Optical and Photonic Glasses

Lesson 16:

Infrared Absorption and Raman Activity

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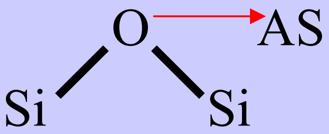
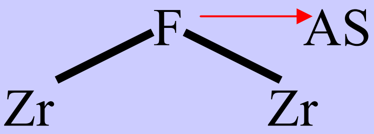
Infared absorption occurs between vibrational energy levels of the structural units of the glass.

For example:



or



these ***A**symmetric **S**tretching* vibrations are IR-active, according to the basic *selection rule* which states that a variation of **dipole moment** must take place at the equilibrium configuration, with a non-zero derivative with respect to a vibrational coordinate, for the vibration to cause IR light absorption. (Also, for *fundamental* modes, the rule $\Delta v = \pm 1$).

Usually, the IR cut-off of a glass occurs at a frequency which is ~ double or triple the frequency of the highest energy IR fundamental vibration, corresponding to the first or second *overtone* modes. (The selection rule for *overtone* modes is $\Delta v = \pm 2, \pm 3, \ldots$).

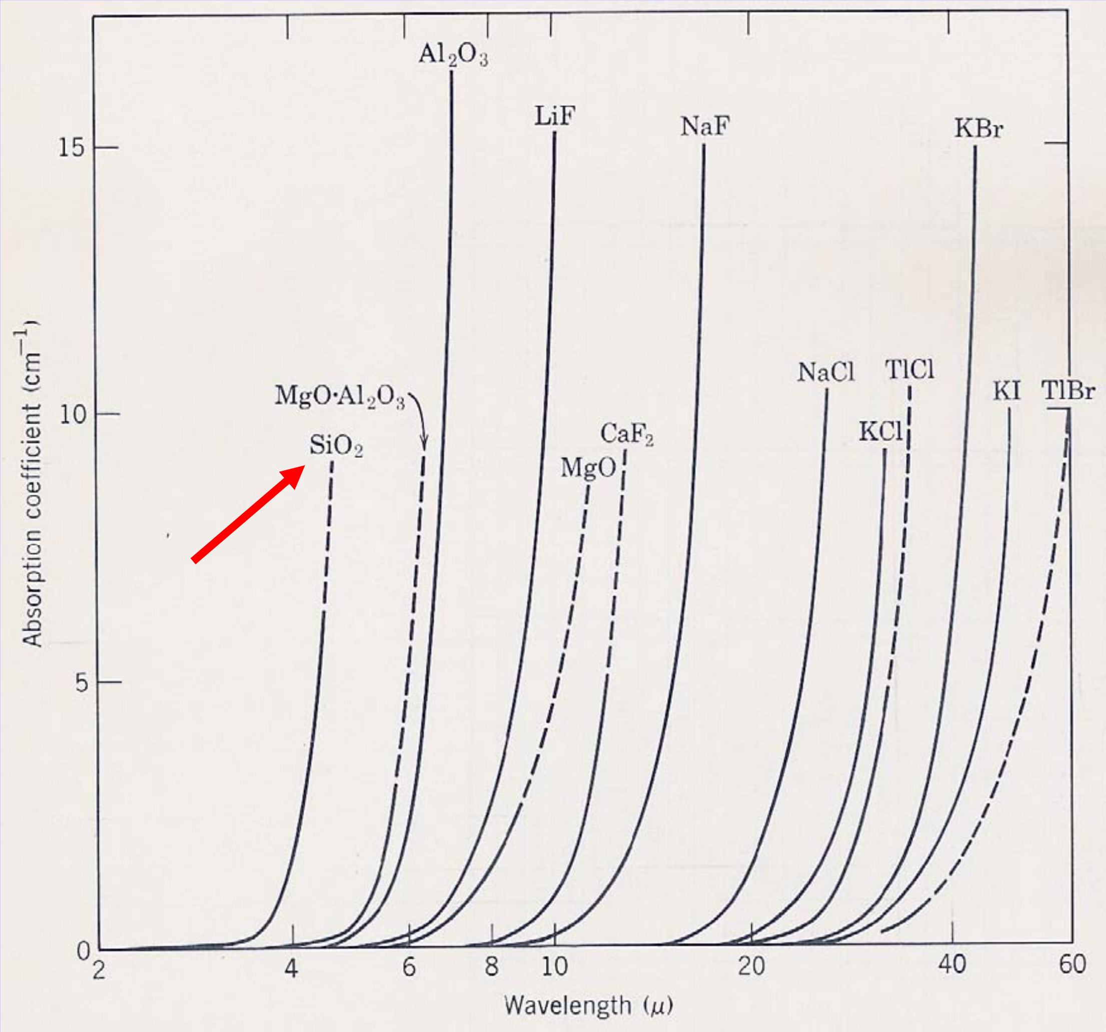
The vibrational frequency of a harmonic oscillator like an isolated $Si\text{-}O^-$ unit may be approximated as:

$$\upsilon = 1/2\pi \, (k / \mu)^{1/2} \qquad \text{(in units of } s^{-1}\text{)}$$

k being the bond *force constant* (in N/m) and $\mu = m_O m_{Si}/(m_O+m_{Si})$ the *reduced mass* (in kg). (The appearance of *overtone* modes is due to *anharmonicity*).

Vibrational absorption in the IR

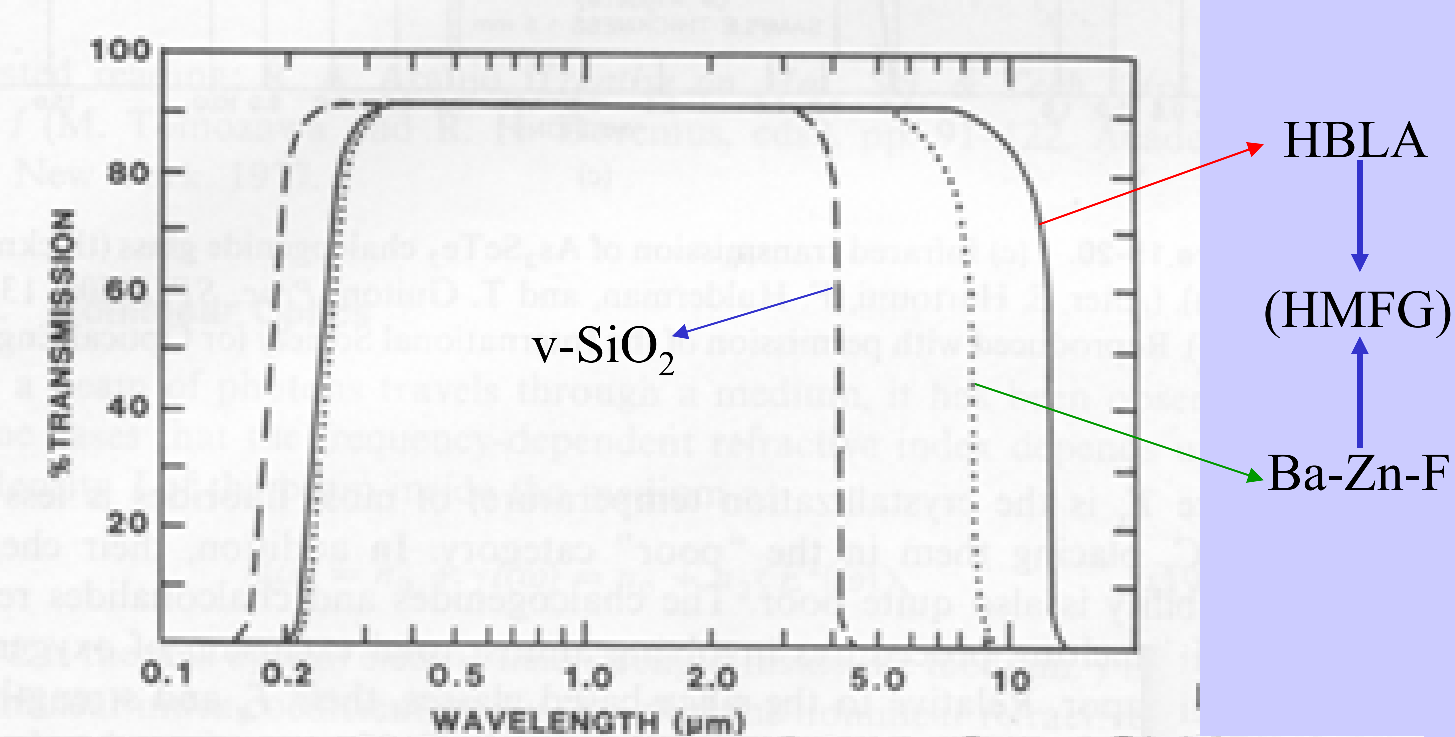
For good IR transparency (long λ cut-off), heavy atoms bonded by weak forces are needed, like in alkali bromides or iodides, which, however, are not glass formers.

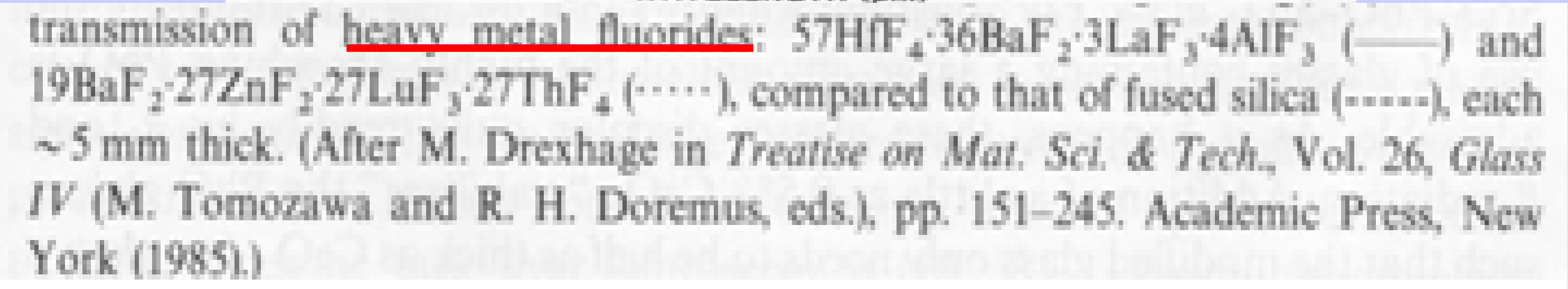


Multiphonon Infrared absorption edges of ionic crystals.

(Adapted from: *Introduction to ceramics*, W.D. Kingery et al., John Wiley, 1976)

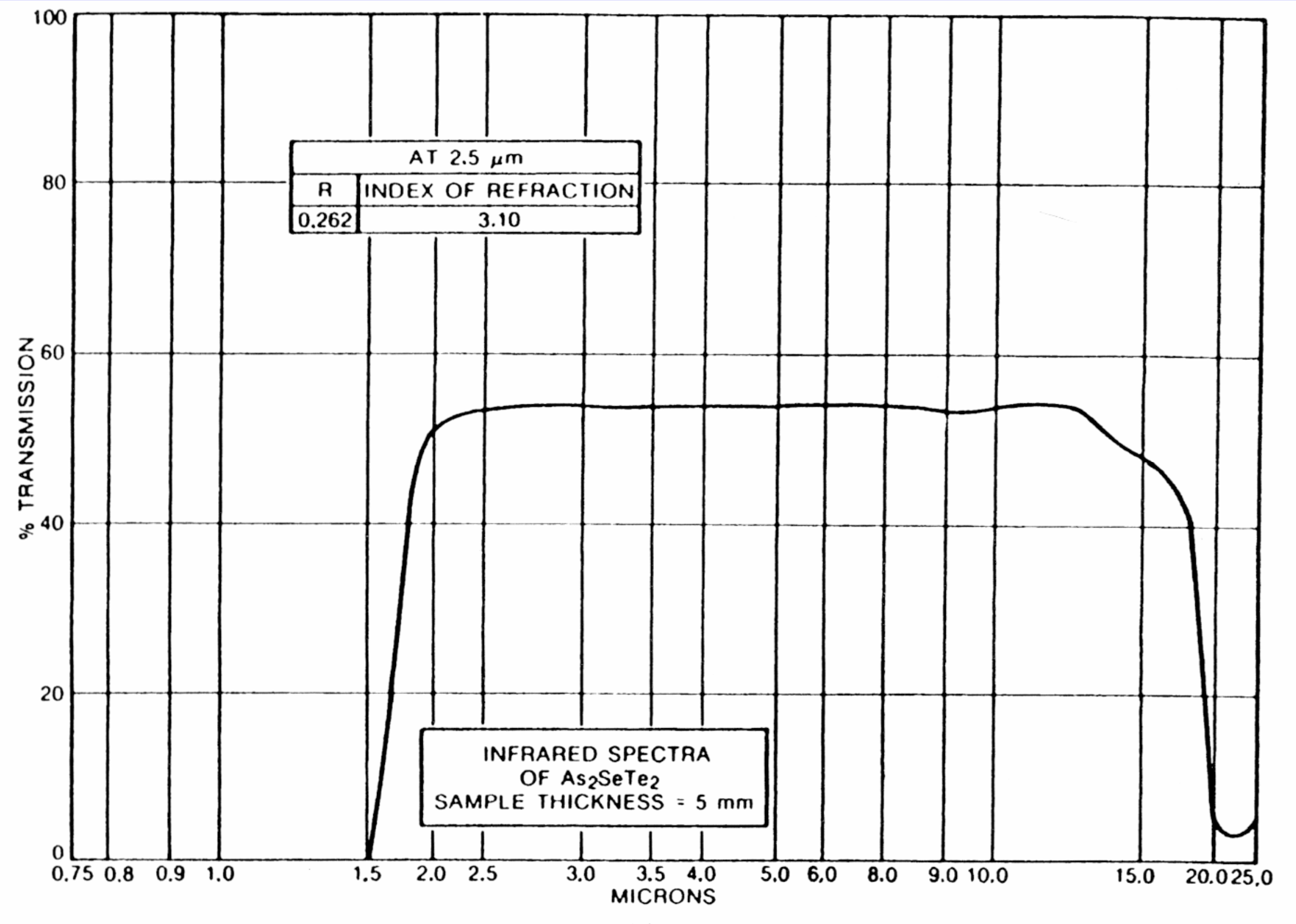
For the purpose of IR transparency, therefore, the best alternatives to oxide glasses are the heavy metal fluoride glasses (HMFG) and the chalcogenide glasses (ChG).




transmission of heavy metal fluorides: $57HfF_4 \cdot 36BaF_2 \cdot 3LaF_3 \cdot 4AlF_3$ (——) and $19BaF_2 \cdot 27ZnF_2 \cdot 27LuF_3 \cdot 27ThF_4$ (·····), compared to that of fused silica (-----), each ~5 mm thick. (After M. Drexhage in *Treatise on Mat. Sci. & Tech.*, Vol. 26, *Glass IV* (M. Tomozawa and R. H. Doremus, eds.), pp. 151–245. Academic Press, New York (1985).)

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

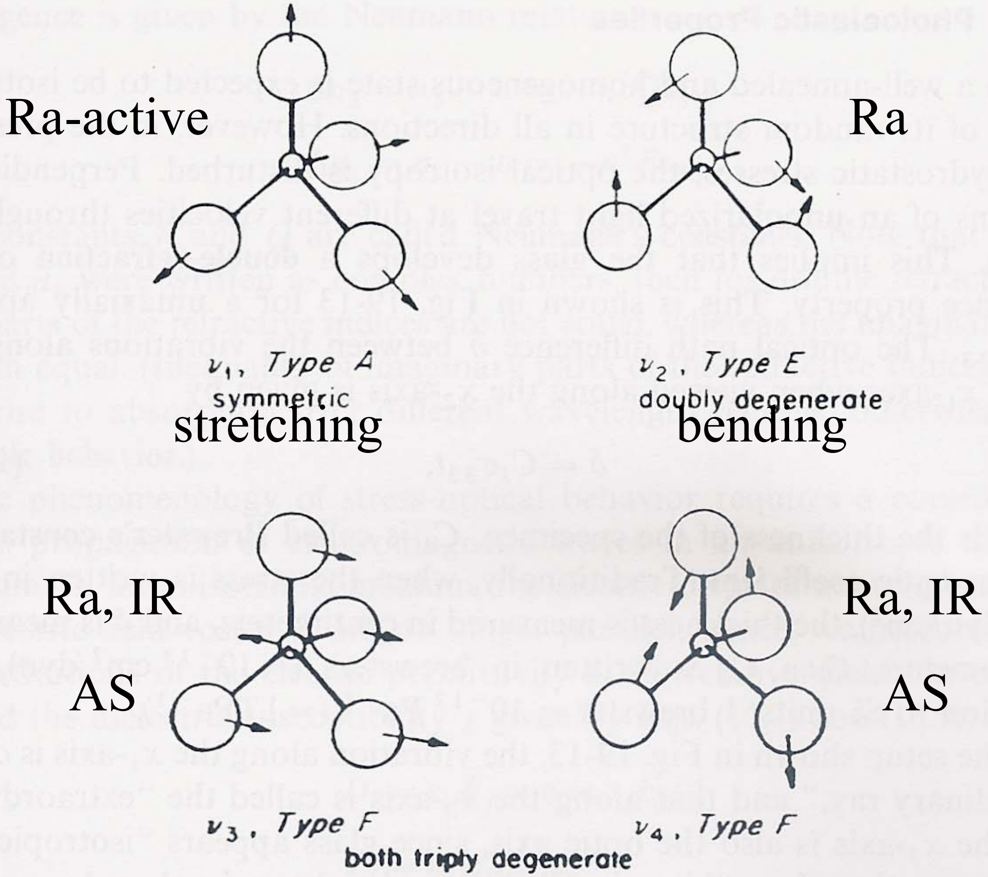
Chalcogenide glass



Infrared transmission of As_2SeTe_2 chalcogenide glass (thickness = 5 mm). (After E. Hartouni, F. Hulderman, and T. Guiton, *Proc. SPIE* **505**, 131–140 (1984). Reproduced with permission of the International Society for Optical Engineering.)

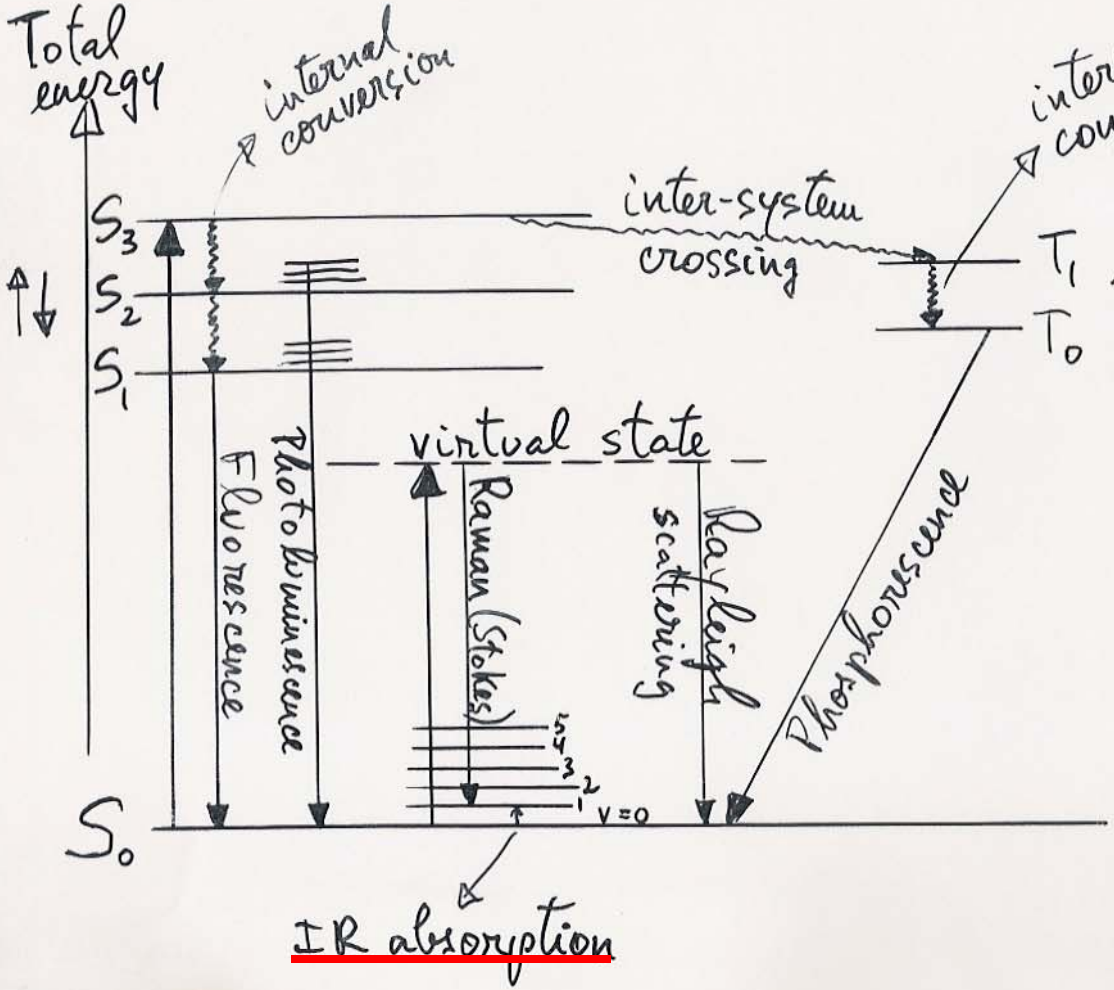
(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

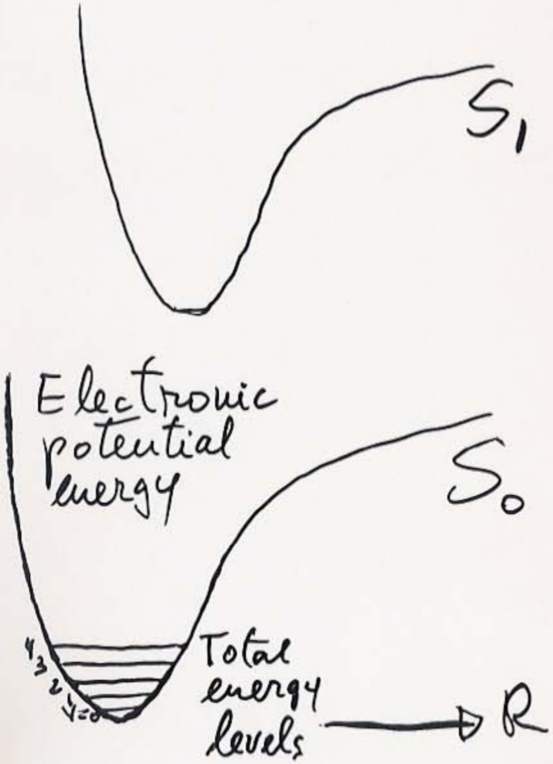
Some glass vibrational modes are not IR-active, but they may be Raman-active. **Raman** spectroscopy is an inelastic light scattering technique complementary to IR absorption (or reflection) spectroscopy, whose basic *selection rule* requires a non-zero value of the **polarizability** derivative with respect to a vibrational coordinate, at the equilibrium configuration of the vibrating unit. (Also, $\Delta v = \pm 1$, for Stokes or anti-Stokes spectra).



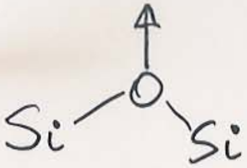
Four normal modes of vibration of an XY_4 tetrahedral molecule. Modes ν_1 and ν_2 are only Raman-active; modes ν_3 and ν_4 are both Raman- and IR-active.

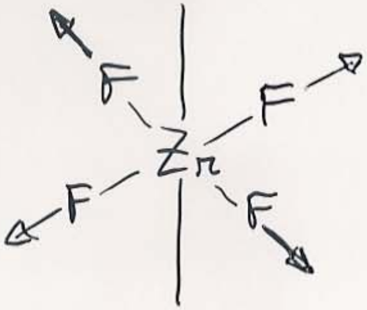
(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)





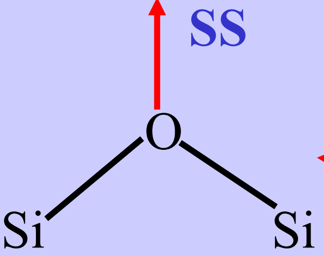
Example of Raman-active vibrations :

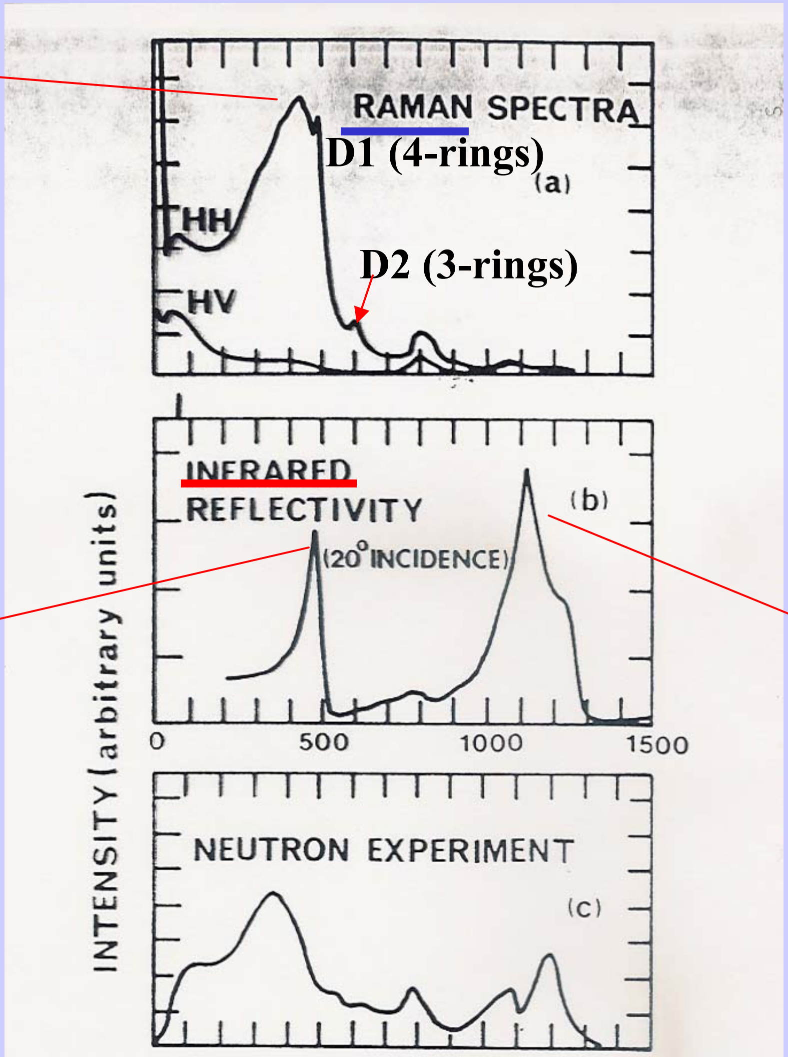




Raman shift: $h\nu_{vib} = h\nu_{exc} - h\nu_{Stokes\ Raman}$

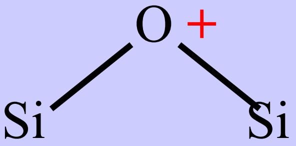
Vibrational spectra of v-SiO$_2$

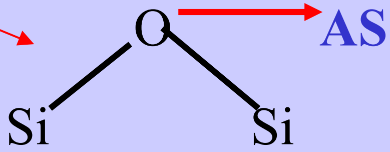




Vibrational spectra of v-SiO$_2$: (a) polarized Raman spectra; (b) infrared reflection spectrum at near-normal incidence; (c) experimental one-phonon inelastic neutron scattering, after subtraction of two-phonon estimate;

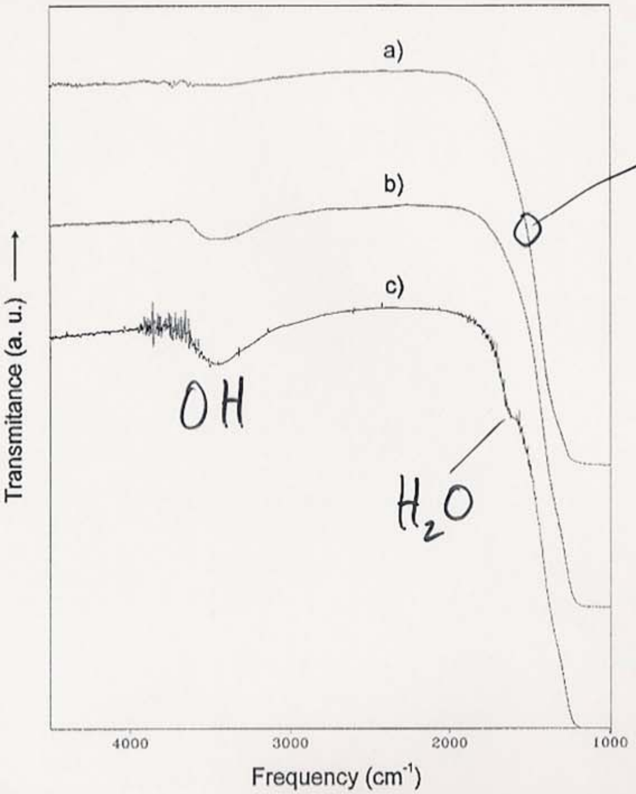
(Adapted from: F.L. Galeener et al., Phys. Rev. B, 1983)





IR absorption (as well as Raman) spectroscopy is also a means of detecting impurities in glass, such as OH groups, or H_2O molecules, e.g. in fluorozirconate glasses (HMFG).

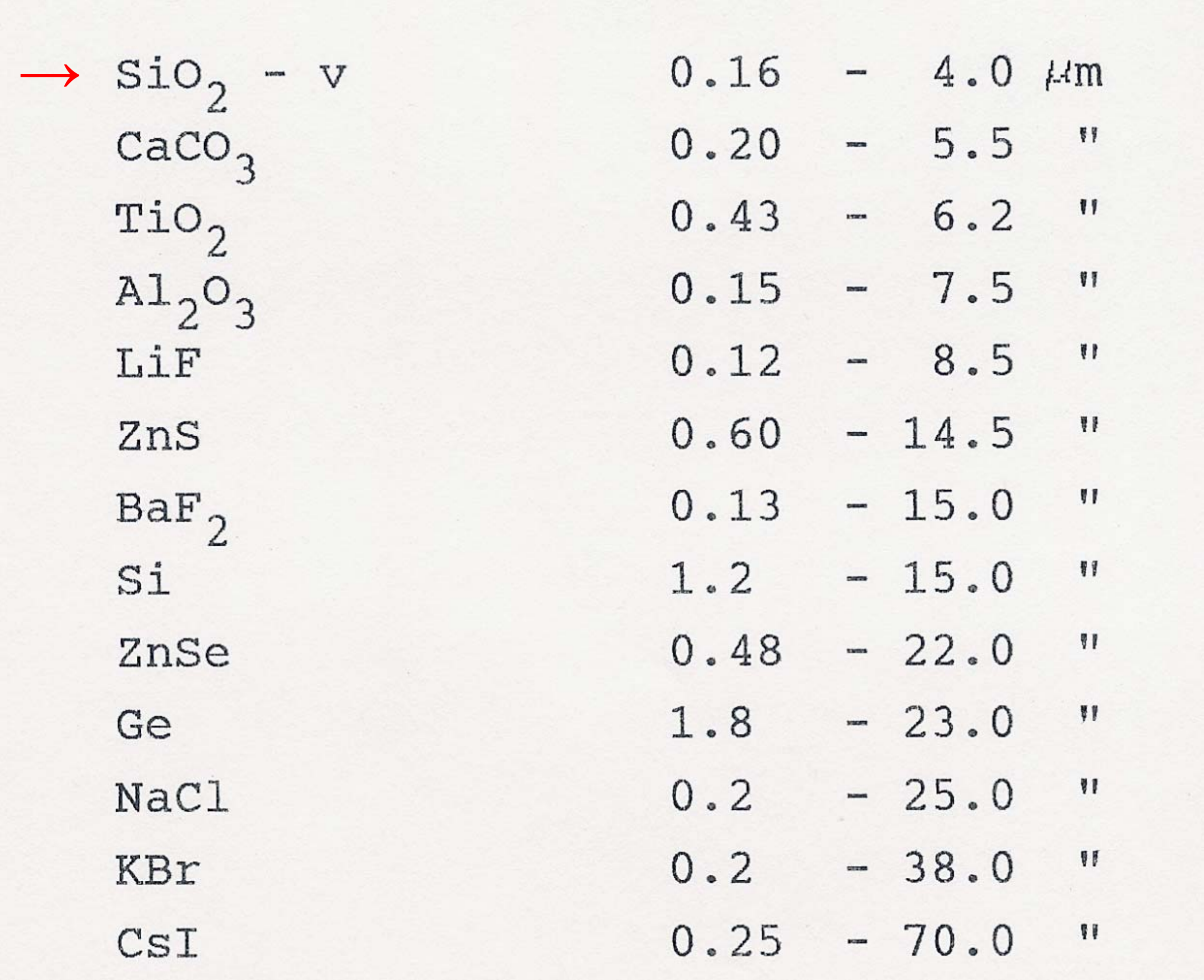
M.C. Gonçalves
(unpublished)



$1500\ cm^{-1}$ → 3-phonon
(multiphonon regime
of transparency)

IR transmission spectra for ZBLAN$_{6.6}$ glasses with different OH levels: a) [OH]=1.42×10^{-4} mol l^{-1}, l=6.75 mm; b) [OH]=3.44×10^{-4} mol l^{-1}, l=4.5 mm; c) [OH]=4.11×10^{-4} mol l^{-1}, l=5.7 mm.

Limits of transparency of different optical materials in the optical region of the electromagnetic spectrum (≥ 10% T, for 2 mm thickness)



→ SiO_2 - v	0.16	-	4.0	μm
$CaCO_3$	0.20	-	5.5	"
TiO_2	0.43	-	6.2	"
Al_2O_3	0.15	-	7.5	"
LiF	0.12	-	8.5	"
ZnS	0.60	-	14.5	"
BaF_2	0.13	-	15.0	"
Si	1.2	-	15.0	"
ZnSe	0.48	-	22.0	"
Ge	1.8	-	23.0	"
NaCl	0.2	-	25.0	"
KBr	0.2	-	38.0	"
CsI	0.25	-	70.0	"

(Adapted from: *Introduction to ceramics*, W.D. Kingery et al., John Wiley, 1976)