

A semiclassical route to the calculation of IR spectra

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Abstract

Semiclassical vibrational spectroscopy is based on the evolution of classical trajectories and is able to reproduce quantum effects with good accuracy at the cost of a reasonable computational effort. Nevertheless, semiclassical vibrational power spectra do not simulate all the features of the experimental IR spectra, since intensities in power spectra are not directly related to the IR absorptions. Therefore, we developed an innovative strategy with the aim of calculating IR spectra within the semiclassical framework. To do this, we started from the general definition of the absorption spectrum as the Fourier transform of the transition dipole moment autocorrelation function; we then added the Herman-Kluk approximation to the quantum propagator and made use of the time-averaging procedure to promote the convergence of the phase-space integrals. Finally, we tested the accuracy of this new method on some simple analytical systems and small molecules in the gas phase.

Theoretical derivation

We start from the definition of an absorption spectrum as the Fourier transform of the transition dipole moment autocorrelation function

$$I(E) = \frac{\text{Re}}{\pi\hbar} \int_0^{+\infty} dt e^{iEt/\hbar} \langle \hat{\mu}(0) \hat{\mu}(t) \rangle$$

We consider the quantum mechanical expression of the dipole moment autocorrelation function

$$\langle \hat{\mu}(0) \hat{\mu}(t) \rangle = \text{Tr} [e^{-\beta\hat{H}} \hat{\mu} e^{i\hat{H}t/\hbar} \hat{\mu} e^{-i\hat{H}t/\hbar}]$$

and we set $e^{-\beta\hat{H}} = \hat{1}$, reaching the limit of high temperatures.

To approximate the quantum propagators we employ the Herman-Heller-Kluk-Kay (HHKK) representation^{1,2}

$$e^{-\frac{i}{\hbar}\hat{H}t} \approx \left(\frac{1}{2\pi\hbar} \right)^F \iint d\mathbf{p}_0 d\mathbf{q}_0 C_t(\mathbf{p}_0, \mathbf{q}_0) e^{iS_t(\mathbf{p}_0, \mathbf{q}_0)/\hbar} |\mathbf{p}_t \mathbf{q}_t\rangle \langle \mathbf{p}_0 \mathbf{q}_0|$$

where $C_t(\mathbf{p}_0, \mathbf{q}_0)$ is the pre-exponential factor, depending on the elements of the monodromy matrix, defined as $\partial \mathbf{i}_t / \partial \mathbf{j}_0$, with $\mathbf{i}, \mathbf{j} = \mathbf{p}, \mathbf{q}$, $S_t(\mathbf{p}_0, \mathbf{q}_0)$ is the corresponding classical action, and $|\mathbf{p}_t \mathbf{q}_t\rangle, \langle \mathbf{p}_0 \mathbf{q}_0|$ are coherent states defined in the configuration space as

$$\langle \mathbf{q} | \mathbf{p}_t \mathbf{q}_t \rangle = \left(\frac{\det(\Gamma)}{\pi^F} \right)^{\frac{1}{4}} e^{-\frac{1}{2}(\mathbf{q}-\mathbf{q}_t)^T \Gamma (\mathbf{q}-\mathbf{q}_t) + \frac{i}{\hbar} \mathbf{p}_t^T (\mathbf{q}-\mathbf{q}_t)}$$

The time-averaging (TA) procedure developed by Kaledin and Miller³ is employed to promote the convergence of the phase-space integrals, leading to

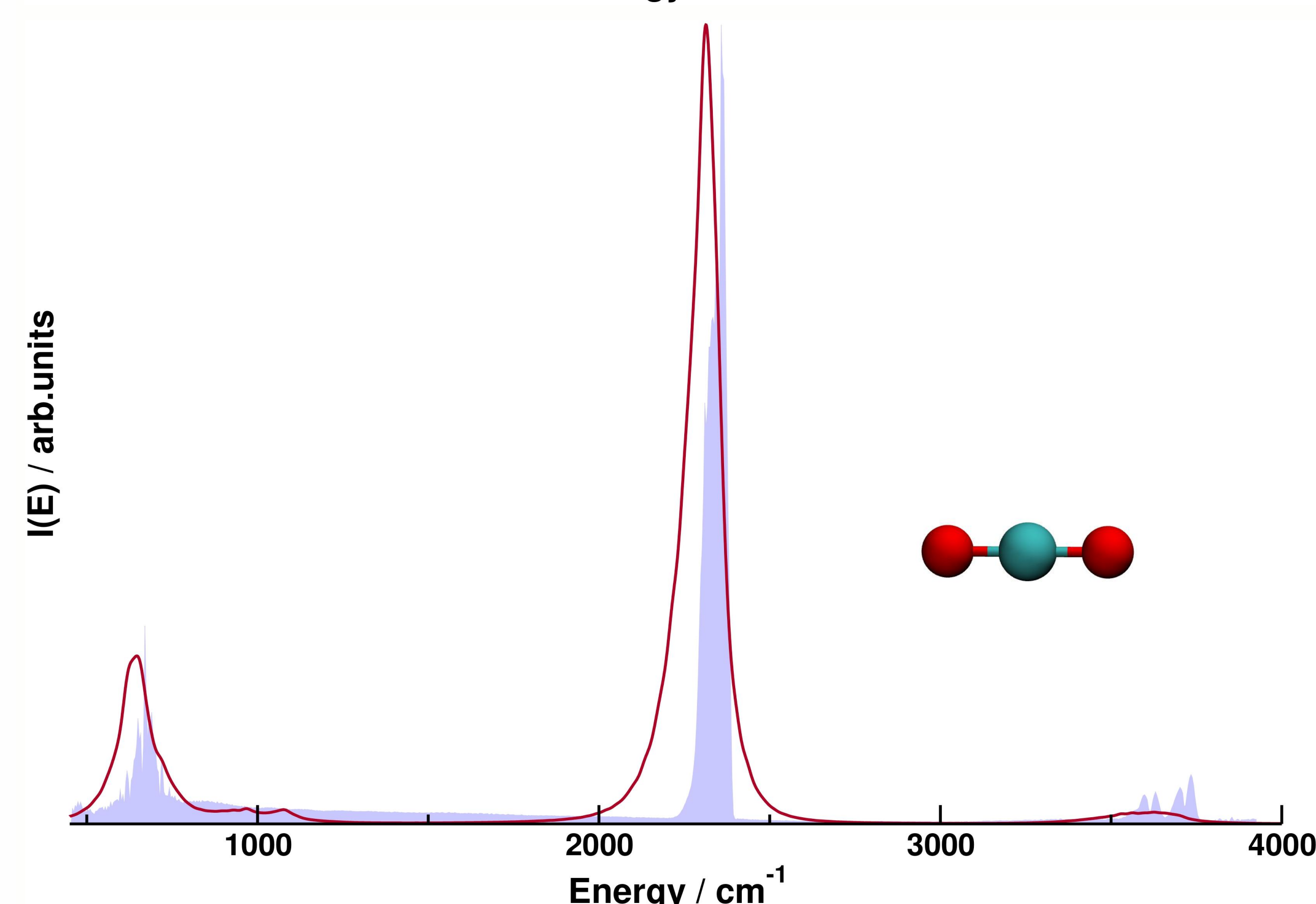
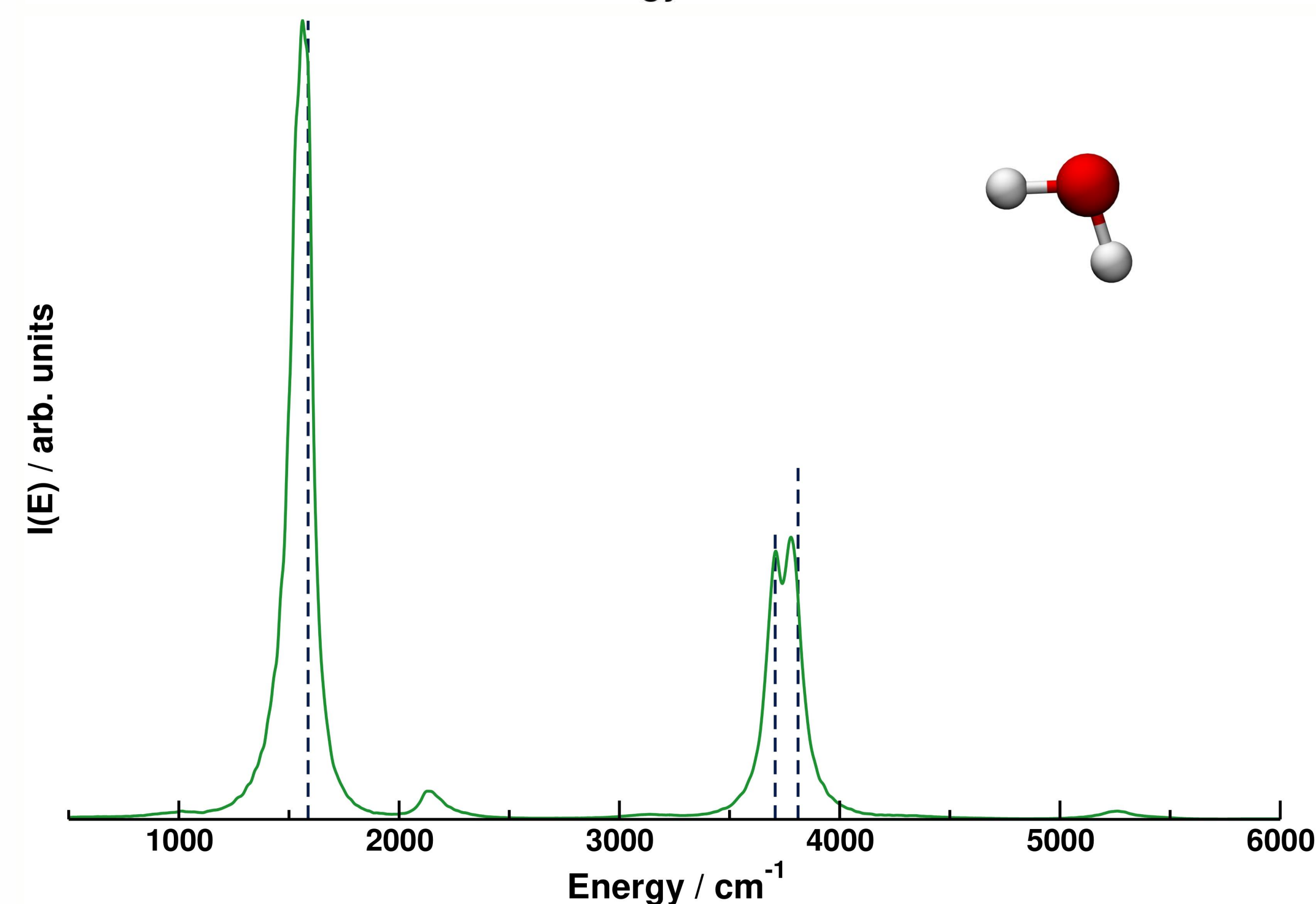
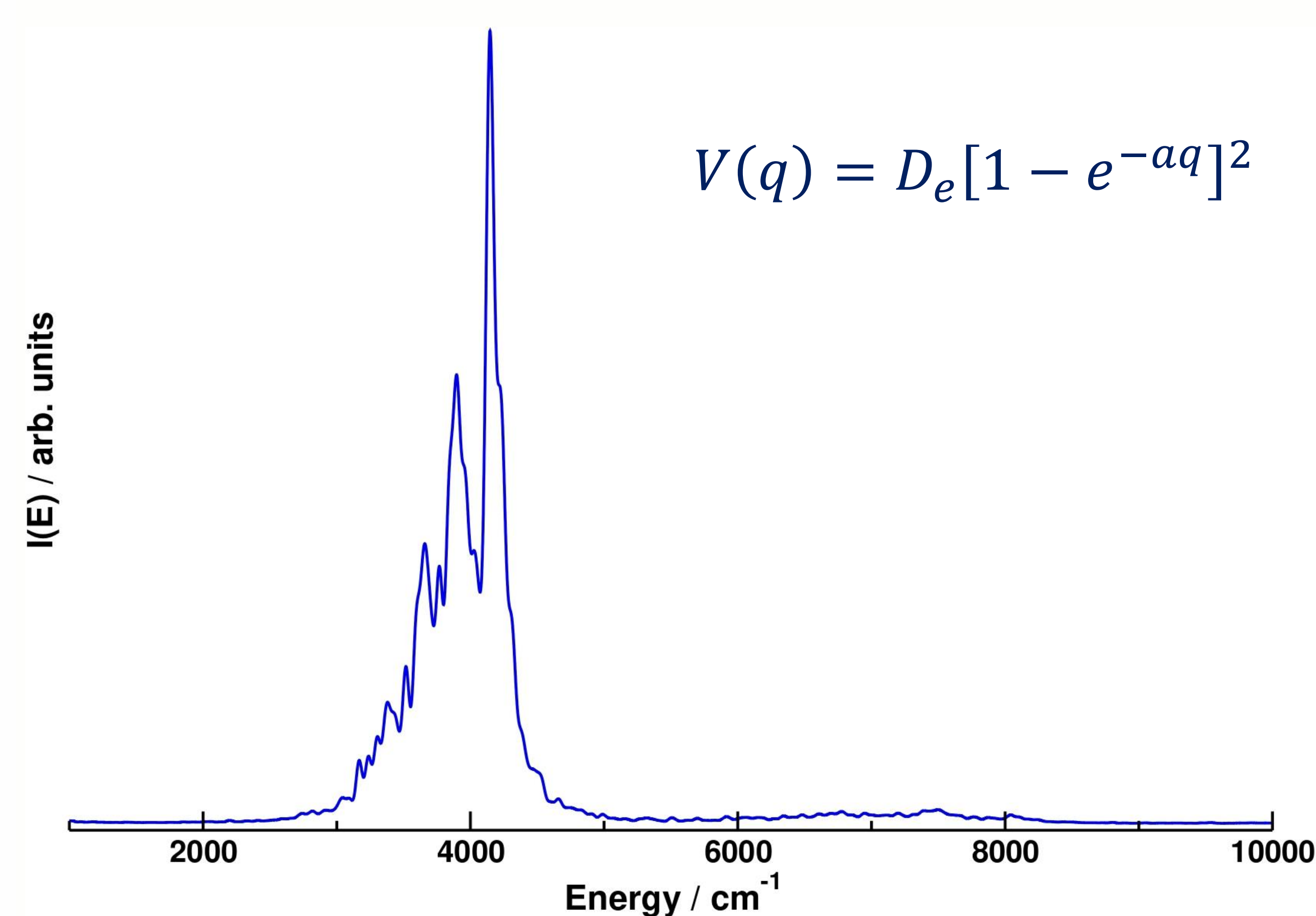
$$I(E) = \frac{(2\pi\hbar)^{-2F}}{2\pi\hbar T} \iint d\mathbf{p}_0 d\mathbf{q}_0 \iint d\mathbf{p}'_0 d\mathbf{q}'_0 \times \left| \int_0^T dt e^{i[S_t(\mathbf{p}'_0, \mathbf{q}'_0) - S_t(\mathbf{p}_0, \mathbf{q}_0) + Et + \phi'(t) - \phi(t)]/\hbar} \langle \mathbf{p}_t \mathbf{q}_t | \hat{\mu} | \mathbf{p}'_t \mathbf{q}'_t \rangle \right|^2$$

with T being the total simulation time and $\phi(t), \phi'(t)$ the phases of the pre-exponential factors $C_t(\mathbf{p}_0, \mathbf{q}_0)$ and $C_t(\mathbf{p}'_0, \mathbf{q}'_0)$.

We finally make use of the linearization approximation to the transition dipole moment operator

$$\boldsymbol{\mu}_{0N}(\mathbf{q}) - \boldsymbol{\mu}_{0N}(\mathbf{q}_{eq}) \approx \sum_{\alpha=1}^{N_v} \left. \frac{\partial \boldsymbol{\mu}_{0N}}{\partial q_\alpha} \right|_{\mathbf{q}_{eq}} (q_\alpha - q_{eq,\alpha})$$

Results



References

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