xy, yz, xy)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

$$\Gamma_{vib} = A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u}$$



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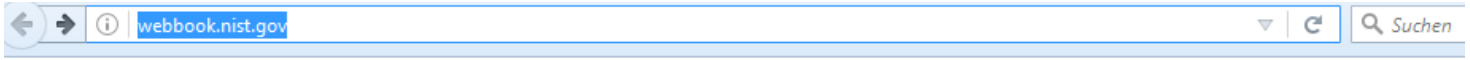
Online Datenbank zu IR-Spektren

http://webbook.nist.gov



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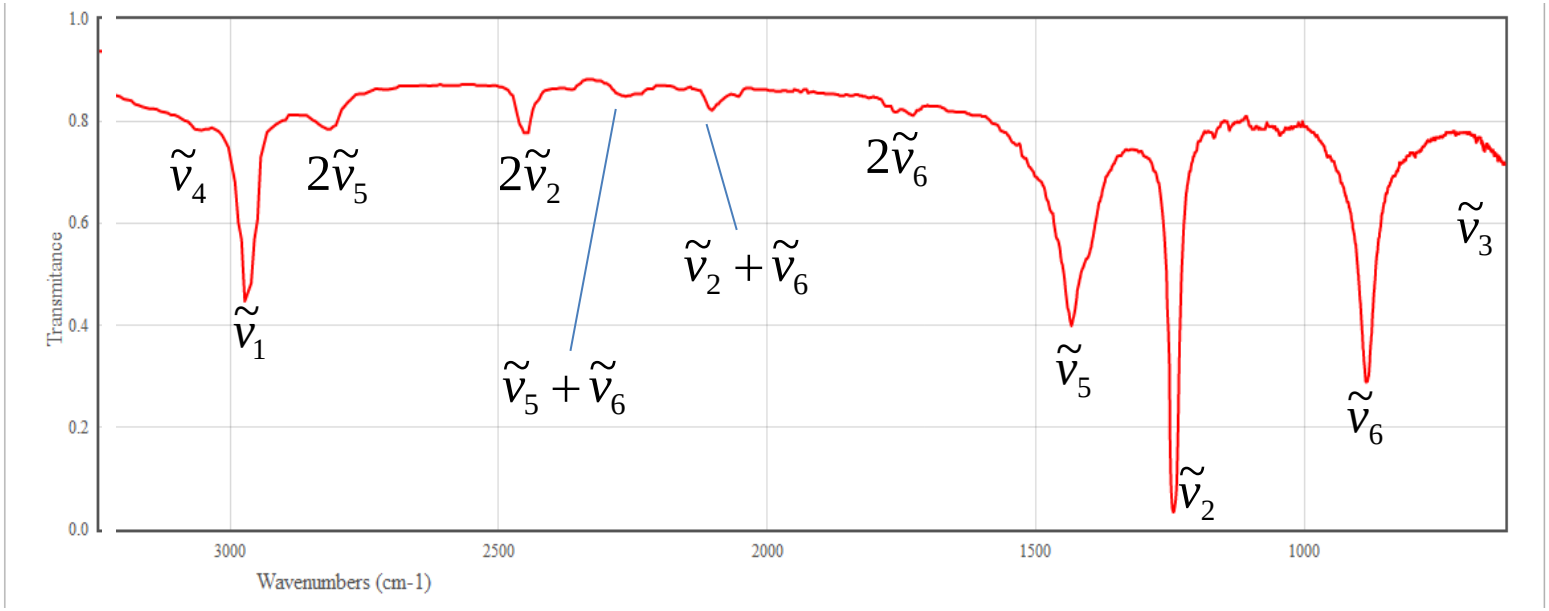
- **UV/Vis spectra for over 1600 compounds.**
- **Gas chromatography data for over 27,000 compounds.**
- **Electronic and vibrational spectra for over 5000 compounds.**
- **Constants of diatomic molecules (spectroscopic data) for over 600 compounds.**

Schwingungen mehratomiger Moleküle: CH_3I

http://webbook.nist.gov/cgi/cbook.cgi?ID=C74884&Mask=80



A_1

$$\tilde{\nu}_1 = 2970 cm^{-1}$$
$$\tilde{\nu}_2 = 1252 cm^{-1}$$
$$\tilde{\nu}_3 = 533 cm^{-1}$$

$$\tilde{\nu}_4 = 3060 cm^{-1}$$
$$\tilde{\nu}_5 = 1440 cm^{-1}$$
$$\tilde{\nu}_6 = 880 cm^{-1}$$

E

Gruppenschwingungen im IR

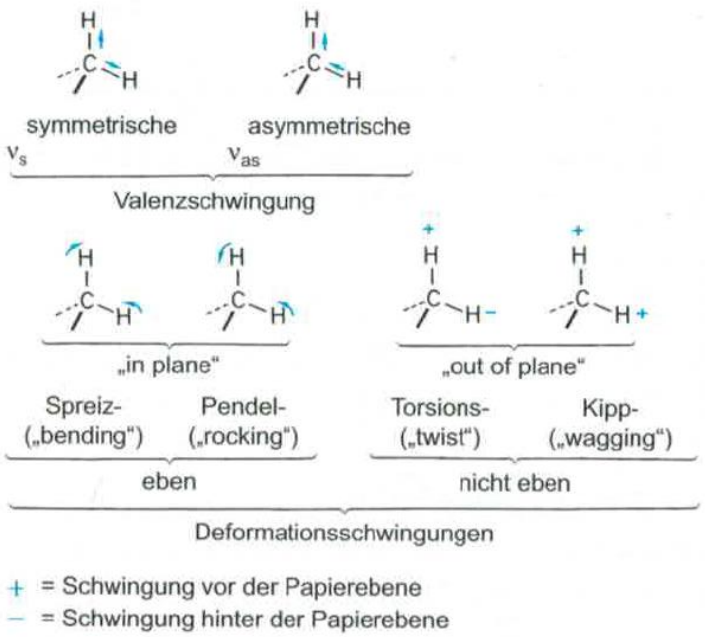


Table 6.3 Typical bond-stretching and angle-bending group vibration wavenumbers $\tilde{\nu}$.

Bond-stretching		Bond-stretching	
Group	$\tilde{\nu}$/cm^{-1}	Group	$\tilde{\nu}$/cm^{-1}
≡C–H	3300	–O–H	3600‡
=C–H except O=C–H	3020	>N–H	3350
	2800	>P=O	1295
>C–H	2960	>S=O	1310
		Angle-bending	
–C≡C–	2050	≡C–H	700
>C=C<	1650	=C(H)–H	1100
>C–C<	900		
>Si–Si<	430	–C(H)(H)–H	1000
>C=O	1700		
–C≡N	2100		
>C–F	1100		
>C–Cl	650	C(H)(H)	1450
>C–Br	560		
>C–I	500	C≡C–C	300

Hesse, Meier & Zeeh, Spektroskopische Methoden

Hollas, Modern Spectroscopy

Symmetrie von Gruppenschwingungen

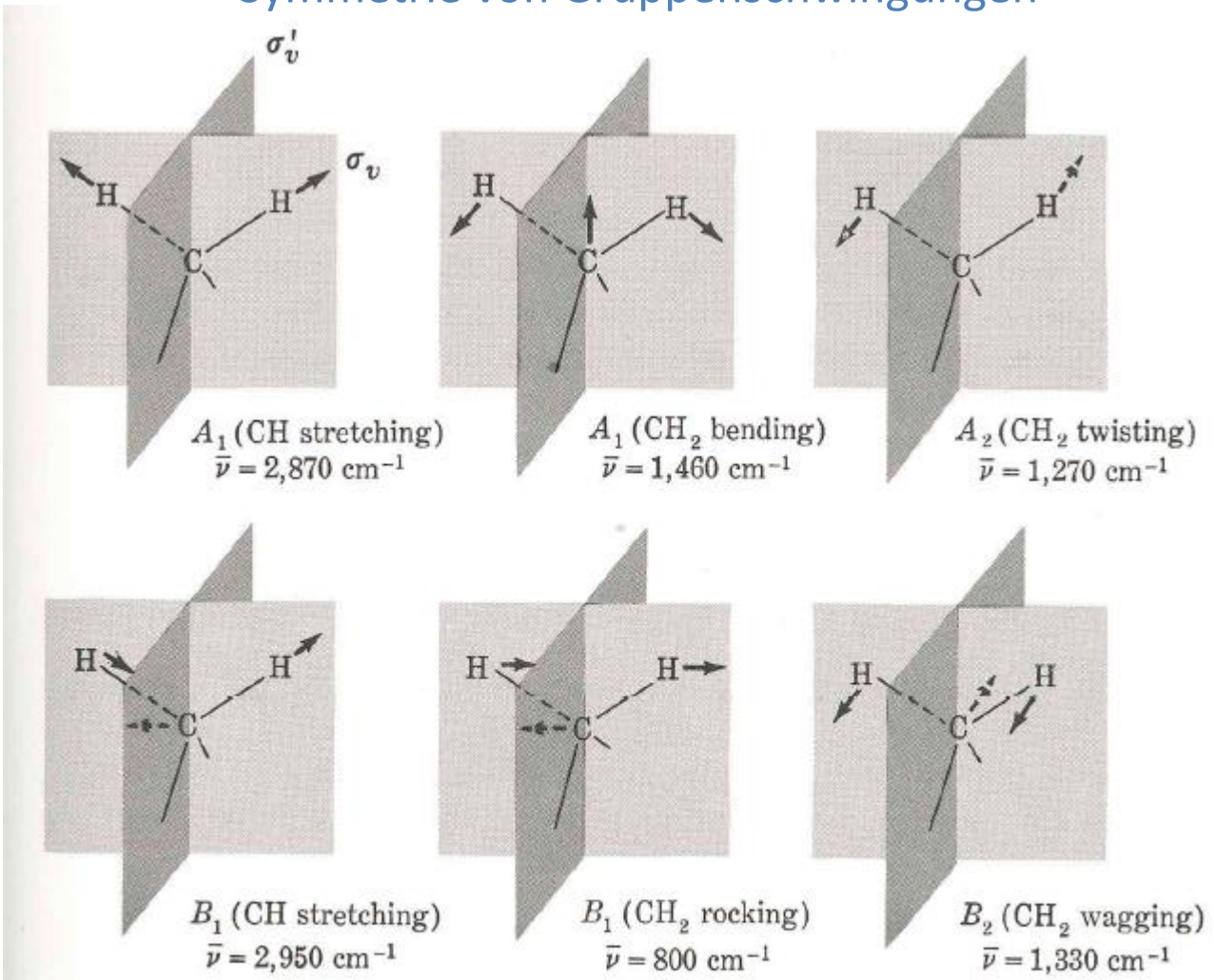


Fig. 8-21 Various vibrational modes of the methylene group. (*By permission of G. M. Barrow, "Introduction to Molecular Spectroscopy," McGraw-Hill Book Company, New York, 1962.*)

Raymond Chang, Basic Principles of Spectroscopy