Translational density of states [Relative translation: $m \to \mu$]

$$\rho_{trans}^{(1D)}(\varepsilon) = \frac{\sqrt{2m}}{h} l \varepsilon^{-1/2} \tag{2.1.2}$$

$$\rho_{trans}^{\circ\,(3D)}(\varepsilon) = 2\pi \left(\frac{\sqrt{2m}}{h} \right)^3 \varepsilon^{1/2} = c_{trans} \varepsilon^{1/2} \tag{2.1.5}$$

Rotational density of states

$$\rho_{rot}^{(n_r)}(\varepsilon) \sim c_{rot}^{(n_r)} \varepsilon^{\frac{n_r}{2}-1}, \quad c_{rot}^{(n_r)} = \frac{\Gamma(n_r)}{\sigma B_{(\mathrm{av})}^{n_r/2}} \tag{2.2.11}$$

$$B = \frac{h^2}{8\pi^2 I} \quad \text{(rotational constant)} \tag{2.2.2}$$

Vibrational density of states

$$\rho_{vib-cl}^{(n_v)}(\varepsilon_{cl}) = \frac{1}{\Gamma(n_v) \prod_{i=1}^{n_v} h\nu_i} \varepsilon_{cl}^{n_v-1} = c_{vib-cl}^{(n_v)} \varepsilon_{cl}^{n_v-1} \tag{2.3.5}$$

$\Gamma(n) = (n-1)!, \quad \Gamma(1) = \Gamma(2) = 1$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k_f}{\mu}} \quad \text{(vibrational frequency)} \tag{2.3.2}$$

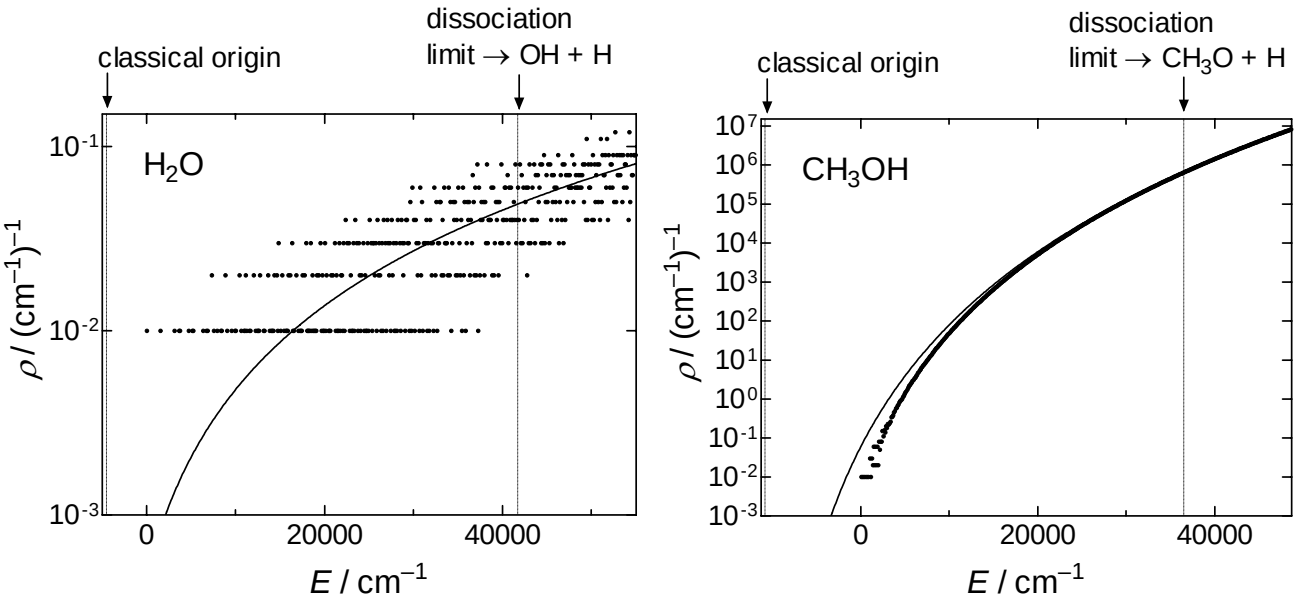

Fig. 2 Comparison of ρ by eq. 2.3.5 (—) and exact ρ (·····). (H_2O [left] / CH_3OH [right])

Problem-2.2

Estimate the vibrational density of states for ethane [D(C-C) = 377 kJ mol^{-1}] at around dissociation threshold by eq. 2.3.5. Use the following vibrational frequencies [Unit: cm^{-1}; Values in parentheses are degeneracy of the vibration.]

2954, 1388, 995, 289, 2896, 1379, 2969(2), 1468(2), 1190(2), 2985(2), 1469(2), 822(2)

Note that the ε_{cl} in eq. 2.3.5 is the energy from classical origin.