R-Quiz: Raman Quiz

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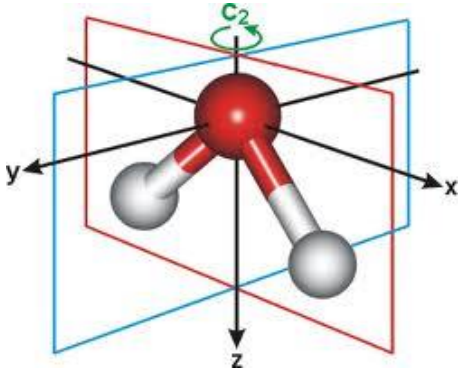


Quiz: Five Advantages
(ARS = Audience Response System)

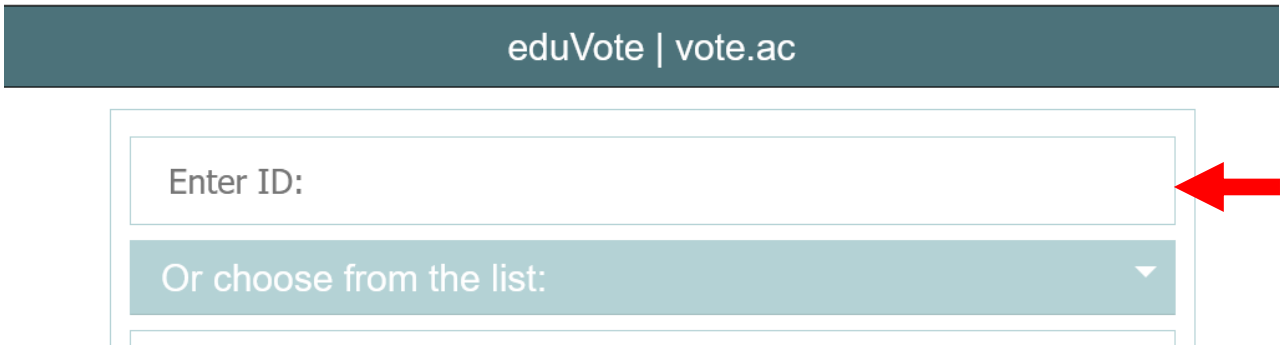
- **Activation** of Students (game, competition, explicit answer)
- **Anonymity** ("Unfortunately, nobody will know how smart I am")
- **Feedback** on State of Knowledge (Students & Lecturer)
- Internal **Comparison with Peer Group** (Students)
- Reflection on **Learning Objectives** and Focus (Lecturer)

Which Categories of Questions? (STEM Perspective)

1. Definitions (Technical Terms, Physicochemical Quantities)
2. Qualitative Understanding (Concepts)
3. Quantitative Understanding (Equations/Proportionalities)
4. Estimations (Mental Arithmetics)

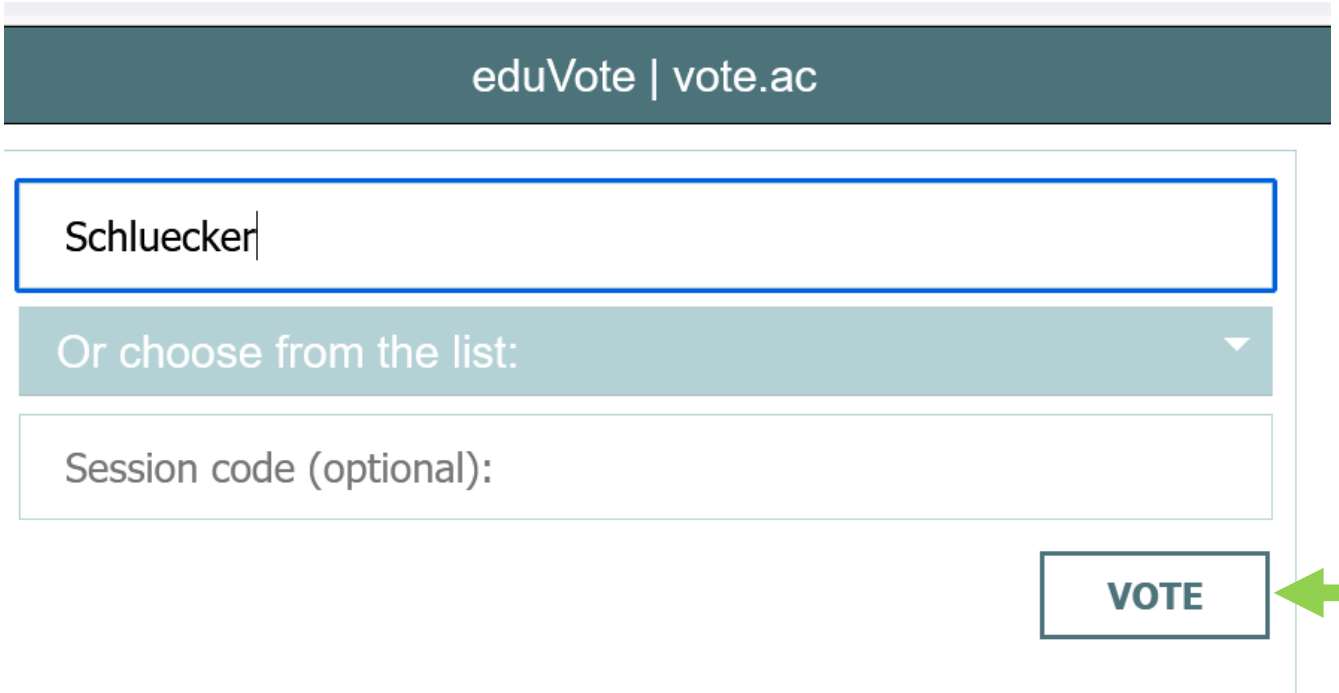
Quiz Participation: Internet Connection Required (WiFi or mobile data)

Open Your Web Browser and go to the Website vote.ac ! It looks like this:



Fill in here
Enter ID: Schluecker

Your ID field should then look like this:



Please wait !
Click on "Vote" AFTER the quiz has been started

Getting Started: Test Run

Answer D is correct, while answers A, B and C are wrong.

Which answer is correct? Choose A, B, C or D AFTER the voting started!

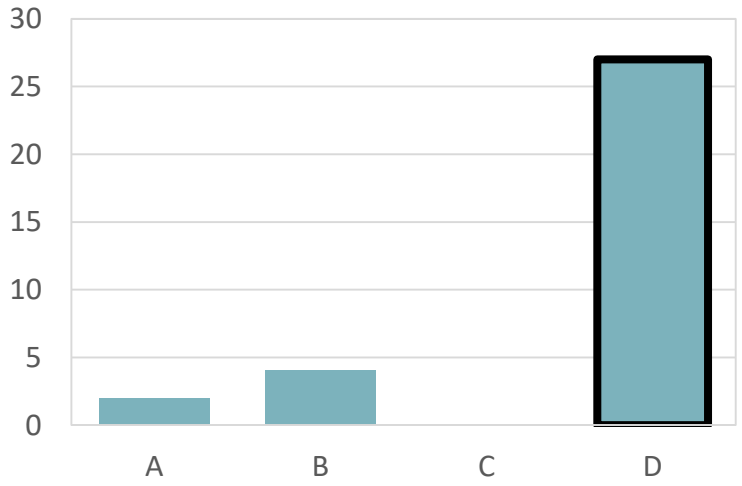
A. Answer A is correct

B. Answer B is correct

C. Answer C is correct

D. Answer D is correct

Please wait for instructions before voting !



Umfrage zurücksetzen

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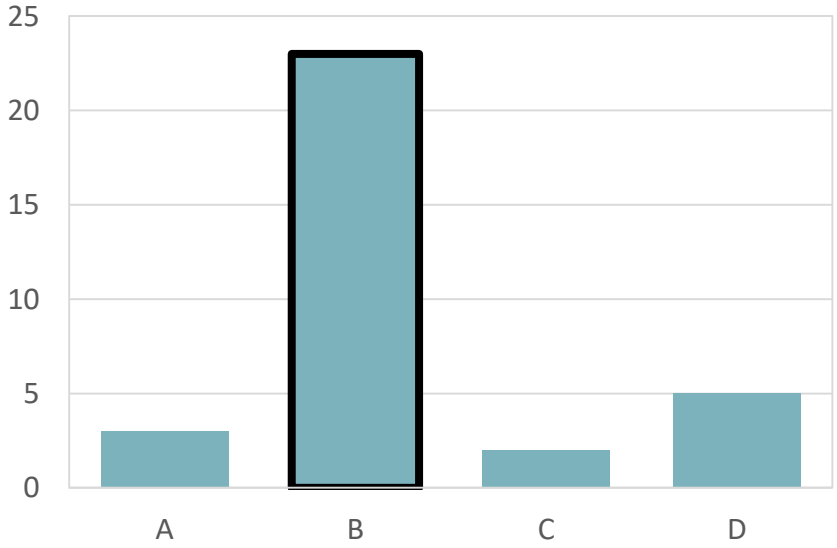
$$I_{\rho\sigma}^{if} = c_2 \omega^4 N I_0 \left|\alpha_{\rho\sigma}\right|^2$$

Please wait until voting has been started !

You change the laser excitation wavelength from 1064 nm (Nd: YAG fundamental) to 532 nm (frequency-doubled). The laser power is the same in both cases and the spectrometer/CCD system has the same sensitivity at 532 and 1064 nm. We also neglect the role of molecular electronic resonances (i.e. conventional Raman scattering, not resonance Raman scattering)

By which factor does the Raman intensity change?

A) 4-fold increase
B) 16-fold increase
C) 4-fold decrease
D) 16-fold decrease



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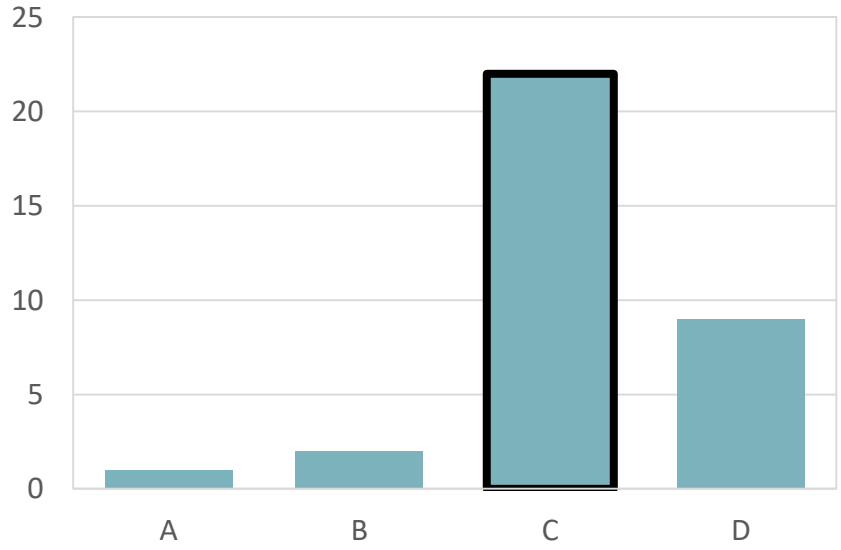
$$\mu = \alpha_0 E_0 \cos\omega_0 t + \frac{1}{2}\left(\frac{\partial\alpha}{\partial q}\right)_0 q_0 E_0 \cos(\omega_0 - \omega_R)\, t + \frac{1}{2}\left(\frac{\partial\alpha}{\partial q}\right)_0 q_0 E_0 \cos(\omega_0 + \omega_R)\, t$$

Which requirement applies to vibrational Raman scattering?

(1) Molecule must have permanent dipole moment
(2) Change of electric dipole moment when passing through the equilibrium position
(3) Change of polarizability when passing through the equilibrium position
(4) Molecule must be polarizable

A) 1
B) 2
C) 3
D) 4



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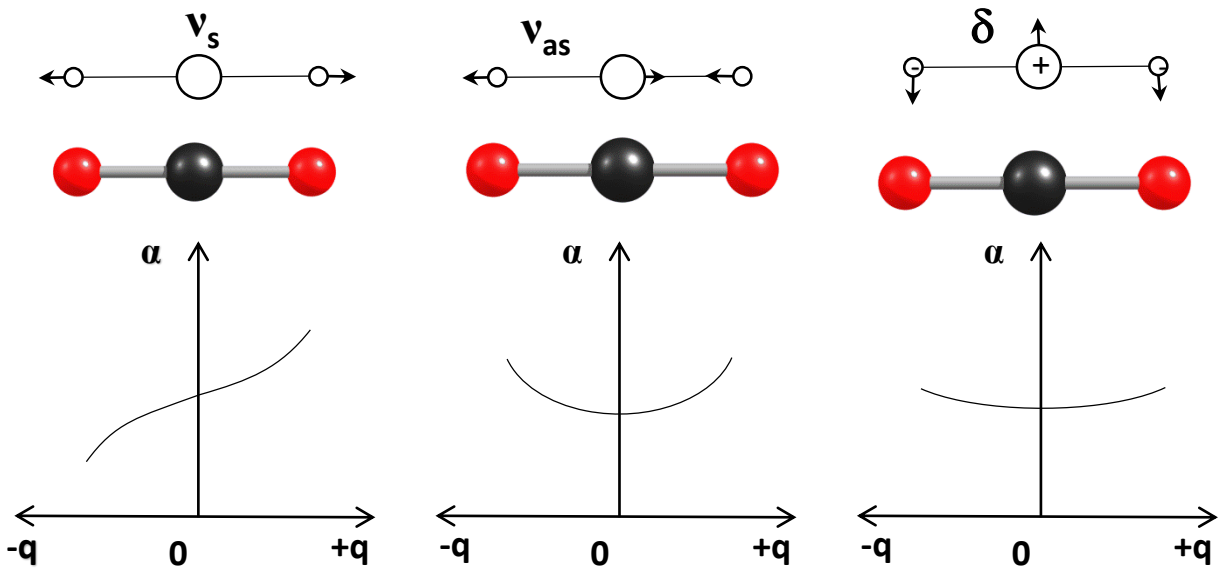
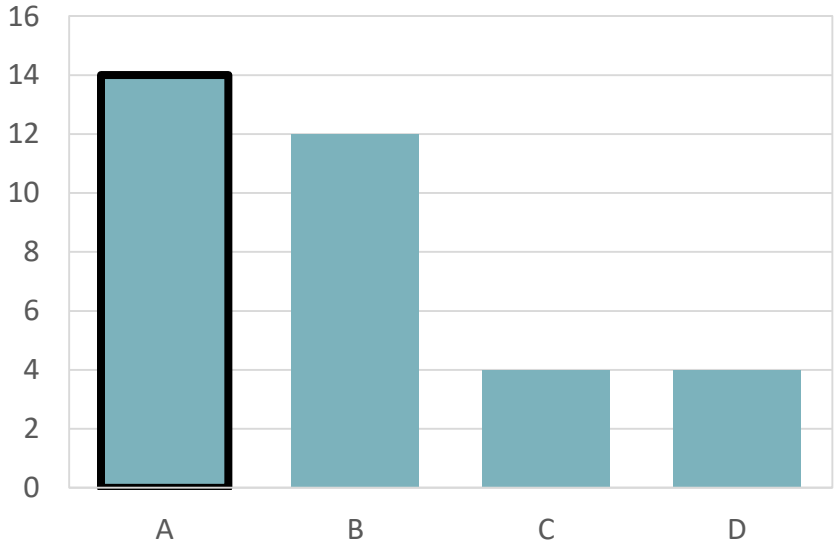
$$\mu = \alpha_0 E_0 \cos\omega_0 t + \frac{1}{2}\left(\frac{\partial\alpha}{\partial q}\right)_0 q_0 E_0 \cos(\omega_0 - \omega_R)\, t + \frac{1}{2}\left(\frac{\partial\alpha}{\partial q}\right)_0 q_0 E_0 \cos(\omega_0 + \omega_R)\, t$$

Which normal modes of CO_2 are Raman-active?



A) ν_S
B) $\nu_S + \nu_{as}$
C) $\nu_S + \nu_{as} + \delta$
D) None



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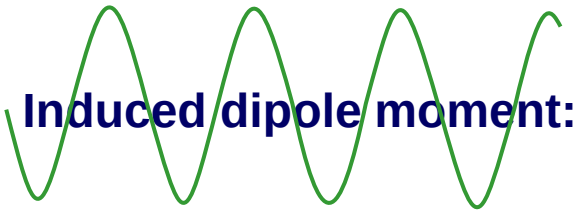
Classical Description of the Raman Effect

Incident electric field:

$$E = E_0 \cdot \cos \omega_0 t \qquad (1)$$



Induced dipole moment:

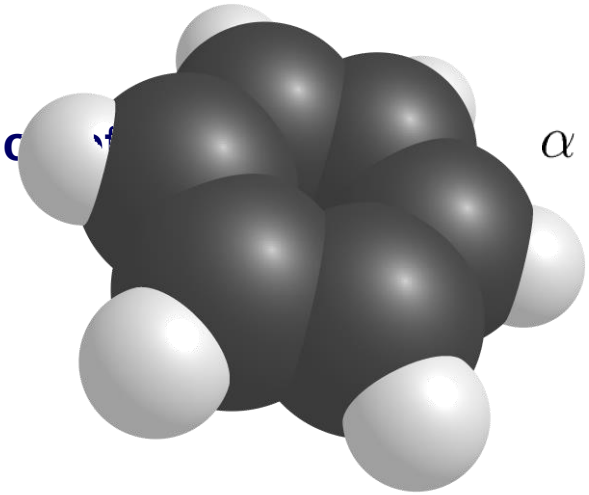
$$\mu = \alpha E \qquad (2)$$

(1) in (2):

$$\mu = \alpha E_0 \cos \omega_0 t \qquad (3)$$

Oscillating molecule:

$$q = q_0 \cdot \cos \omega_R t \qquad (4)$$



Expansion of α:

$$\alpha = \alpha(q) = \alpha_0 + \left(\frac{\partial \alpha}{\partial q}\right)_0 q + \ldots \qquad (5)$$

Classical Description of the Raman Effect

(5) in (3):

$$\mu = \left[\alpha_0 + \left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 \cos \omega_R t\right] E_0 \cdot \cos \omega_0 t \qquad \textbf{(6)}$$

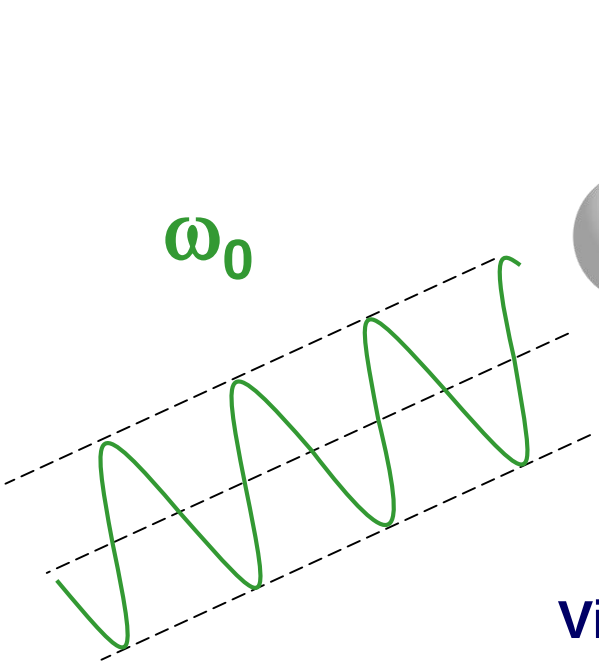
Applying trigonometric formula

$$\mu = \underbrace{\alpha_0 E_0 \cos \omega_0 t}_{\text{Rayleigh scattering}} + \underbrace{\frac{1}{2}\left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 E_0 \cos\left(\omega_0 - \omega_R\right) t}_{\text{Stokes Raman scattering}}$$

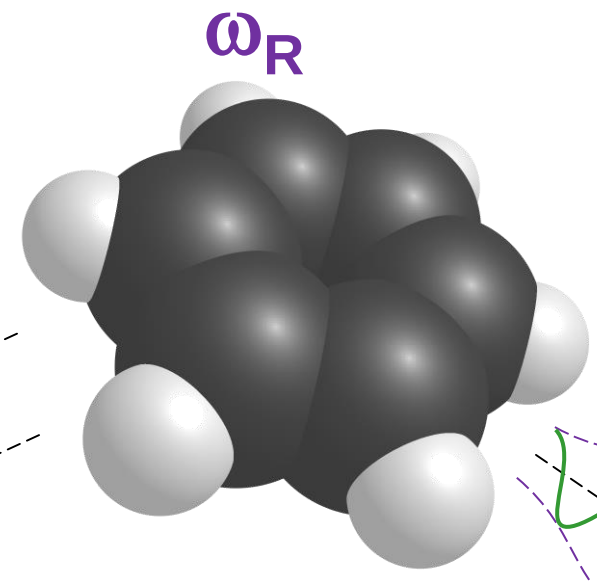
$$+ \underbrace{\frac{1}{2}\left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 E_0 \cos\left(\omega_0 + \omega_R\right) t}_{\text{Anti-Stokes Raman scattering}} \qquad \textbf{(7)}$$

Classical Description of Raman Scattering

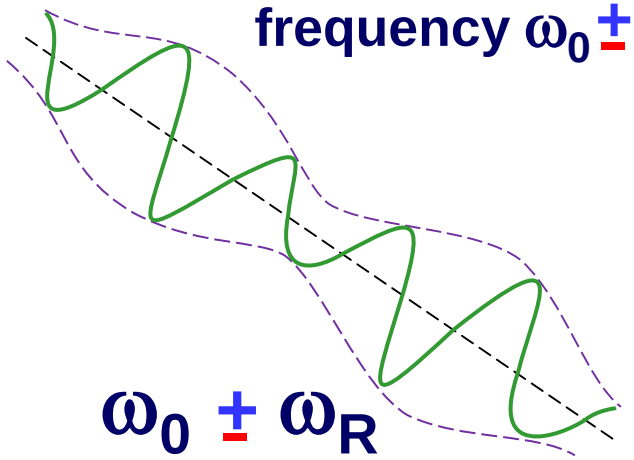
Modulation of the incident electric field by vibrating molecule



Incident electric field with angular frequency ω_0



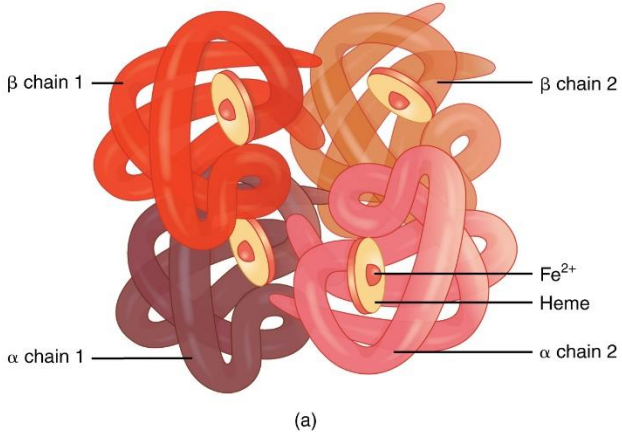
Vibrating molecule with angular frequency ω_R

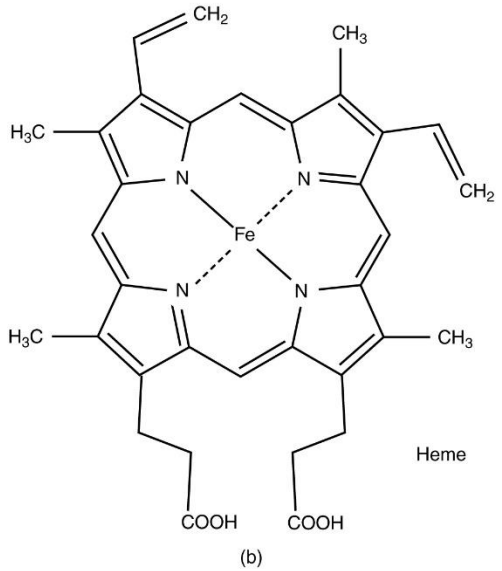


Modulated electric field with angular frequency $\omega_0 \pm \omega_R$

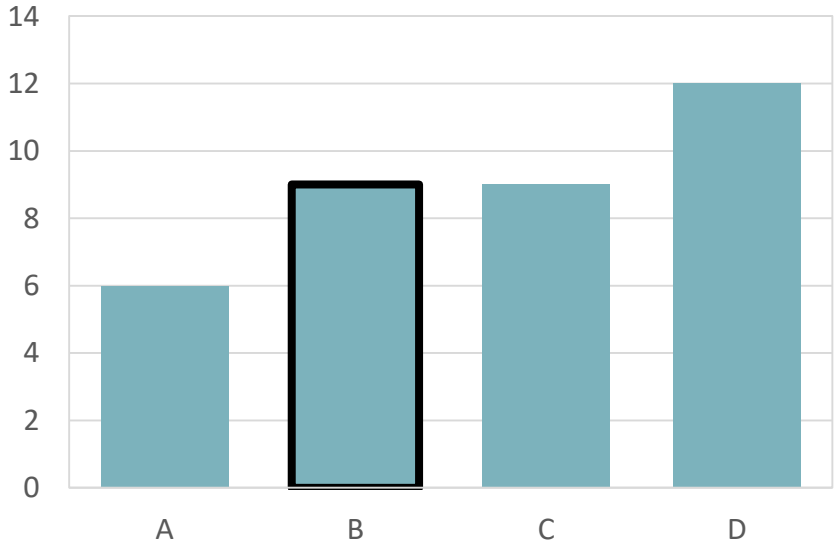
$\omega_0 \pm \omega_R$

Resonance Raman scattering (RRS): Which laser excitation wavelengths for selectively exciting i) AmI/II/III ii) Heme iii) Tyr/Trp ?





	AmI/II/III i)	Heme ii)	Tyr/Trp iii)
A)	266	633	325
B)	197	419	229
C)	229	419	197
D)	419	785	532



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Resonance Raman Scattering of Hemoglobin (Hb)

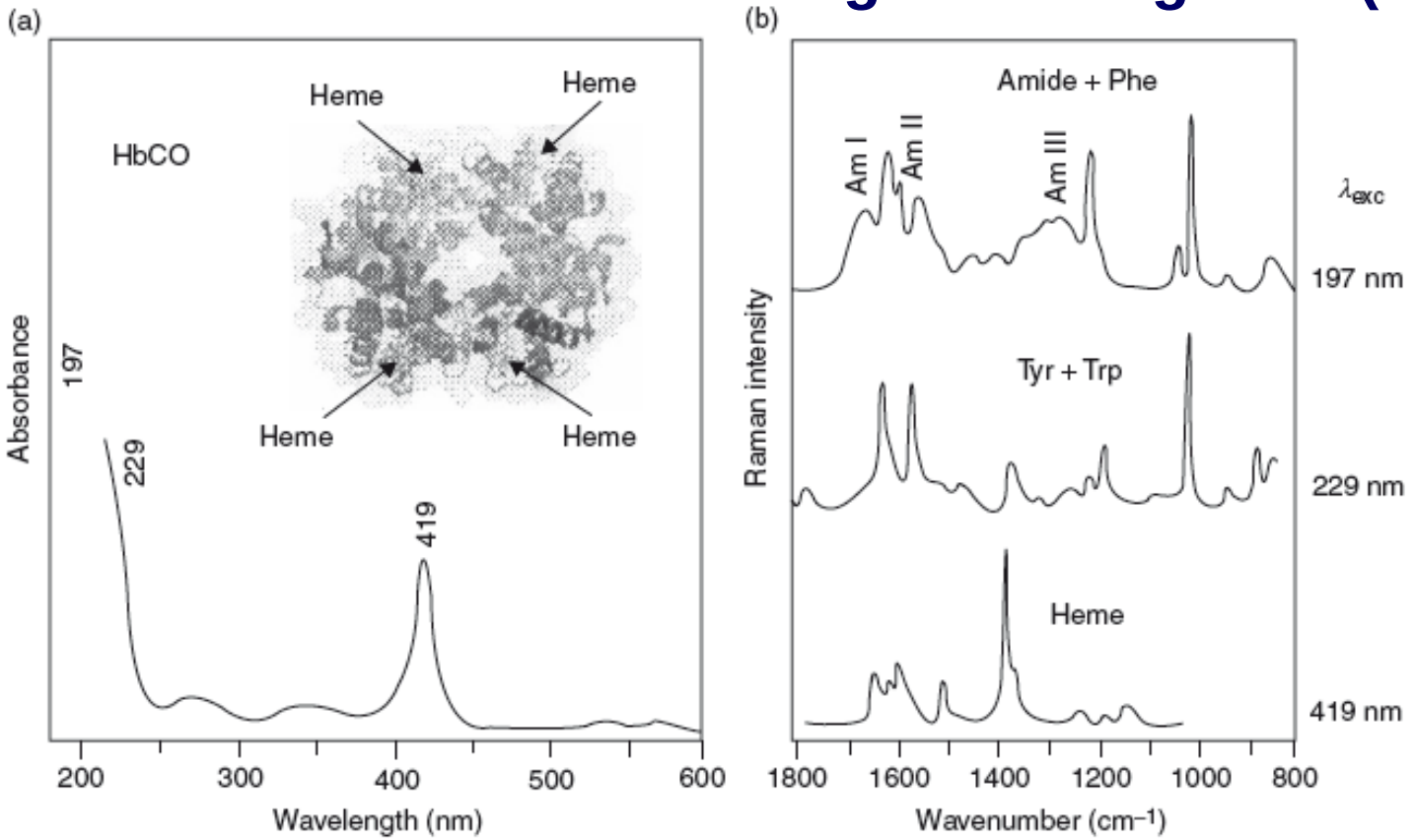


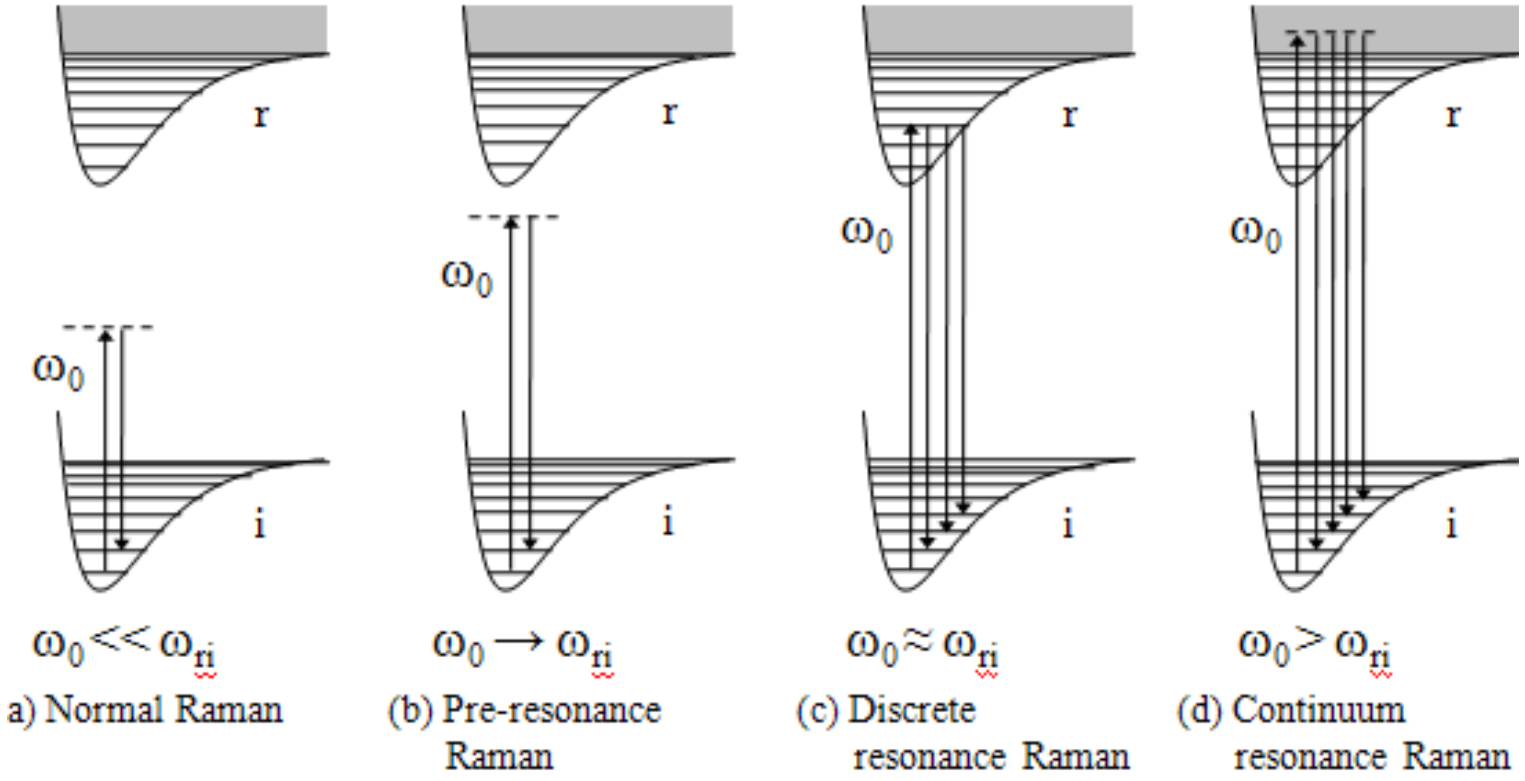
Figure 7 (a) Absorption spectrum and structure of HbCO; (b) Raman spectra of HbCO obtained with 197, 229, and 419 nm laser excitation, respectively. Adapted from Balakrishnan G, Weeks CL, Ibrahim M, Soldatova AV, and Spiro TG (2008) Protein dynamics from time resolved UV Raman spectroscopy. *Current Opinion in Structural Biology* 18: 623, with permission from Elsevier.

Schlücker S and Srivastava SK. Resonance Raman Applications. In: John Lindon, George Tranter and David Koppenaal, editors. Encyclopedia of Spectroscopy and Spectrometry, 2nd edition, Vol 3. Oxford: Elsevier; 2010. pp. 2426–2434.

Raman vs. Resonance Raman Scattering

Kramers-Heisenberg-Dirac (KHD) Dispersion Relation

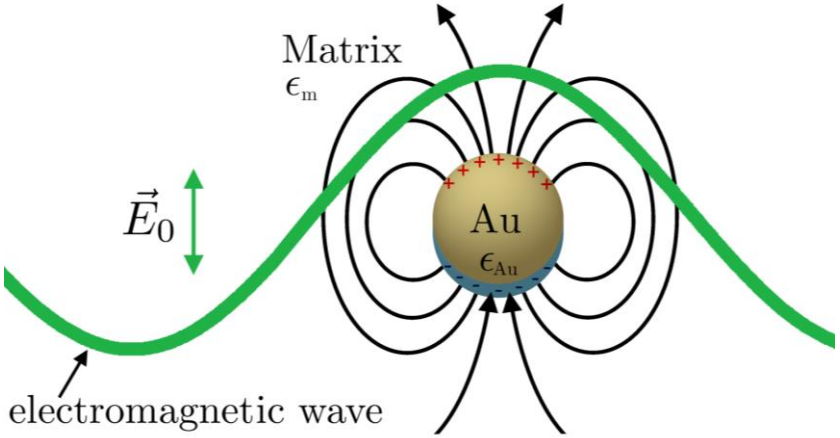
$$(\alpha_{\rho\sigma})_{fi} = \sum_r \left[\frac{\langle f|\mu_\rho|r\rangle\langle r|\mu_\sigma|i\rangle}{\hbar\omega_{ri} - \hbar\omega_0 - i\Gamma_r} + \frac{\langle f|\mu_\sigma|r\rangle\langle r|\mu_\rho|i\rangle}{\hbar\omega_{rf} + \hbar\omega_0 - i\Gamma_r} \right]$$

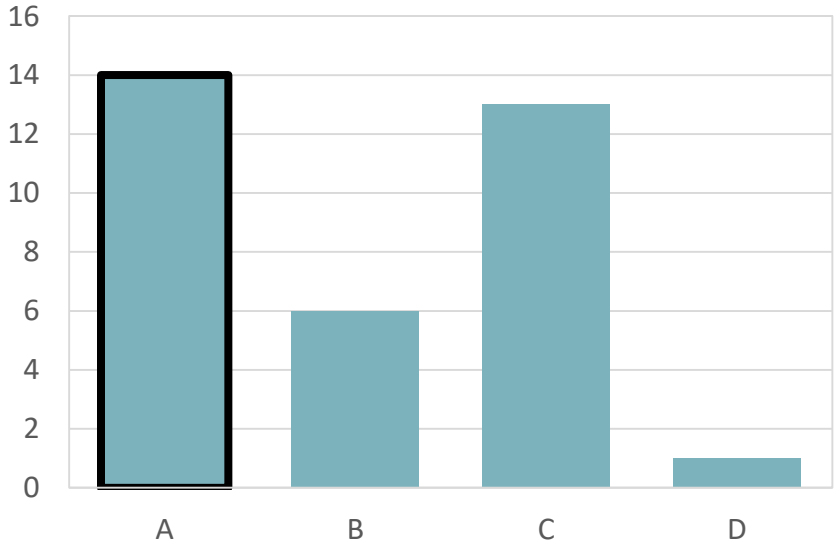


Schlücker S and Srivastava SK. Resonance Raman Applications. In: John Lindon, George Tranter and David Koppenaal, editors. Encyclopedia of Spectroscopy and Spectrometry, 2nd edition, Vol 3. Oxford: Elsevier; 2010. pp. 2426–2434.

Surface-Enhanced Raman Scattering (SERS):
The local enhancement of the electric field induced by the LSPR-supporting nanostructure is 50.
How large is approximately the associated enhancement of the Raman signal?

A) 6.250.000
B) 2.500.000
C) 2.500
D) 50





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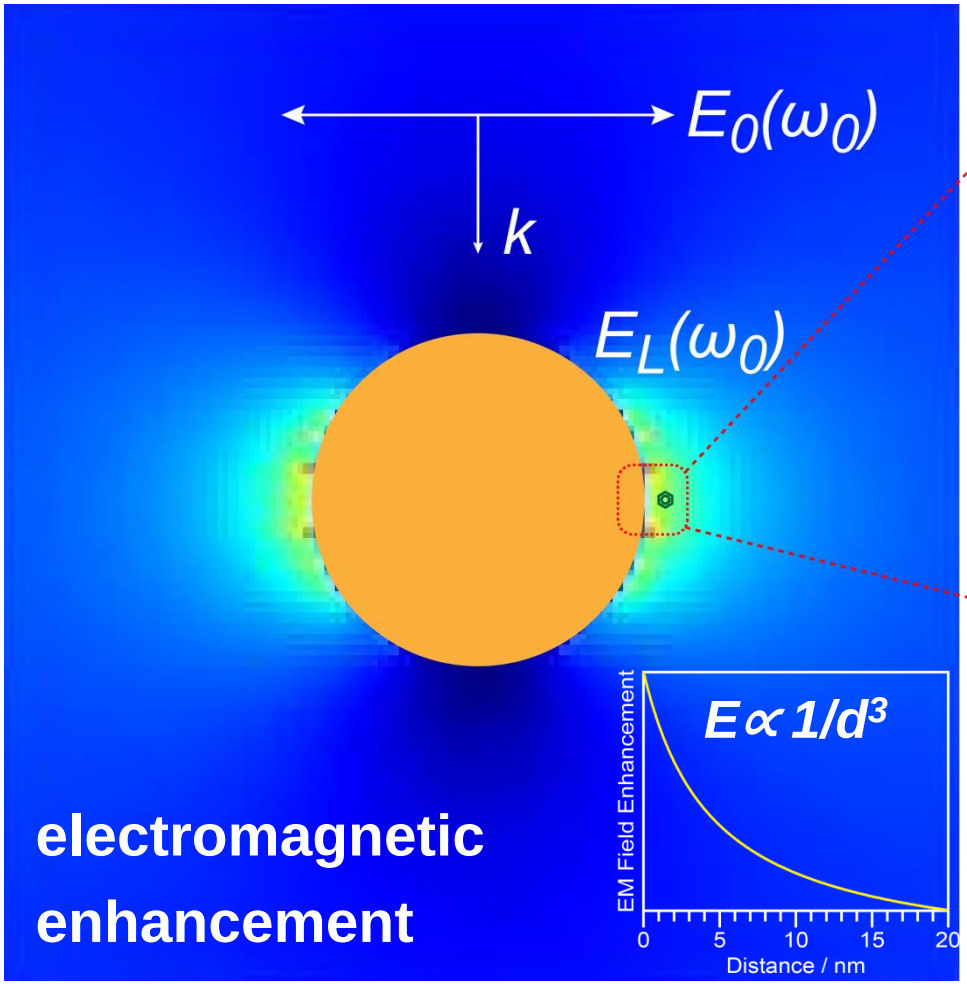
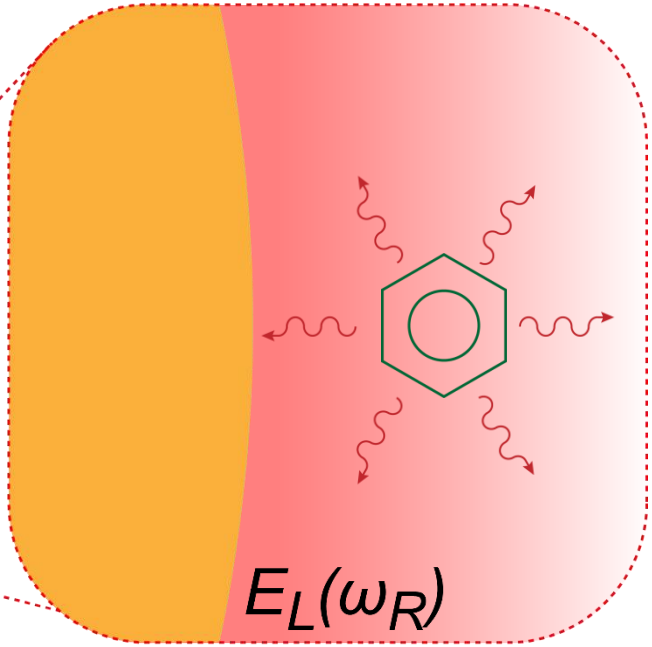
Raman vs. Surface-Enhanced Raman Scattering





SERS:

$$I_{SERS} \propto |E_L(\omega_0)|^2 \cdot |E_L(\omega_R)|^2 \approx |E_{loc}|^4$$

$\propto 1/d^{12}$ — Surface selectivity

Sensitivity

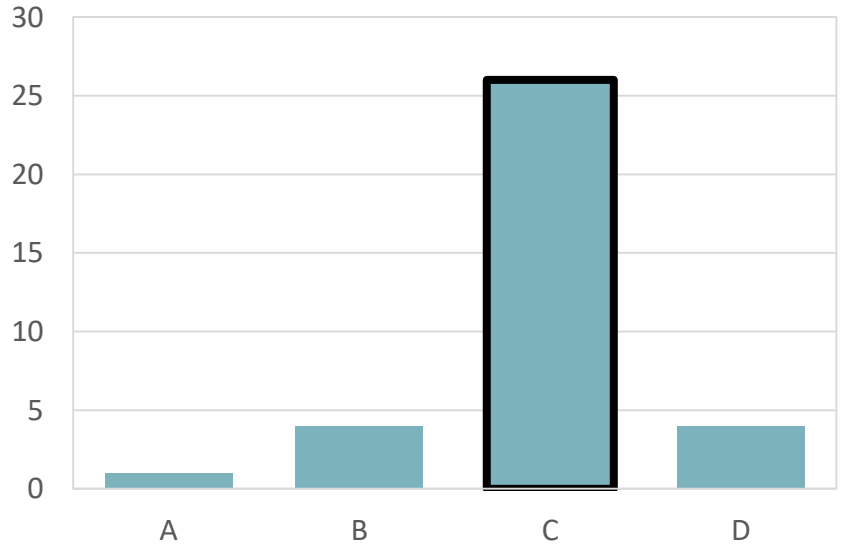
Coherent Anti-Stokes Raman Scattering (CARS):

i) Frequencies of pump and Stokes laser for Raman-resonant signal:
(1) Sum vs. (2) Difference frequency

ii) Order of nonlinearity:
(1) $\chi^{(2)}$/three-wave mixing vs. (2) $\chi^{(3)}$/four-wave mixing

iii) (1) Non-Raman-resonant background vs.
(2) background-free technique

iv) Concentration dependence: (1) linear vs. (2) quadratic



	i)	ii)	iii)	iv)
A)	(1)	(1)	(1)	(1)
B)	(1)	(2)	(2)	(1)
C)	(2)	(2)	(1)	(2)
D)	(2)	(1)	(2)	(2)

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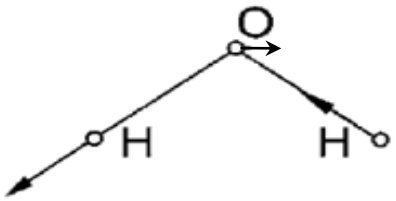
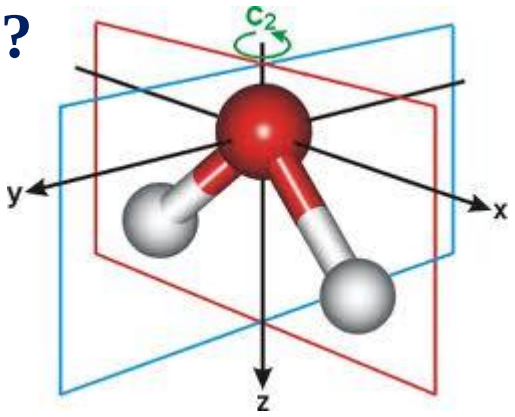
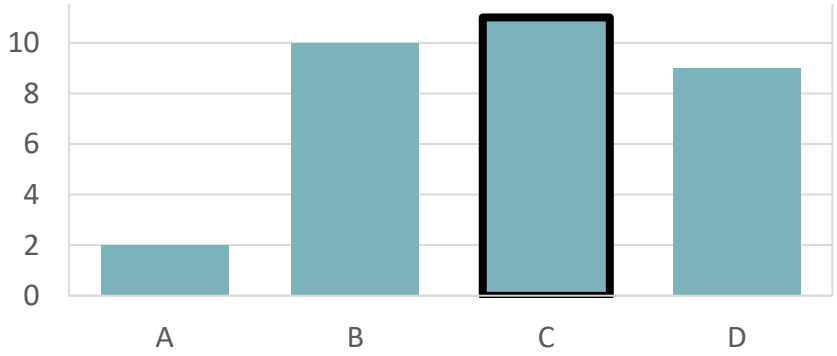
Which symmetry does the antisymmetric stretching mode of water have? In other words: According to which irreducible representation does it transform?





C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

A) A_1
B) A_2
C) B_1
D) B_2



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