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SMR 1302 - 13

WINTER SCHOOL ON LASER SPECTROSCOPY AND APPLICATIONS

19 February - 2 March 2001

Molecular Spectroscopy and Secondary Frequency Standards

Part I and Part II

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D-30167 Hannover, Germany

These are preliminary lecture notes, intended only for distribution to participants.

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Molecular spectroscopy and secondary frequency standards

Part 1 Methods and potential determination

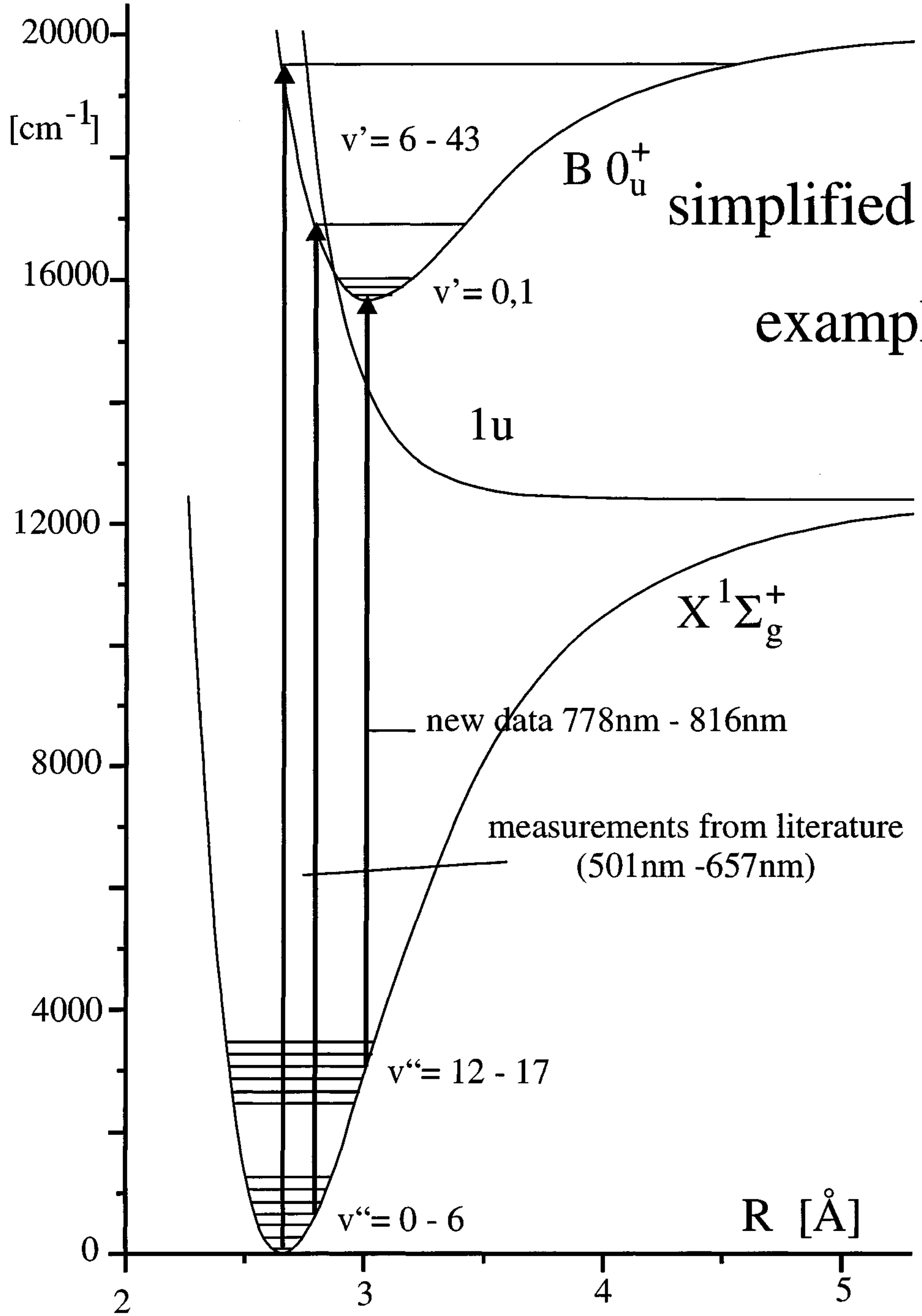
Eberhard Tiemann

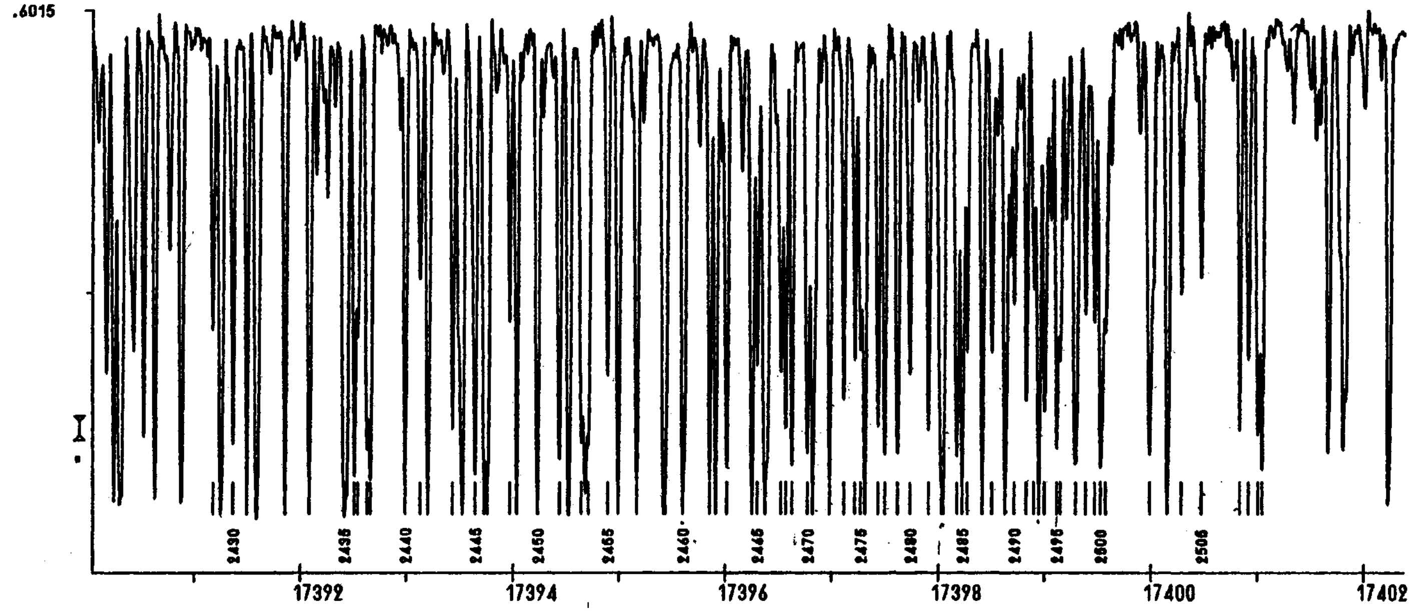
University Hannover, Institute of Quantum Optics

1. High resolution molecular spectroscopy
2. Precision laser sources, stabilization techniques
3. Frequency measurements
4. Vibrational and rotational structure
5. Determination of potential functions
6. Born-Oppenheimer approximation and its correction

simplified potential scheme

example I_2




.6015
2430
2435
2440
2445
2450
2455
2460
2465
2470
2475
2480
2485
2490
2495
2500
2505
17392
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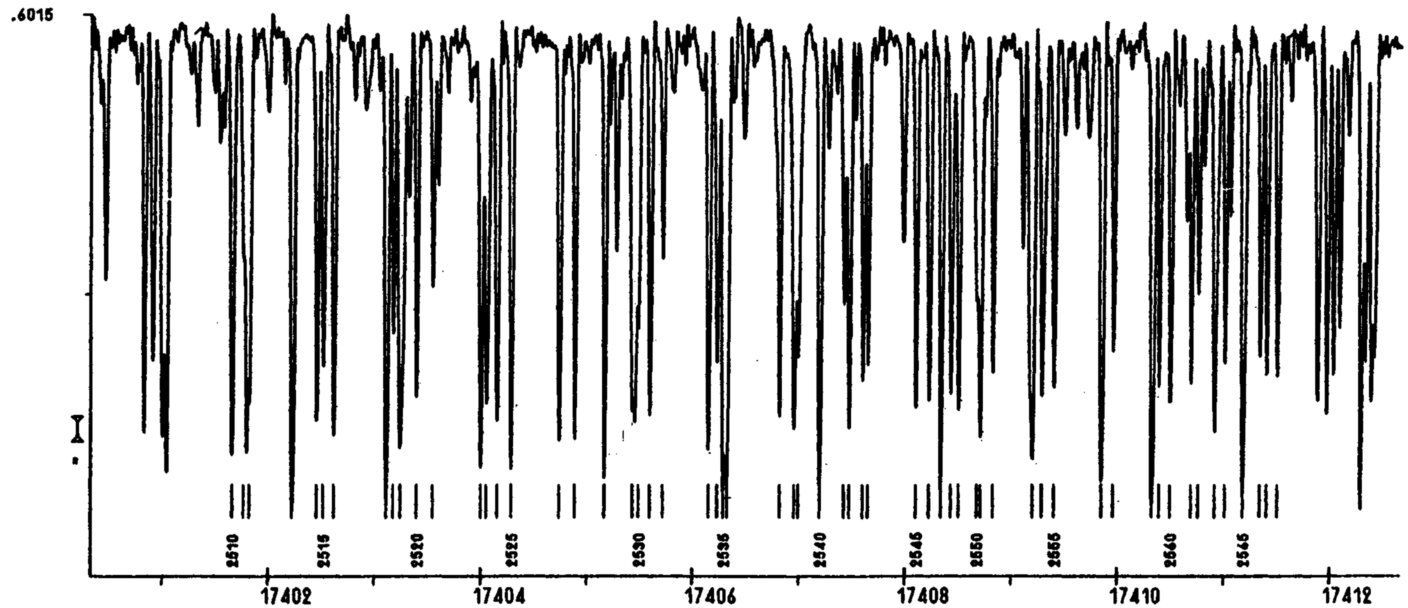
17396
17398
17400
17402


.6015
2510
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2535
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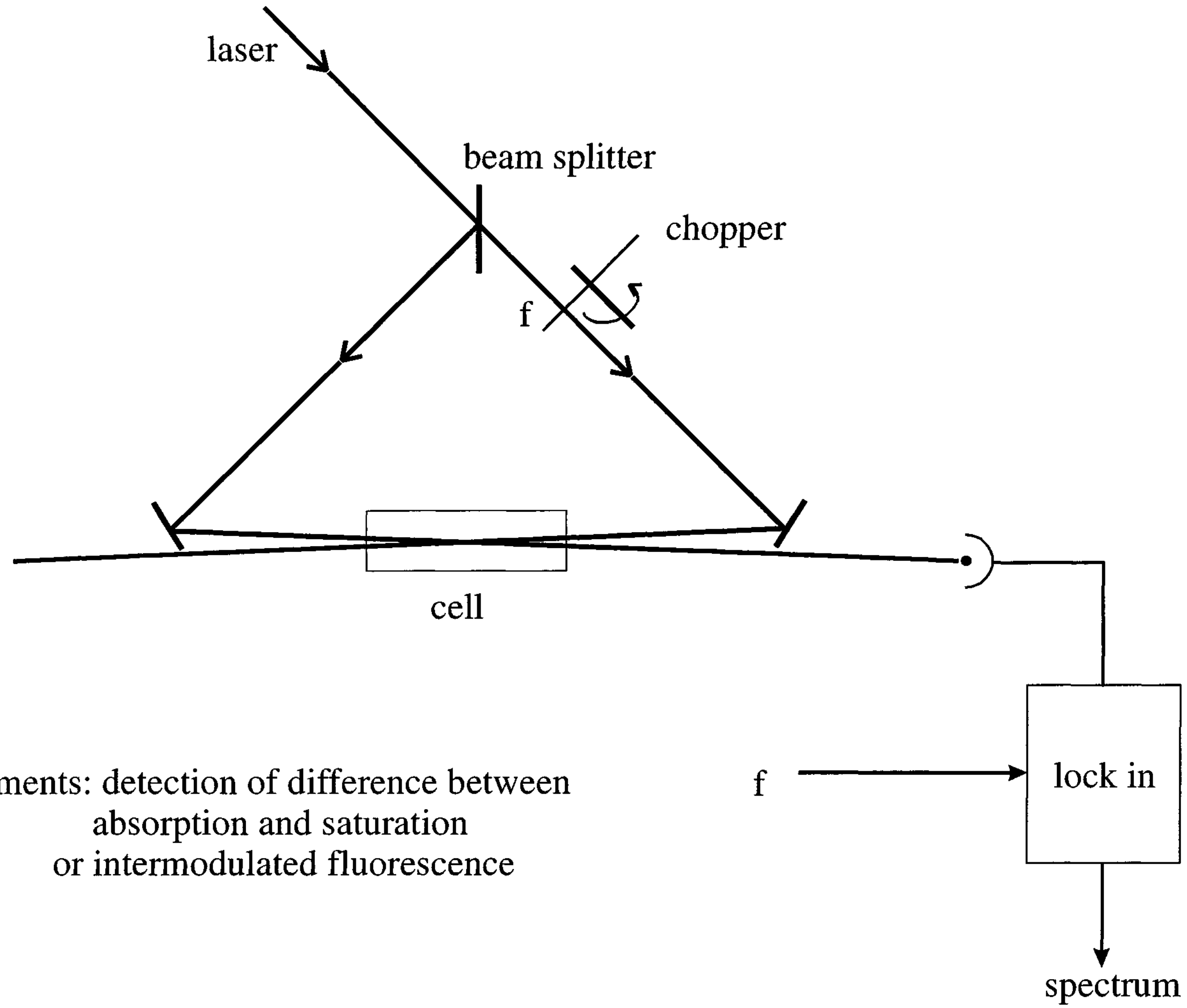
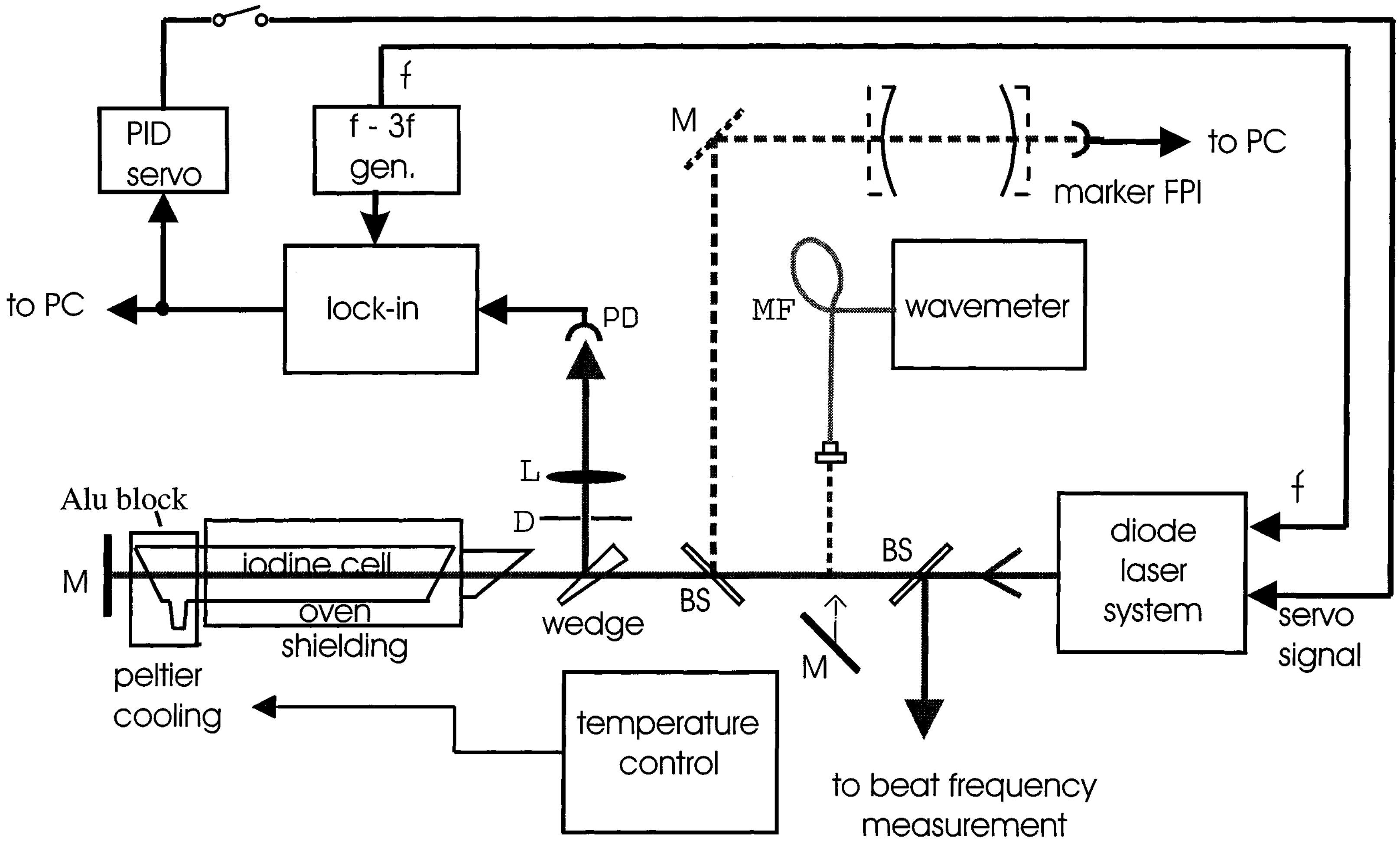
2560
2565
17402
17404
17406
17408
17410
17412

I2] 3

Saturation spectroscopy



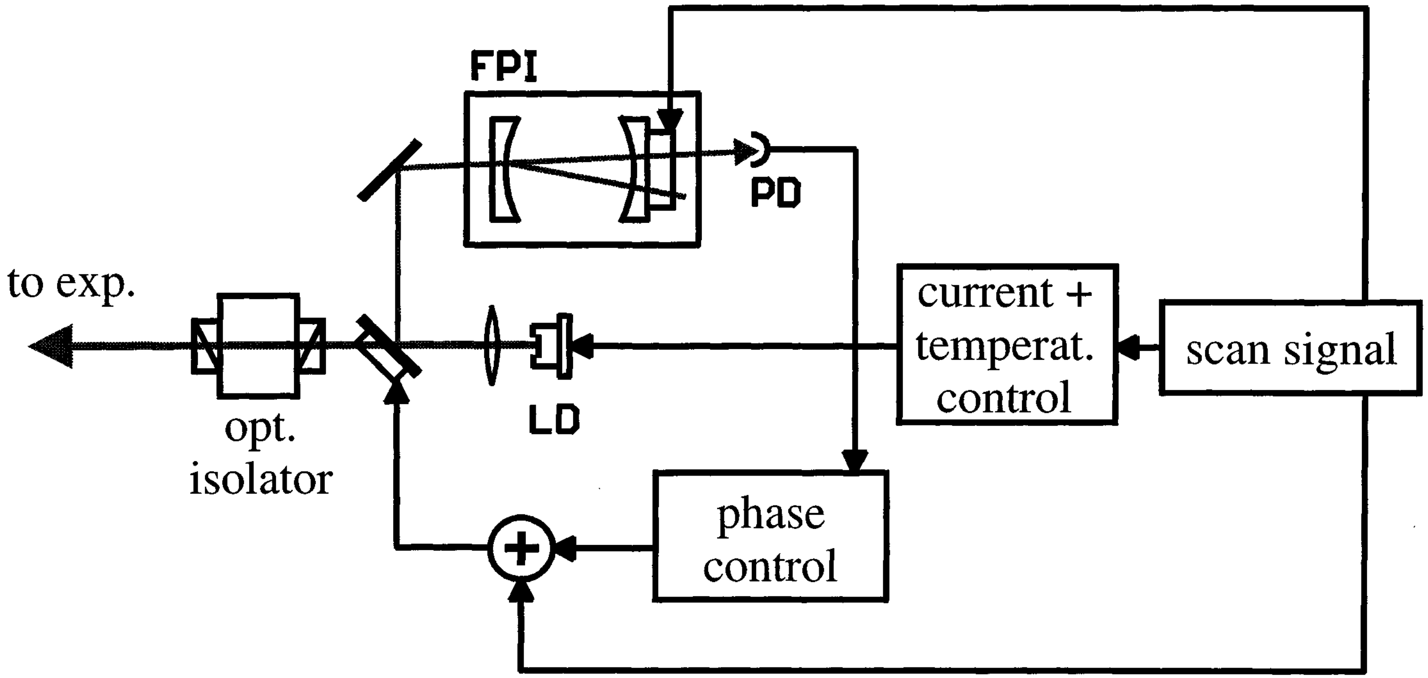
improvements: detection of difference between
absorption and saturation
or intermodulated fluorescence



sattaufb3_4.cdr

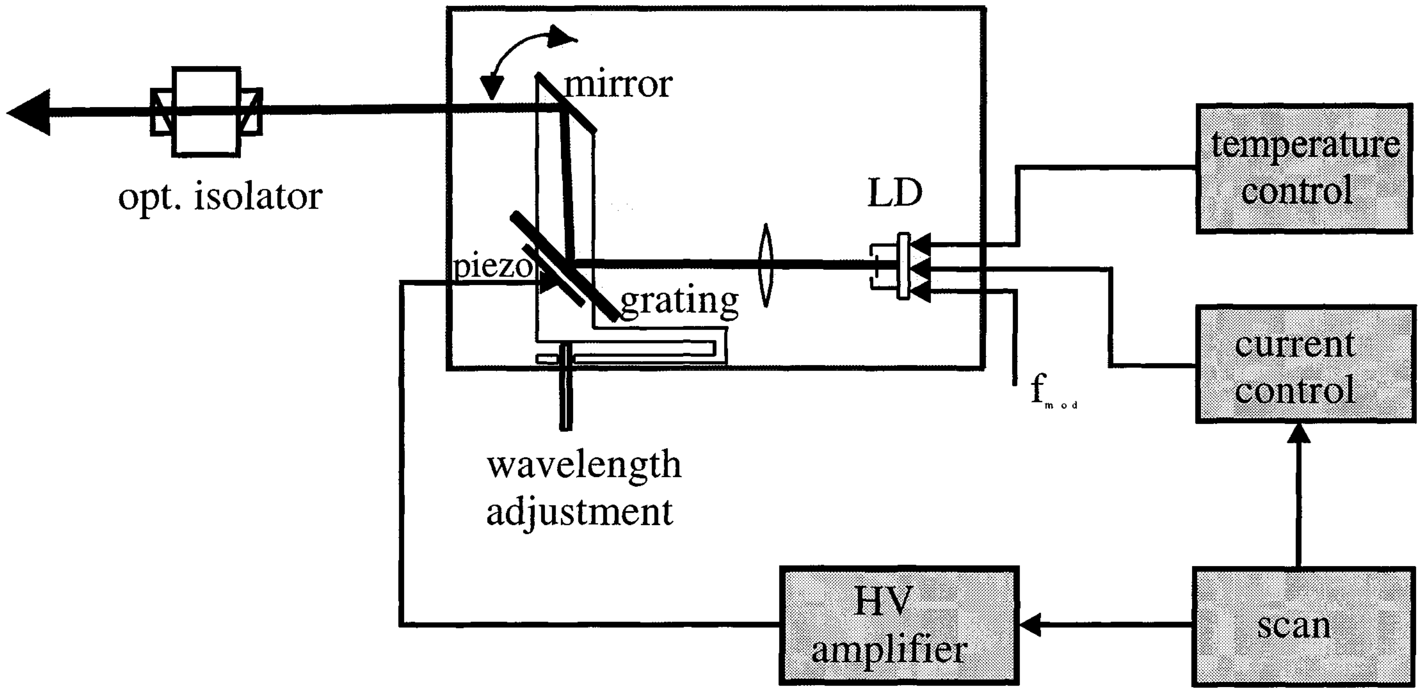
Stabilizing lasers

Hollberg setup:



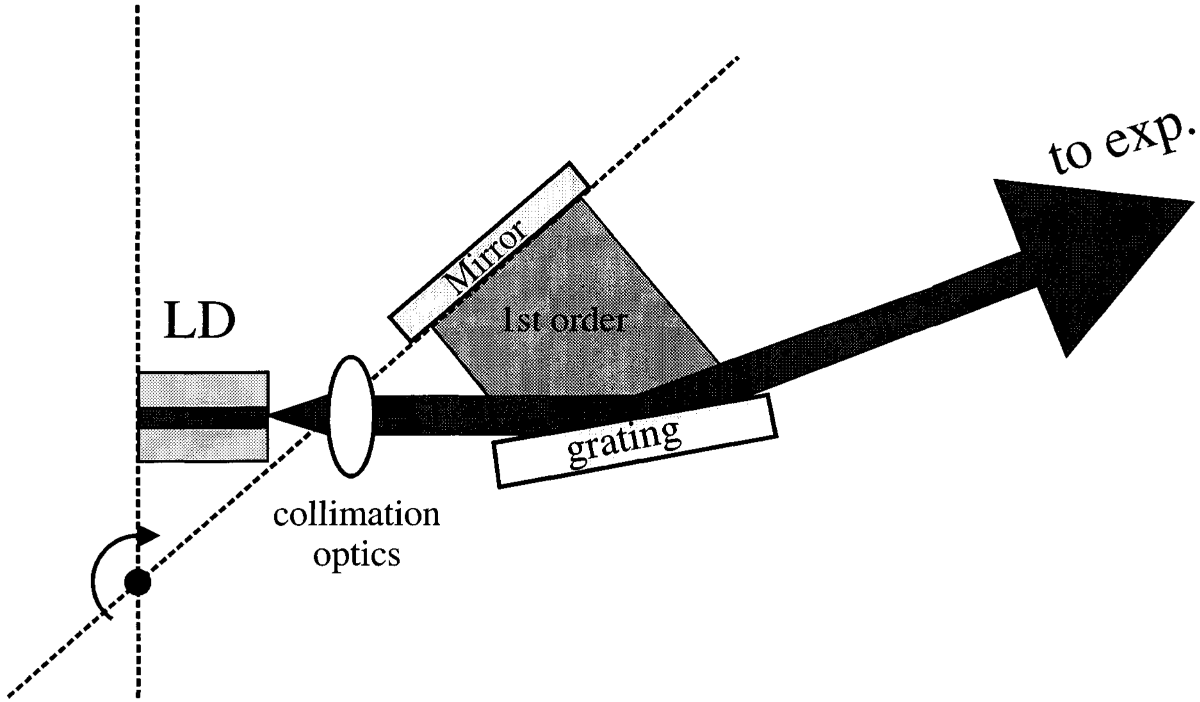
B. Dahmani et al., Opt.Lett. **12**, 876 (1987)

extended cavity diode laser in Littrow configuration



L.Ricci et al., Opt. Comm. ,**117**, 541 (1995)

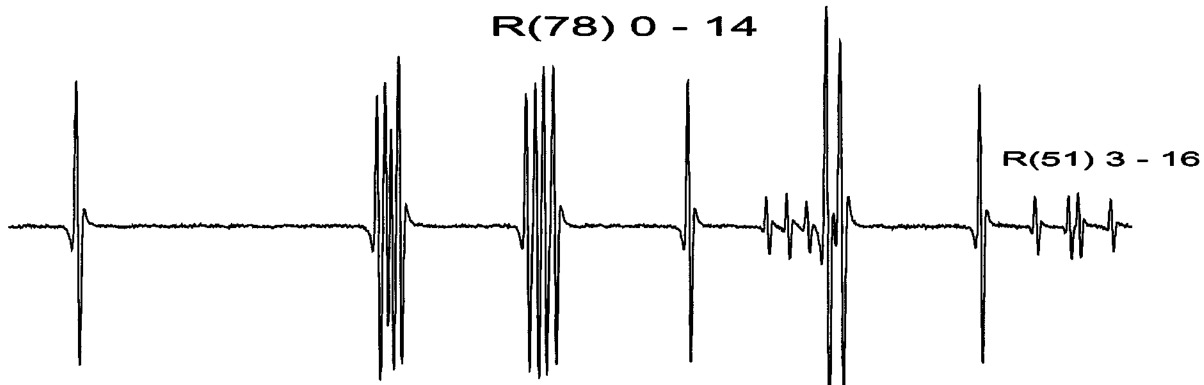
Littman setup:



e.g. K.C. Harvey, C.J. Myatt, Opt.Lett 16, 911 (1996)

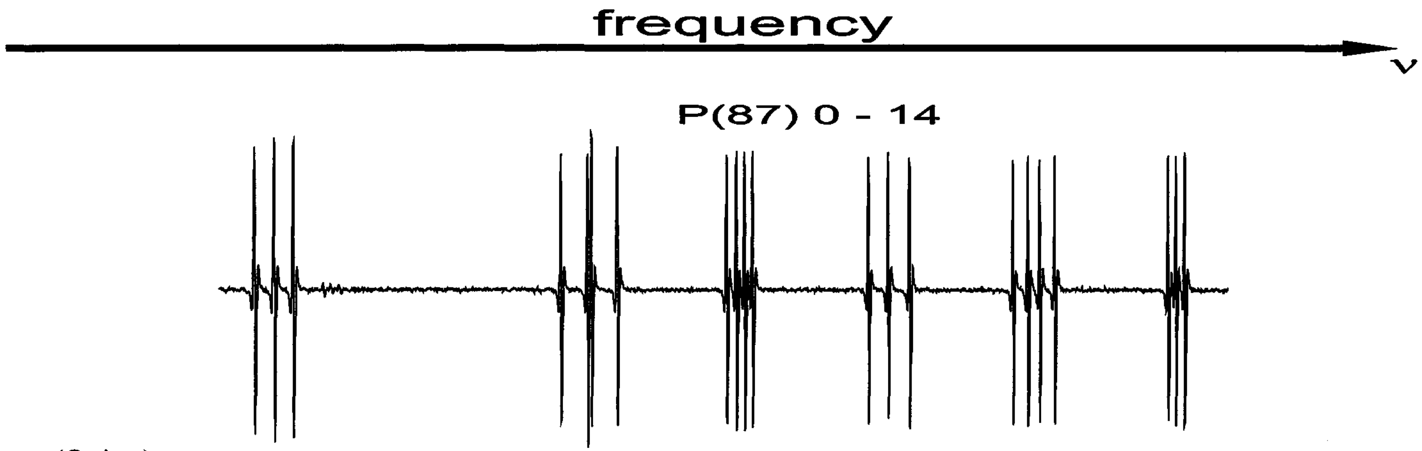
littmann.cdr

Saturation spectrum as third derivative profiles

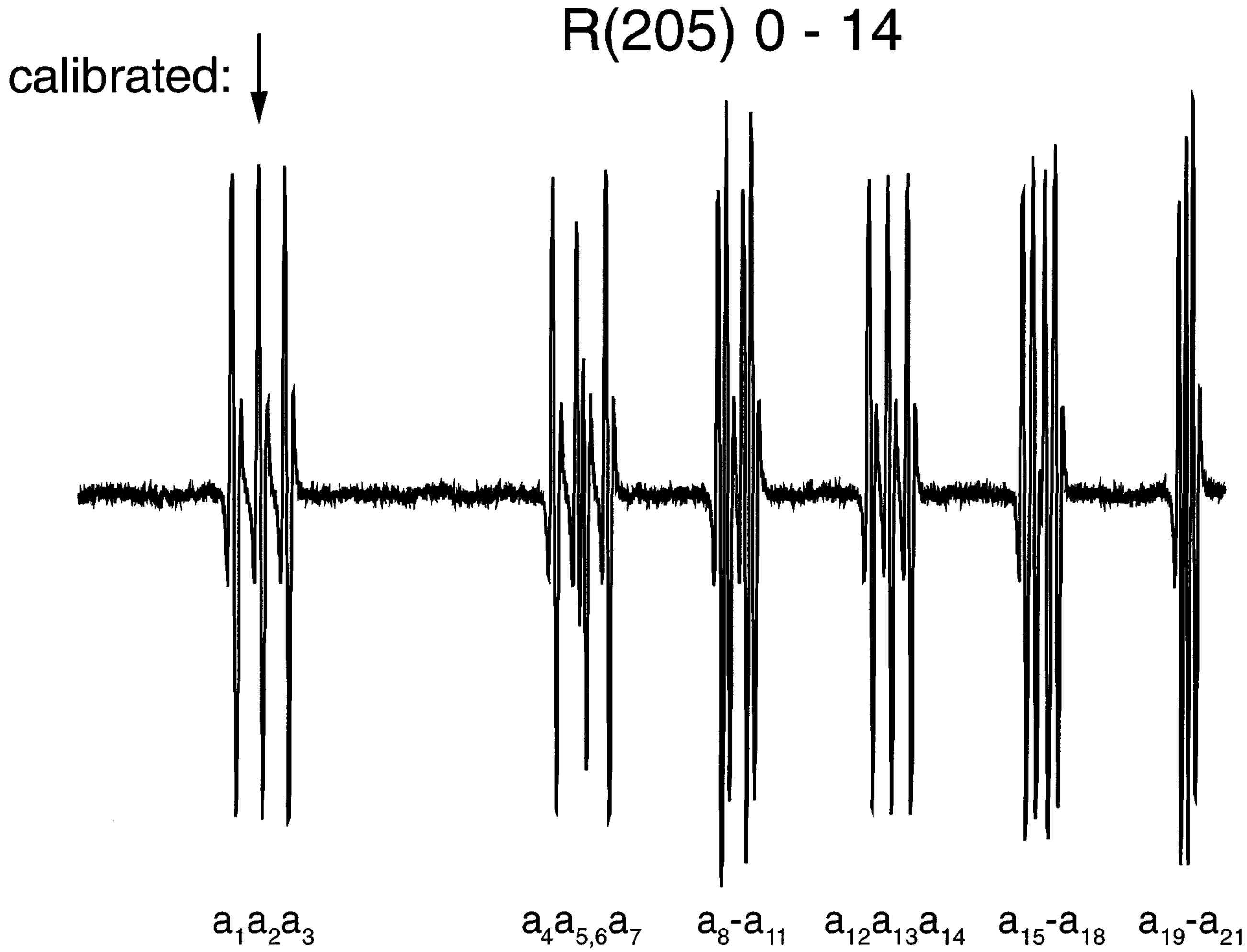


nomenclature of assignment of lines:

used here (Quinn):	a_1	$a_2 - a_5$	$a_6 - a_9$	a_{10}	$a_{11} - a_{14}$	a_{15}
used by Cerez et al.:	o	nmlk	jihg	f	edcb	a
used by Sansonetti:	t	rqpo	nmlk	i	gfed	b

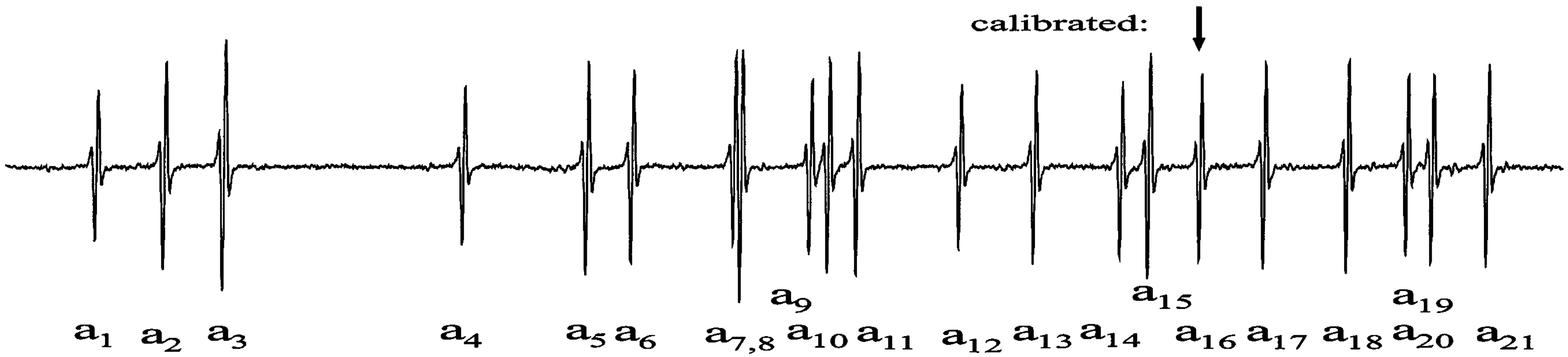


used here (Quinn):	$a_1 - a_3$	$a_4 - a_7$	$a_8 - a_{11}$	$a_{12} - a_{14}$	$a_{15} - a_{18}$	$a_{19} - a_{21}$
Cerez & Sansonetti:	uts	rqpo	nmlk	jih	gfed	cba

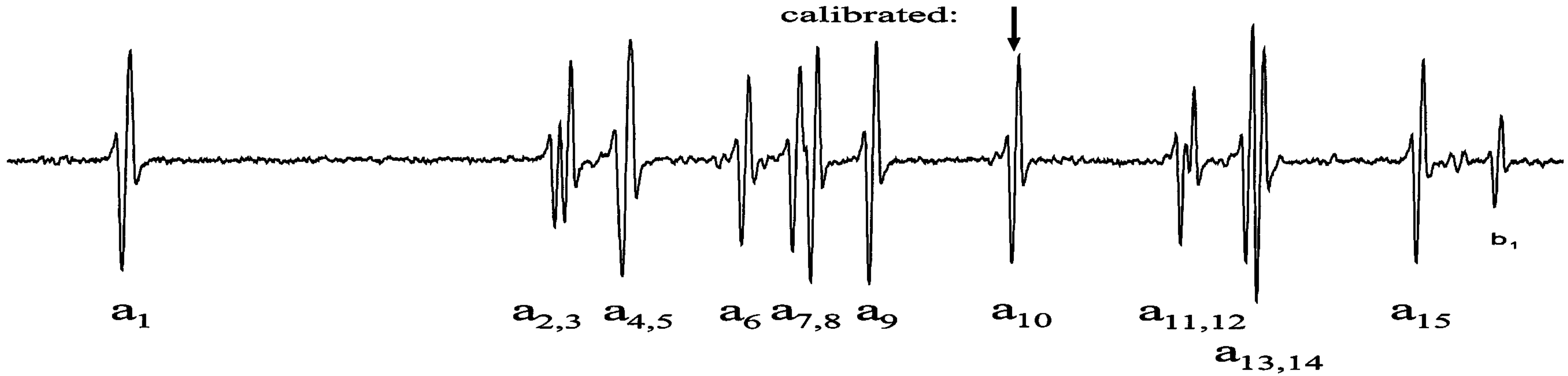

R(205) 0 - 14
calibrated:
a1a2a3
a4a5,6a7
a8-a11
a12a13a14
a15-a18
a19-a21

Low rotational angular momentum J

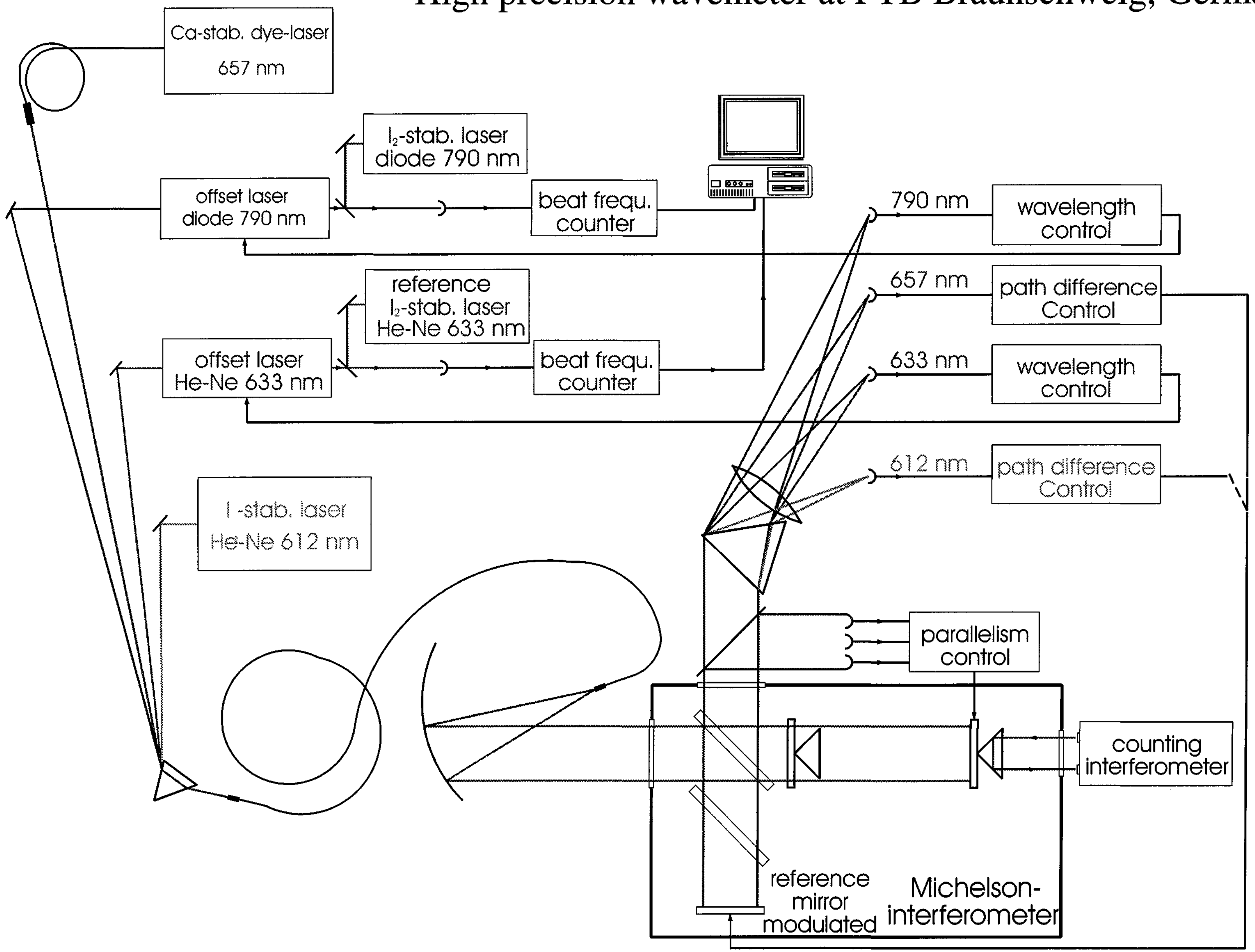
P(19) 0-14

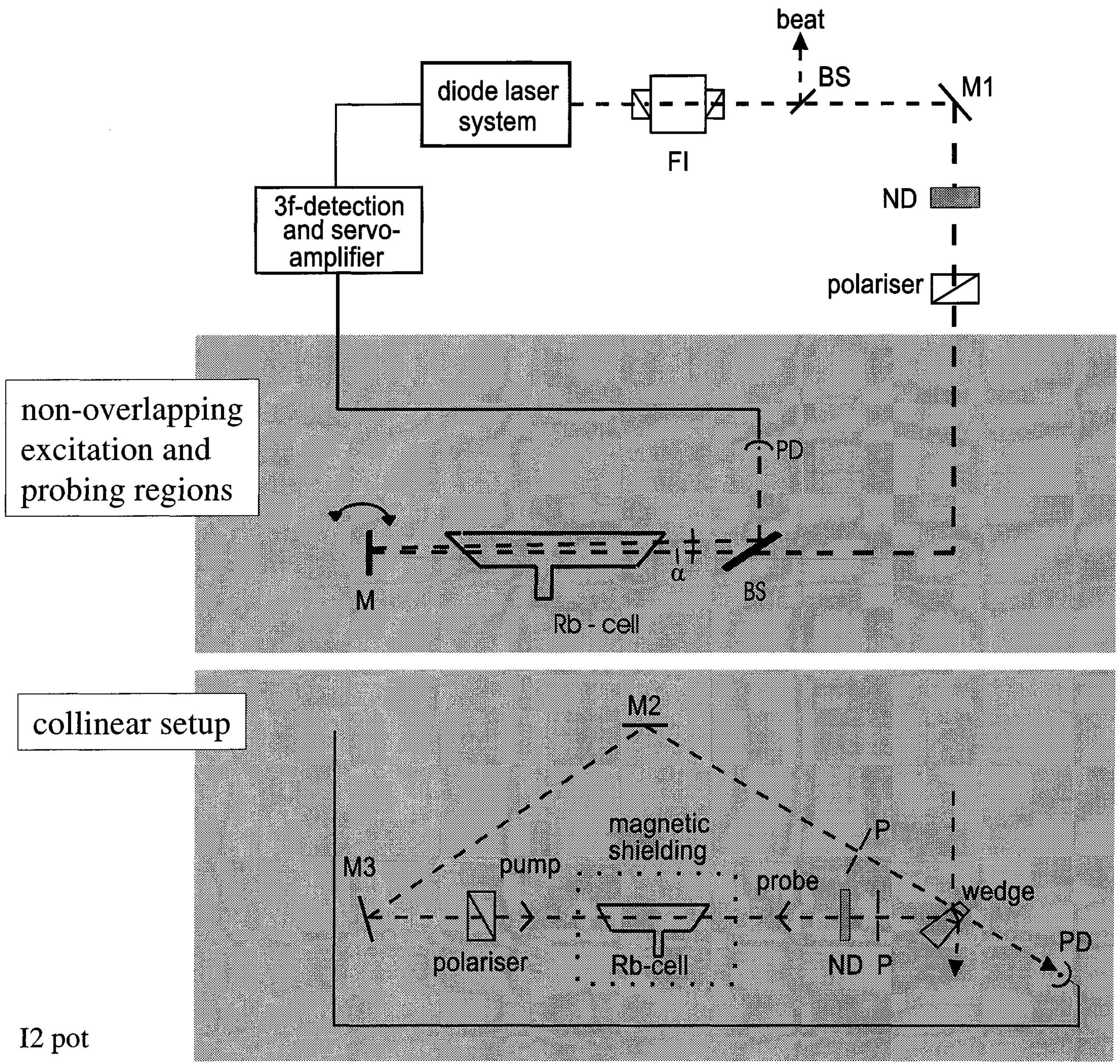


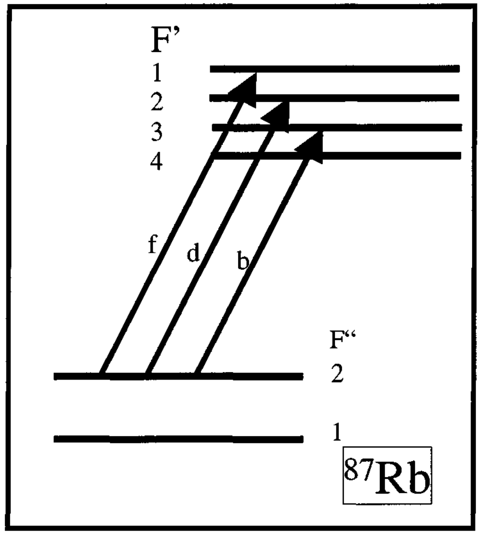
R(16) 0-14



High precision wavemeter at PTB Braunschweig, Germany

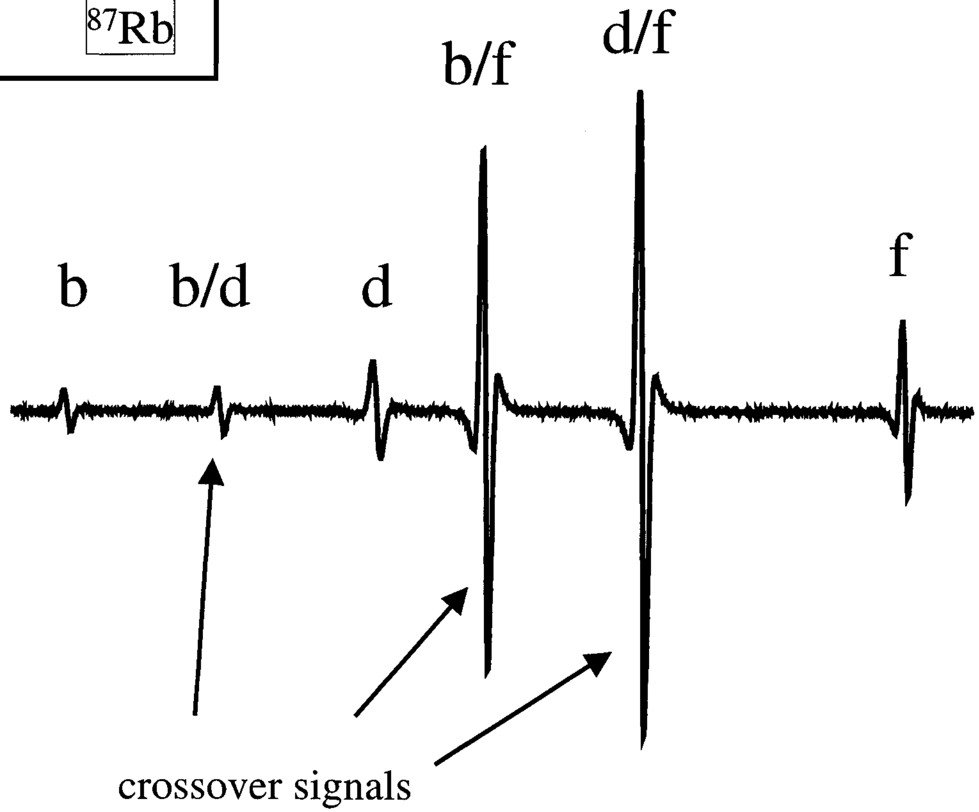



beat
BS
M1
diode laser system
FI
ND
3f-detection and servo-amplifier
polariser
non-overlapping excitation and probing regions
PD
α
M
BS
Rb - cell
collinear setup
M2
magnetic shielding
P
M3
pump
probe
wedge
PD
polariser
Rb-cell
ND
P

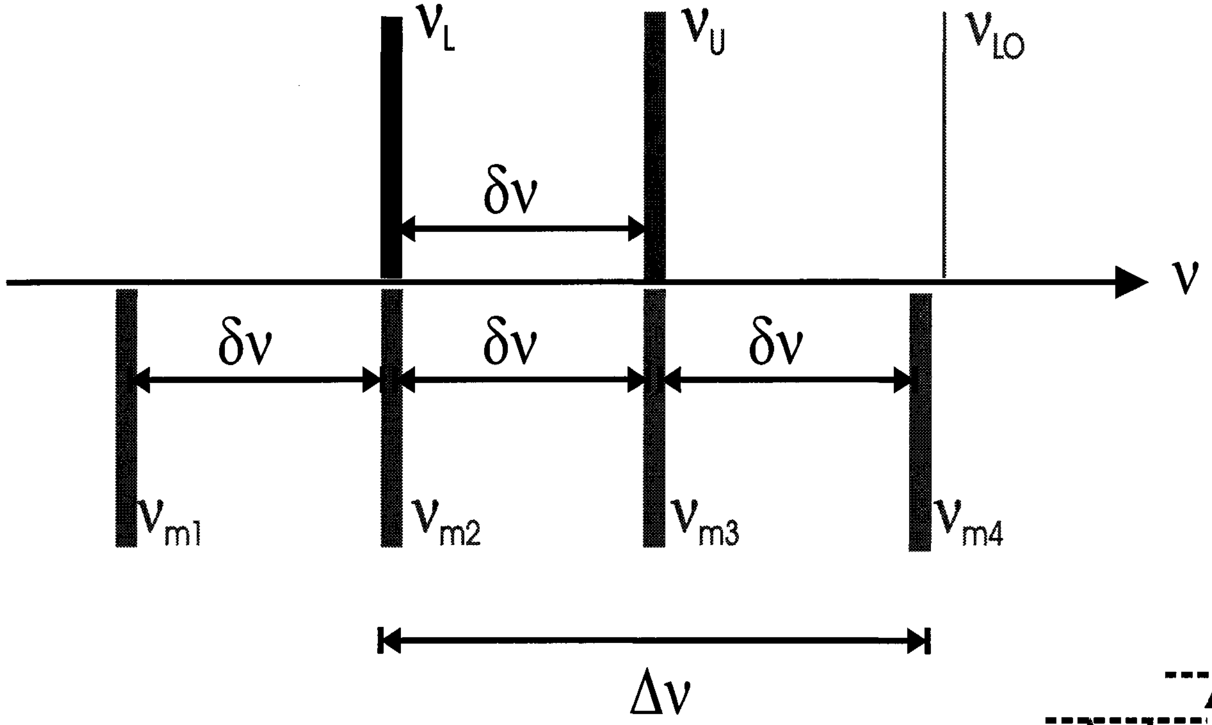


Calibration with reference spectrum

part of the hyperfine spectrum
of the D2 line of ^{87}Rb



Optical Extrapolation

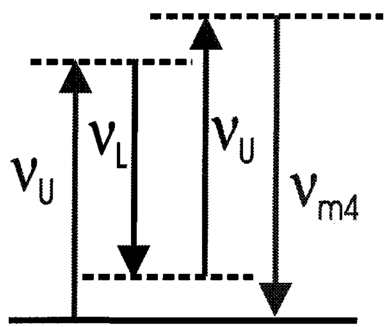


ν_U : upper mixing frequency

ν_L : lower mixing frequency

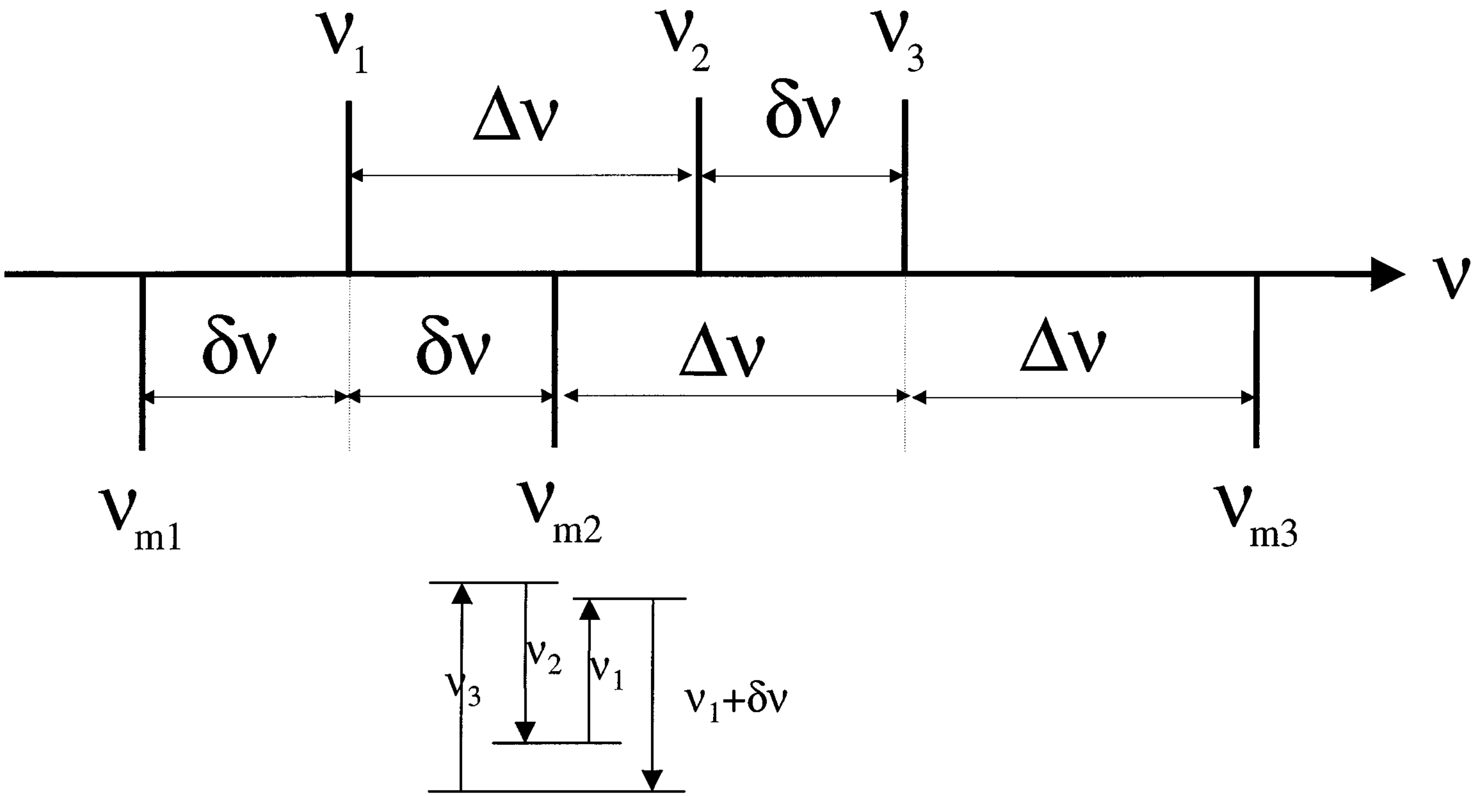
ν_{LO} : frequency of probe laser

$\nu_{m...}$: mixing products



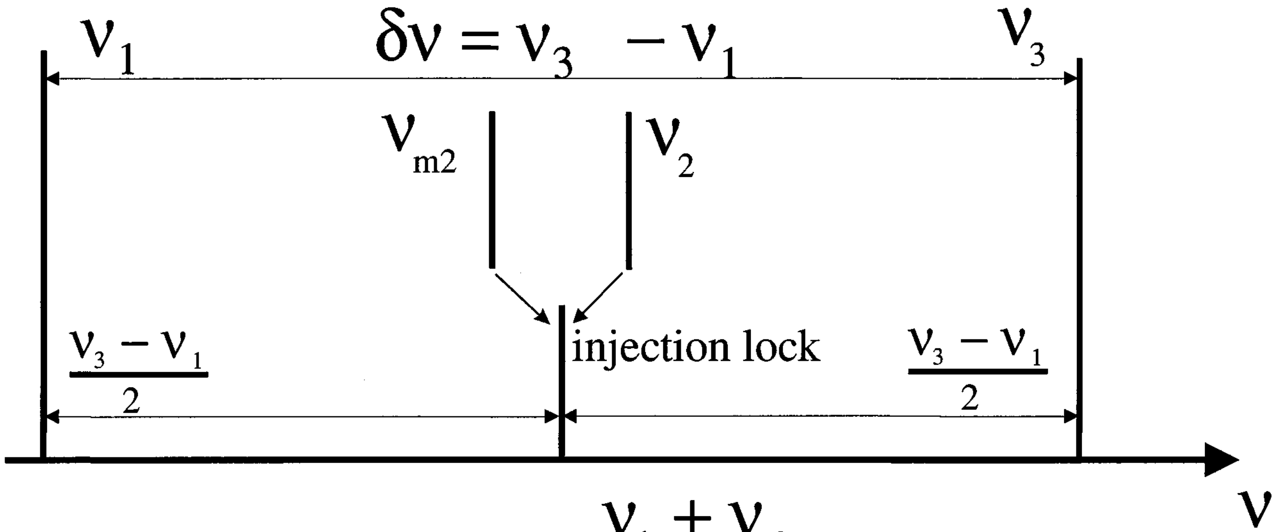
I2 pot Ch. Koch, H.R. Telle, J. Opt. Soc.Am. **B 13**, 1666 (1996)

scheme for 4-colour mixing:

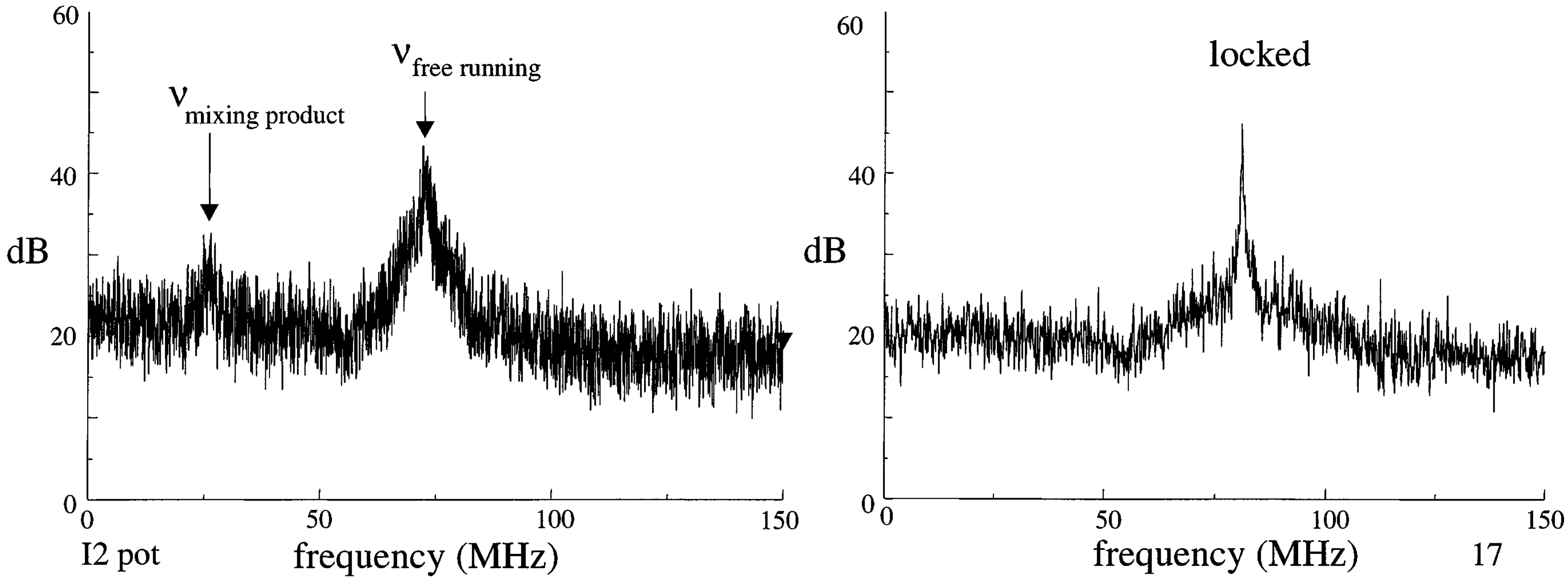


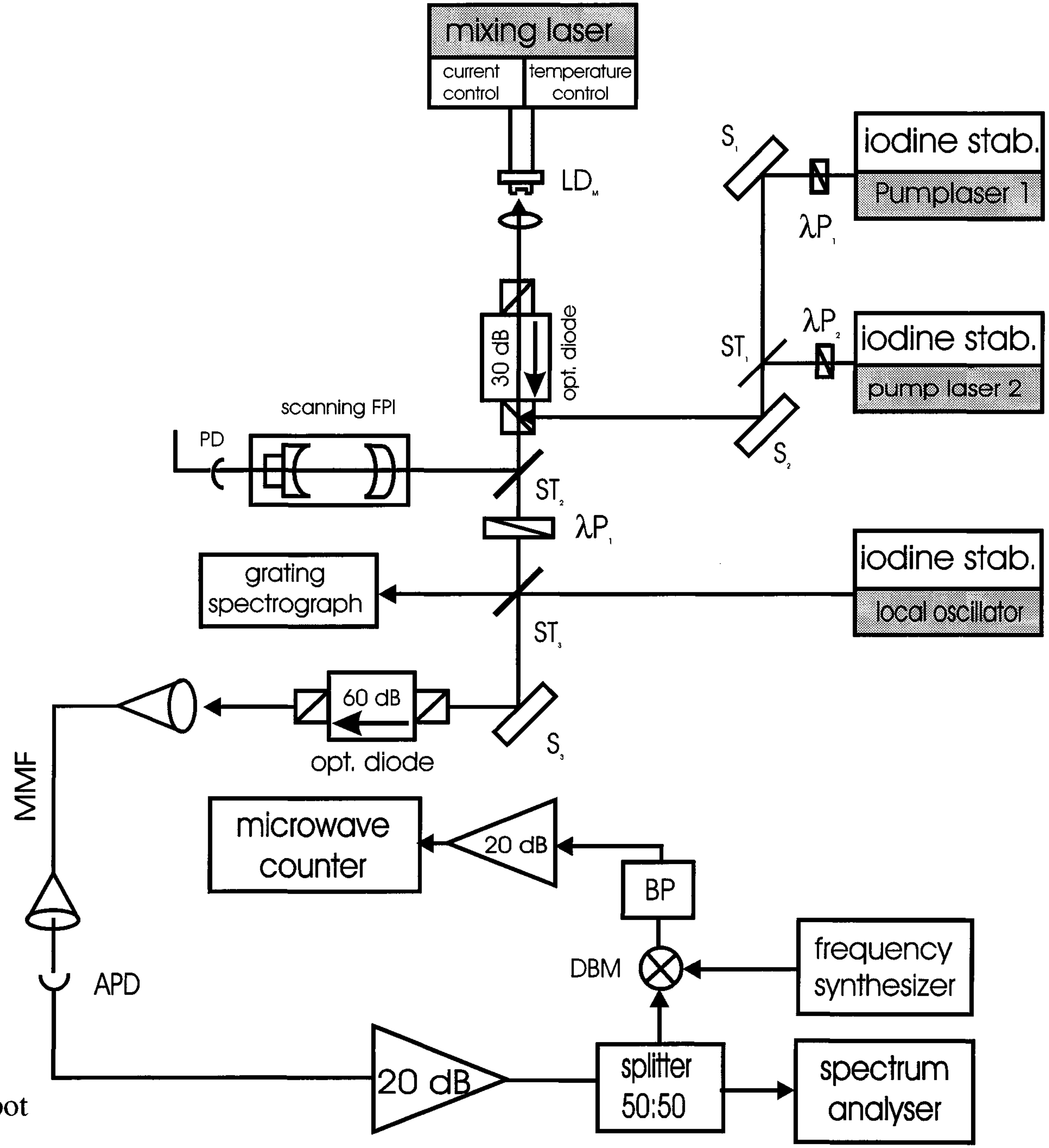
4_col_mix.cdr

optical interval division by 4-wave mixing:



$$\nu_{m2} = \nu_2 = \frac{\nu_1 + \nu_3}{2}$$





mixing laser
current control
temperature control
LD_M
S_1
iodine stab.
Pumplaser 1
λP_1
λP_2
iodine stab.
pump laser 2
ST_1
30 dB
opt. diode
scanning FPI
PD
S_2
ST_2
λP_1
grating spectrograph
iodine stab.
local oscillator
ST_3
60 dB
opt. diode
S_3
MMF
microwave counter
20 dB
BP
DBM
frequency synthesizer
APD
20 dB
splitter 50:50
spectrum analyser

Beat frequency of
Ca standard and methane standard

B.Bodermann et al, Appl.Phys. B67, 95 (1998)

Wavemeter measurements

B.Bodermann et al Metrologia 35, 105 (1998)

Calibration with Rb lines

B.Bodermann et al, Eur.Phys.J. D11, 213 (2000)

I2 pot

Übergang:	Komp.	Frequenz [MHz]	Unsicherheit [MHz]	Methode
P(172) 0 - 16	a10	367565102,563	0,060	Beat
R(44) 0 - 17	a10	367586099,783	0,060	Beat
P(34) 0 - 17	a10	367599333,367	0,070	Beat
P(239) 0 - 15	a2	367606843,764	0,065	Beat
R(180) 0 - 16	a1	367614603,485	0,044	Diff.freq.
R(42) 0 - 17	a10	367615714,545	0,043	Diff. freq.
P(171) 0 - 16	a14	367634198,367	0,070	Beat
P(105) 0 - 15	a14	377087649,357	0,077	Rb D1
R(205) 0 - 14	a12	377105264,775	0,077	Rb D1
R(113) 0 - 15	a12	377117726,171	0,077	Rb D1
P(104) 0 - 15	a10	377131003,300	0,077	Rb D1
P(88) 0 - 15	a15	377770986,011	0,050	Beat
P(228) 1 - 14	b10	377796446,422	0,080	Beat
R(96) 0 - 15	a10	377796992,463	0,048	Wellenlänge
P(166) 0 - 14	a1	379431381,762	0,048	Wellenlänge
R(19) 0 - 15	a2	379431541,326	0,062	Beat
R(16) 0 - 15	a9	379448164,055	0,055	Beat
R(174) 0 - 14	a1	379459701,975	0,059	Beat
R(96) 0 - 14	a10	383617264,515	0,049	Wellenlänge
P(87) 0 - 14	a2	383633241,143	0,050	Beat
P(70) 0 - 14	a10	384205192,831	0,060	Rb D2
R(188) 0 - 13	a10	384208473,543	0,055	Rb D2
R(117) 2 - 15	b13	384208927,438	0,080	Rb D2
P(43) 3 - 16	a13	384219193,630	0,072	Rb D2
P(243) 0 - 12	b12	384219408,307	0,250	Rb D2
R(78) 0 - 14	a10	384222471,557	0,060	Rb D2
P(148) 1 - 14	a1	384235614,628	0,075	Rb D2
R(56) 0 - 14	a10	384783612,796	0,124	VWM
P(31) 0 - 14	a07	385074236,842	0,137	VWM
P(19) 0 - 14	a16	385218641,076	0,045	Rb 2 - Phot
R(26) 0 - 14	a10	385233438,207	0,042	Rb 2 - Phot
R(139) 1 - 14	a13	385266729,747	0,043	Rb 2 - Phot
R(18) 0 - 14	a9	385291965,716	0,050	Rb 2 - Phot
R(16) 0 - 14	a10	385302700,723	0,043	Rb 2 - Phot
R(138) 1 - 14	a10	385322745,915	0,047	Beat
R(240) 0 - 12	a10	385347591,290	0,047	Beat
P(164) 0 - 13	a1	385363327,790	0,110	Beat
P(129) 1 - 14	b2	385363816,382	0,120	Beat

Large set of measurements

- assignment of spectrum
- rotational and vibrational energy levels
- analysis of hyperfine structure
- determination of molecular parameters
- determination of potentials
- recalculation of the total spectrum
- predictions ? !

radial Schrödinger equation:

$$\left\{-\frac{\hbar^2}{2m_r}\frac{\partial^2}{\partial R^2}+\frac{\hbar^2 J(J+1)}{2m_r R^2}+V(R)\right\}\chi(R)=E_{\mathrm{v},J}\chi(R)$$

Dunham potential:

$$V(R)=d_0\cdot\xi^2\cdot\left(1+\sum_{i>0}d_i\cdot\xi^i\right) \qquad \xi=\frac{R-R_e}{R_e}$$

representation of energy levels:

$$E(\mathrm{v},J)=\sum_{k,l}Y_{k,l}\left(\mathrm{v}+\frac{1}{2}\right)^k\left[J(J+1)\right]^l \quad k,l=0,1,2,\ldots$$

transition frequencies:

$$\nu(\mathrm{v}'',J'',\mathrm{v}',J')=T_e+E(\mathrm{v}',J')-E(\mathrm{v}'',J'')$$

„X“-representation of **potential**: for better convergence behavior

$$V(R) = \sum_i a_i X^i \qquad i = 0,1,2,\ldots \qquad X = \frac{R - R_e}{R + a \cdot R_e}$$

effective Hamiltonian including Born-Oppenheimer (BO) corrections

$$H_{eff} = -\frac{\hbar^2}{2m_r}\frac{\partial}{\partial R}[1+\beta(R)]\frac{\partial}{\partial R} + \frac{\hbar^2 \cdot [1+\alpha(R)] \cdot J \cdot (J+1)}{2m_r R^2} + V(R) + V_{kor}(R)$$

non-adiabatic BO corrections (→ $\beta(R)$, $\alpha(R)$) adiabatic BO correction (→ $V_{kor}(R)$) observed by isotope variation

$$1 + \alpha(R) = \sum_i b_i X^i$$

isotope dependent (→ b_i)

$$a_j = a_j^0 + a_j^A \frac{m_e}{M_A} + a_j^B \frac{m_e}{M_B}$$

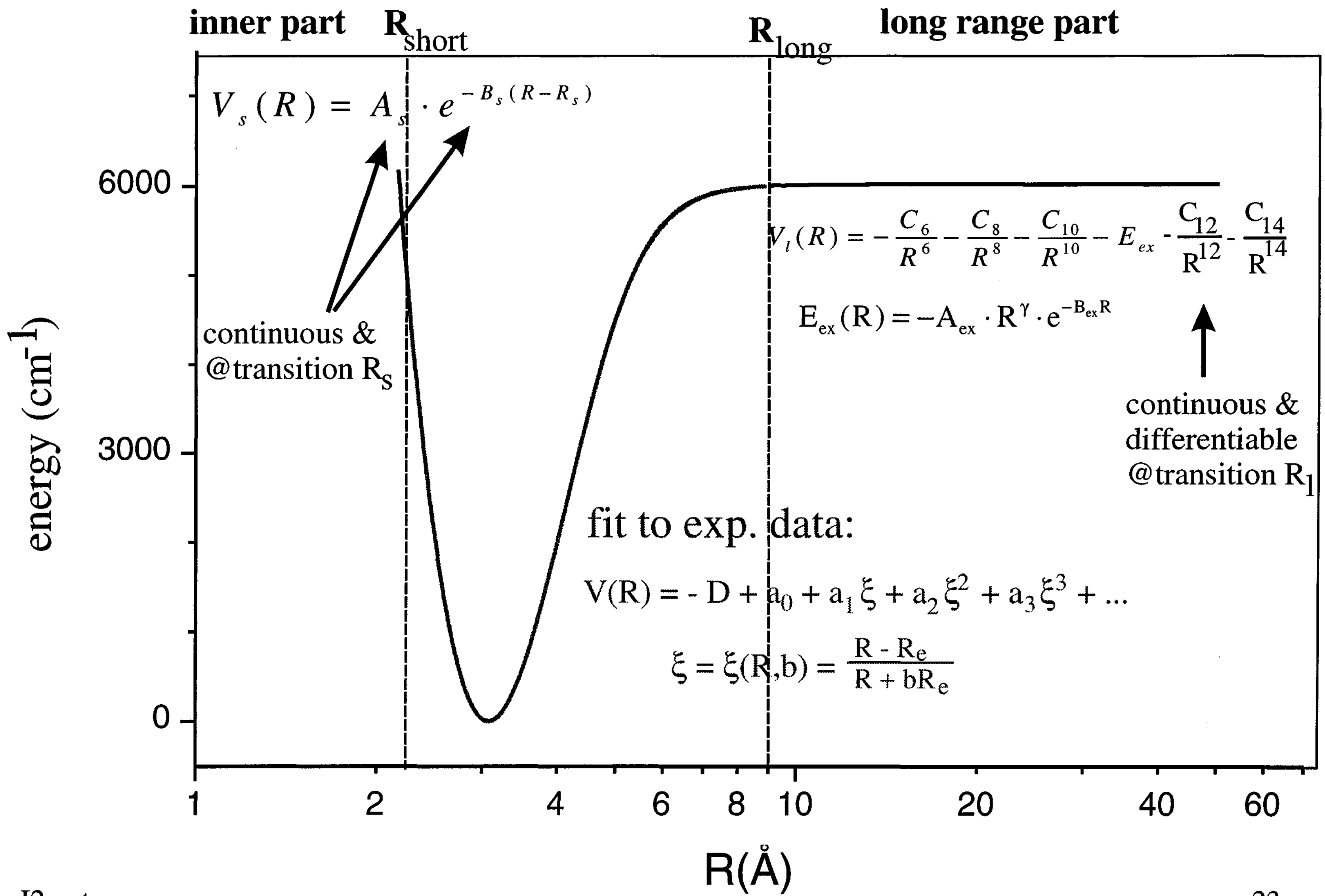
effective Schrödinger equation:

$$\left\{ -\frac{\hbar^2}{2m_r}\frac{\partial^2}{\partial R^2} + \frac{\hbar^2 \cdot \sum_i b_i X^i}{2m_r R^2} J \cdot (J+1) + \sum_j a_j X^j \right\} \chi(R) = E_{v,J} \cdot \chi(R)$$

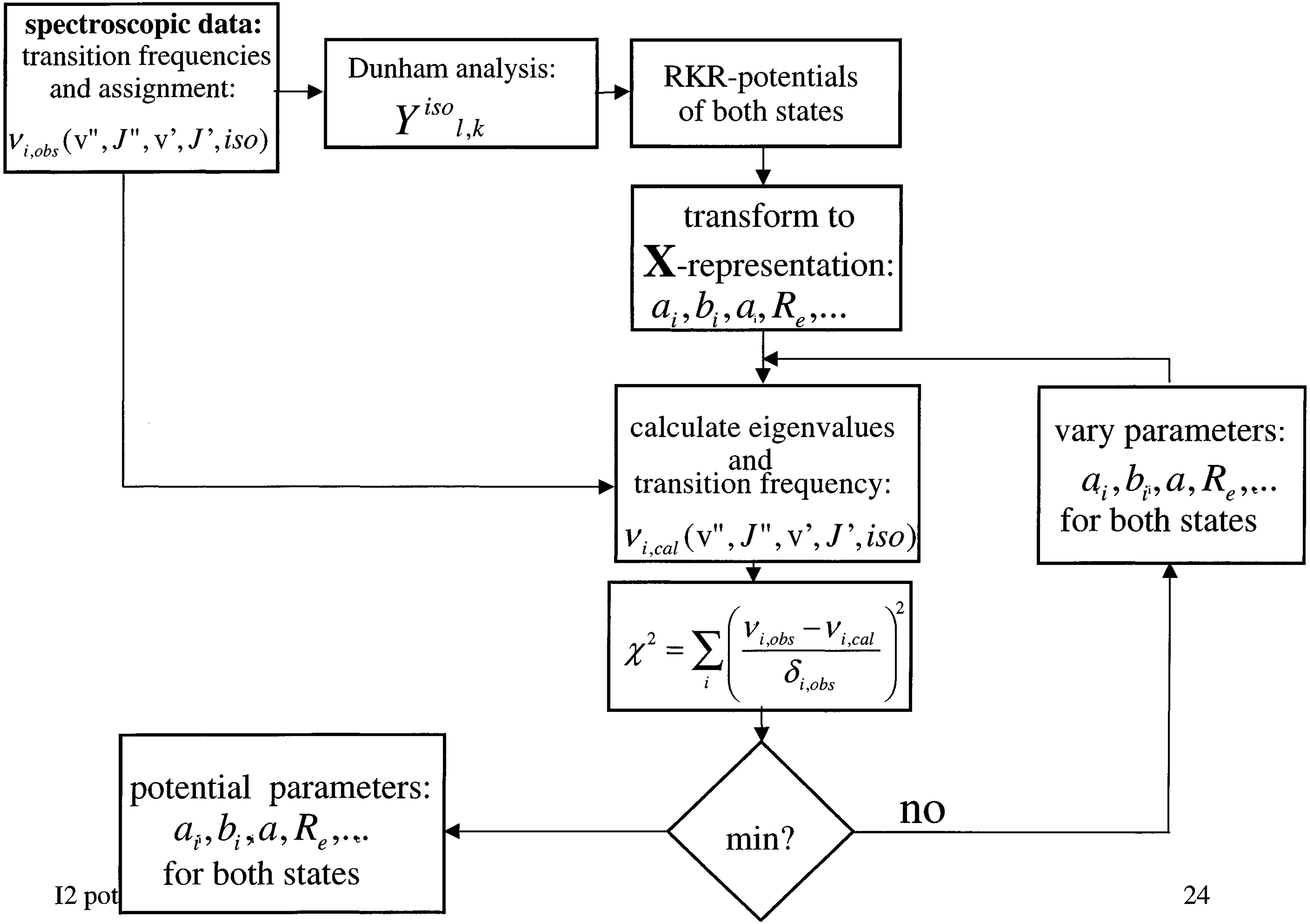
R.M.Hermann, A.Asgharian, J.Mol.Spectrosc. **19**, 305 (1966)

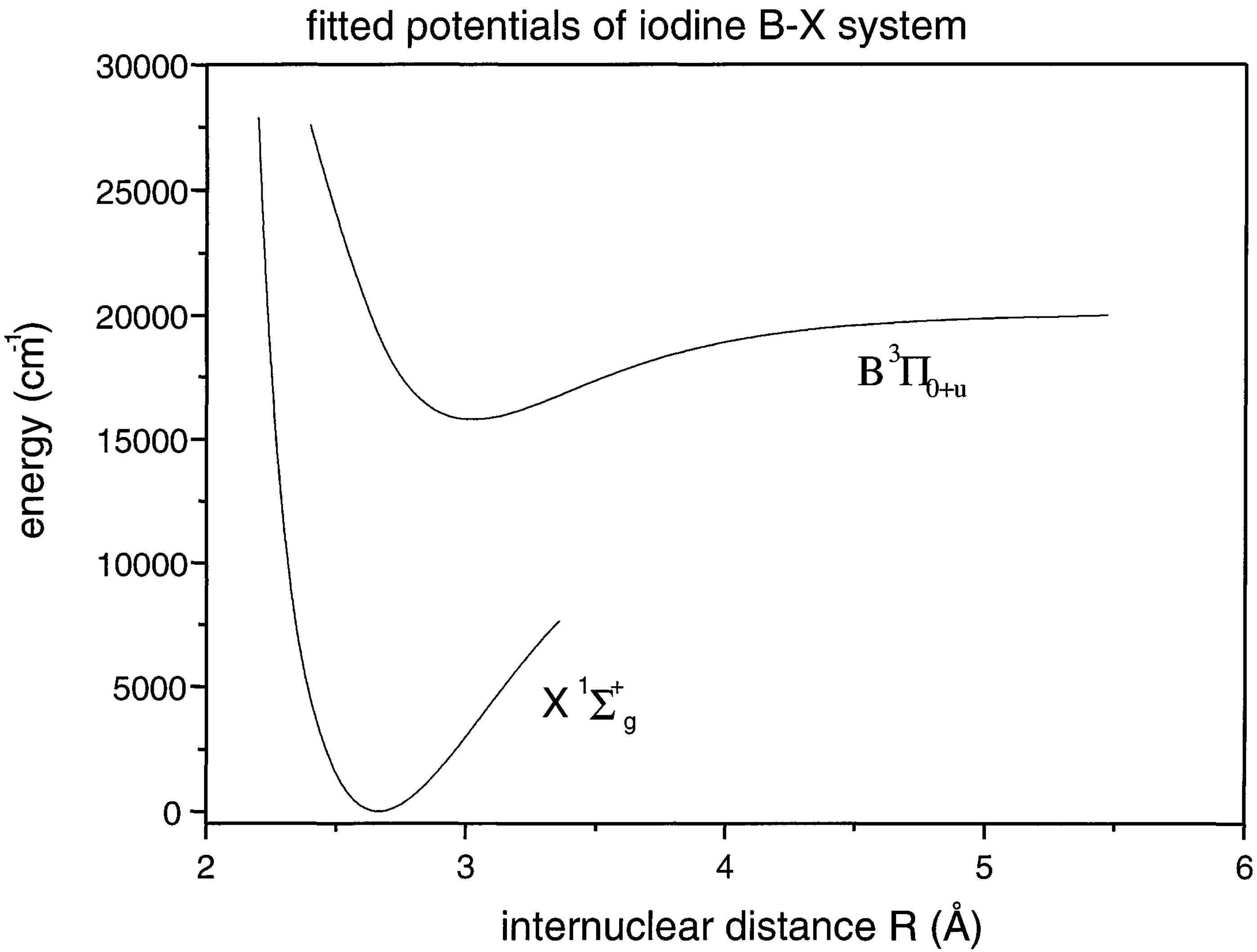
J.K.G.Watson, J.Mol.Spectrosc. **80**, 411 (1980)

Construction of the adiabatic potentials

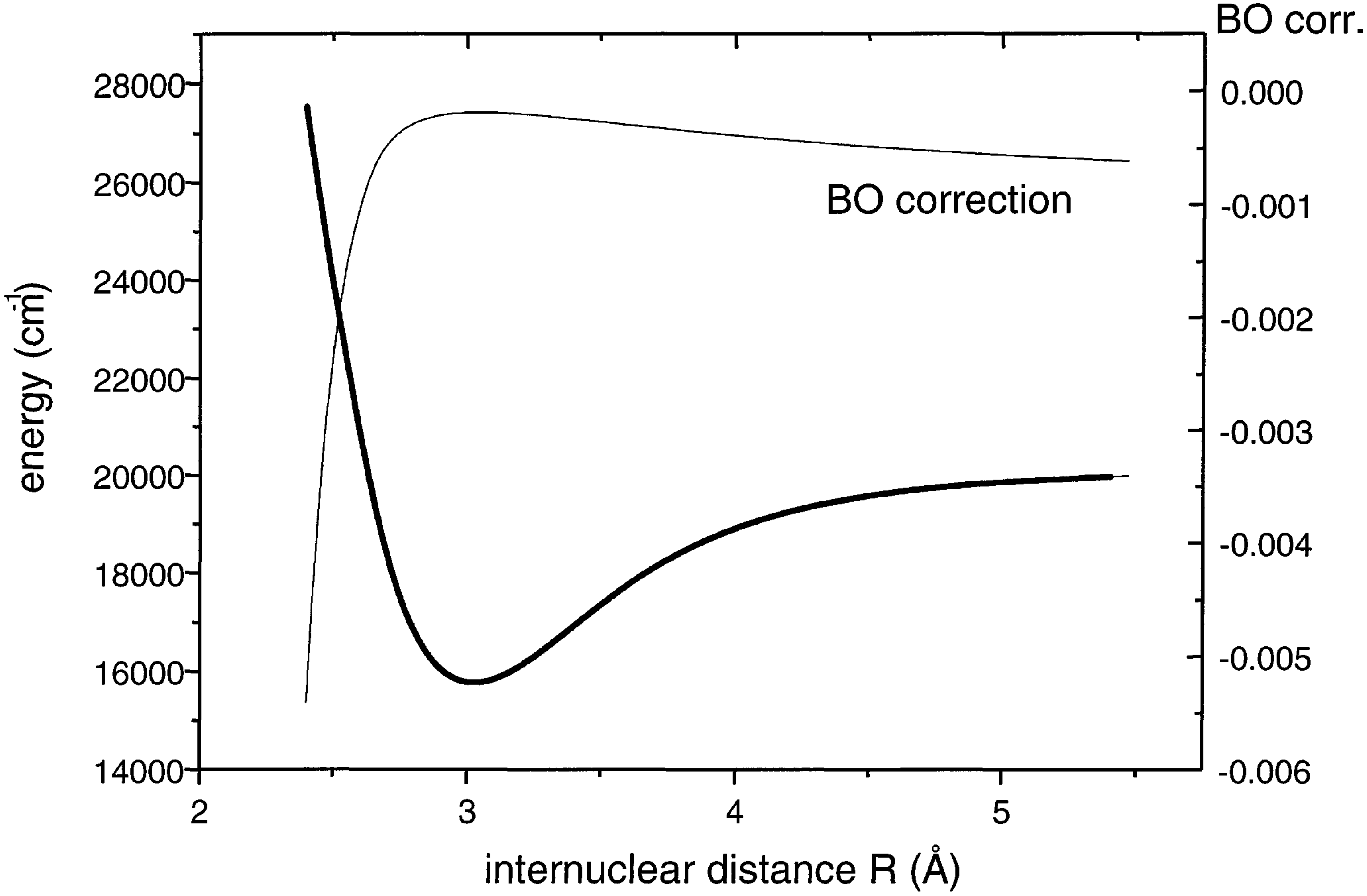


determination of molecular potentials

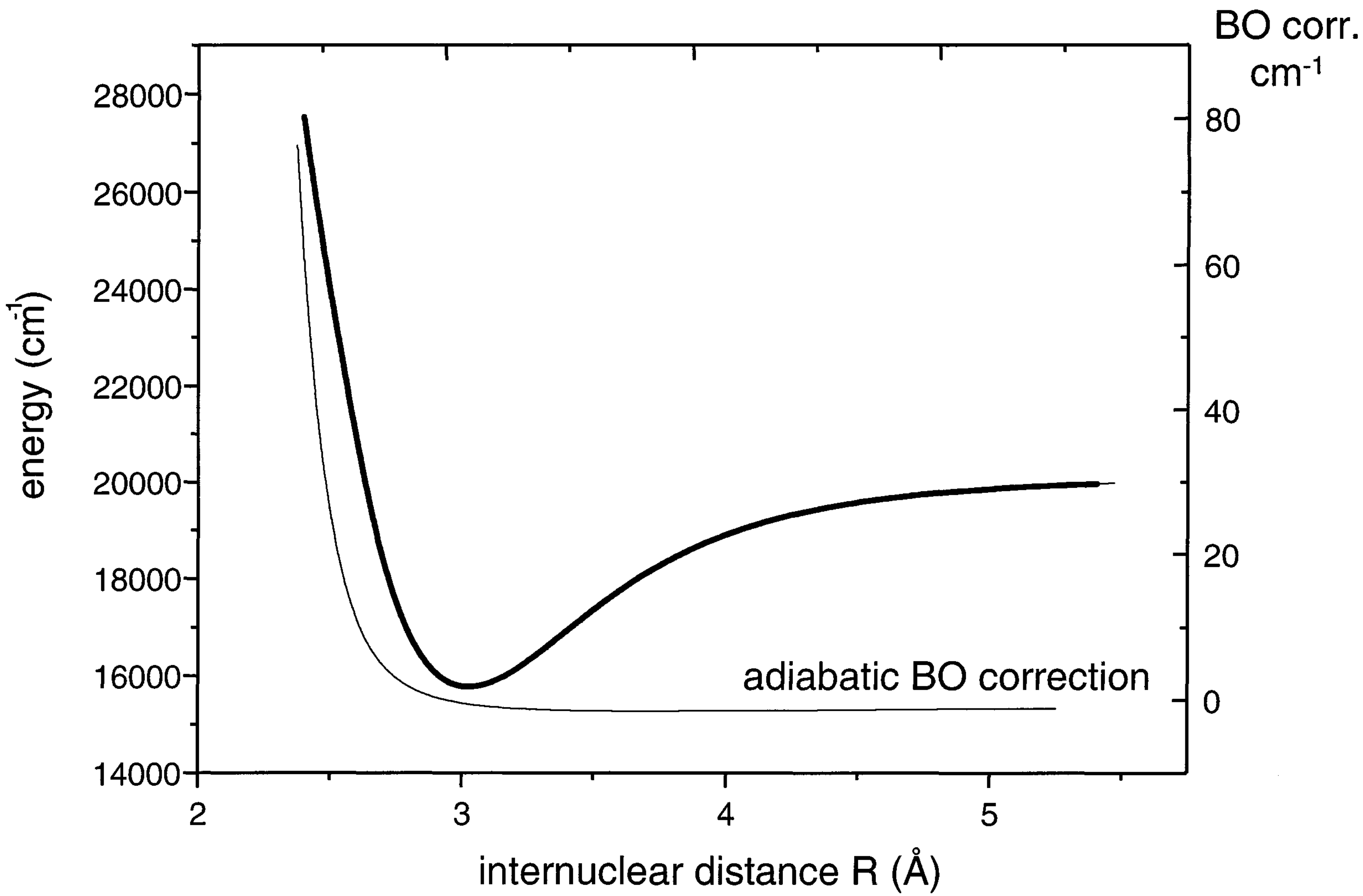



fitted potentials of iodine B-X system
30000
25000
20000
15000
10000
5000
0
energy (cm-1)
2
3
4
5
6
internuclear distance R (Å)
B 3Π0+u
X 1Σ+g

B state potential and BO correction for J **non-adiabatic**



B state potential and **adiabatic** BO correction



The fit describes all observations of vibrational and rotational structure within experimental accuracy

To give error limits for potential parameters is not meaningful:
- the correlation is too high and
- the result depends strongly on the truncation of the power series

Extrapolation out of the region of observation degrades quickly in reliability

Molecular spectroscopy and secondary frequency standards

Part 2 Hyperfine analysis and precise global prediction

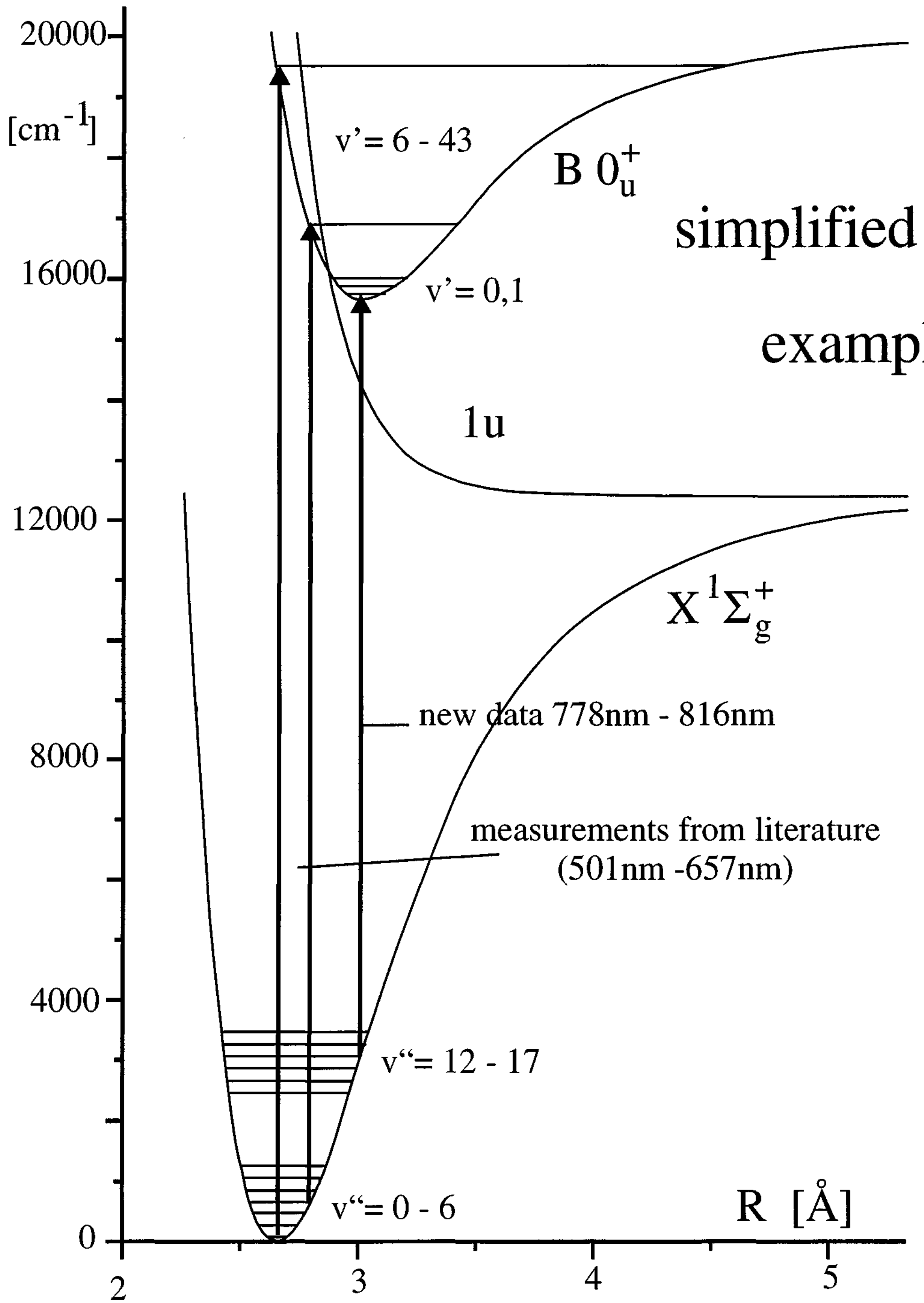
Eberhard Tiemann

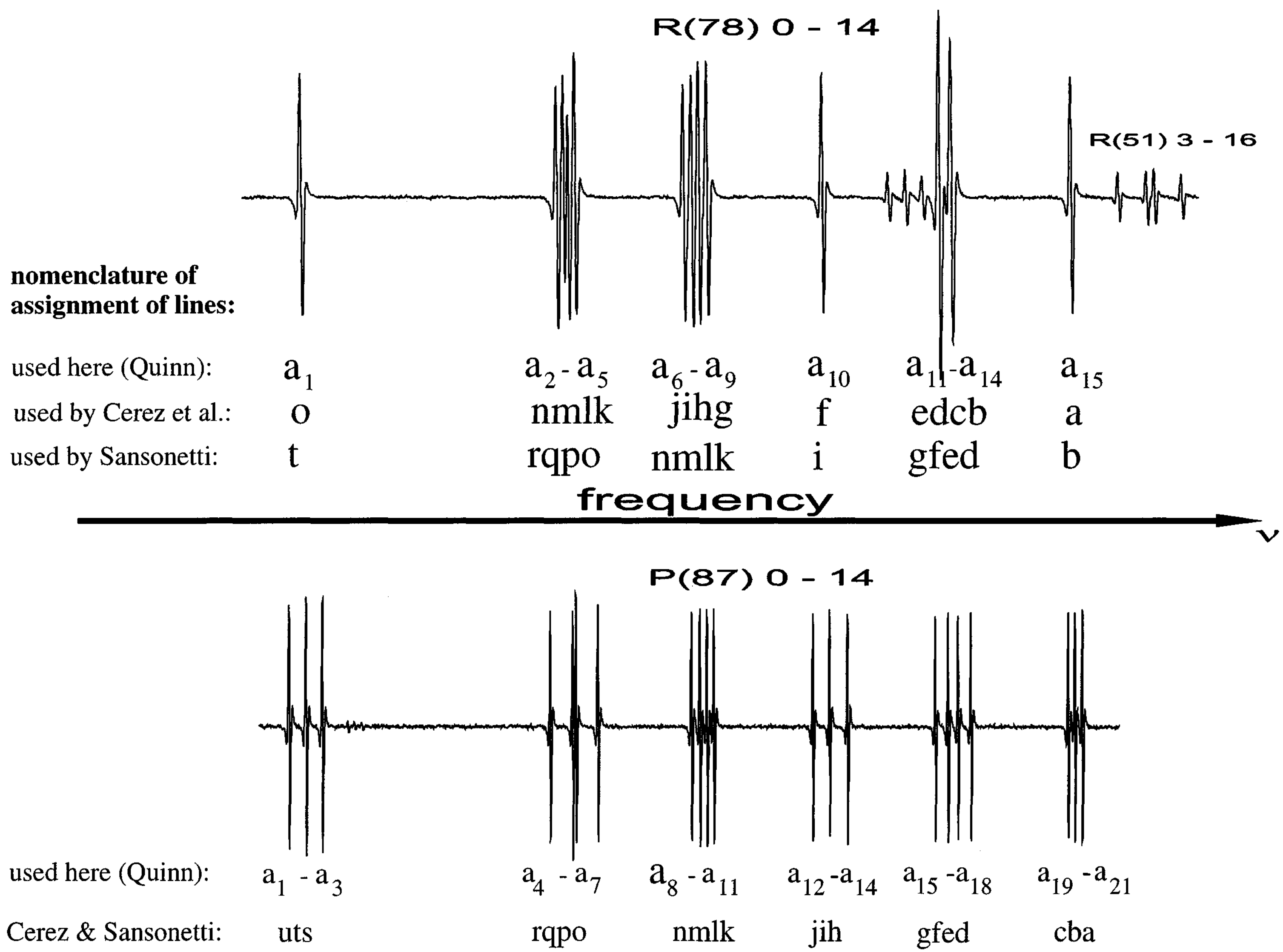
University Hannover, Institute of Quantum Optics

1. Hyperfine interactions, effective hamiltonian
2. Fitting to molecular parameters
3. Interpretation of quantum number dependence
4. Iodine atlas as reference and its numerical reconstruction

simplified potential scheme

example I_2




R(78) 0 - 14
R(51) 3 - 16
nomenclature of assignment of lines:
used here (Quinn): a_1 a_2 - a_5 a_6 - a_9 a_{10} a_{11} - a_{14} a_{15}
used by Cerez et al.: o nmlk jihg f edcb a
used by Sansonetti: t rqpo nmlk i gfed b
frequency
ν
P(87) 0 - 14
used here (Quinn): a_1 - a_3 a_4 - a_7 a_8 - a_{11} a_{12} - a_{14} a_{15} - a_{18} a_{19} - a_{21}
Cerez & Sansonetti: uts rqpo nmlk jih gfed cba

Hamiltonian for hyperfine structure

$$\hat{H}_{hfs} = \hat{H}_{quadrupole} + \hat{H}_{spin-rot.} + \hat{H}^{tensor}_{spin-spin} + \hat{H}^{scalar}_{spin-spin}$$

$eqQ_{A/B}$ $C_{sr\ A/B}$ d δ molecular parameters

angular momentum coupling

$\vec{F}_A = \vec{J} + \vec{I}_A$ $\vec{F} = \vec{F}_A + \vec{I}_B$ yields the basis $\left|(J, I_A)F_A I_B F, M_F\right\rangle$

effective hamiltonian, e.g. $\hat{H}_{spin-rot.} = c_{sr}\vec{J}\cdot\vec{I}$

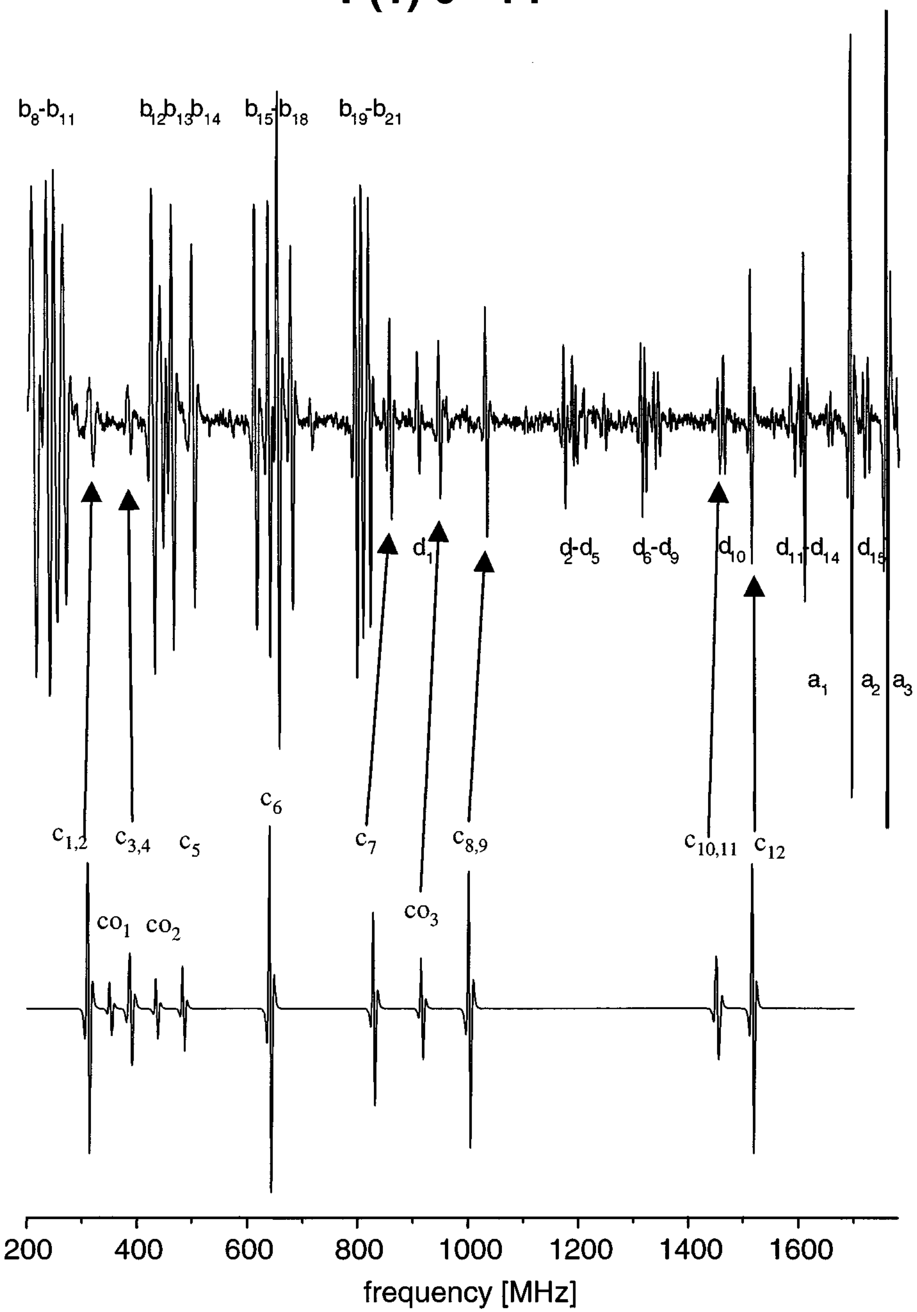
Literature:

A.R.Edmonds, Angular momentum in quantum mechanics
Princeton University Press (1964)

M.Broyer, J.Vigué, J.C.Lehmann, J.Physique 39, 347 (1987)

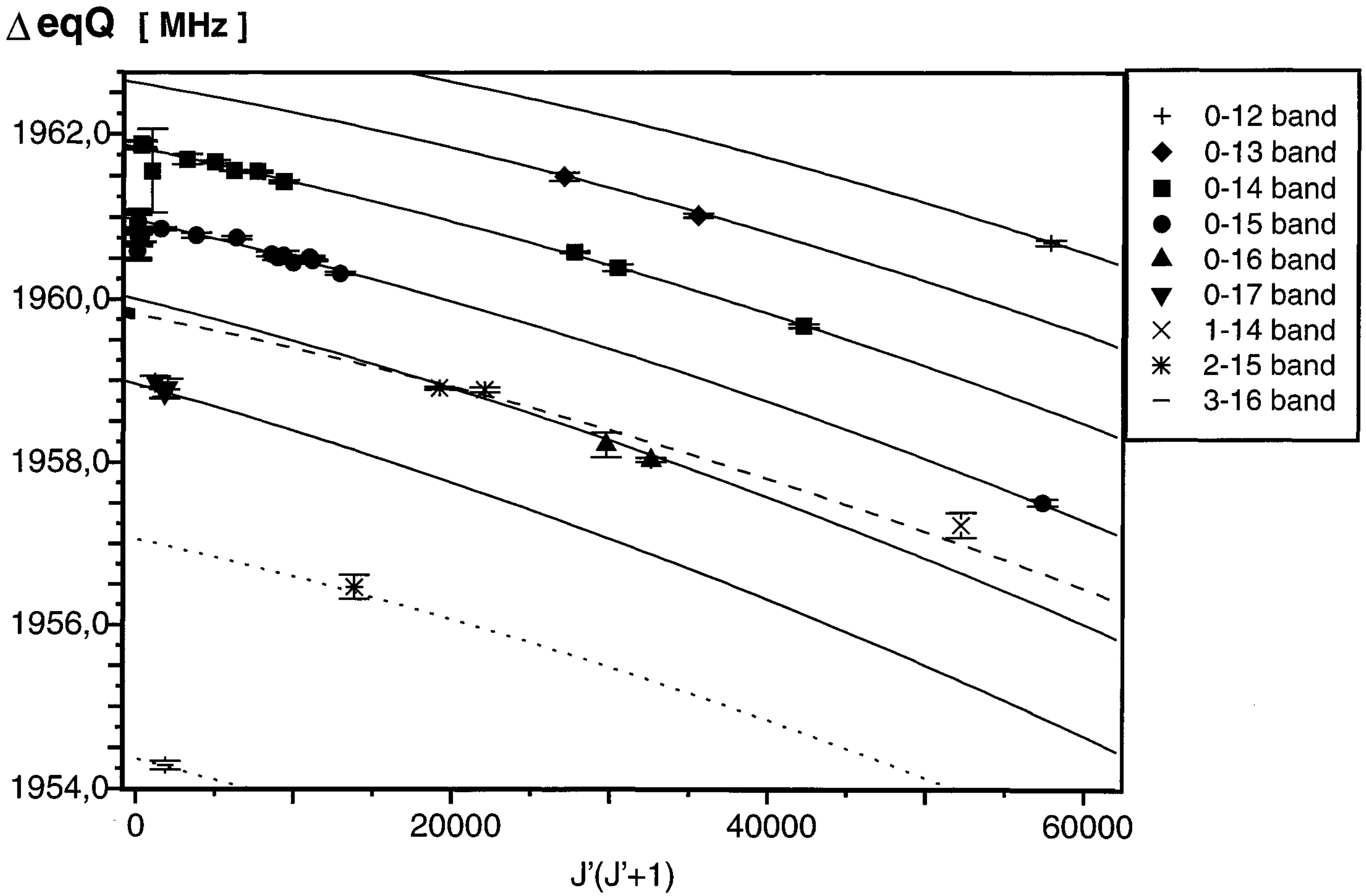
E.Hirota, High resolution spectroscopy of transient molecules,
Springer Berlin 1986

P(1) 0 - 14



Simulation
to identify weak lines

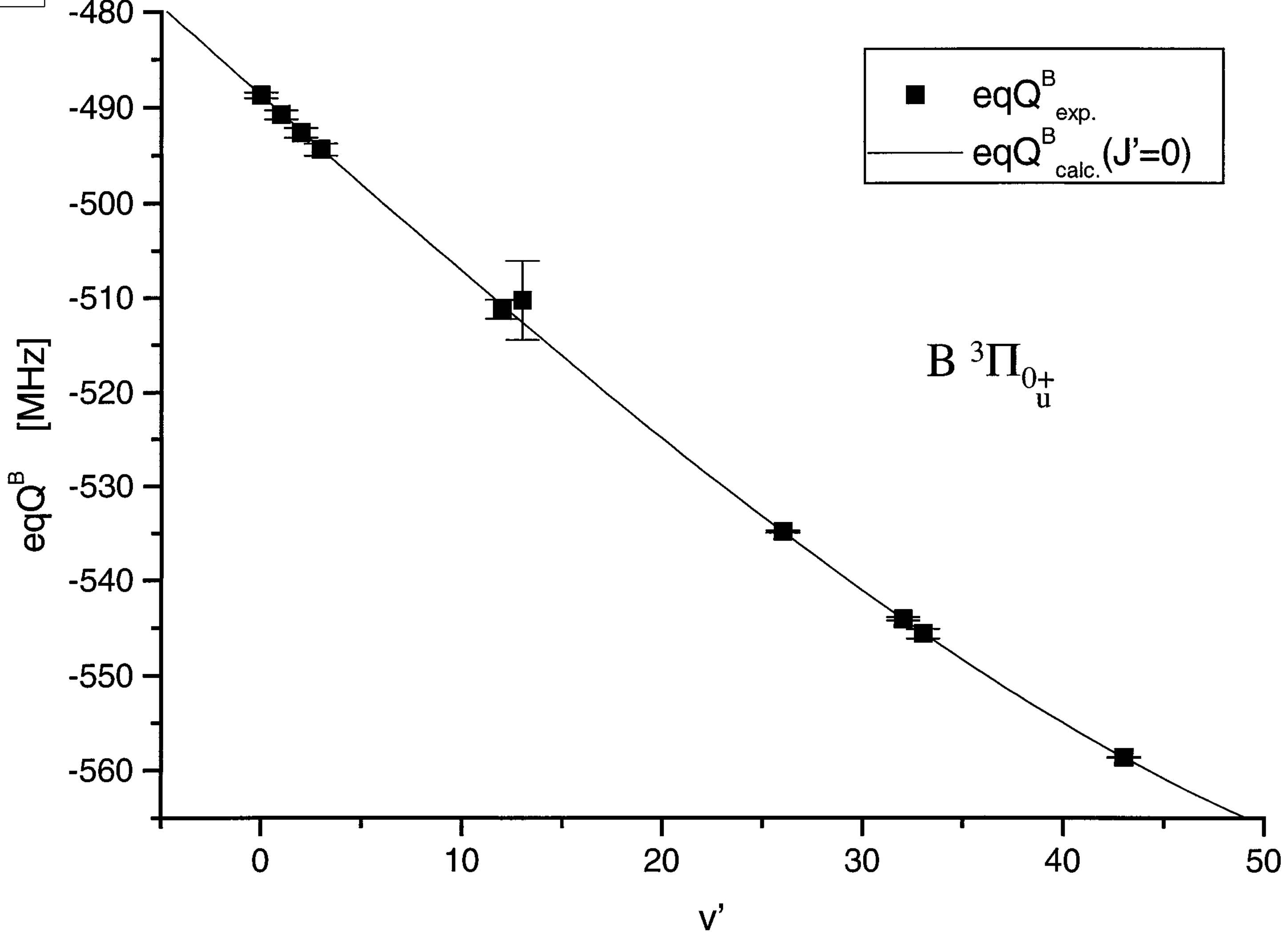
nuclear quadrupole coupling $\Delta eqQ = eqQ_B(v',J') - eqQ_X(v'',J'')$



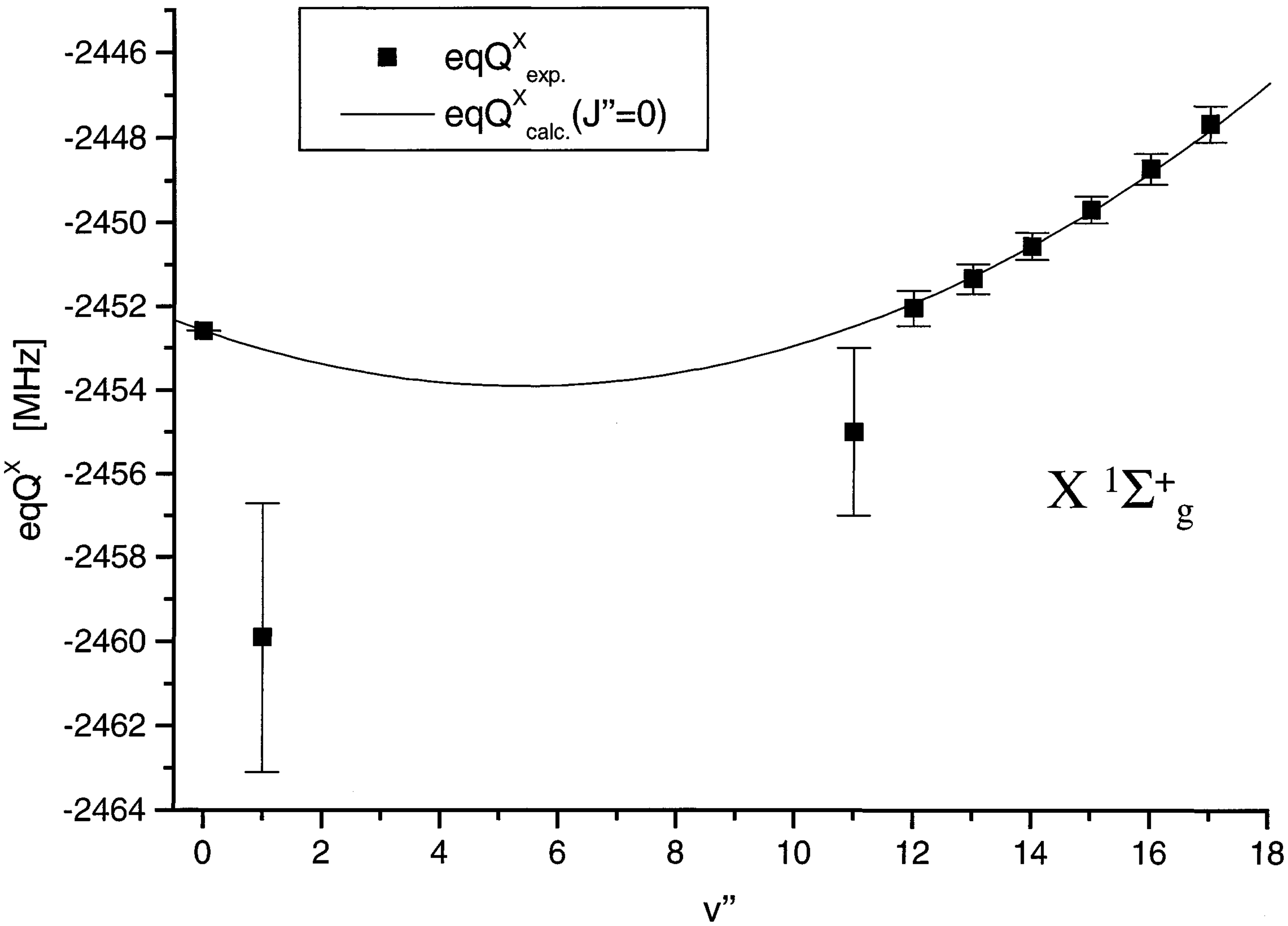
solid line: variation of the ground state X

dotted line: variation of the excited state B

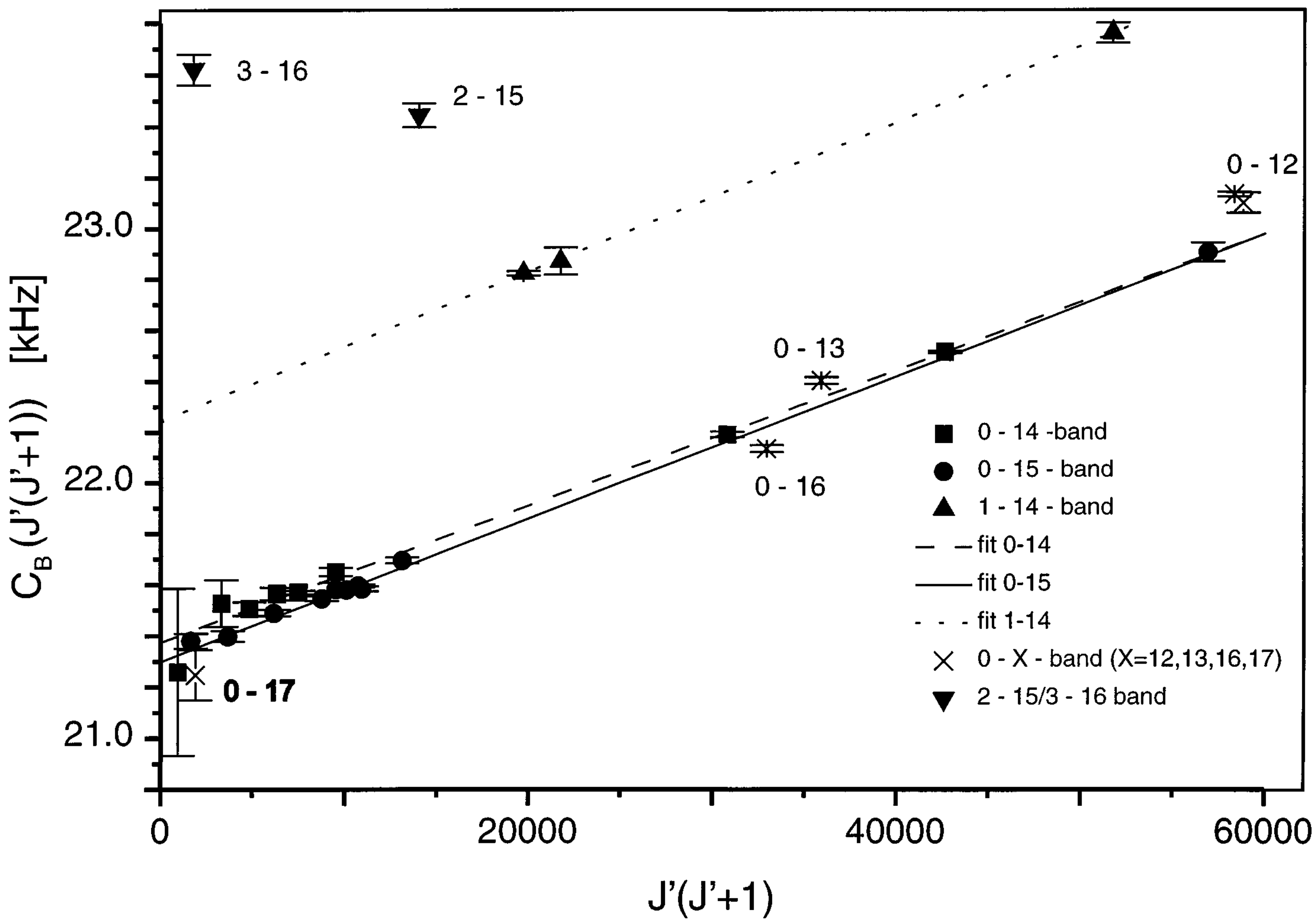
Variation of eqQ with v‘ gives the function of electric field gradient with internuclear separation



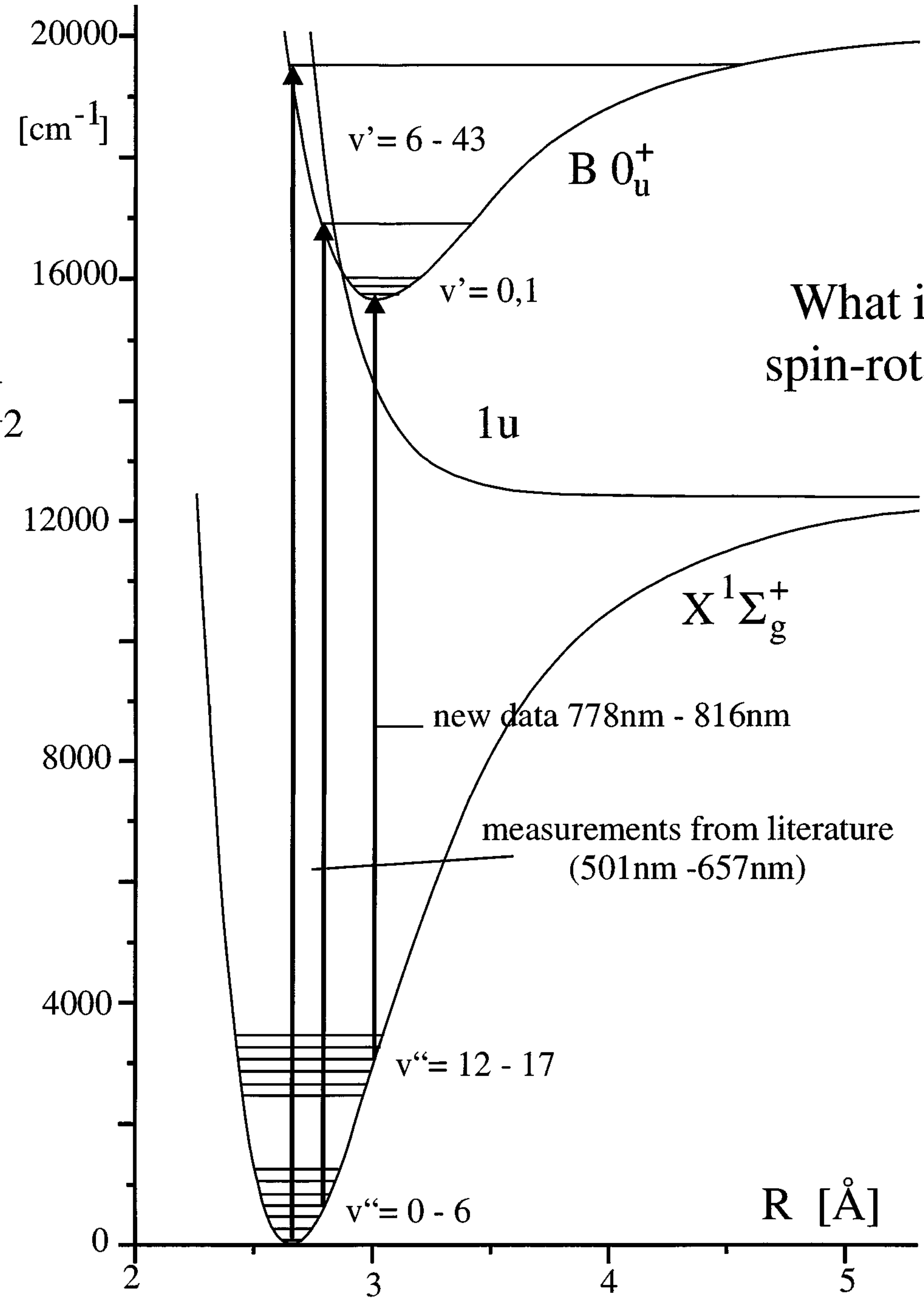
ground state, small variation of eqQ



variation of spin-rotation coupling of the excited state B

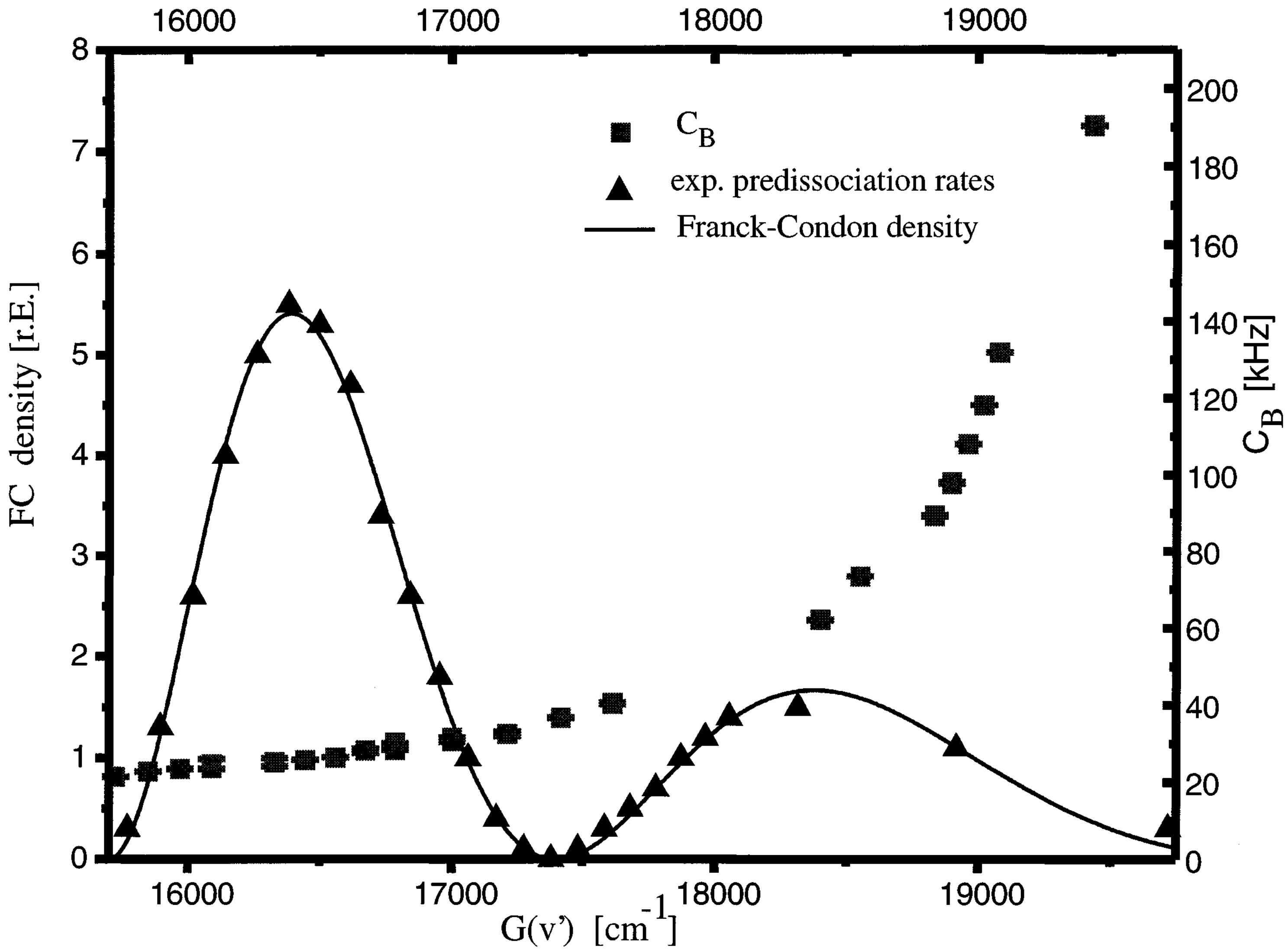


example I_2

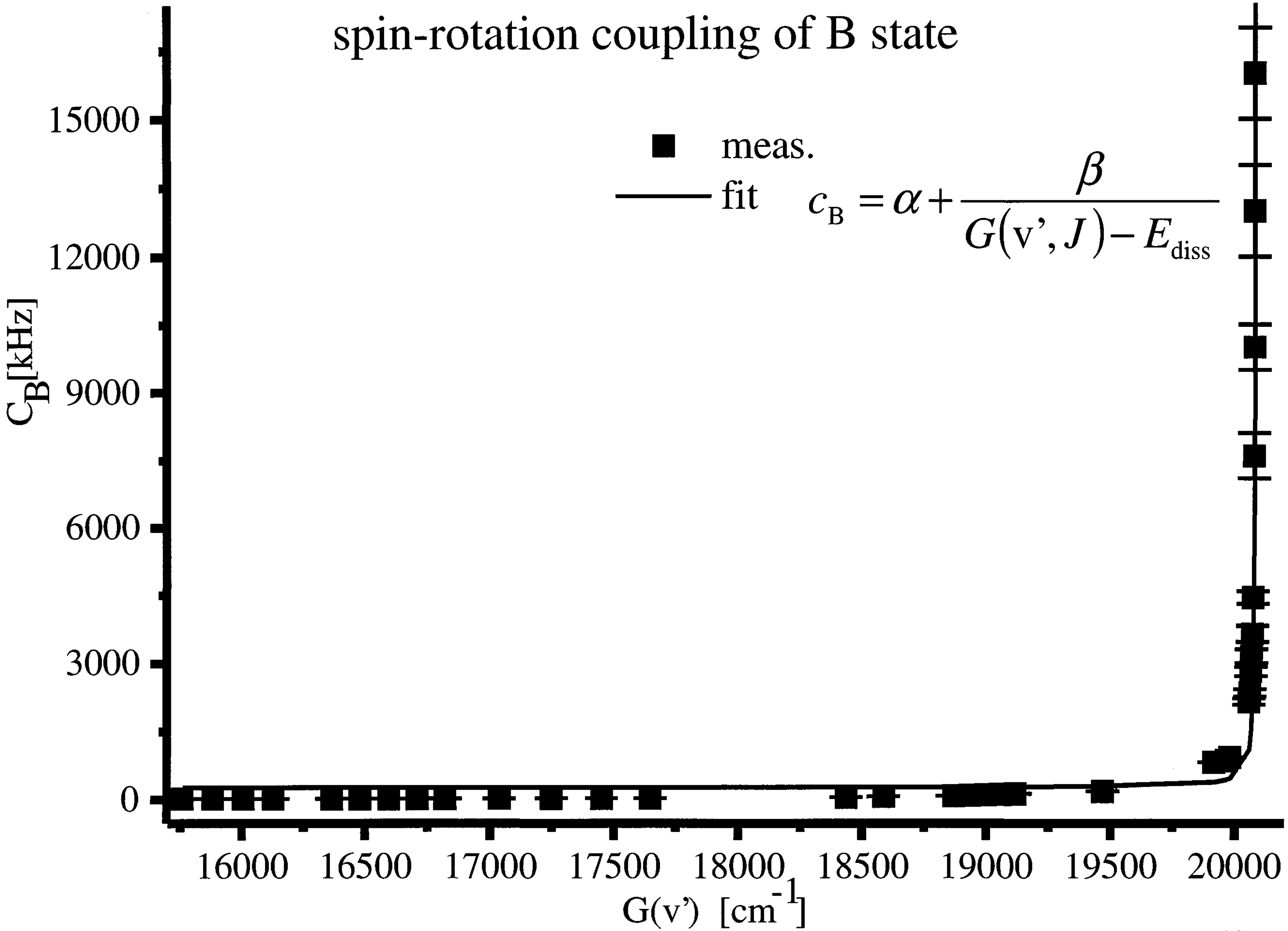


What is the origin of spin-rotation coupling ?

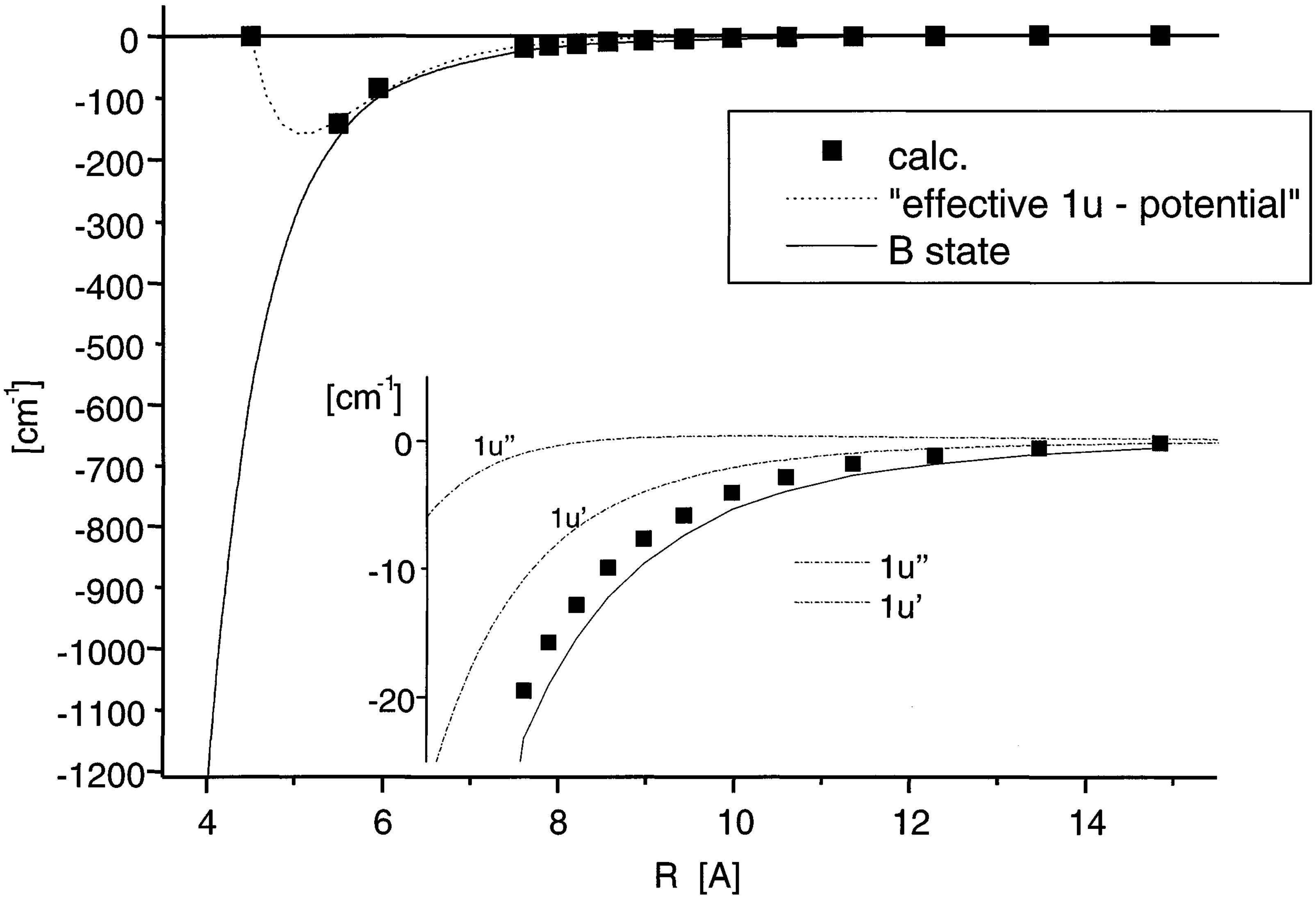
Is the spin-rotation coupling produced by the repulsive state 1u?



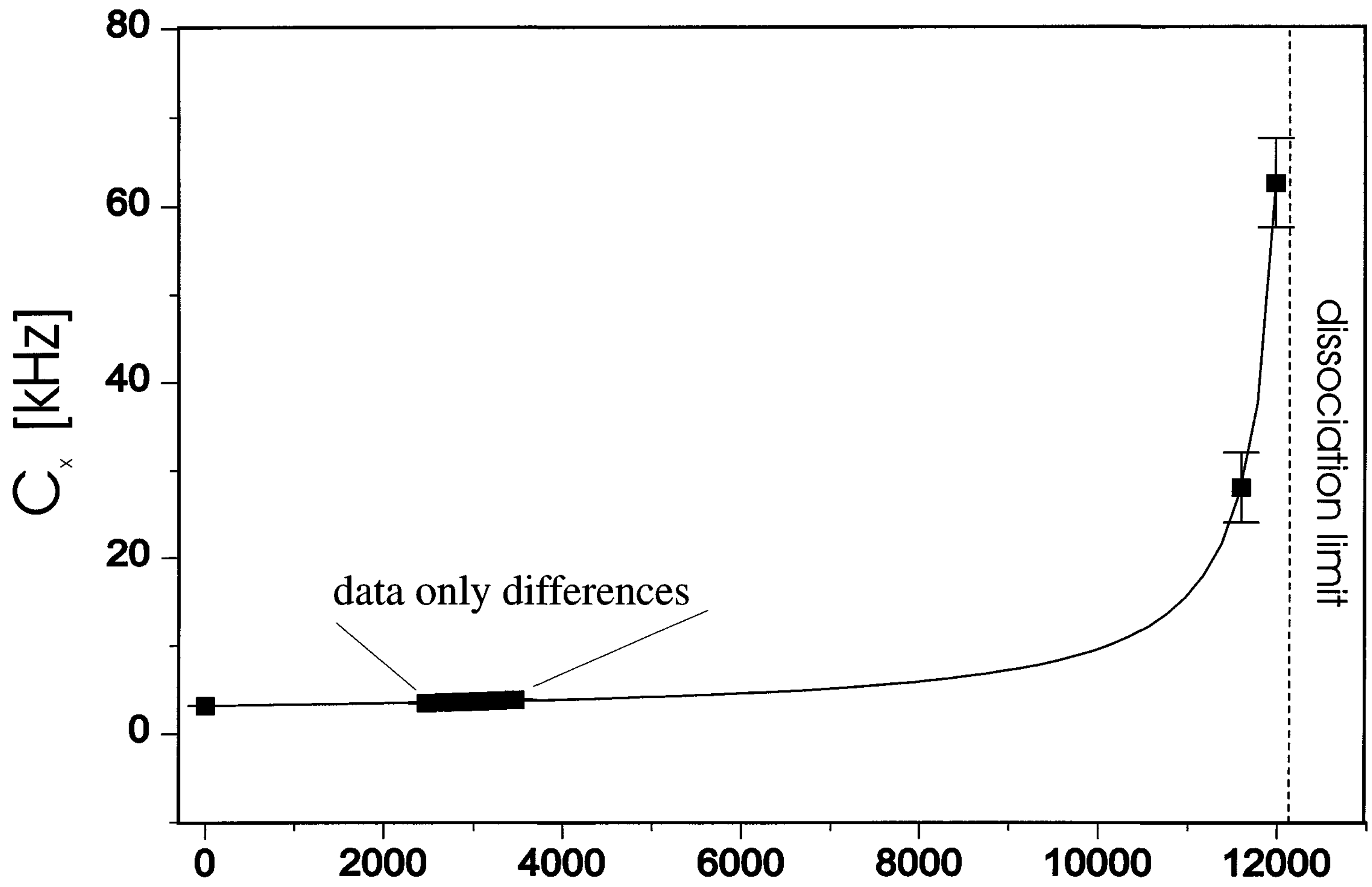
No! There is no similarity between the Franck-Condon density of State B and 1u and the function of C_B


spin-rotation coupling of B state
meas.
fit
$c_B = \alpha + \frac{\beta}{G(v', J) - E_{diss}}$
C_B[kHz]
15000
12000
9000
6000
3000
0
16000
16500
17000
17500
18000
18500
19000
19500
20000
G(v') [cm^{-1}]

Potential form from asymptotic behavior of the spin-rotation coupling

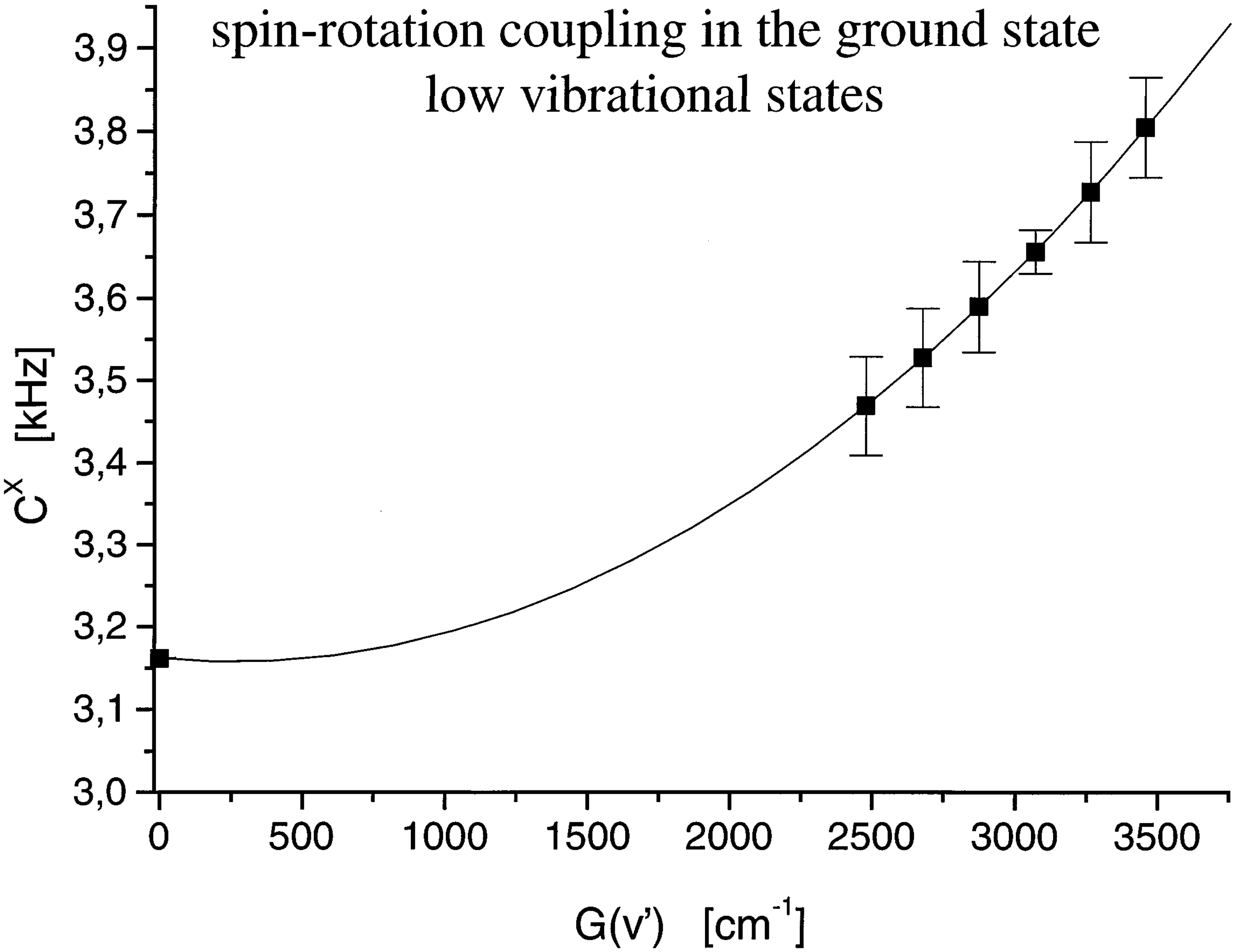


spin-rotation coupling in the ground state



G(v") [cm⁻¹]

$$C_X = 1.95(38) + 3.8(1.1)\cdot 10^{-2}\cdot\left(v'' + \frac{1}{2}\right) + \frac{14677(4824)}{12343(85) - G(v'')} \quad [\mathrm{kHz}]$$


spin-rotation coupling in the ground state
low vibrational states
C^X [kHz]
3,0
3,1
3,2
3,3
3,4
3,5
3,6
3,7
3,8
3,9
0
500
1000
1500
2000
2500
3000
3500
G(v') [cm^{-1}]

nuclear spin-rotation interaction:

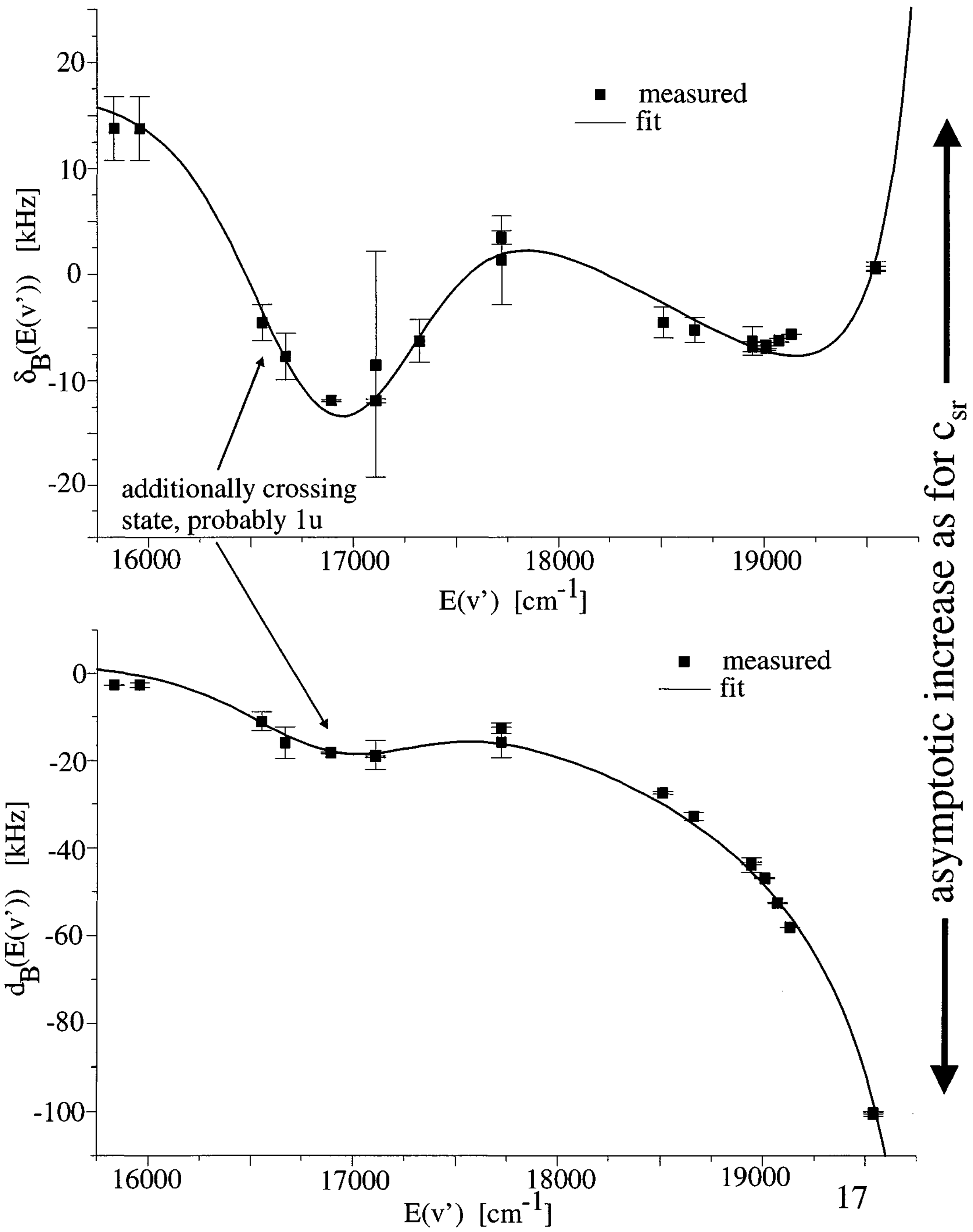
$$C_X = 1.95(38) + 3.8(1.1)\cdot 10^{-2}\cdot\left(v'' + \frac{1}{2}\right) + \frac{14677(4824)}{12343(85) - G(v'')} \quad [\text{kHz}]$$

$$C_B = -5.539(32) - 0.3173(21)\cdot\left(v' + \frac{1}{2}\right) - 3.502\cdot 10^{-4} J'(J'+1) -$$

$$1.080\cdot 10^{-5}\cdot\left(v' + \frac{1}{2}\right)\cdot J'(J'+1) + \frac{119706(156) + 1.6422(37)\cdot J'(J'+1)}{20005.6(4) - G(v'')} \quad [\text{kHz}]$$

scalar spin-spin coupling

tensorial spin-spin coupling



Iodine as a reference spectrum

- Calculation of vibrational and rotational structure
  from potentials
- Determination of hyperfine structure from reliable formulas
- Construction of the spectrum with line profiles
  according to experimental conditions
- Calculation of relative intensities with
  the Franck-Condon approximation
- Accuracy in the range of 10^{-8} - 10^{-10}
  depending on the primary calibration
- Stability of the calibration better than one year