more-information

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February 4, 2021

Presented here is a more informative, but still a stripped-down version of the derivation of the expression for the level splitting of low vibrationally-excited states in asymmetrically-stretched systems.

An expression which is valid for asymmetrically-stretched systems

$$\langle \phi_n^{(l)} | e^{-\beta \hat{H}} | \phi_n^{(r)} \rangle = \frac{2\hbar\Omega_n}{\Delta_n} \sinh\left(\frac{\beta\Delta_n}{2}\right) \mathrm{e}^{-\beta E} \tag{1}$$

where the level splitting is given by

$$\boxed{\Delta_n = 2\sqrt{d_n^2 + (\hbar\Omega_n)^2}} \tag{2}$$

and

$$d_n = \frac{E_n^{(l)} - E_n^{(r)}}{2} \tag{3}$$

$$E = \frac{E_n^{(l)} + E_n^{(r)}}{2} \tag{4}$$

with $E_n^{(l/r)} = \hbar\omega_{l/r}(n + \frac{1}{2})$.

We then note that we can choose to expand this using a complete set of position states such that

$$\begin{aligned} \langle \phi_n^{(l)} | e^{-\beta \hat{H}} | \phi_n^{(r)} \rangle &= \int \mathrm{d}x' \int \mathrm{d}x'' \, \langle \phi_n^{(l)} | x' \rangle \, \langle x' | \mathrm{e}^{-\beta \hat{H}} | x'' \rangle \, \langle x'' | \phi_n^{(r)} \rangle \\ &= \int \mathrm{d}x' \int \mathrm{d}x'' \, K(x', x'', \beta\hbar) \phi_n^{(l)}(x') \phi_n^{(r)}(x'') \end{aligned} \tag{5}$$

where we defined $K(x', x'', \beta\hbar) = \langle x' | \mathrm{e}^{-\beta \hat{H}} | x'' \rangle$.

We can now then choose to evaluate this with instanton theory. In order to do this, we first need the forms of the wavefunction at the left/right well, which just so happen to coincide well with the harmonic oscillator wavefunctions, i.e.

$$\phi_n^{(l)}(x') = \frac{1}{\sqrt{2^n n!}} \left(\frac{\alpha_l}{\pi}\right)^{\frac{1}{4}} \mathrm{e}^{-\frac{m\omega_l}{2\hbar}(x'-x_0)} \tag{6}$$

$$\phi_n^{(r)}(x'') = \frac{1}{\sqrt{2^n n!}} \left(\frac{\alpha_r}{\pi}\right)^{\frac{1}{4}} \mathrm{e}^{-\frac{m\omega_r}{2\hbar}(x''+x_0)} \tag{7}$$

Then finally, we need the semiclassical form of $K(x', x'', \beta\hbar)$, of which the derivation is presented in Richardson, *Int. Rev. Phys. Chem.* **37**, 171-216 (2018).

With all the information now at hand, one can now evaluate Eq. 5 with instanton theory. [a] Equating the result back to Eq. 1, we now obtain an expression for Ω_n as

$$\Omega_n \sim \Gamma_n A_{\mathrm{inst}} \mathrm{e}^{-S/\hbar} \tag{8}$$

where S is the action of the optimised instanton path.

It can be noted that $\Omega_0 \sim A_{\mathrm{inst}} \mathrm{e}^{-S/\hbar}$. Here this is written for simplicity's sake, but expression is effectively the same as the one given in Jahr, Laude and Richardson, *J. Chem. Phys.* **153**, 094101 (2018). The starting point of the derivation outlined here

[a] How this is done will not be shown here, as it is intended to be a short document. Do look forward to our future work as we intend to show how this would be done then!