A Time Averaged Approach to IR Spectroscopy

Cecilia Lanzi[1], Chiara Aieta[1], Michele Ceotto[1], Riccardo Conte[1]

[1] Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milan, Italy

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 IR absorptions. Therefore, we developed a new semiclassical approach to the calculation of molecular IR spectra, by employing the time average technique upon symmetrization of the quantum dipole-dipole autocorrelation function. We tested the accuracy of this new method on a few simple analytical systems and small molecules in the gas phase. Overall the method features excellent accuracy in calculating absorption intensities and provides estimates for the frequencies of vibrations in agreement with the corresponding power spectra.

Theoretical derivation

1) QM definitions of IR absorption spectrum and absorption lineshape

$$\alpha(\omega,T)=\omega(1-e^{-\beta\hbar\omega})\sigma(\omega,T)$$

$$\sigma(\omega,T)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\,e^{-i\omega t}\,\langle\hat{\mu}(0)\hat{\mu}(t)\rangle$$

2) Herman – Kluk (HK) Semiclassical Initial Value Representation (SC-IVR)[1]

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

3) Kaledin and Miller’s time averaging procedure[2]

$$I=\iint d\mathbf{p}_0 d\mathbf{q}_0 A(\mathbf{p}_0,\mathbf{q}_0)\quad\equiv\quad I_{TA}=\iint d\mathbf{p}_0 d\mathbf{q}_0\frac{1}{T}\int_0^T dt\,A(\mathbf{p}_t,\mathbf{q}_t)$$

4) Time-averaged semiclassical absorption lineshape

$$\sigma(\omega,T)=\frac{(2\pi\hbar)^{-2F}}{2\pi T_s}\iint d\boldsymbol{p}_0 d\boldsymbol{Q}_0\iint d\boldsymbol{p}'_0 d\boldsymbol{Q}'_0\times\left|\int_0^{T_s}dt\,e^{\frac{i}{\hbar}\left[S_t(\boldsymbol{p}'_0,\boldsymbol{Q}'_0)-S_t(\boldsymbol{p}_0,\boldsymbol{Q}_0)-\hbar\omega t+\phi'(t)-\phi(t)\right]}\left\langle\boldsymbol{p}_t\boldsymbol{Q}_t\middle|\hat{\mu}\hat{B}(\beta/2)\middle|\boldsymbol{p}'_t\boldsymbol{Q}'_t\right\rangle\right|^2$$

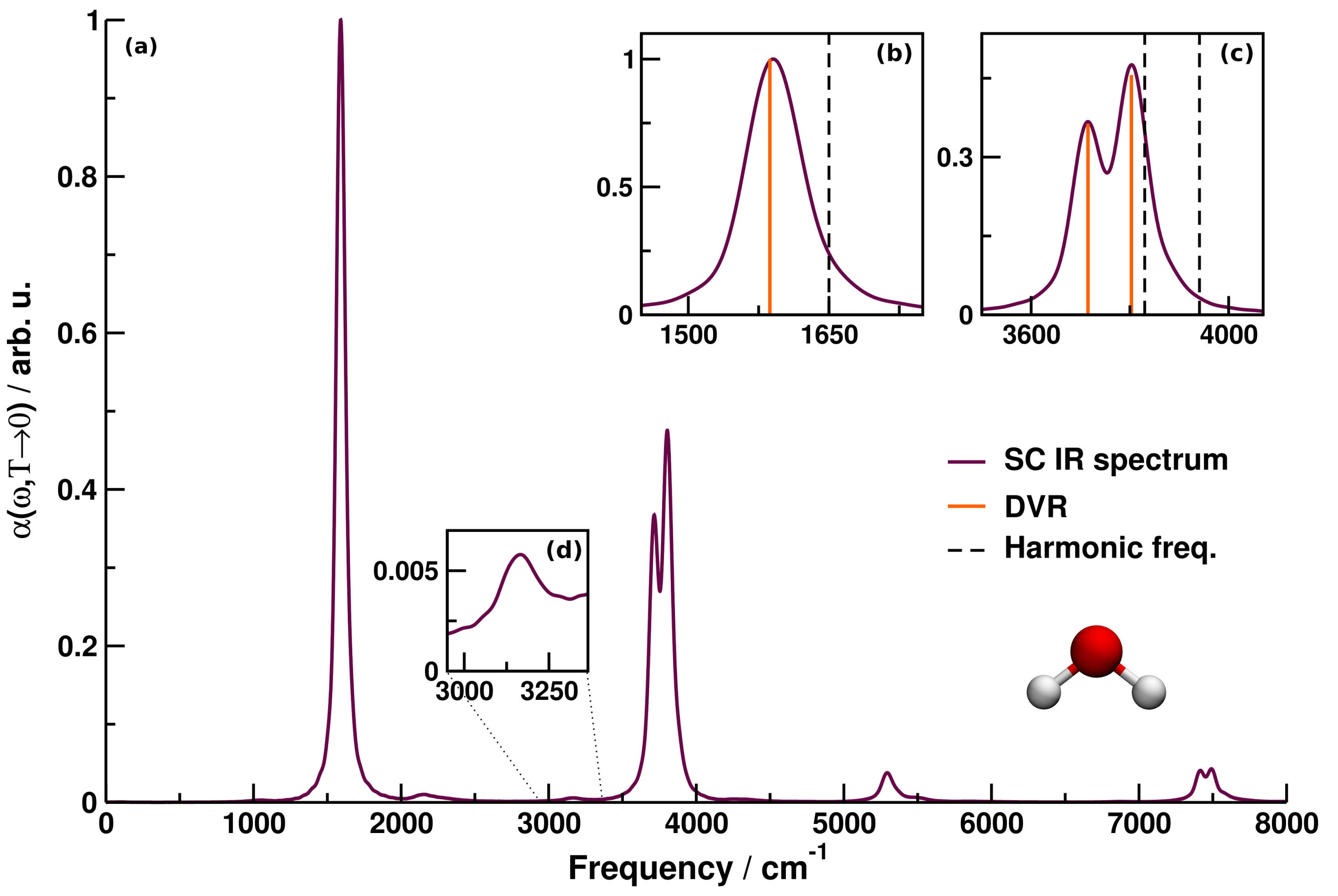
5) Linearization of the transition dipole moment operator

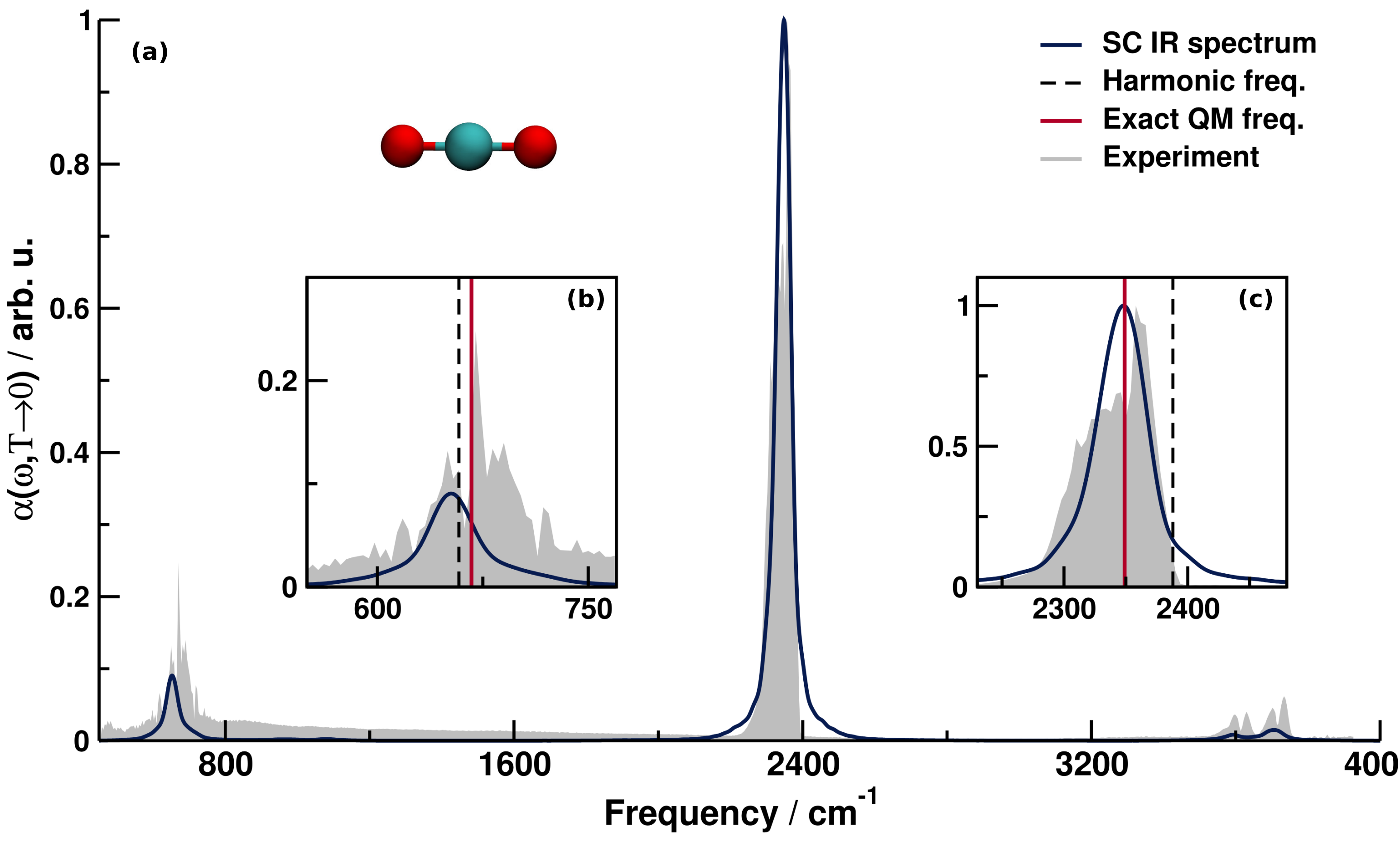
$$\boldsymbol{\mu}(\boldsymbol{q})-\boldsymbol{\mu}(\boldsymbol{q}_{eq})\simeq\sum_{j=1}^{N_\nu}\left.\frac{\partial\boldsymbol{\mu}}{\partial q_j}\right|_{\boldsymbol{q}_{eq}}(q_j-q_{eq,j})$$

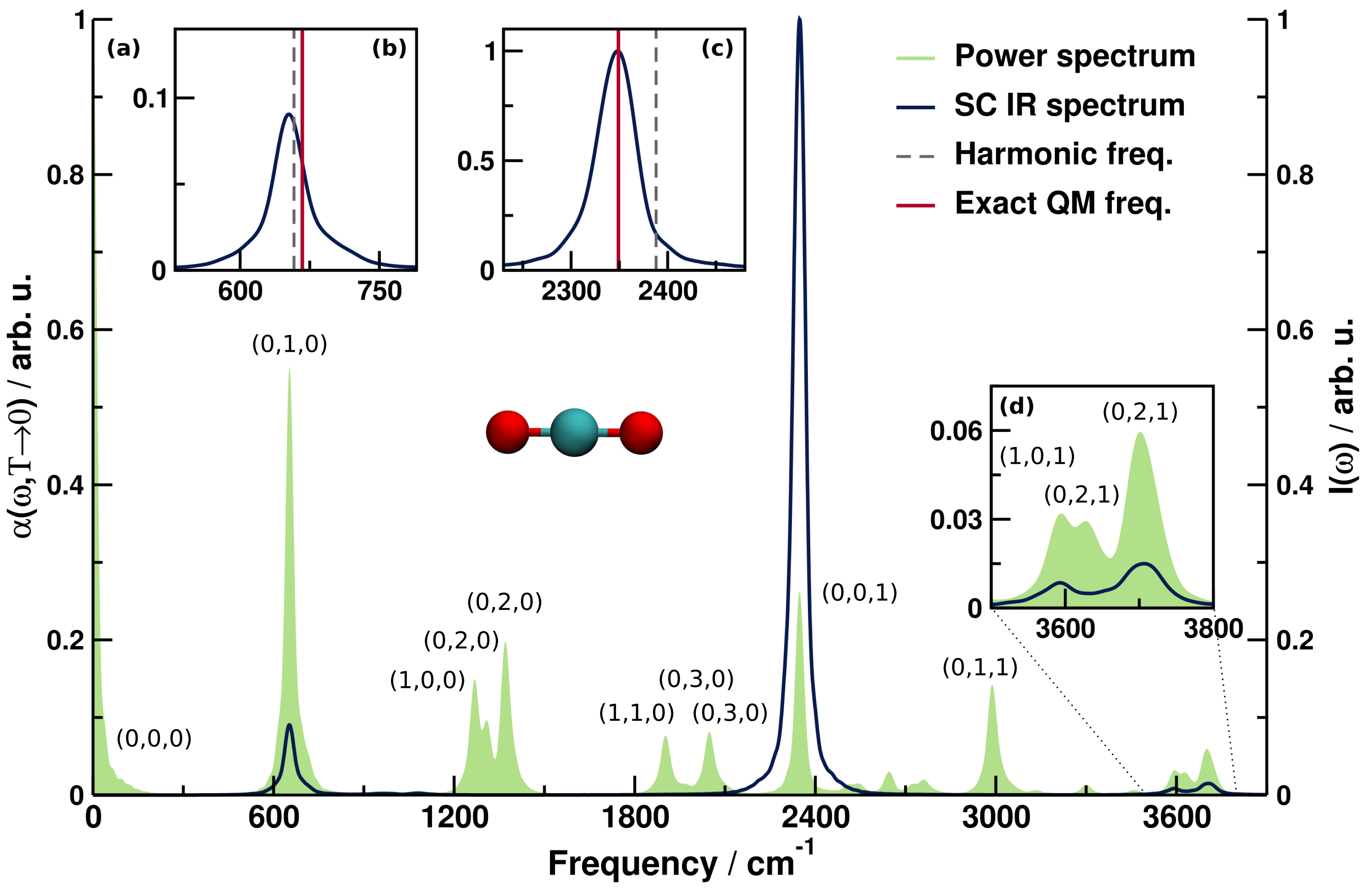
6) Boltzmann operator in the low-temperature limit (T → 0)

$$\hat{B}(\beta)=\frac{e^{-\beta\hat{H}}}{Z}\approx\left|\Psi_0\right\rangle\left\langle\Psi_0\right|$$

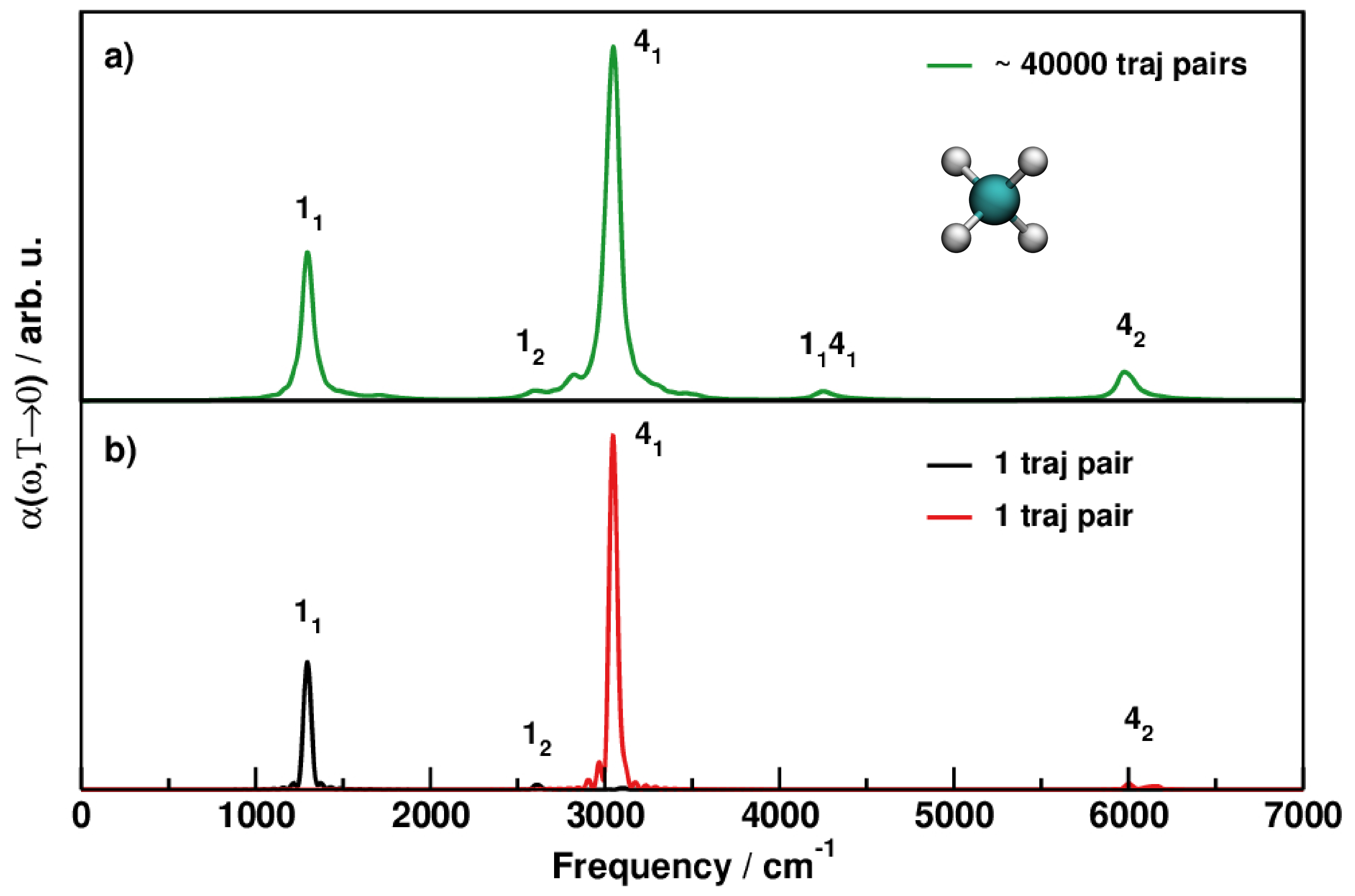
Results







Work in progress



References

[1] M. F. Herman and E. Kluk, *Chem. Phys.* **91**, 27 (1984)

[2] A. L. Kaledin and W. H. Miller, *J. Chem. Phys.* **118**, 7174 (2003)

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