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A 51

Infrarot - Absorptions - Spektroskopie

22.2.17

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Praktikum: A51
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Objective

The objective of the experiment is to measure the rotational-vibrational spectrum of carbon monoxide CO with a Fourier transform infrared spectrometer FTIR. Afterwards we interpret the spectrum and determine the resonant vibrational frequencies, rotational constants, moments of inertia and bond lenghts of CO.

Basics

The FTIR provides an absorption spectrum by using a Michelson interferometer. All wavelengths are measured simultaneously. The obtained interferogram is converted into an absorption spectrum using an fast fourier transformation-algorithm.

Absorption occurs by changing the vibrational and rotational states of the sample, but only certain energys can be absorbed. This leads to the individual peaks in the spectrum.

The oscillation in the CO-Molecule can approximately be described as the oscillation of point masses in a harmonic potential.

Related Schrödinger equation: $-\frac{\hbar}{2\mu}\frac{\partial^2}{\partial x^2}\Psi(x) + \frac{1}{2}kx^2\Psi(x) = E\Psi(x)$

Solved by $E_{vib}(v) = hc\tilde{\nu}_0\left(v+\frac{1}{2}\right)$ $v=0,1,2,\dots$ $\tilde{\nu}_0 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

The rotation of the molecule follows the principle of the rigid rotator.

Energy states $E_{rot}(J) = hcBJ(J+1)$; $J=0,1,2,\dots$ $B = \frac{h}{8\pi^2 cI} = \frac{\hbar}{4\pi cI}$

B is the rotational constant that is used to derive the bond length and the moment of inertia.

$I = \frac{\hbar}{4\pi cB}$; $I = \mu r^2$

In order to interpret the spectrum following selection rules must be observed:

Source: Description of experiment
Atkins, Physikalische Chemie, WILEY-VCH, Weinheim 2013

global rules: for rotational ~~exiton~~ excitation a molecule must have a permanent electric dipole moment.
for vibrational excitation the electric dipole moment has to change as a function of the nuclei distance.

Also the specific selection rules limit the possible quantum numbers.

two atomic oscillator $\Delta v = \pm 1$; ~~the~~ two atomic ridged rotator $\Delta J = \pm 1$

If one ~~o~~ compares the reality with the previous considerations, one can see deviations. These come from the anharmonicity of the [illegible] oscillator. Therefore corrections have to be implied.

Equations for data evaluation

Fundamental: $\tilde{\nu}_{R(J)} - \tilde{\nu}_{P(J)} = B_1(4J+2)$; $\frac{1}{2}(\tilde{\nu}_{R(J-1)} + \tilde{\nu}_{P(J)}) = \tilde{\nu}_{1\leftarrow 0} - \alpha_e J^2$
$\tilde{\nu}_{R(J-1)} - \tilde{\nu}_{P(J+1)} = B_0(4J+2)$

Overtone: $\tilde{\nu}_{R(J)} - \tilde{\nu}_{P(J)} = B_2(4J+2)$; $\frac{1}{2}(\tilde{\nu}_{R(J-1)} + \tilde{\nu}_{P(J)}) = \tilde{\nu}_{2\leftarrow 0} - 2\alpha_e J^2$
$\tilde{\nu}_{R(J-1)} - \tilde{\nu}_{P(J+1)} = B_0(4J+2)$

Rotational constant $B_v = B_e - \alpha_e(v + \frac{1}{2})$

Anharmonicity $\frac{\tilde{\nu}_{v\leftarrow 0}}{v} = \tilde{\nu}_e - \tilde{\nu}_e x_e(v+1)$

Experimental procedure

First a background spectrum was measured, so there was no sample between the light source and the detector. After that another spectrum was measured but this time the CO cuvette is in the beam path. The resolution value amounts to 0.5 and 5 scans per sample were measured.

Data evaluation

The rotational constants B_0, B_1 and B_2 are determined by the gradient of the linear regression of the measured wavenumbers (graphs attached). With those constants the moments of Inertia I are calculated by the equation given in the basics. Also the bondlength R of the CO-Molecule is calculated that way: $R = \sqrt{\frac{I}{\mu}}$ (conversion of the equation in the basics). The calculation of the anharmonicity constant x_e is a consequence of the linear regression of the equation $\frac{\tilde{\nu}_{v\leftarrow0}}{v} = \tilde{\nu}_e - \tilde{\nu}_e x_e (v+1)$. The gradient is given by the Program originLab and to get x_e it had to be divided by $\tilde{\nu}_e$. All results are listet in a table in the annex.

Critical discussion

$\tilde{\nu}_{0\to1}$ exists more often than $\tilde{\nu}_{0\to2}$ which is a result of the Boltzmann-distribution so the intensity of the harmonic oscillator is smaller.

As the results of the rotational constants deviate from the literature all the other results cannot be exactly equal with the literature, too.

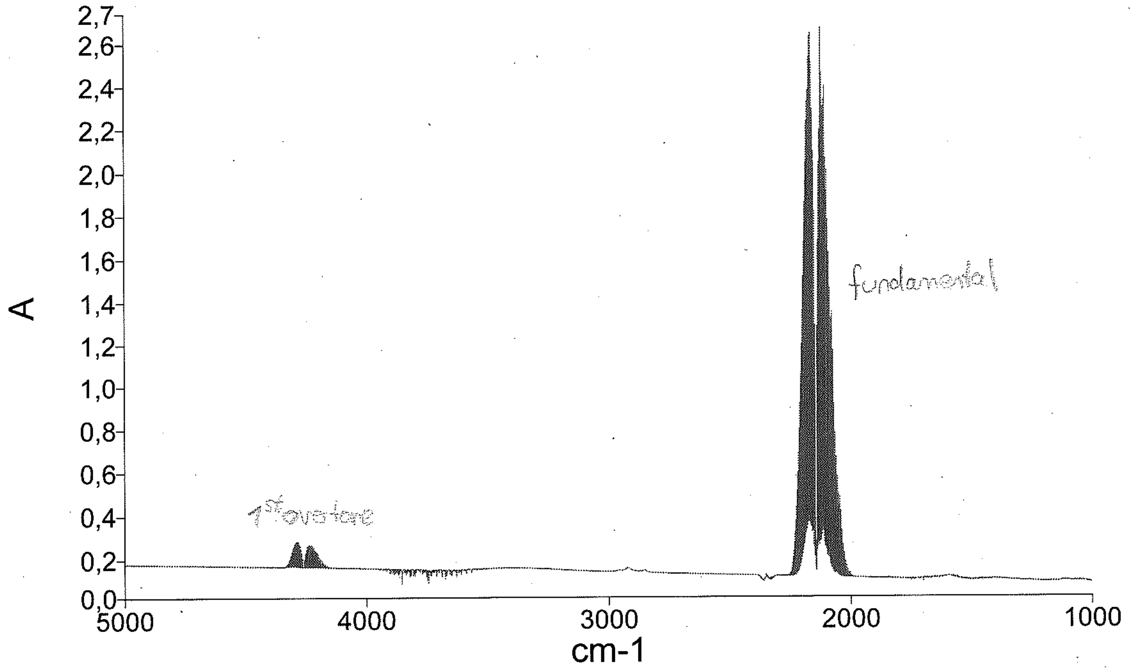
Centrifugal forces stretch the bond of the molecule, so the rotational constants get smaller and cause asymmetrical behaviour.

The Q-branch shouldn't be in the CO-spectrum because of the selection rules. In the fundamental there is a small peak in the Q-branch which indicates that the carbonmonoxide molecule is not an ideal harmonic oscillator. Only in this model the selection rules forbit the Q-branch.

Source for literature data:

- description of experiment
- Atkins, Physikalische Chemie, WILEY-VCH, Weinheim 2013
- Pyler, E.K.; Blaine, L.R.; Connor, W.S J. Opt. Soc. Amer. 1955, 45, 102-106
- Rank, D.H.; Guenther, A.H.; Saksena, G.D.; Shearer, J.A. J. Opt. Soc. Amer. 1957, 47, 688-689

Anwender	Praktikum
DatumUhrzeit	Mittwoch, 22. Februar 2017 11:01



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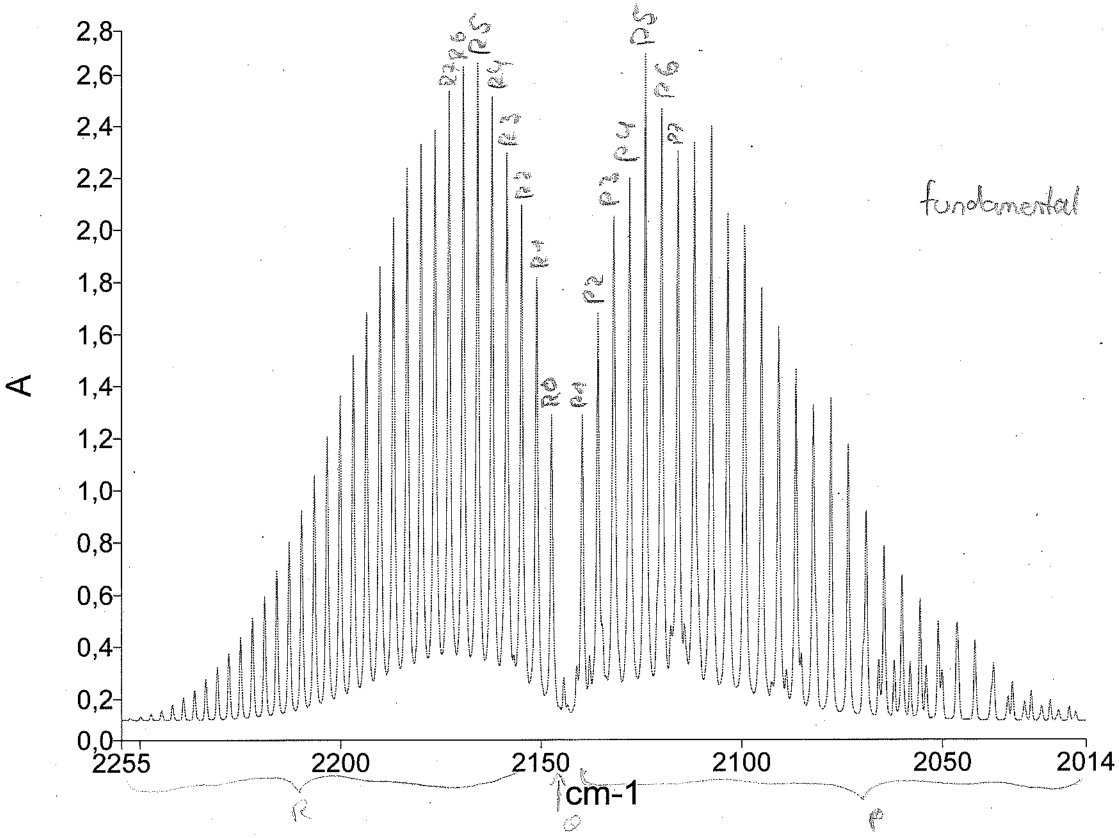

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Praktikum date
Mittwoch, Februar 22
2017

PerkinElmer Spectrum Version 10.03.06
Mittwoch, 22. Februar 2017 11:03

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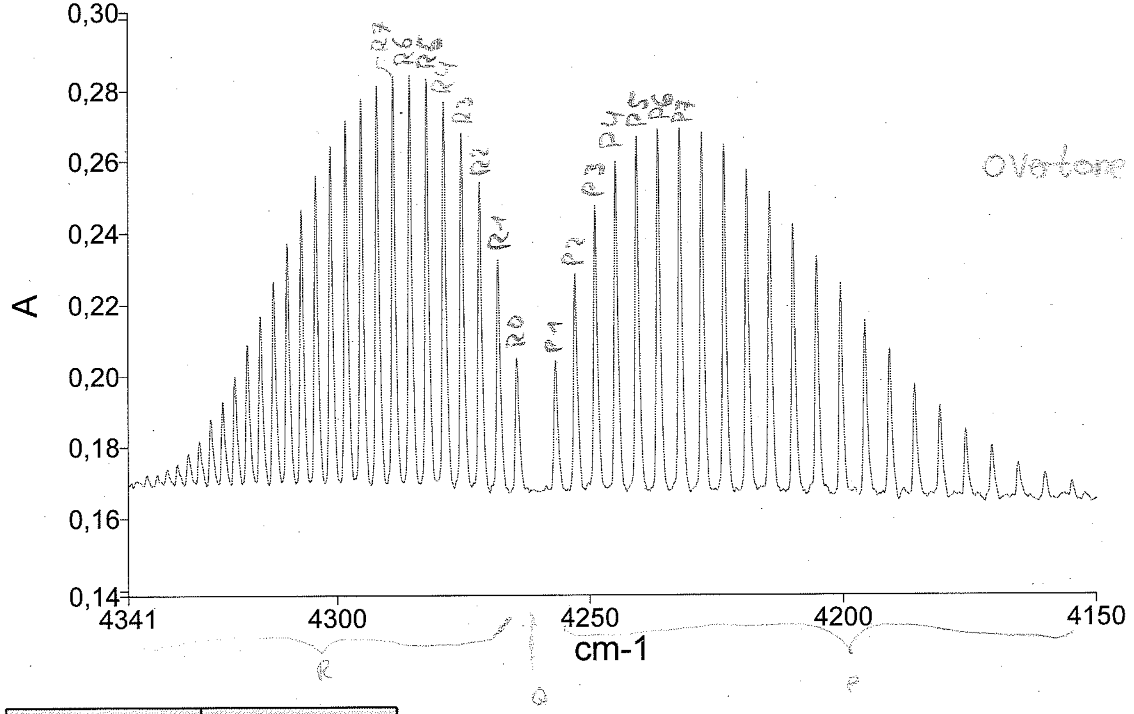
DatumUhrzeit Mittwoch, 22. Februar 2017 11:03



Probenname	Beschreibung
Praktikum47_2	Sample 016 By Praktikum date Mittwoch, Februar 22 2017

Quellspektren-Ergebnisse
Name des Spektrums

Liste der Peakflächen/Peakhöhen			
Name des Peaks	X (cm-1)	Y (A)	
1	4312,53	0,2265	
2	4309,82	0,2372	
3	4307,03	0,2465	
4	4304,19	0,2559	
5	4301,27	0,2641	R10
6	4298,27	0,2718	R9
7	4295,19	0,2777	R8
8	4292,06	0,2813	R7
9	4288,85	0,2842	R6
10	4285,57	0,2842	R5
11	4282,21	0,2833	R4
12	4278,79	0,2767	R3
13	4275,3	0,268	R2
14	4271,74	0,254	R1
15	4268,1	0,2324	R0
16	4252,86	0,2285	P1
17	4248,88	0,2474	P2
18	4244,82	0,26	P3
19	4240,69	0,267	P4
20	4236,5	0,269	P5
21	4232,23	0,2691	P6
22	4227,9	0,2681	P7
23	4223,5	0,2645	P8
24	4219,04	0,2572	P9
25	4214,5	0,2511	P10
26	4209,89	0,2421	

Liste der Peakflächen/Peakhöhen

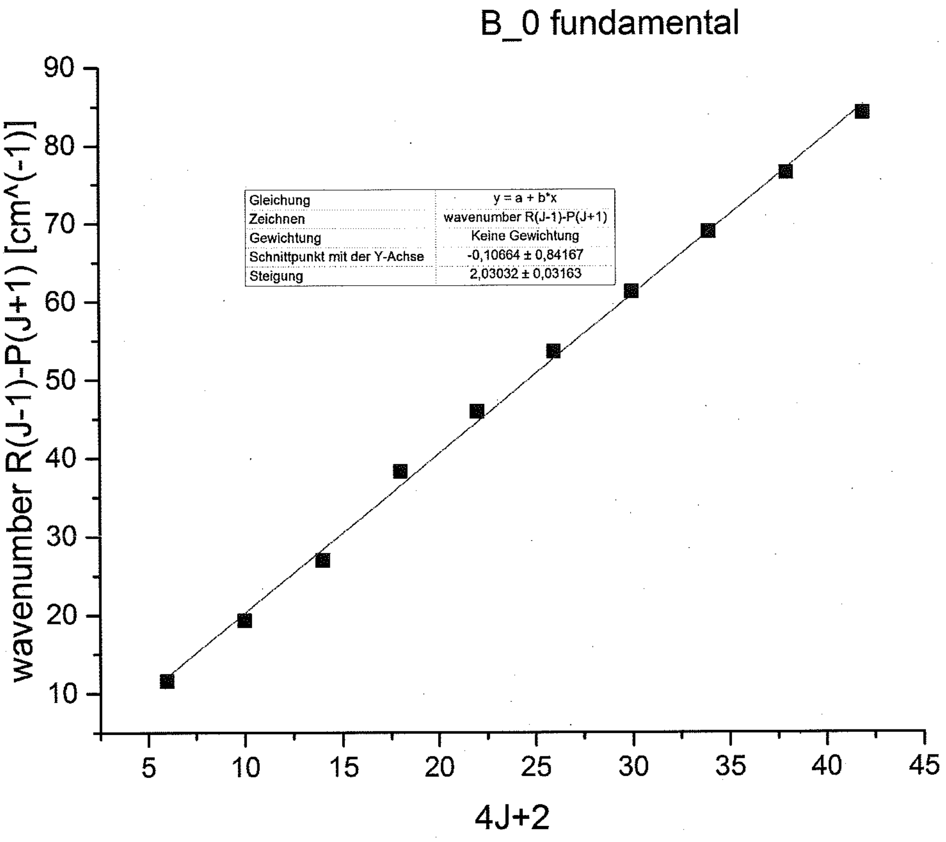
Name des Peaks	X (cm-1)	Y (A)	
27	4205,22	0,2331	
28	4200,49	0,2257	
29	3842,52	0,1577	
30	3417,13	0,1626	
31	2241,94	0,1782	
32	2239,2	0,2045	
33	2236,43	0,2368	
34	2233,62	0,2755	
35	2230,77	0,3201	
36	2227,89	0,3735	
37	2224,96	0,4365	
38	2221,99	0,511	
39	2218,98	0,596	
40	2215,93	0,6923	
41	2212,85	0,8039	
42	2209,72	0,9239	
43	2206,57	1,0588	
44	2203,37	1,2064	
45	2200,13	1,3632	
46	2196,86	1,5207	
47	2193,54	1,6836	
48	2190,2	1,8613	
49	2186,81	2,0503	R10
50	2183,4	2,2362	R9
51	2179,93	2,3282	R8
52	2176,45	2,3835	R7
53	2172,91	2,5383	R6
54	2169,38	2,6341	R5
55	2165,79	2,6491	R4
56	2162,15	2,5173	R3

Liste der Peakflächen/Peakhöhen

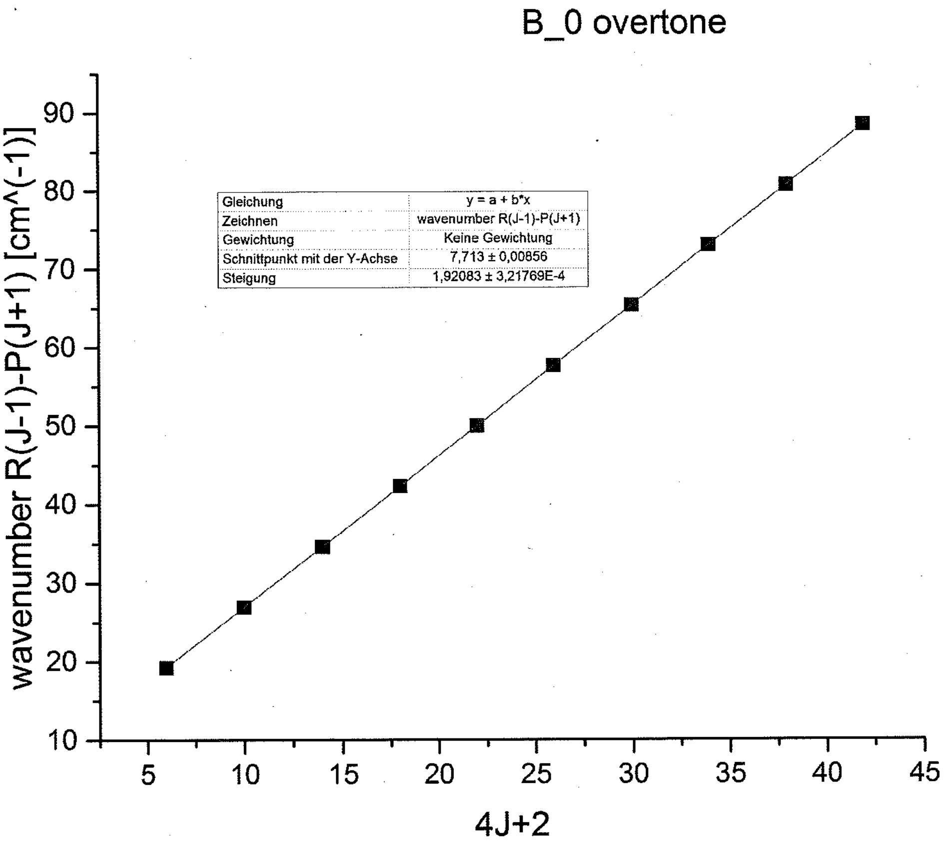
Name des Peaks	X (cm-1)	Y (A)	
58	2154,79	2,0964	R2
59	2151,01	1,8173	R1
60	2147,3	1,2876	R0
61	2144,28	0,2791	Q
62	2141,03	0,3248	Q
63	2139,63	1,289	P1
64	2137,82	0,3632	
65	2135,73	1,6825	P2
66	2131,77	2,0511	P3
67	2127,85	2,2008	P4
68	2123,9	2,6783	P5
69	2119,87	2,4705	P6
70	2115,8	2,303	P7
71	2114,22	0,4882	
72	2111,71	2,3388	P8
73	2107,55	2,4003	P9
74	2103,44	2,0664	P10
75	2099,28	2,0147	
76	2095,05	1,7803	
77	2090,8	1,6299	
78	2088,91	0,3084	
79	2086,51	1,4679	
80	2082,2	1,326	
81	2077,8	1,3516	
82	2073,5	1,1763	
83	2069,08	0,9196	
84	2065,99	0,3476	
85	2064,61	0,7855	
86	2062,07	0,3439	
87	2060,13	0,6739	

Liste der Peakflächen/Peakhöhen

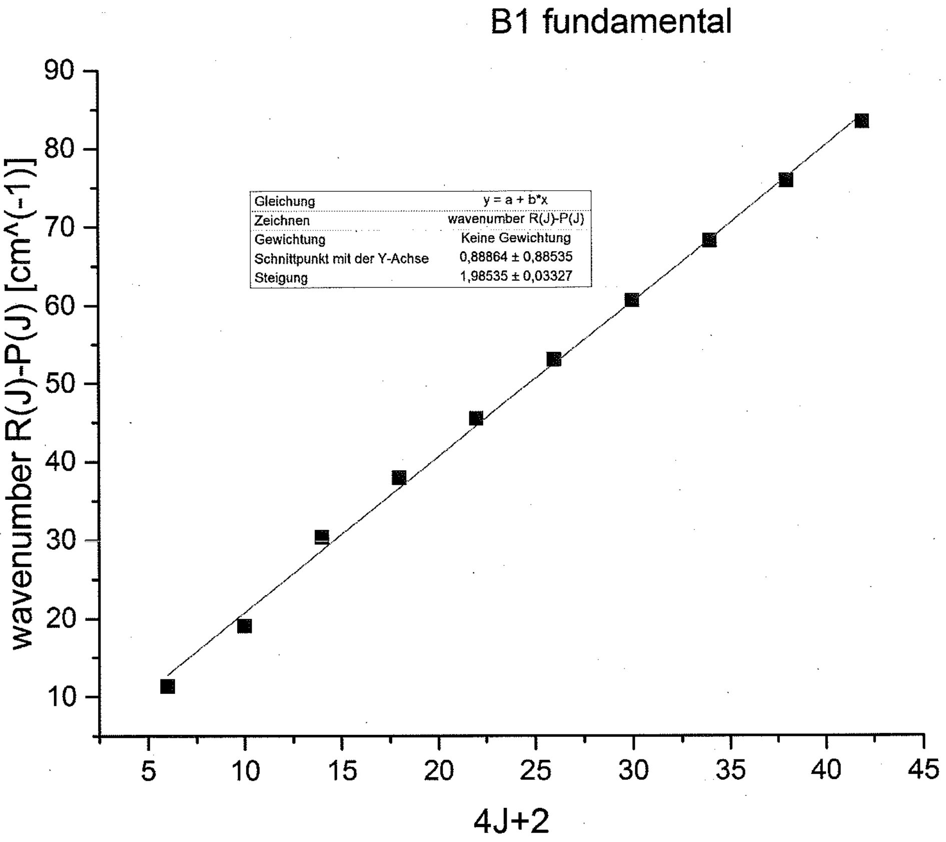
Name des Peaks	X (cm-1)	Y (A)
89	2055,61	0,582
90	2054,13	0,3242
91	2051,08	0,4994
92	2050,12	0,3104
93	2046,41	0,4916
94	2041,91	0,4222
95	2037,29	0,3326
96	2033,67	0,2073
97	2032,58	0,2658
98	2029,49	0,1883
99	2027,88	0,2276
100	2025,27	0,1718
101	2023,14	0,1931
102	2018,38	0,1691



Gleichung	y = a + b*x
Zeichnen	wavenumber R(J-1)-P(J+1)
Gewichtung	Keine Gewichtung
Schnittpunkt mit der Y-Achse	-0,10664 ± 0,84167
Steigung	2,03032 ± 0,03163

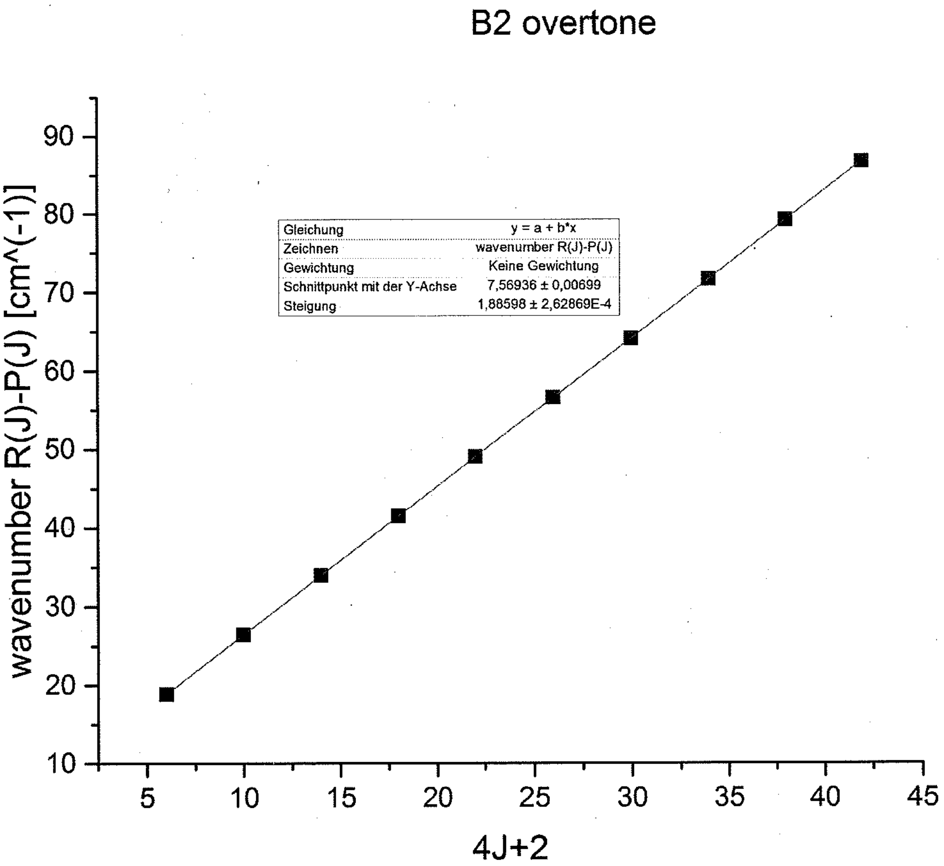


Gleichung	y = a + b*x
Zeichnen	wavenumber R(J-1)-P(J+1)
Gewichtung	Keine Gewichtung
Schnittpunkt mit der Y-Achse	7,713 ± 0,00856
Steigung	1,92083 ± 3,21769E-4



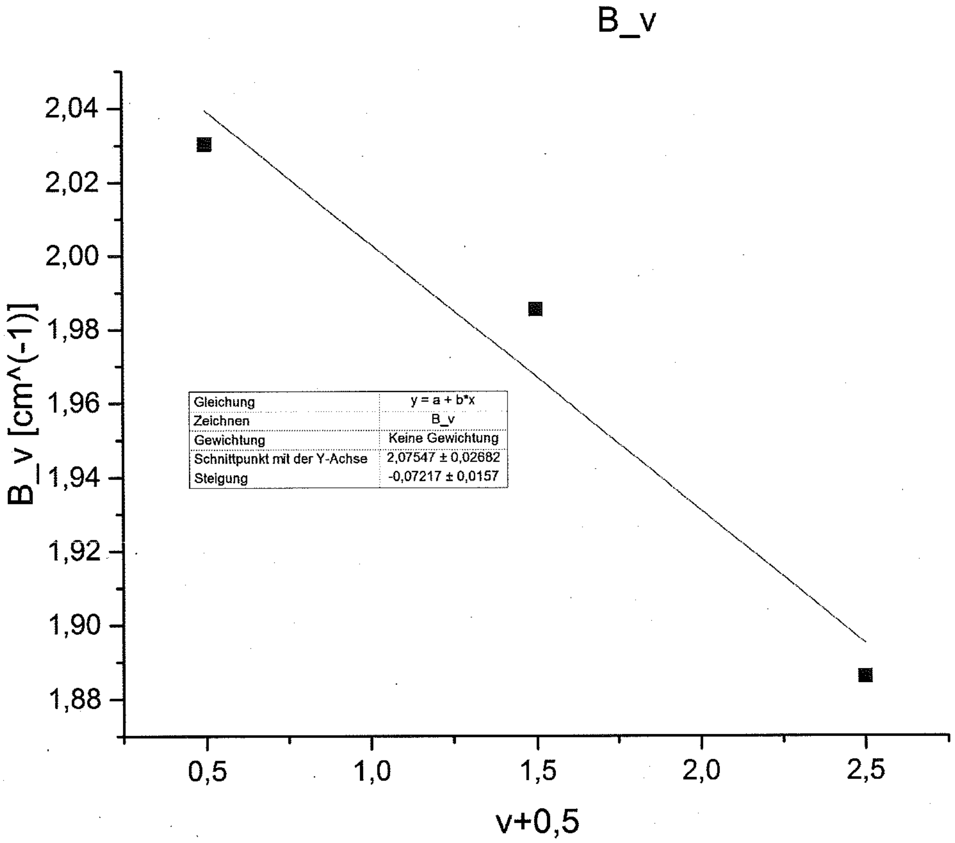
B1 fundamental

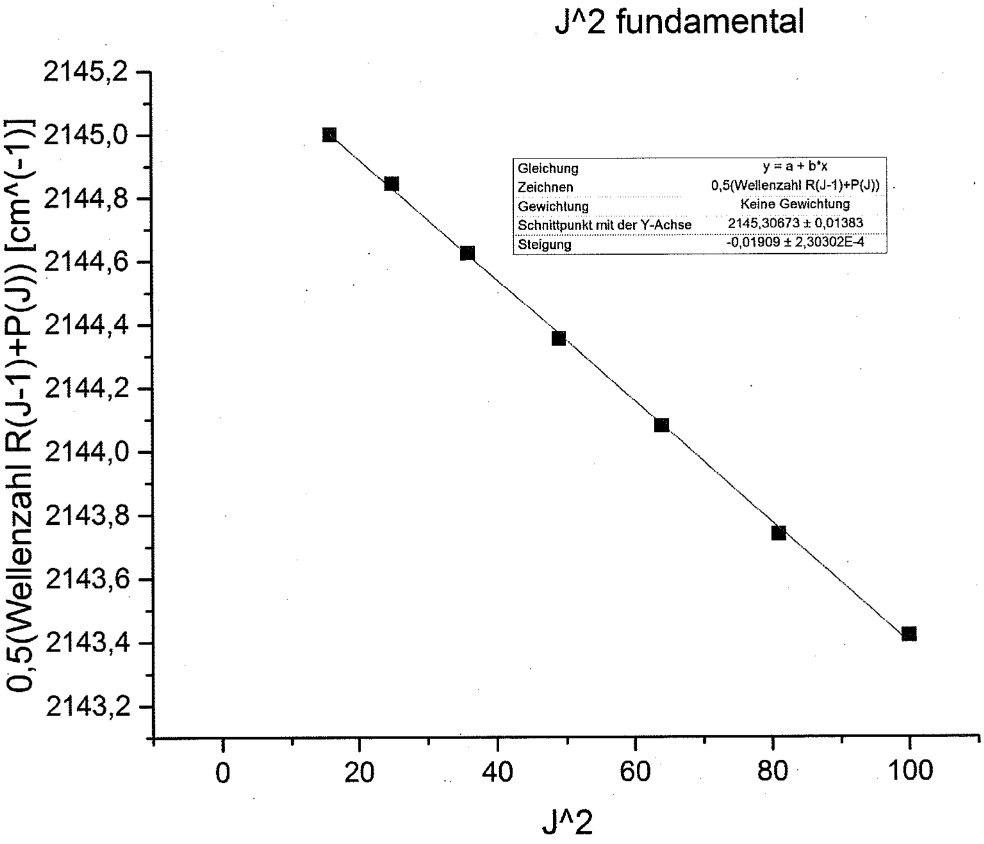
Gleichung	y = a + b*x
Zeichnen	wavenumber R(J)-P(J)
Gewichtung	Keine Gewichtung
Schnittpunkt mit der Y-Achse	0,88864 ± 0,88535
Steigung	1,98535 ± 0,03327

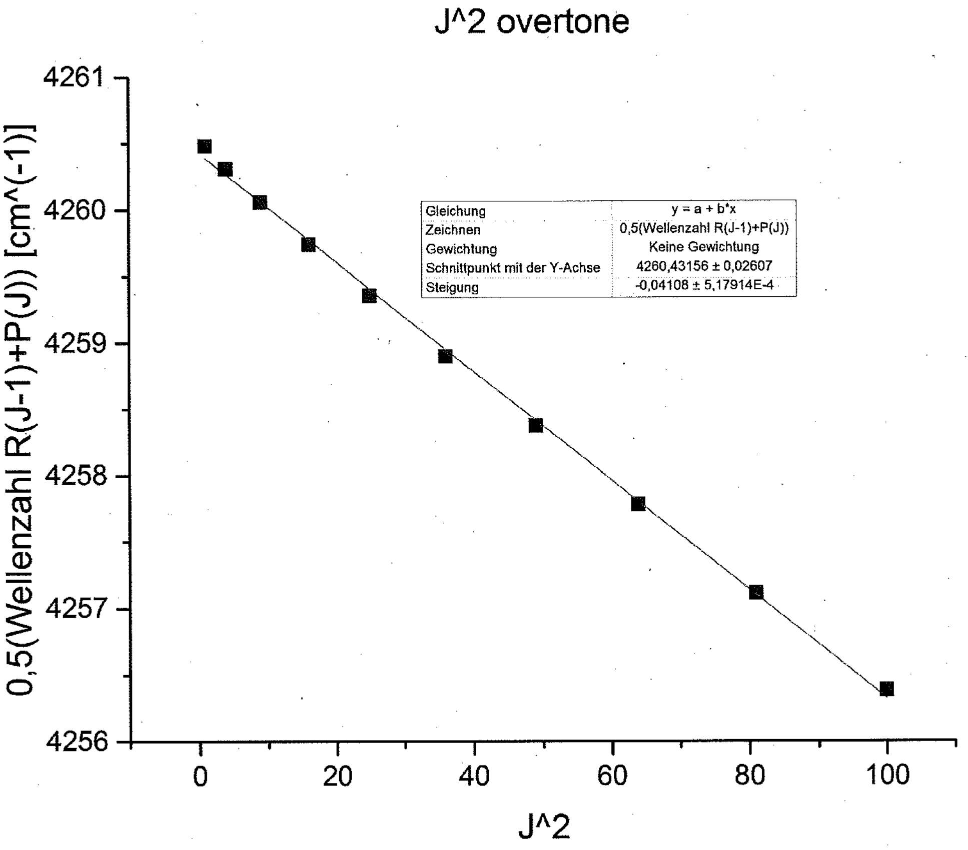


B2 overtone

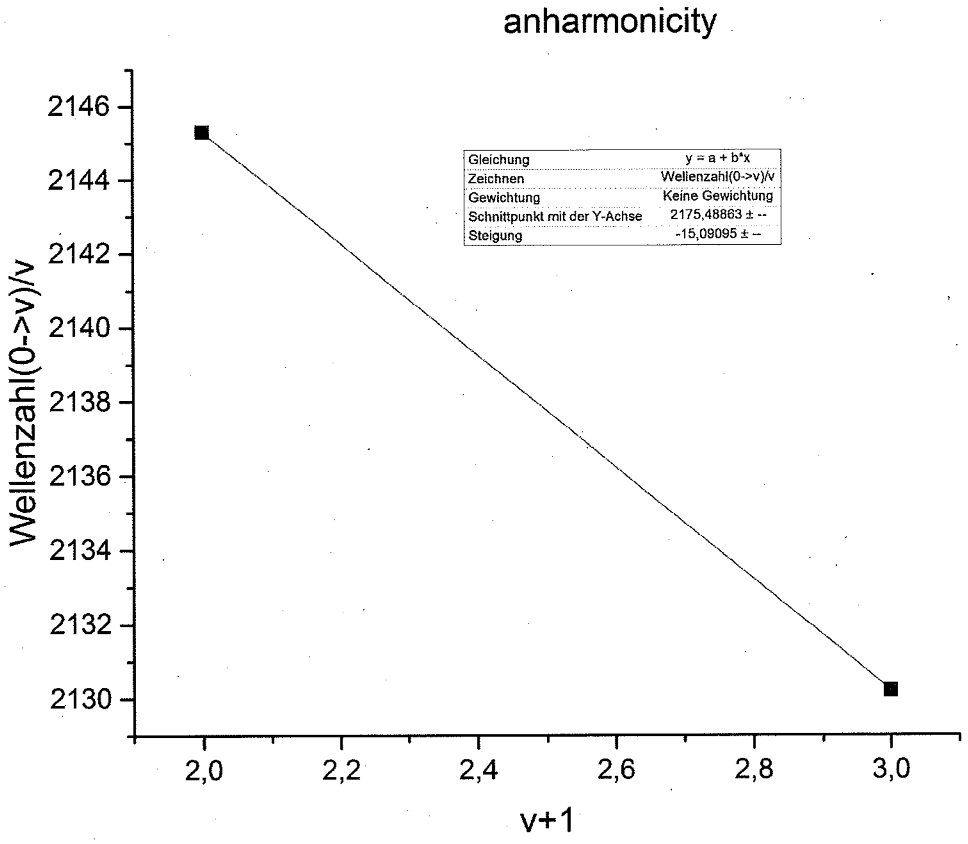
Gleichung	y = a + b*x
Zeichnen	wavenumber R(J)-P(J)
Gewichtung	Keine Gewichtung
Schnittpunkt mit der Y-Achse	7,56936 ± 0,00699
Steigung	1,88598 ± 2,62869E-4


B_v
B_v [cm^(-1)]
2,04
2,02
2,00
1,98
1,96
1,94
1,92
1,90
1,88
0,5
1,0
1,5
2,0
2,5
v+0,5
Gleichung
y = a + b*x
Zeichnen
B_v
Gewichtung
Keine Gewichtung
Schnittpunkt mit der Y-Achse
2,07547 ± 0,02682
Steigung
-0,07217 ± 0,0157


J^2 fundamental
0,5(Wellenzahl R(J-1)+P(J)) [cm^(-1)]
2145,2
2145,0
2144,8
2144,6
2144,4
2144,2
2144,0
2143,8
2143,6
2143,4
2143,2
0
20
40
60
80
100
J^2
Gleichung
y = a + b*x
Zeichnen
0,5(Wellenzahl R(J-1)+P(J))
Gewichtung
Keine Gewichtung
Schnittpunkt mit der Y-Achse
2145,30673 ± 0,01383
Steigung
-0,01909 ± 2,30302E-4



Gleichung	y = a + b*x
Zeichnen	0,5(Wellenzahl R(J-1)+P(J))
Gewichtung	Keine Gewichtung
Schnittpunkt mit der Y-Achse	4260,43156 ± 0,02607
Steigung	-0,04108 ± 5,17914E-4



Gleichung	y = a + b*x
Zeichnen	Wellenzahl(0->v)/v
Gewichtung	Keine Gewichtung
Schnittpunkt mit der Y-Achse	2175,48863 ± --
Steigung	-15,09095 ± --

measurand	measured value	error	literature	
B_0	2,03032	0,01597588	1,9326 cm^{-1}	→ graphics named like measurand
B_1	1,98535	0,03327	1,9051 cm^{-1}	
B_2	1,88598	0,00026287	1,8875 cm^{-1}	
I_0	1,37236E-46	1,0799E-50	1,456E-46 $kg*m^2$	
I_1	1,40345E-46	2,3519E-50	1,4693E-46 $kg*m^2$	
I_2	1,47739E-46	2,0592E-52	1,4830E-46 $kg*m^2$	
R_0	7,52794E-10	7,1855E-42	1,1306E-10 m	
R_1	7,61272E-10 !	1,5475E-41	1,1358E-10 m	
R_2	7,8107E-10	1,3206E-43	1,1411E-10 m	
$\tilde{\nu}_{(0\to1)}$	2145,30673		2143,2 cm^{-1}	→ graphic "J^2 fundmental"
$\tilde{\nu}_{(0\to2)}$	2130,21578		4259,8 cm^{-1}	→ graphic "J^2 overtone"
$\tilde{\nu}_e$	2175,48863		2169,8 cm^{-1}	→ graphic "anharmonicity"
x_e	0,006936809		6,125E-03 cm^{-1}	
α_e (fundamental)	0,01909		1,75E-2 cm^{-1}	
α_e (overtone)	0,02054			
B_e	2,07547	0,02682	1,9313 cm^{-1}	→ in the graphic called "B_v"

For the errors in the table above the Gaussian law of errors was used: $\Delta y = \sqrt{\sum_i \left(\frac{\partial y}{\partial x_i} \Delta x_i\right)^2}$

$\Rightarrow \Delta I_i = \frac{h}{8\pi^2 c \cdot B_i^2} \Delta B_i$

$\Rightarrow \Delta R_i = \frac{1}{2} \cdot \frac{1}{\sqrt{\frac{I}{\mu}}} \cdot \Delta I_i$

The error of B_i was given by the statistical error of the linear regression with the program originLab (shown in the graphs attached)

Soure of literature:

1. Pyler, E.K; Blaine, L.R.; Connor, W.S J. Opt. Soc. Amer. 1955, 45, 102-106
2. Rank, D.H.; Guenther, A.H.; Saksena, G.D.; Shearer, T.A. J. opt. Soc. Amer. 1957, 47, 686-689