ⓐ Since molecules do not interact, we can express the canonical partition sum as

$$Z(T,V,N) = \frac{Z_1^N}{N!}$$

, and the partition function for a single molecule can be express as a ~~sum~~ product of the rotational and the translational contributions :

$$Z_1 = Z_{trans} + Z_{rot.} \; ;$$

$$Z_{trans} = \frac{V}{(2\pi\hbar)^3} \int d^3p \, e^{-\beta|\vec{p}|^2/2m} = \frac{V}{\lambda^3} \; , \; \lambda = \left(\frac{(2\pi\hbar)^2}{2\pi mT} \right)^{1/2}$$

$$Z_{rot} = \sum_{l=0}^{\infty} (2l+1) e^{-\beta l(l+1)\hbar^2/2I}$$

$$\therefore \; Z = \frac{1}{N!} \left(\frac{V}{\lambda^3} \sum_{l=0}^{\infty} (2l+1) e^{-\beta l(l+1)\hbar^2/2I} \right)^N$$

ⓑ At sufficiently high temperatures, we might expect that the spacing between rotational energy levels becomes sufficiently small compared ~~to~~ with T, so that the above sum could be replaced with an integral. However, as temperature is lowered this replacement is not valid any more; however, corrections ~~to~~ the approximation of the sum by the integral can be calculated by means of Euler-Maclaurin formula :

$$\sum_{k=0}^{\infty} f(k) = \int_0^{\infty} f(k)\,dk + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f'''(0) - \dots$$

This formula is valid for smooth functions $f(k)$ which vanish, along with all its derivatives, as $k \to \infty$. Of course, this formula is useful only in circumstances where all but a few terms of the series can be neglected. Let us define $\Theta = \frac{\hbar^2}{2I}$ and $f(l) = (2l+1)e^{-l(l+1)\frac{\Theta}{T}}$. If $T \gg \Theta$, we can keep just a few terms in a power series expansion of Z_{rot} in powers of $\frac{\Theta}{T}$. These two series, however, do not agree term by term:

$$f(l) = \sum_{n=0}^{\infty} (2l+1) \frac{[-l(l+1)]^n}{n!}\left(\frac{\Theta}{T}\right)^n =$$

$$= (2l+1) - (2l^3+3l^2+l)\frac{\Theta}{T} + \dots$$

The coefficient of $\left(\frac{\Theta}{T}\right)^n$ is a polynomial of degree $2n+1$ in l, and will contribute to all terms of the Euler-Maclaurin series up to $f^{(2n+1)}(0)$. Thus, to obtain our answer correct to order $\frac{\Theta}{T}$, we need the terms up to $f'''(0)$. In this way we find:

$$Z_{rot} = \int_0^{\infty} f(l)\,dl + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f'''(0) - \dots$$

$$= \frac{T}{\Theta} + \frac{1}{3} + \frac{1}{15}\frac{\Theta}{T} + O\left(\left(\frac{\Theta}{T}\right)^2\right)$$

The internal energy and specific heat are then given by

$$E = -N\left(\frac{\partial(\ln Z_{trans})}{\partial\beta} + \frac{\partial(\ln Z_{rot})}{\partial\beta}\right) =$$

$$= \frac{5}{2}NT\left(1 - \frac{2}{15}\frac{\theta}{T} - \frac{2}{225}\left(\frac{\theta}{T}\right)^2 + O\left[\left(\frac{\theta}{T}\right)^3\right]\right)$$

$$c_v = \left(\frac{\partial E}{\partial T}\right)_v = \frac{5}{2}N\left[1 + \frac{2}{225}\left(\frac{\theta}{T}\right)^2 + O\left[\left(\frac{\theta}{T}\right)^3\right]\right]$$

At high T, $c_v \to \frac{5N}{2}$ (as in the classical equipartition theorem)

At low temperatures $T \ll \theta$, successive terms of the sum over l decrease rapidly, and we keep just the first two:

$$Z_{rot} \approx 1 + 3e^{-\frac{2\theta}{T}} + \dots$$

$$\Downarrow$$

$$c_v \approx \frac{3}{2}N + \underbrace{12N\left(\frac{\theta}{T}\right)^2\left(e^{-\frac{2\theta}{T}} + \dots\right)}_{\text{rotational contribution}}$$

It vanishes as $T \to 0$.