INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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SMR/100 - 59

WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

(24 January - 25 March 1983)

CARS Spectroscopy

Part II

a) Lasers for CARS
b) Electronic Enhancement of CARS-Spectra

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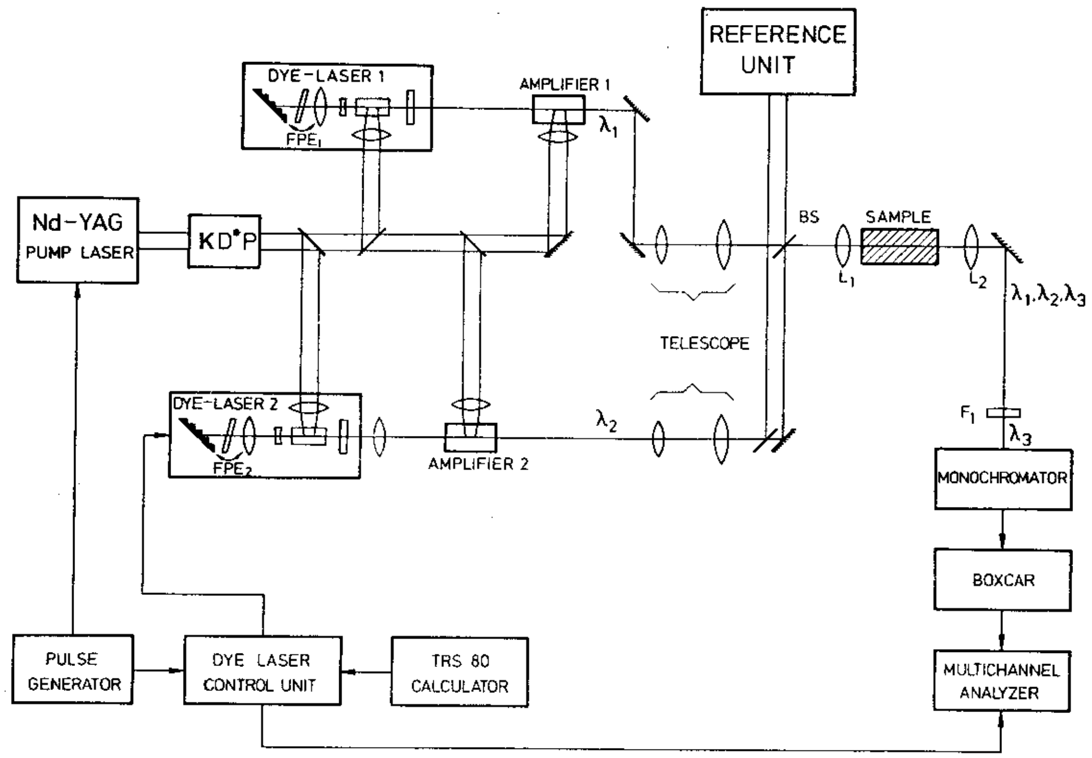
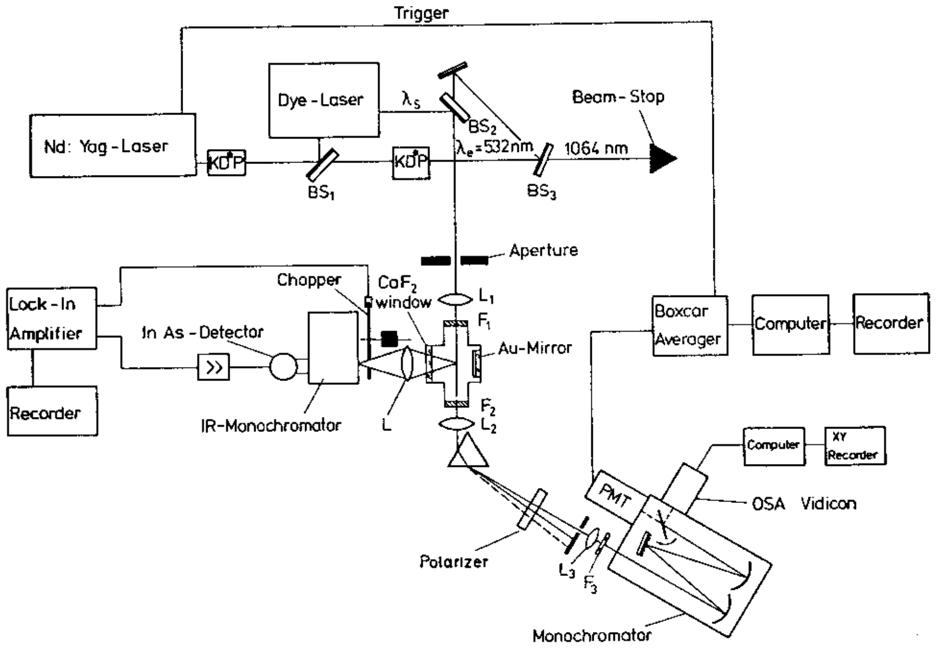
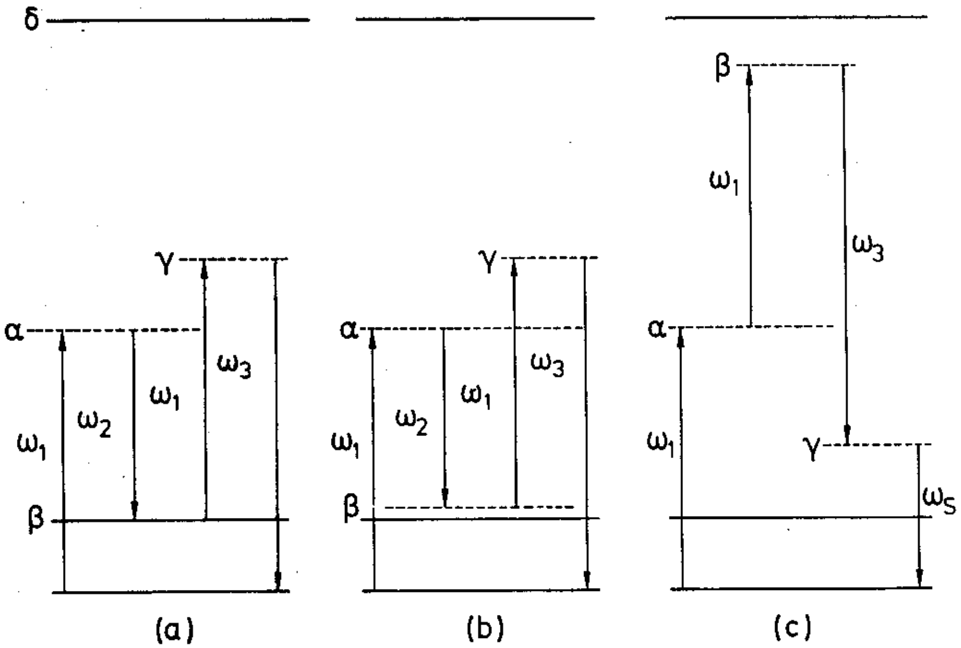

REFERENCE UNIT
DYE-LASER 1
FPE1
AMPLIFIER 1
λ1
Nd-YAG PUMP LASER
KD*P
BS
SAMPLE
L1
L2
λ1,λ2,λ3
TELESCOPE
DYE-LASER 2
FPE2
AMPLIFIER 2
λ2
F1
λ3
MONOCHROMATOR
BOXCAR
PULSE GENERATOR
DYE LASER CONTROL UNIT
TRS 80 CALCULATOR
MULTICHANNEL ANALYZER


Trigger
Dye-Laser
λS
Beam-Stop
Nd: Yag-Laser
KDP
BS1
KDP
BS2
λe=532nm
BS3
1064 nm
Aperture
Lock-In Amplifier
Chopper
CaF2 window
L1
F1
In As-Detector
Au-Mirror
Boxcar Averager
Computer
Recorder
Recorder
IR-Monochromator
L
F2
L2
Computer
XY Recorder
PMT
OSA Vidicon
Polarizer
L3
F3
Monochromator



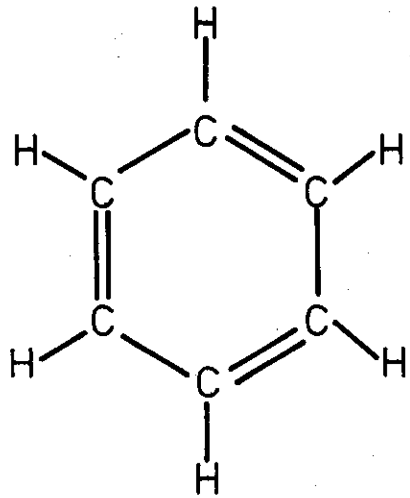
CARS-Type Experiments

2-Photon-Type Experiments

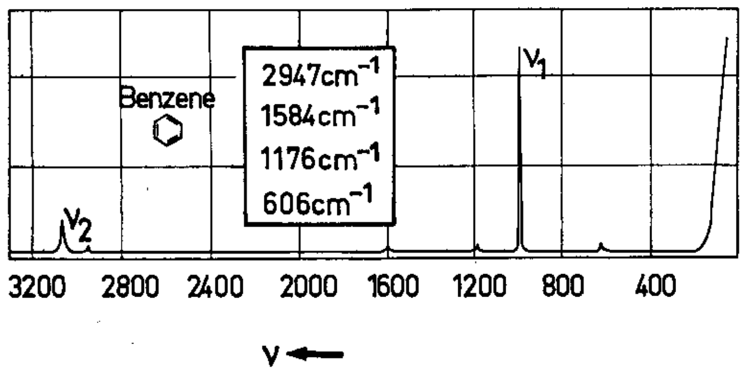
Benzene:

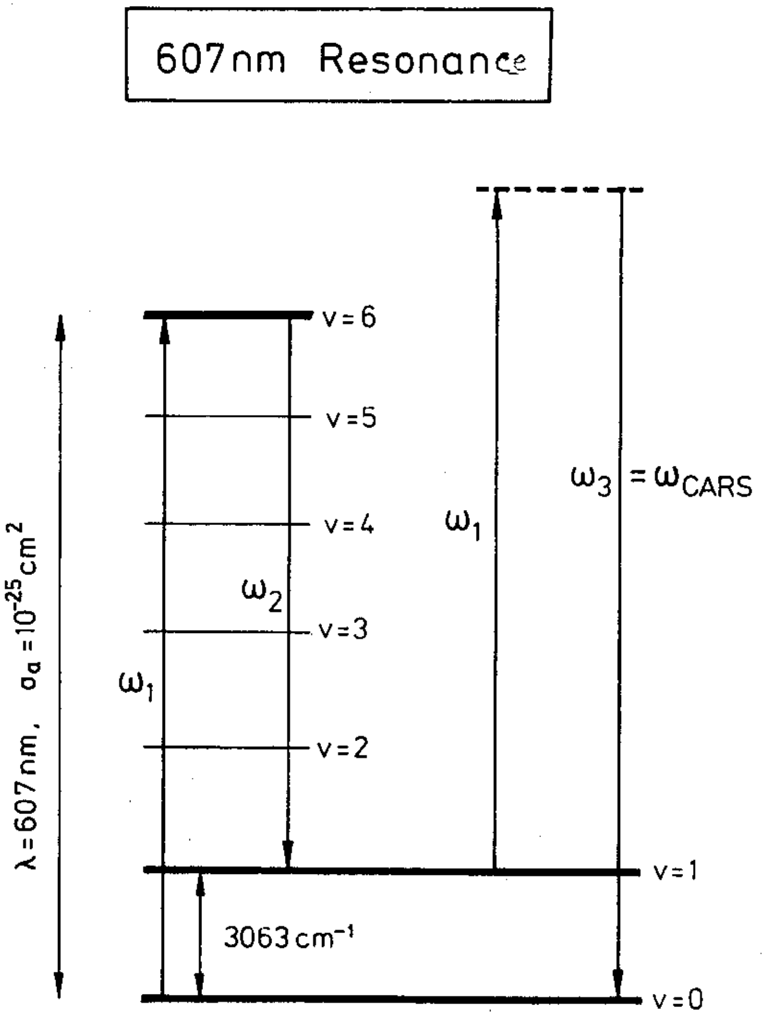
ν_1 - mode

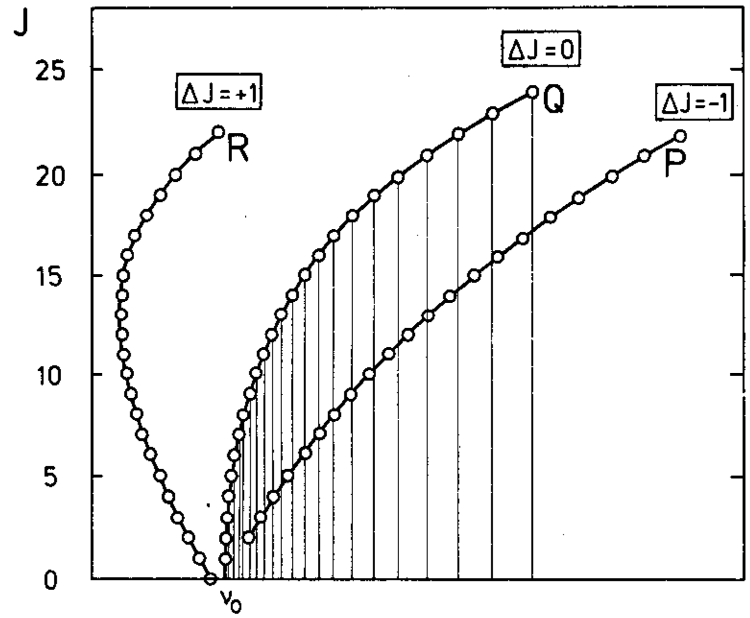
ν_2 - mode



$$\nu_1 = 992\,cm^{-1} \quad ; \quad \nu_2 = 3063\,cm^{-1}$$





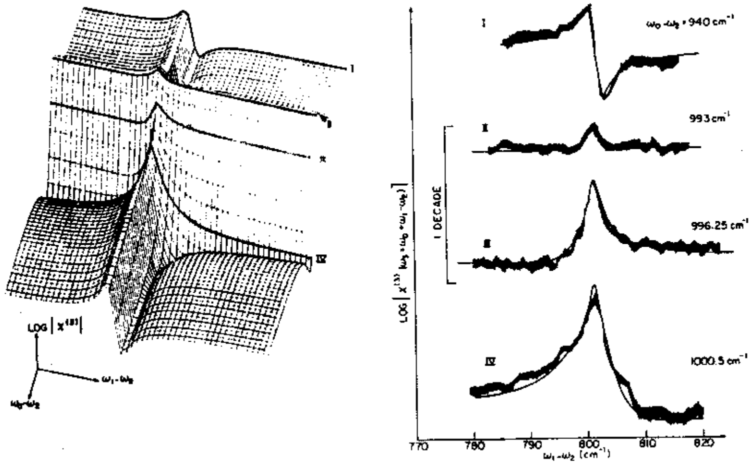


Fortrat — Diagramm

III/4

(7)

R.T. Lynch et al. Opt Comm. 16 (1976), 372



$$\chi^{(3)}(\omega_3=\omega_0+\omega_1-\omega_2) = \chi^{(3)}_{NR} + \frac{A_M}{\Omega_M-\Omega_a-i\Gamma_M} + \frac{A_{M'}}{\Omega_M-\Omega_b-i\Gamma_{M'}}$$

$\Omega_M = 992\ cm^{-1}$ (benzene)

$\Omega_M = 801\ cm^{-1}$ (cyclohexane)

$\Omega_a = \omega_0-\omega_2$

$\Omega_b = \omega_1-\omega_2$

IV/1

(5)

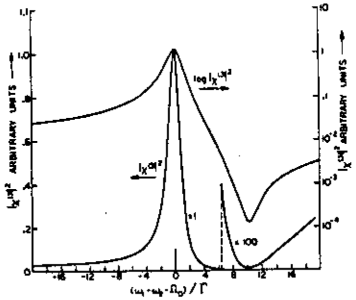


Fig. 7.4. The CARS line shape of (7.60) for $N(\alpha^R_{eff})^2/4MD\chi^{NR}_{eff} = 10\Gamma$ on linear and logarithmic scales. This plot corresponds to the frequency dispersion of $|\chi^{(3)}|^2$. The deep minimum occurs when the non-resonant background is cancelled by the real part of the resonant Raman susceptibility

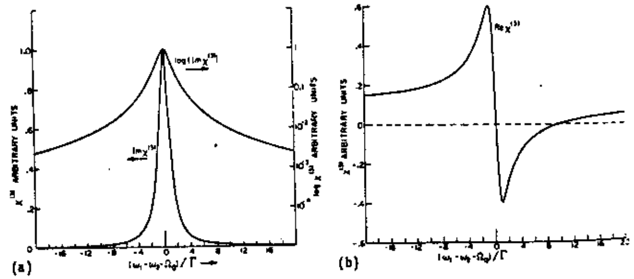
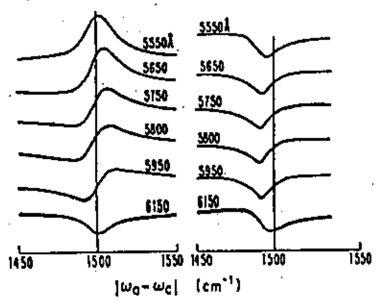
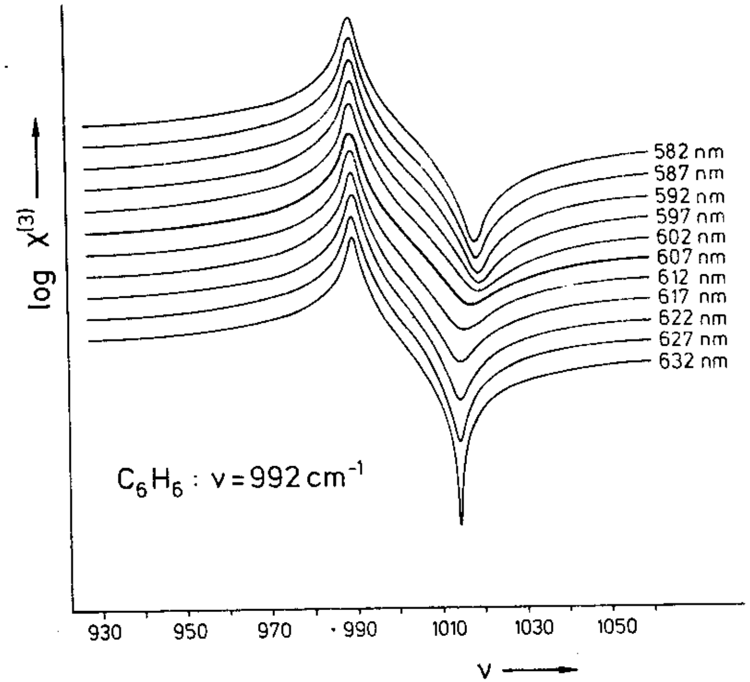


Fig. 7.5a,b. The real and imaginary parts of the Lorentzian resonance responsible for the CARS line shape in Fig.7.4. Part (a) shows $Im(\chi^{(3)})$ on linear and logarithmic scales while (b) gives $Re(\chi^{(3)})$



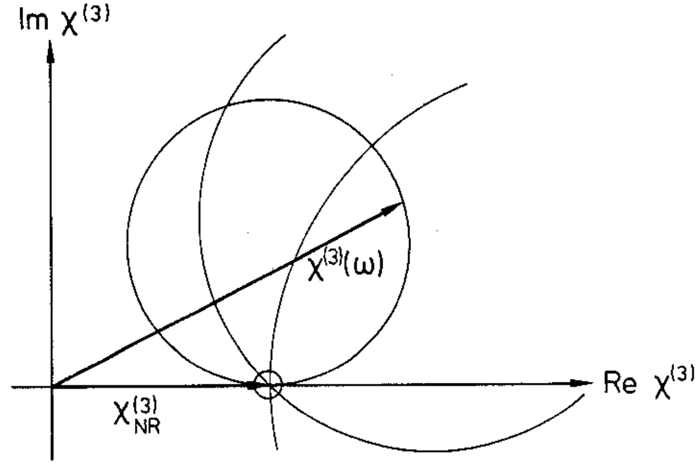
IV/2

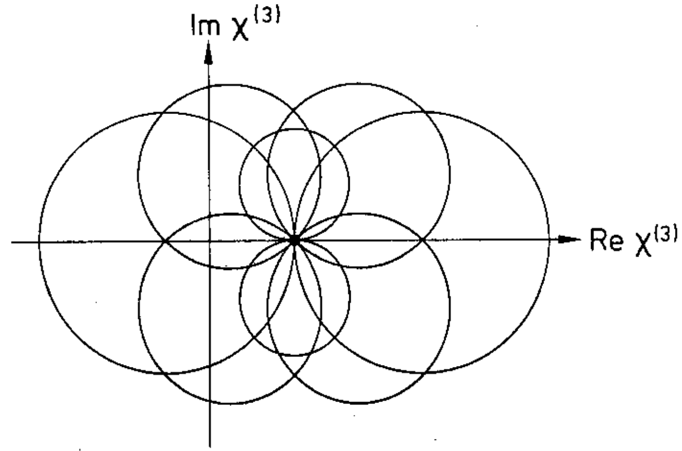


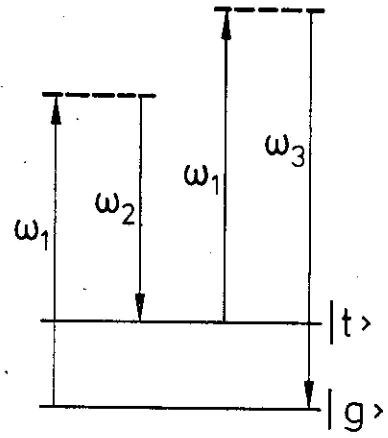
$\chi^{(3)} = A \cdot \bar{\chi}^{(3)} + B \cdot \bar{\bar{\chi}}^{(3)}$

$(B \approx 0{,}02\, A)$

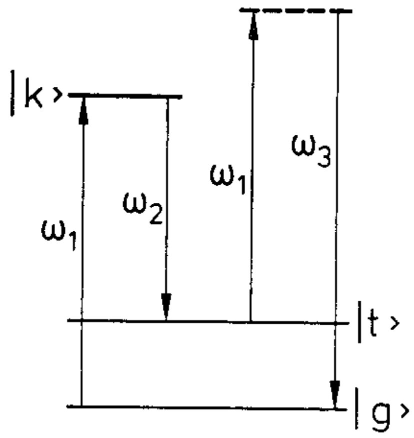
$\chi^{(3)}$-Geometrie



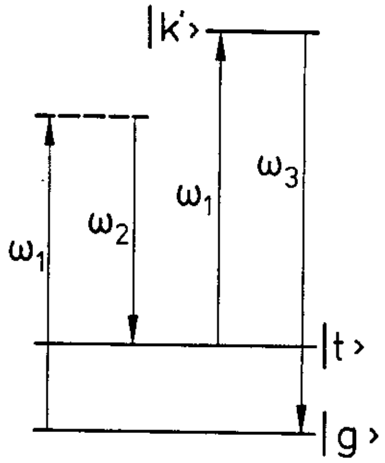




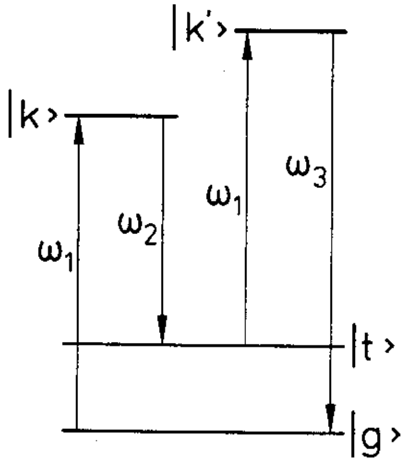
CARS



$\boxed{\omega_1 \equiv \omega_e^{kg}}$



$\boxed{\omega_3 \equiv \omega_e^{k'g}}$



$\boxed{\omega_1 \equiv \omega_e^{kg}}$ $\boxed{\omega_3 \equiv \omega_e^{k'g}}$

Theoretical Approach:

Perturbation Theory

$$\frac{\delta\rho}{\delta t} = -\frac{i}{\hbar}\left[H_0+V,\rho\right] + \left.\frac{\delta\rho}{\delta t}\right|_{damp}$$

$$V = -\vec{\mu}\cdot\vec{E}(t)$$

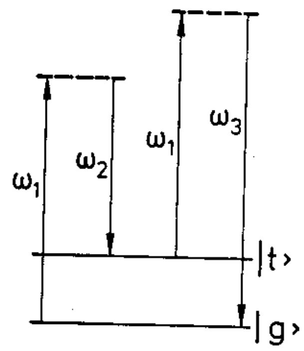
$$P_{NL}^{(3)}(\omega_a,t) = N\sum_{m,n}\rho_{nm}^{(3)}\,\vec{\mu}_{mn}$$

$$\rho_{nm}^{(3)} \sim \left[V(t)\right]^3 \text{ in } \omega_a$$

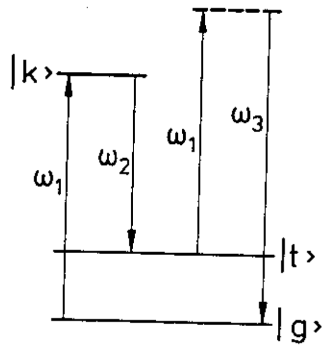
$$P_{NL}^{(3)}(\omega_a,t) = \chi^{(3)}(\omega_a)\cdot E_L^2\cdot E_S^*$$

$$\times \ \exp\left\{i\,(2k_L-k_S)\,z-\cdots\right\}+c.c$$

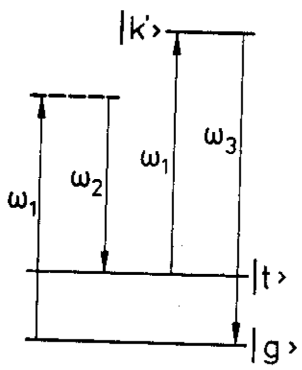
$$\chi^{(3)}(\omega_a) \equiv \chi_{NR}^{(3)}+\sum_{a,b}\chi_R^{ab}$$



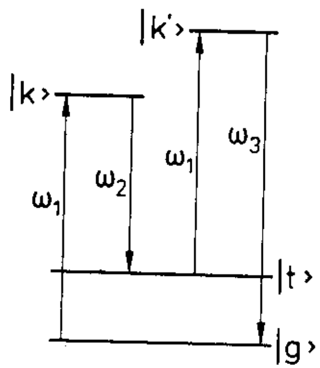
CARS



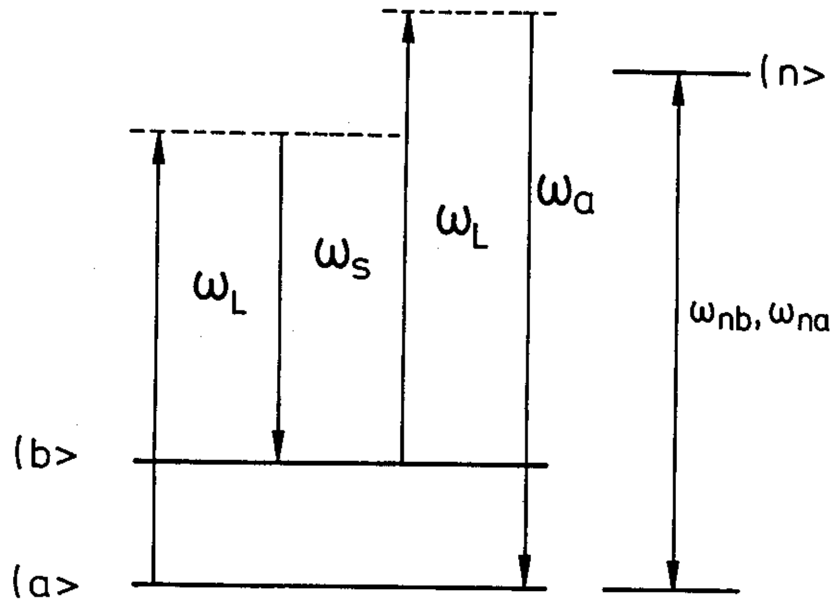
$\boxed{\omega_1 \equiv \omega_e^{kg}}$



$\boxed{\omega_3 \equiv \omega_e^{k'g}}$



$\boxed{\omega_1 \equiv \omega_e^{kg}}$ $\boxed{\omega_3 \equiv \omega_e^{k'g}}$



$$\chi_{\Sigma}^{(3)}(\omega_a) = \tilde{\chi}_{NR} + N \cdot \chi^{(3)}(\omega_a)$$

$$\chi^{(3)}(\omega_a) = \chi_{NR} + \sum_{a,b} \chi_R^{ab}$$

$$\chi_R^{ab} = \frac{1}{3!\hbar^3}\,\frac{1}{\omega_{ba}-(\omega_L-\omega_s)-i\Gamma_{ba}}$$

$$\times\left\{\sum_{n'}\left(\frac{P_{an'}\;P_{n'b}}{\omega_{n'a}-\omega_a-i\Gamma_{n'a}}+\frac{P_{an'}\;P_{n'b}}{\omega_{n'b}+\omega_a+i\Gamma_{n'b}}\right)\right.$$

$$\times\sum_n\left(\rho_{aa}^{(0)}-\rho_{nn}^{(0)}\right)\left(\frac{P_{bn}\;P_{na}}{\omega_{na}+\omega_s-i\Gamma_{na}}+\frac{P_{bn}\;P_{na}}{\omega_{na}-\omega_L-i\Gamma_{na}}\right)$$

$$-\sum_{n'}\left(\frac{P_{an'}\;P_{n'b}}{\omega_{n'a}-\omega_a-i\Gamma_{n'a}}+\frac{P_{an'}\;P_{n'b}}{\omega_{n'b}+\omega_a+i\Gamma_{n'b}}\right)$$

$$\left.\times\sum_n\left(\rho_{bb}^{(0)}-\rho_{nn}^{(0)}\right)\left(\frac{P_{bn}\;P_{na}}{\omega_{nb}-\omega_s+i\Gamma_{nb}}+\frac{P_{bn}\;P_{na}}{\omega_{nb}+\omega_L+i\Gamma_{nb}}\right)\right\}$$

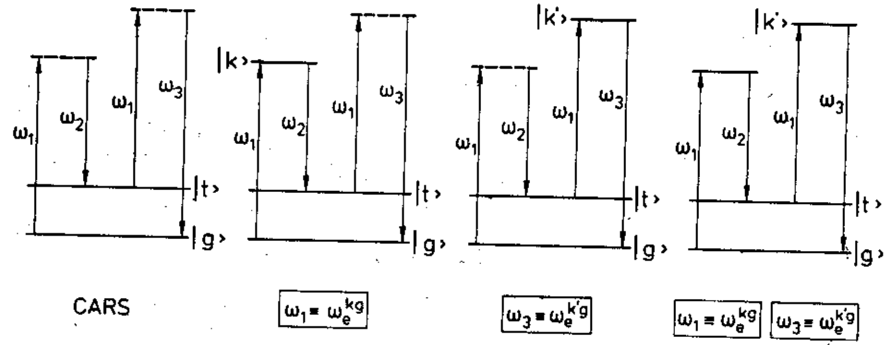
$$\chi_R^{ab} = \frac{1}{3!\hbar^3}\,\frac{1}{\omega_{ba}-(\omega_L-\omega_S)-i\Gamma_{ba}}\times$$

$$\times\left\{\frac{\tilde{\tilde{\chi}}_e}{(\omega_{na}-\omega_a-i\Gamma_{na})(\omega_{na}-\omega_L-i\Gamma_{na})}+\tilde{\chi}_e^{(3)}\right\}$$

$$\left|\frac{\tilde{\tilde{\chi}}_e}{\Delta\omega-i\Gamma_{na}}\right| \gtrless \tilde{\chi}_e^{(3)}$$

$$\chi^{(3)}\left[\mathrm{esu}\right] = \left|\frac{\chi_\Sigma^{(3)}}{\Gamma_{ba}}\right|$$

$$C_6H_6:\ \left|\chi_\Sigma^{(3)}/\Gamma_{ba}\right| \gg \chi_{NR}^{(3)}$$



|k›
|k'›
|t›
|g›
ω1
ω2
ω3
CARS
ω1 = ωe^kg
ω3 = ωe^k'g
ω1 = ωe^kg
ω3 = ωe^k'g