Department:	ID#:	Name:

4. Intramolecular Motions

4.1 Vibration

⟨Vibrational density of states⟩

[example] vibrational density of states of CH_3OH at dissociation limit to CH_3O + H

number of vibrational modes: $n_v = 3\,n_{atom} - 6 = 3\cdot6-6 = 12$

dissociation energy: $D(CH_3O–H) = 436.8$ kJ mol^{-1} = 3.651×10^4 cm^{-1} (1 cm^{-1} = 11.963 J)

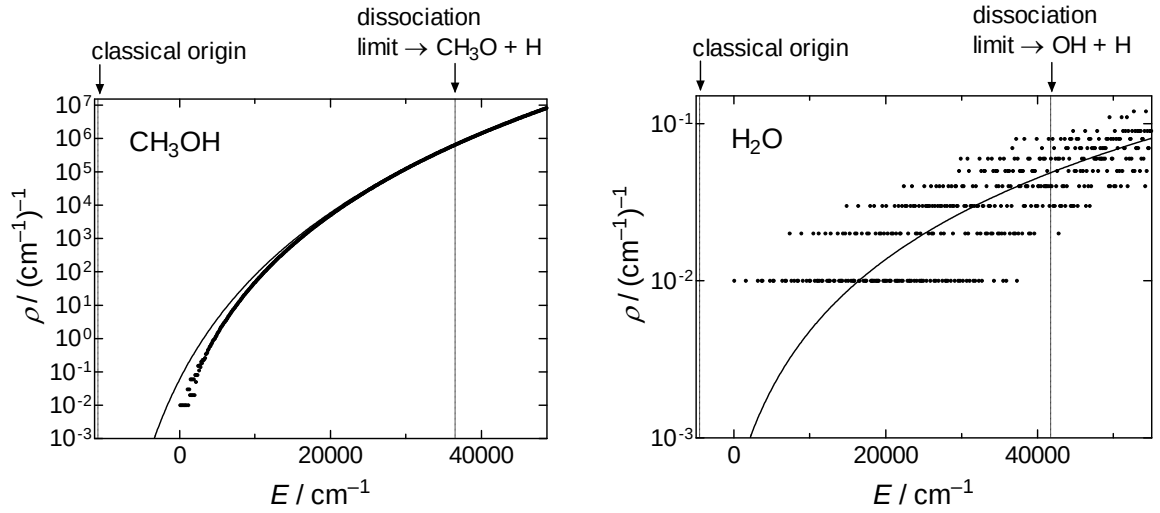
vibrational frequencies (cm^{-1}): 3681, 3000, 2844, 1477, 1455, 1345, 1060, 1033, 2960, 1477, 1165, 200

zero point energy: (3681+3000+2844+1477+1455+1345+1060+1033+2960+1477+1165+200) / 2
= 1.085×10^4 cm^{-1}

$\Gamma(n_v) = 11! = 3.992\times10^7$

$\Pi(h\nu_i) = 3681\cdot3000\cdot2844\cdot1477\cdot1455\cdot1345\cdot1060\cdot1033\cdot2960\cdot1477\cdot1165\cdot200 = 1.013\times10^{38}$ cm^{-12}

$\rho = [(3.651 + 1.085)\times10^4]^{11} / (3.992\times10^7 \times 1.013\times10^{38}) = 6.65\times10^5$ cm (= 1 / cm^{-1} = states per cm^{-1})



[Exercise-4] Estimate the vibrational density of states of H_2O at dissociation limit to H + OH from Eq. (4.6)

$D(H–OH) = 499.1$ kJ mol^{-1}

vibrational frequencies (cm^{-1}): 3657, 1595, 3756
