Quasi-Rigid-Rotor-Harmonic-Oscillator Approximation

Huiwen Tan

February 23, 2025

Under the rigid rotor harmonic oscillator (RRHO) approximation, the contribution of mode K to the vibrational entropy is

$$S_{\mathrm{v},K}^{\mathrm{RRHO}} = R\left[\frac{\Theta_{\mathrm{v},K}}{T(e^{\Theta_{\mathrm{v},K}/T}-1)} - \ln(1-e^{-\Theta_{\mathrm{v},K}/T})\right] \tag{1}$$

where the characteristic vibrational temperature $\Theta_{\mathrm{v},K} = h\nu_K/k_B$. However, this approximation yields an infinite vibrational entropy at the limit frequency $\nu \to 0$, which results in low-lying modes caused by hindered or near-free rotation of single bonds not being properly treated. In Grimme's quasi-RRHO approximation [1], the vibrational entropy contribution of low-frequency modes below the cutoff ν_0 is replaced with free rotor entropy,

$$S_{\mathrm{R},K} = R\left[\frac{1}{2} + \ln\left(\frac{8\pi^3\mu'_K k_B T}{h^2}\right)^{1/2}\right] \tag{2}$$

The effective moment of inertia is expressed as

$$\mu'_K = \frac{\mu_K B_{\mathrm{av}}}{\mu_K + B_{\mathrm{av}}} \tag{3}$$

where B_{av} is the average molecular moment of inertia and $\mu_K = h/8\pi^2\nu_K$ is the moment of inertia for a free-rotor with the same frequency as normal mode K. Then, the vibrational entropy is obtained by interpolating between the harmonic oscillator entropy and the free rotor entropy,

$$S_{\mathrm{vib},K}^{\text{quasi-RRHO}} = w(\nu_K)S_{\mathrm{v},K}^{\mathrm{RRHO}} + [1-w(\nu_K)]S_{\mathrm{R},K} \tag{4}$$

where $w(\nu_K)$ is given by the damping function of Head-Gordon [2],

$$w(\nu_K) = \frac{1}{1+(\nu_0/\nu_K)^\alpha} \tag{5}$$

By default, $\alpha = 4$ and $\nu_0 = 100\ \mathrm{cm}^{-1}$ are used. Therefore, the total vibrational entropy is $S_{\mathrm{v}}^{\text{qusai-RRHO}} = \sum_K S_{\mathrm{vib},K}^{\text{quasi-RRHO}}$, and the total entropy is

$$S_{\mathrm{tot}}^{\text{quasi-RRHO}} = S_{\mathrm{t}} + S_{\mathrm{r}} + S_{\mathrm{v}}^{\text{quasi-RRHO}} + S_{\mathrm{e}} \tag{6}$$

where S_{t}, S_{r} and S_{e} are translational entropy, rotational entropy, and electronic entropy, respectively.

The quasi-RRHO approximation can also be extended to the calculation of enthalpy. In the RRHO approximation, the contribution of vibrational mode K to the internal thermal energy can be expressed as

$$E_{\mathrm{v},K}^{\mathrm{RRHO}} = R\Theta_{\mathrm{v},K}\left(\frac{1}{2} + \frac{1}{e^{\Theta_{\mathrm{v},K}/T}-1}\right) \tag{7}$$

The vibrational internal energy modified by qRRHO approximation is [3]

$$E_{\mathrm{v}}^{\text{quasi-RRHO}} = \sum_{K} \left(w(\nu_K) E_{\mathrm{v},K}^{\mathrm{RRHO}} + [1 - w(\nu_K)] \frac{1}{2} RT \right) \tag{8}$$

The enthalpy can then be calculated from the total electronic energy E_0 by including the thermal correction $H_{\mathrm{corr}}^{\text{quasi-RRHO}}$,

$$\begin{aligned} H_{\mathrm{tot}}^{\text{quasi-RRHO}} &= E_0 + H_{\mathrm{corr}}^{\text{quasi-RRHO}} \\ &= E_0 + E_{\mathrm{tot}}^{\text{quasi-RRHO}} + RT \\ &= E_0 + (E_{\mathrm{t}} + E_{\mathrm{r}} + E_{\mathrm{v}}^{\text{quasi-RRHO}} + E_{\mathrm{e}}) + RT \end{aligned} \tag{9}$$

where E_{t}, E_{r}, and E_{e} are the contributions of translation, rotation and electronic motion to internal thermal energy, respectively. Therefore, the Gibbs free energy with the quasi-RRHO approximation is

$$G_{\mathrm{tot}}^{\text{quasi-RRHO}} = H_{\mathrm{tot}}^{\text{quasi-RRHO}} - TS_{\mathrm{tot}}^{\text{quasi-RRHO}} \tag{10}$$

References

(1) Grimme, S. *Chemistry – A European Journal* **2012**, *18*, 9955–9964.

(2) Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

(3) Li, Y.-P.; Gomes, J.; Mallikarjun Sharada, S.; Bell, A. T.; Head-Gordon, M. *The Journal of Physical Chemistry C* **2015**, *119*, 1840–1850.