

Quantumness of classical-trajectory-based methods for vibrational spectroscopy

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Classical-trajectory-based methods calculate the vibrational spectrum of a molecular system as the Fourier transform of an appropriate time correlation function. In this paper, we assess the quantumness of different approaches derived from the path-integral representation of quantum mechanics. We focus on power spectra obtained by means of semiclassical (SC) dynamics, centroid molecular dynamics (CMD), ring polymer molecular dynamics (RPMD) and its thermostatted version (TRPMD). Our calculations also include classical and quasi-classical trajectory (QCT) simulations as examples of results based on a purely classical propagator. Calculations are performed for a 3-dimensional anharmonic model system, and the non-rotating gas-phase water molecule. We show that typical features of classical calculations like sum-of-frequency combination bands and overtones, difference bands, and spectroscopic signals at negative frequencies are found for classical, QCT, CMD and (T)RPMD spectra. Conversely, these features are basically absent in semiclassical calculations, which show just a reminiscence of the underlying classical trajectory. The overall accuracy of the results compared to quantum mechanical values is always better for SC methods. Classical results depend on the initial sampling distributions, and their accuracy is of the same order of CMD, RPMD, and TRPMD simulations, i.e. an order of magnitude lower than for semiclassical approaches. Our main conclusion is that when it comes to molecular vibrational spectroscopy calculations, semiclassical methods have a predominant quantum character, being able to include also real-time coherence effects, while CMD, RPMD and TRPMD are prevalently classical reproducing just the anharmonicity related to the zero point energy or quantum statistical distribution.

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I. INTRODUCTION

The numerical complexity of quantum mechanics makes exact calculations of large or complex systems unfeasible. This is true also in the field of vibrational spectroscopy, where quantum exact calculations are limited to low-dimensional systems (up to a few atoms).^{1,2} Quantum methods based on highly accurate approximations have been developed in both a time-independent^{3–5} and a time-dependent fashion.⁶ However, they all face scalability issues, and treatment of larger systems, if doable at all, requires the introduction of additional approximations at the cost of a reduction in accuracy and precision.^{7,8}

To overcome the curse of dimensionality, methods based on classical trajectories able to regain approximate quantum effects have been developed.^{9–13} The rationale for such a choice lies in the fact that classical trajectories are computationally affordable also for very large systems. Therefore, the main challenge for classical-trajectory-based approaches is to reproduce accurately quantum effects.

Imaginary-time path integral molecular dynamics (PIMD) methods,¹⁴ which include centroid molecular dynamics (CMD),^{15,16} quasi-centroid molecular dynamics (QCMD),^{17,18} ring polymer molecular dynamics (RPMD),¹⁹ its thermostatted version (TRPMD),^{20,21} and some recent developments²² are among the most popular approaches when vibrational spectroscopy is the target of investigation. Due to their affordable computational times, they are often used for studying condensed-phase systems, but numerous applications to isolated molecules have also been reported,^{23–25} as well as comparative studies.^{26,27} In spite of their popularity, they present some shortcomings in performing spectral evaluations.¹⁶ For instance, with limitation to frequency calculations, signals approximating overtones and combination bands are known to be calculated as more blue shifted than fundamentals.²⁸ Fermi resonances are another potential source of inaccuracy.²⁸ In general, CMD and RPMD are methods able to include zero-point energy effects in the calculation, but they neglect real-time quantum coherences. Plé and Althorpe (and their co-workers), in separate studies,^{29,30} attributed the inaccuracy of PIMD-derived methods to the approximations they make to the underlying Matsubara dynamics, and, by correcting the Matsubara dynamics, results closer to quantum exact ones can be recovered. However, the correction could be unpractical and straightforward application of these methods in their original, uncorrected formulation is still very much employed in studies of nuclear quantum effects (NQE).³¹ Plé et al.²⁹ also showed, through adoption of the adaptive quantum thermal bath method, that sampling can

improve the description of the absorption intensity of the signals which approximate overtones and combination bands, however without correcting the frequency blue shift issue.

If one wants to include approximate zero-point energy effects into a vibrational frequency calculation in a simpler way, quasi-classical trajectory dynamics (QCT) is an option.^{32–35} In QCT, the initial conditions of the dynamics are harmonically quantized. The following NVE dynamics is purely classical, so that no real-time NQEs are found and the revealed anharmonicity is related to the initial quantization of energy. Vibrational frequencies calculated through QCT are energy-dependent (a typical feature of classical approaches),³⁶ but the method can be accurate regarding fundamentals.³⁷ Combination bands and overtones obtained from the same trajectory are simply the sum of frequencies or multiple integers of fundamental frequencies, another characteristic that QCT shares with purely classical and harmonic approaches (*vide infra*).³⁸ Accuracy of QCT results for fundamentals can be improved by tailoring a trajectory per mode with initial conditions in which the specific mode under investigation is harmonically excited. However, if these multiple trajectories are summed up and averaged, combination bands are no longer found at a frequency exactly equal to the sum of the frequencies obtained for the contributing fundamentals. This happens because different trajectories are employed for the different modes contributing to the combination band. The dependence of QCT results on the trajectory energies is once more evident.

Differently from harmonic approaches, which produce a stick spectrum, QCT, CMD, and RPMD calculate the frequencies of vibration by Fourier transforming velocity (dipole) autocorrelation functions.³⁹

Semiclassical (SC) dynamics approaches are also based on classical trajectories and can be derived from a stationary phase approximation to the real-time path integral formulation of quantum mechanics.^{40–42} Therefore, differently from previous methods, they are able to account for real-time quantum coherences, and they reproduce approximate but very accurate NQEs. SC methods adopt classical-trajectory-based quantities like the stability matrix and the classical action, which are appropriately employed in the SC Herman-Kluk propagator.⁴³ The way frequencies are calculated by SC methods is through the Fourier transform of the survival amplitude of a quantum reference state. The Herman-Kluk propagator is based on a multi-dimensional phase-space integration, which is difficult to converge as the dimensionality of the system increases. A way to overcome the issue was introduced by Kaledin and Miller with the time average (TA) technique.^{44,45} In the last 10-15 years, constant theoretical developments of SC dynamics have opened

the way to SC calculations based on on-the-fly dynamics,^{46,47} simulations of larger and larger molecular systems including solvated ones,^{48,49} calculations of vibronic^{50–52} and IR spectra,^{53–56} and investigations of SC wavefunctions and nuclear densities.^{57,58} The field is still attracting much interest as new theoretical approaches are being developed.⁵⁹ Remarkably, a technique based on filter diagonalization instead of time averaging has successfully been developed quite recently.⁶⁰ The flexibility and wide range of applicability of SC methods is demonstrated by advances in fields like chemical kinetics including tunneling of heavy atoms,⁶¹ where comparisons among SC and RPMD methods have already been performed,⁶² and non-adiabatic dynamics.^{52,63–68} Current perspectives in the semiclassical field can be found in Refs. 69,70. SC approaches are certainly more elaborated and demand more human effort than CMD or RPMD ones. So, it is interesting to examine whether the additional effort required by SC approaches is rewarded by better quantum spectroscopic results or not.

In this manuscript, we compare the different accuracy and ability of SC, CMD and RPMD methods to describe quantum anharmonic effects in vibrational spectroscopy when using an ensemble of trajectories (in the case of SC we present calculations based also on a single representative trajectory). We reach our goal by looking at the frequencies calculated with the different approaches for fundamentals, combination bands, and overtones and comparing the results to classical and quantum estimates. Calculations are performed on a 3-dimensional model system and on the isolated, non-rotating water molecule. Furthermore, we look for the presence of the fingerprints of classical mechanics. In this way, we are able to provide a metric of the "quantumness" of each approach we investigate (i.e. how close each method is to quantum approaches rather than to classical ones).

The paper is organized as follows: We start by reminding the reader of some peculiar features of spectra based on classical mechanics. Then, the several approaches we employ are described in the Methodology Section. This is followed by the Results and Discussion Section where the performance of SC, CMD, and RPMD is assessed and compared to classical and quantum exact results for a model system and the water molecule. A Summary and Conclusions Section ends the paper.

II. FINGERPRINTS OF SPECTRA BASED ON CLASSICAL MECHANICS

In classical mechanics, the study of the equations of motion of a set of coupled anharmonic oscillators leads to the determination of the classical fundamental frequencies. For a non-linear molecule made of N atoms, $3N-6$ classical fundamental frequencies of vibration are found. However, the classical mechanics of molecular vibrations is also characterized by other periodic motions superposed on the fundamental ones. Their frequencies are anticipated by the method of successive approximations to be at the sums and differences of the fundamental frequencies.³⁸ On the one hand, classical signals are found at exact sums of the fundamental frequencies, i.e. they are in a sense "harmonic". This is the meaning of expressions like "harmonic overtones" or "harmonic combination bands". Often, these types of signals are (in our opinion improperly) labeled as combination bands and overtones, which are purely quantum mechanical features and, opposite to classical sums of frequencies, are anharmonic. On the other hand, classical signals related to differences of fundamental frequencies are not present in quantum mechanical power spectra, so their presence on a calculated power spectrum can reveal the classical character of the method employed. Furthermore, a classical approach features peaks at negative frequencies, providing another possible way to assess the classical character of the method.

In Figure 1 we anticipate the QCT simulation of a three-dimensional model presented below. We employ a single classical trajectory where the lower frequency mode has been singly excited, the second mode doubly excited, and the third mode initially contains just its contribution to the harmonic zero-point energy. Using an arcsinh scale for the power spectrum, it is possible to appreciate the numerous peaks present in this classical simulation. However, only the signals labeled as 100, 010, and 001 represent the 3 classical fundamental frequencies of vibration of the system. All other frequencies are due to the anharmonicity of the potential and coupling between modes. As anticipated, they are located at frequencies that can be obtained by algebraically combining integer multiples of the 3 classical fundamental frequencies, including negative integers as indicated by a bar on top of the excitation index. These combinations of frequencies are unrelated and generally different from the quantum combination and overtone frequencies.

Classical methods, as far as fundamental frequencies are concerned, are able to reproduce a certain degree of anharmonicity, which depends on the trajectory energy (for instance the zero-point energy in QCT) and related to the shape of the potential energy surface (PES). Nuclear quantum effects which cannot be obtained with a classical propagator manifest themselves in two

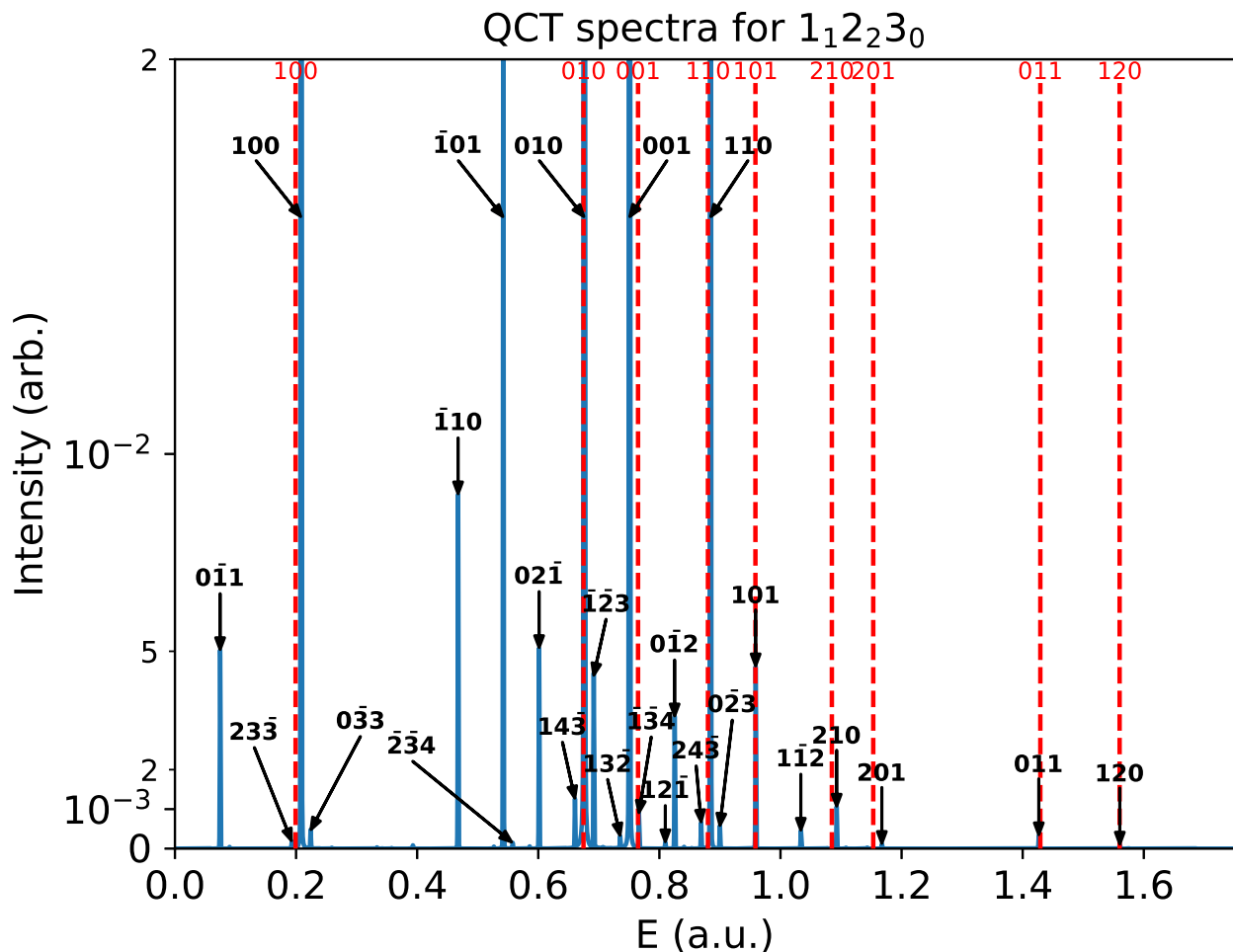


Figure 1. QCT spectra of model I (vide infra) from a single trajectory with energy corresponding to the $1_1 2_2 3_0$ energy shell. Intensities are in arcsinh scale for clarity. Each peak is marked with the corresponding 3 mode indexes, with negative numbers noted with a bar on the top. All peak positions are (within resolution) equal to the sum of the corresponding integer multiples of the fundamental frequencies. The red vertical dashed lines mark some of the quantum eigenvalues.

main ways: One is the possible presence of a tunnel effect between two molecular conformations separated by a low-energy barrier. This case is usually associated with hydrogen(s) migration (like in tropolone)⁷¹ or molecular structure inversions and torsions (like in ammonia and water trimer),^{72,73} and the result is the splitting of the spectroscopic signal. The other common way in which NQEs shape a vibrational spectrum is by means of an additional anharmonicity or frequency shift of peaks compared to harmonic and classical estimates. Sometimes, this effect is labeled as "quantum anharmonicity" meaning it is due to the quantum nature of molecules. Quantum anharmonicity, in the meaning we have just reported, can affect fundamental frequencies of vibration

and it is responsible for the anharmonicity of spectral combination bands and overtones compared to classical harmonic sum-of-frequency signals. Quantum anharmonicity can be essentially reconducted to quantum nuclear delocalization, quantum coherence and quantum interference effects, all of which can be described by trajectory-based methods only if they account for real-time quantum coherences.

III. METHODOLOGY

For numerically exact benchmarks, we use the DVR method with harmonic oscillator basis to solve the time-independent Schrödinger's equation⁷⁴. The basis is set according to the normal modes and harmonic frequencies at the global minimum of the potential. The resulting coefficients are then used to assign mode indexes to the eigenstates.

For semiclassical calculations, we use the Herman-Kluk propagator^{10,43},

$$e^{-i\hat{H}t/\hbar} = \frac{1}{(2\pi\hbar)^D} \int d\mathbf{p}_0 \int d\mathbf{q}_0 C_t(\mathbf{p}_0, \mathbf{q}_0) \times e^{iS_t(\mathbf{p}_0, \mathbf{q}_0)/\hbar} |\mathbf{p}_t, \mathbf{q}_t\rangle \langle \mathbf{p}_0, \mathbf{q}_0|, \quad (1)$$

where S_t is the classical action of the trajectory,

$$S_t(\mathbf{p}_0, \mathbf{q}_0) = \int_0^t \mathbf{p}_{t'} \dot{\mathbf{q}}_{t'} - H(\mathbf{p}_{t'}, \mathbf{p}_{t'}) dt', \quad (2)$$

and C_t is the pre-exponential factor

$$C_t(\mathbf{p}_0, \mathbf{q}_0) = \sqrt{\frac{1}{2^D} \left| \frac{\partial \mathbf{q}_t}{\partial \mathbf{q}_0} + \Gamma^{-1} \frac{\partial \mathbf{p}_t}{\partial \mathbf{p}_0} \Gamma - i\hbar \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \Gamma + \frac{i}{\hbar} \Gamma^{-1} \frac{\partial \mathbf{p}_t}{\partial \mathbf{q}_0} \right|}} \quad (3)$$

of a D -dimensional system. The width matrix Γ of the coherent states $|\mathbf{p}_t, \mathbf{q}_t\rangle$ and $\langle \mathbf{p}_0, \mathbf{q}_0|$ is chosen to be diagonal and to coincide with the harmonic one. The power spectrum of a chosen reference state is

$$\begin{aligned} I_\chi(E) &\equiv \langle \chi | \delta(E - \hat{H}) | \chi \rangle \\ &= \frac{1}{\pi\hbar} \text{Re} \int_0^\infty dt e^{iEt/\hbar} \langle \chi | e^{-i\hat{H}t/\hbar} | \chi \rangle \\ &\equiv \frac{1}{\pi\hbar} \text{Re} \int_0^\infty dt e^{iEt/\hbar} A_\chi(t). \end{aligned} \quad (4)$$

where $A_\chi(t)$ is the autocorrelation of the reference state $|\chi\rangle$,

$$\begin{aligned} A_\chi(t) &\equiv \langle \chi | e^{-i\hat{H}t/\hbar} | \chi \rangle = \frac{1}{(2\pi\hbar)^D} \int d\mathbf{p}_0 \int d\mathbf{q}_0 C_t(\mathbf{p}_0, \mathbf{q}_0) \\ &\quad \times e^{iS_t(\mathbf{p}_0, \mathbf{q}_0)/\hbar} \langle \chi | \mathbf{p}_t, \mathbf{q}_t \rangle \langle \mathbf{p}_0, \mathbf{q}_0 | \chi \rangle. \end{aligned} \quad (5)$$

The reference states are selected as linear combinations of multiple coherent states which have different parities for easier recognition of peaks and enhancement of the signal^{75,76},

$$|\chi_\varepsilon\rangle = \prod_i (|p_{\text{eq}}^i, q_{\text{eq}}^i\rangle + \varepsilon_i |p_{\text{eq}}^i, q_{\text{eq}}^i\rangle), \quad (6)$$

where ε_i is the parity of the i -th mode, $\mathbf{q}_{\text{eq}}$ is the equilibrium position and $p_{\text{eq}}^i = \sqrt{\omega_i}$ is the harmonic zero-point momentum. This approach is denominated multiple coherent semiclassical initial value representation (MC SCIVR).⁷⁵ The phase space integration is done with Monte Carlo sampling of the initial conditions from a Husimi distribution,

$$f(\mathbf{p}_0, \mathbf{q}_0) \propto |\langle \mathbf{p}_0, \mathbf{q}_0 | \mathbf{0}, \mathbf{q}_{\text{eq}} \rangle|^2. \quad (7)$$

From the same distribution of initial conditions, the classical (CL) spectra are obtained from the velocity autocorrelation function or, as reported in the following, from the normal mode momentum $\mathbf{p}$ autocorrelation function,

$$\begin{aligned} I(\omega) &= \int_{-\infty}^{+\infty} e^{i\omega\tau} \langle G_{pp}(\tau) \rangle d\tau \\ G_{pp}(\tau) &= \frac{1}{T} \int_0^T \mathbf{p}(t+\tau) \cdot \mathbf{p}(t) dt, \end{aligned} \quad (8)$$

where T is a sufficiently long time and $\langle \cdot \rangle$ is the average over the trajectories. Both semiclassical and classical autocorrelation functions can be calculated more efficiently with the time-averaging (TA) technique, which adopts Liouville's theorem to obtain a positive-definite spectrum from fewer or shorter trajectories,^{44,45,77–80}

$$\begin{aligned} I_\chi(E) &= \frac{1}{(2\pi\hbar)^{D+1}T} \int d\mathbf{p}_0 \int d\mathbf{q}_0 \left| \int_0^T e^{i[Et+S_t(\mathbf{p}_0, \mathbf{q}_0)+\phi_t(\mathbf{p}_0, \mathbf{q}_0)]/\hbar} \langle \chi | \mathbf{p}_t, \mathbf{q}_t \rangle dt \right|^2, \\ I(\omega) &= \frac{1}{2T} \left\langle \left| \int_0^T e^{i\omega t} \mathbf{p}(t) dt \right|^2 \right\rangle, \end{aligned} \quad (9)$$

where the average in the second equation is over the several trajectories. We also test the cross-correlation filter diagonalization (CCFD) method⁶⁰, which is a semiclassical IVR-based method featuring very efficient extraction of frequencies from short-time propagation.

In addition to the multiple-trajectory methods, it is possible to work also with a single, longer trajectory. We do this for QCT simulations, where a single trajectory is run per each spectral feature to calculate the corresponding frequency of transition from the ground state. More specifically, the QCT spectra are obtained by employing, for each spectral feature, a trajectory starting from

$\mathbf{q}_{\text{eq}}$ with initial momentum $p_i = \sqrt{(2n_i + 1)\omega_i}$, which matches the energy level under harmonic approximation (n_i counts the quanta of excitation in the i -th normal mode and ω_i is its harmonic frequency). The QCT dynamics is performed in the NVE ensemble. Some ZPE leakage is present since harmonic quantization applies only initially and is lost during trajectory propagation. The initial parts of the same single trajectories are employed in single-trajectory time-averaged SC-IVR calculations to verify their accuracy compared to the fully converged time-averaged SC-IVR simulations introduced above.

Finally, for the non-rotating gas-phase water molecule we apply PIMD methods to investigate their performance. Standard methods including CMD, RPMD and TRPMD are tested.^{12,13,20,81,82} The finite-temperature PIMD calculations are carried out using the i-pi software,⁸³ while the zero-temperature limit of CMD can be obtained from the displacement of the ground state under linear perturbation, which helps to calculate the otherwise computationally infeasible limit.⁸⁴

IV. RESULTS AND DISCUSSIONS

To demonstrate the accuracy and the differences between each method, we test them on two 3-dimensional systems. The first one is a model (we call it model I) which has unit mass and an analytic potential function,

$$V(x, y, z) = \frac{0.04x^2 + 0.46y^2 + 0.60z^2}{2} - 0.03xyz + 0.0003x^2y^2z^2. \quad (10)$$

It is composed of a harmonic term, an anharmonic term, and a bounding term. All quantities are in atomic units for this model. The vibrational frequencies calculated by several methods are listed in Table I. For DVR calculations we use harmonic basis up to (25, 10, 8), which corresponds to a maximum energy around 6 a.u. for each mode. The time step for propagation is 0.1 a.u. and the length of trajectories is enough for convergence at 24 a.u. for CCFD, 600 a.u. for MC SCIVR (shortly defined as IVR in Table I), 45000 a.u. for classical (CL) and QCT, and 900 a.u. when applying the time-averaging filter to the classical (CL-TA) and semiclassical (TA for short) calculations. We run 10^6 trajectories for MC SCIVR, 10^5 for classical and time averaged MC SCIVR, and 5×10^5 for CCFD. The convergence with respect to sampling is reached.

In Table I mean absolute error (MAE)-DVR shows how much each approximate method is overall accurate, while MAE-IVR how much methods other than MC SCIVR are approximate compared to the full semiclassical approach. The MAE-DVR values clearly demonstrate that all

Table I. Calculated vibrational frequencies (in a.u.) of model I. The labels IVR and TA refers respectively to primitive and time-averaged MC-SCIVR results. The TA[1] label marks the single-trajectory, time-averaged MC-SCIVR results. QCT calculations are also performed with a single trajectory. Other labels are self-explanatory or defined in the text.

Mode	Harm	DVR	CCFD	IVR	TA	TA[1]	CL	CL-TA	QCT
1 ₁	0.200	0.199	0.198	0.199	0.199	0.200	0.200	0.200	0.200
2 ₁	0.678	0.675	0.674	0.674	0.674	0.675	0.677	0.676	0.675
3 ₁	0.775	0.765	0.764	0.765	0.765	0.764	0.764	0.764	0.762
1 ₁ 2 ₁	0.878	0.880	0.879	0.880	0.880	0.880	0.887	0.887	0.883
1 ₁ 3 ₁	0.975	0.959	0.957	0.959	0.959	0.958	0.956	0.957	0.957
1 ₂ 2 ₁	1.078	1.085	1.084	1.085	1.085	1.084	1.091	1.095	1.087
2 ₁ 3 ₁	1.453	1.429	1.428	1.430	1.430	1.429	1.422	1.424	1.424
1 ₁ 2 ₂	1.556	1.560	1.560	1.560	1.559	1.559	1.570	1.570	1.560
MAE-DVR	0.0082	0.0000	0.0009	0.0004	0.0005	0.0006	0.0046	0.0045	0.0020
MAE-IVR	0.0081	0.0004	0.0009	0.0000	0.0001	0.0008	0.0049	0.0049	0.0023

semiclassical methods are an order of magnitude more accurate than the classical ones. Overall, when one looks at the accuracy of the methods presented, as expected, it turns out that time averaging does not affect accuracy too much, so it only increase numerical efficiency.

The spectra related to the values of the time-averaged classical (labeled as CL-TA Table I) and MC-SCIVR (labeled as TA in Table I) methods are plotted in Figure 2 on the top and bottom panels, respectively. We note here that the classical (CL) label refers to the calculation performed according to Eq. (8) with initial conditions sampled from the Husimi distribution of Eq. (7). In the bottom panel, we annotate the highest peak of each mode with the corresponding harmonic quantum numbers for a clear comparison between time-averaged MC-SCIVR and quantum results. Here, the horizontal position of the end point of each arrow is the exact quantum frequency of that mode index, while the vertical position of the arrow is determined according to

$$h_{abc} = C \max_i \frac{|\langle \psi_{abc}^{\text{DVR}} | \chi_i \rangle|^2}{w_i}, \quad (11)$$

where w_i is the FWHM of the time-averaged MC-SCIVR peak, ψ_{abc}^{DVR} is the DVR vibrational eigenfunction for the state characterized by indexes abc , χ_i is the semiclassical coherent reference

state defined in Eq. (6), and C is a global scaling factor. In this way it is possible to compare, in a mode-by-mode fashion, the calculated time-averaged MC-SCIVR intensity with the one expected from the quantum overlap between the exact DVR wavefunction and the arbitrary reference state $|\chi_i\rangle$ employed in time-averaged MC-SCIVR.

In Figure 2 a very good agreement can be observed between the time-averaged MC-SCIVR calculation and the quantum reference, and it takes much attention to tell the difference between the peak and the arrow positions. This proves the ability of the semiclassical method to capture quantum spectral features. For sake of clarity, we remark that all semiclassical peaks reported in Figure 2 are very accurate and have a quantum counterpart even when the dashed line and arrow have not been drawn to improve the readability of the figure.

Conversely, the classical approach reported on the top panel of Figure 2 returns a much different spectrum. Since the Zero Point Energy (ZPE) value is absent in classical calculations, we have to shift the frequency axis to align its zero with the ZPE value of the absolute eigenvalue scale of the semiclassical and DVR calculations.

Furthermore, we have plotted in addition to the exact frequency values (vertical dashed lines) the Fourier transform of the function

$$G_{pp}^{\text{QM}}(\tau) = \text{Tr} \left[e^{-\hat{H}/kT} e^{i\hat{H}\tau} \hat{\mathbf{p}} e^{-i\hat{H}\tau} \hat{\mathbf{p}} \right], \quad (12)$$

which is the quantum analog of the velocity-velocity autocorrelation in Eq. (8). Eq. (12) is evaluated at $kT/2 = 0.277$, which is the expectation value of the kinetic energy per mode according to the employed Husimi distribution. At such temperature, the quantum average energy is approximately equal to that of the trajectories employed in the CL calculation.

First, we note that the classical spectra do not recover the correct intensities, especially for overtones and combination bands. However, one can see a good match (but worse than in the time averaged MC-SCIVR case) between the trajectory-based calculation and the quantum one in the region with positive frequencies, except for the left-most peak near 0.1. That peak is associated with a hot band transition.

In the negative frequency region, the classical spectra are exactly symmetric both in frequency and intensity with respect to the positive frequency region. This is due to the symmetry of the classical correlation function. If one thinks that this is the emission part of the classical spectrum, then the conclusion is that it deviates significantly from the quantum one, whose intensities are much weaker, since the excited vibrational states are barely populated at $kT/2 = 0.277$.

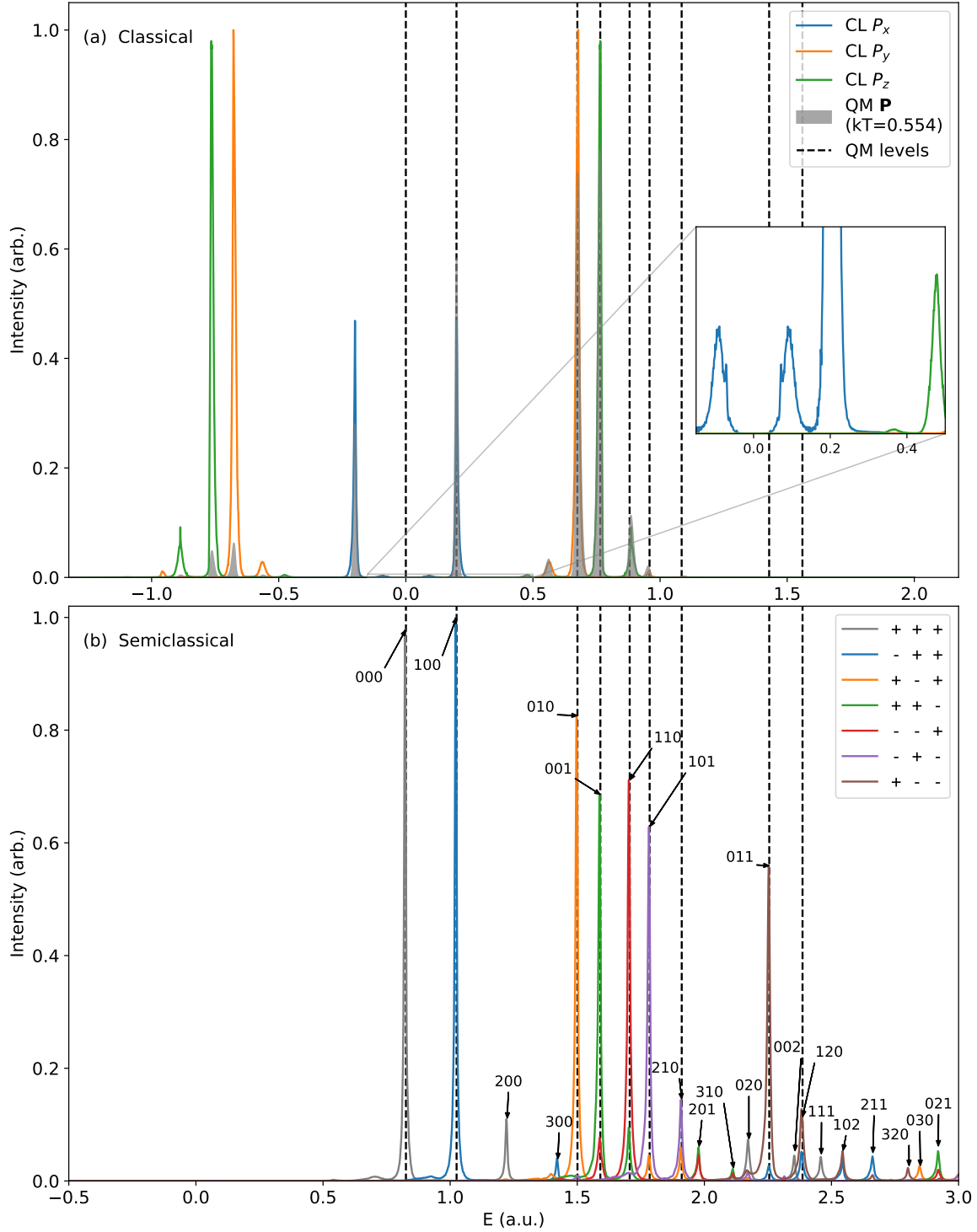


Figure 2. The vibrational power spectra of model I from time averaged (a) classical and (b) MC-SCIVR calculations. The legend on the upper panel denotes the method and the quantity used for the autocorrelation function before the Fourier transform, where $P_{x,y,z}$ refers to the momentum components along the 3 normal-mode directions. The legend on the lower panel shows the parities of the reference states. The inset shows the magnified spectrum in the low-energy region. The vertical dashed lines mark the DVR frequencies in Table I.

We note again that we are using the Husimi distribution for the classical methods rather than the Boltzmann distribution at some physical temperature. This is because if one had employed the Boltzmann distribution at room temperature, the sampling would have fallen into the harmonic part of the potential well. The results would have been harmonic, and even farther away from quantum results, due to the trajectories being trapped in the vicinity of the global minimum.

If one zooms in the energy range just below the main features, small spurious peaks can be observed also in the semiclassical spectra, which indicate that there are still classical features in the method. However, the intensities of these spurious signals can be barely seen by the naked eye and they are always negligible compared to the actual peaks, which, given also their high accuracy in frequency, allow us to insert the semiclassical methods definitely in the group of quantum approaches. Finally, for this first example, the semiclassical methods greatly surpass the classical ones both in terms of accuracy of the frequencies and intensity of the spectra. These conclusions are even more striking when considering the overtones and the combination bands, where the semiclassical peaks are much easier to assign and closer in frequency to the quantum benchmark.

The second investigation we perform concerns the isolated water molecule. Its 3-dimensional PES can be approximated quite reliably and sufficiently for our goals (even if more sophisticated PESs have been constructed) by means of a fourth-order force field,⁸⁵

$$V_w(\mathbf{X}) = \frac{1}{2} (f_{200} \Delta r_{\text{OH}_1}^2 + f_{110} \Delta r_{\text{OH}_1} \Delta r_{\text{OH}_2} + \dots) + \frac{1}{6} (f_{300} \Delta r_{\text{OH}_1}^3 + \dots) + \frac{\dots}{24} \\ = \sum_{2 \leq i+j+k \leq 4} \frac{f_{ijk}}{(i+j+k)!} (r_{\text{OH}_1}(\mathbf{X}) - r_e)^i (r_{\text{OH}_2}(\mathbf{X}) - r_e)^j (\theta_{\text{HOH}}(\mathbf{X}) - \theta_e)^k, \quad (13)$$

where $\mathbf{X}$ is the set of atomic Cartesian coordinates, r_e and θ_e are the equilibrium bond length and bond angle, and i, j, k are the orders of the displacements in the series expansion. After mass scaling and diagonalizing the Hessian matrix at the equilibrium geometry, the Hamiltonian can be expressed in terms of normal-mode coordinates,

$$\hat{H} = \sum_{i=1}^9 \frac{\hat{p}_i^2}{2} + V_w \left(\mathbf{Q}_{\text{eq}} + \sum_{i=1}^9 x_i \mathbf{Q}_i \right), \quad (14)$$

where $\mathbf{Q}_{\text{eq}}$ is the global minimum and $\mathbf{Q}_i$ are unit vectors along the normal-mode directions with descending frequencies. Therefore, x_{1-3} represents the displacements of asymmetric stretching, symmetric stretching and bending modes, while x_{4-9} corresponds to translations and rotations. Here we only keep the former so that the system has merely 3 vibrational degrees of freedom.

The calculated vibrational frequencies are listed in Table II. For DVR calculations we use harmonic basis up to (24, 12, 12), which corresponds to a maximum energy around 0.2 a.u. for each mode. The time step and the length of trajectories are 100 times those of the first model since the energy and frequency scale is completely different. For the sake of clarity, in this case we report frequencies in wavenumbers. At a first glance, the behavior of the methods is similar in the

Table II. Calculated vibrational frequencies (in cm^{-1}) for the isolated and non-rotating water molecule.

Labels are the same as in Table I

Mode	Harm	DVR	CCFD	IVR	TA	CL	TA[1]	QCT	CL-TA
1 ₁	1650.7	1587.4	1582.6	1586.8	1590.0	1565.2	1586.8	1578.0	1567.1
2 ₁	3831.3	3716.3	3711.0	3711.3	3710.4	3704.7	3709.1	3704.7	3702.5
3 ₁	3942.5	3804.1	3808.4	3805.7	3805.7	3796.9	3807.9	3790.3	3796.9
1 ₂	3301.4	3139.5	3130.3	3142.9	3145.1	3083.6	3164.8	3083.6	3091.0
1 ₁ 2 ₁	5482.0	5293.0	5280.8	5291.5	5289.3	5257.5	5306.9	5267.4	5271.8
1 ₁ 3 ₁	5593.2	5351.7	5340.3	5353.0	5353.0	5327.0	5355.2	5295.9	5331.0
2 ₂	7662.6	7418.1	7413.3	7416.0	7414.7	7409.1	7418.2	7409.4	7408.6
2 ₁ 3 ₁	7773.8	7500.8	7499.4	7501.6	7495.0	7493.2	7502.7	7525.8	7494.2
3 ₂	7885.0	7588.8	7578.4	7587.2	7585.1	7580.7	7590.7	7580.6	7578.4
MAE-DVR	191.4	0.0	7.1	2.0	3.7	20.2	6.5	23.7	17.6
MAE-IVR	191.8	2.0	6.3	0.0	2.1	19.8	5.6	23.2	17.2

two investigated cases, except that QCT results are a bit less accurate than CL ones for the water molecule. Once again, when looking at the MAE-DVR values, the semiclassical methods are an order of magnitude more accurate than the classical ones.

We now turn to the PIMD category of methods in order to test their performance on exactly the same ground as the semiclassical ones. The initial configurations are extracted from a long PIMD trajectory with a time step of 10 a.u. and a pile_g thermostat. An initial evolution of 800,000 steps is undertaken for equilibration purposes, and then 10,000 snapshots are recorded at intervals of 20 steps. The 10,000 configurations are then used in all three methods here tested as initial configurations of the dynamics, with the initial velocities re-sampled thermally according to the mass setting of each method.

For CMD simulations we use the partially adiabatic method with a normal-mode frequency of

$\omega = 0.2$ a.u., a time step of 0.1 a.u., and a pile_1 thermostat.

For RPMD we use a time step of 0.5 a.u. no thermostats in the production run. For TRPMD we use a scaling factor of $\lambda = 0.1$ for the pile_1 thermostat, which reduces significantly the spurious resonances at low temperatures.

All trajectories are evolved for 90000 a.u., and the CL-TA method is applied to the centroid momenta to extract the frequencies. The results of methods derived from PIMD are listed in Table III with the temperature and the number of beads marked there. By inspection of MAE values with respect to the DVR results reported in Table III, we can see that the 3 PIMD approaches have quite comparable accuracy, and, upon testing, that it does not improve significantly by changing the number of beads. MAE values are one order of magnitude larger than for SC simulations. Since we have eliminated the rotational degrees of freedom, and the potential has a single global minimum, the curvature problem typical of CMD is expected not to be substantial or not even to arise in this case.

Table III. Calculated vibrational frequencies for the isolated and non-rotating water molecule with PIMD methods. The second row shows the temperatures (in Kelvin) and the third one shows the numbers of beads used in the simulations. The MAE is calculated with respect to DVR results.

Method	CMD						RPMD					TRPMD		
Temp. (K)	0	50	100	300	1000	2000	50	100	300	1000	2000	50	100	300
beads	∞	128	64	16	8	8	128	64	16	8	8	128	64	16
1_1	1588.9	1591.2	1591.2	1595.6	1594.5	1580.2	1591.2	1591.2	1600.0	1593.4	1575.8	1591.2	1591.2	1593.4
2_1	3726.5	3722.3	3724.5	3728.9	3750.8	3728.9	3759.6	3764.0	3753.0	3764.0	3731.1	3759.6	3759.6	3755.2
3_1	3833.1	3827.6	3827.6	3832.0	3847.4	3823.2	3860.6	3860.6	3860.6	3858.4	3827.6	3860.6	3858.4	3858.4
1_2	3177.8	3182.4	3180.2	3185.7	3166.4	3124.1	3204.3	3179.2	3196.7	3173.6	3103.4	3180.2	3180.2	3183.2
$1_1 2_1$	5315.4	5311.3	5313.5	5322.2	5337.6	5298.1	5350.8	5355.2	5350.8	5344.2	5289.3	5353.0	5350.8	5346.4
$1_1 3_1$	5422.0	5417.8	5418.8	5421.0	5410.0	5372.7	5464.1	5451.7	5453.9	5435.0	5354.1	5449.5	5447.4	5446.2
2_2	7453.1	7442.4	7446.8	7453.3	7484.1	7453.3	7517.0	7534.5	7506.0	7512.4	7448.7	7523.6	7521.4	7506.0
$2_1 3_1$	7559.7	7548.6	7549.9	7555.4	7569.7	7545.5	7639.8	7624.5	7602.6	7597.4	7543.3	7620.1	7615.8	7606.2
3_2	7666.3	7655.3	7657.5	7659.6	7682.6	7648.7	7718.9	7723.3	7716.7	7703.5	7653.1	7718.9	7714.5	7714.5
MAE	38.2	33.2	34.5	39.4	49.3	24.5	78.5	76.1	71.2	64.7	25.5	73.0	71.1	67.8
MA shifts	0.0	1.1	1.8	4.8	20.1	15.2	9.7	2.0	4.6	16.1	24.4	2.2	1.8	4.2

For a deeper analysis of these results, we calculate the mean absolute value of the anharmonic shifts. To do this, we define for each calculation a 6-dimensional array named "shifts" whose components are defined in Eq. (15). The MA shifts metric is obtained as the average of the absolute values of the six components. The MA shifts value for DVR is equal to 23.2 and it serves as a

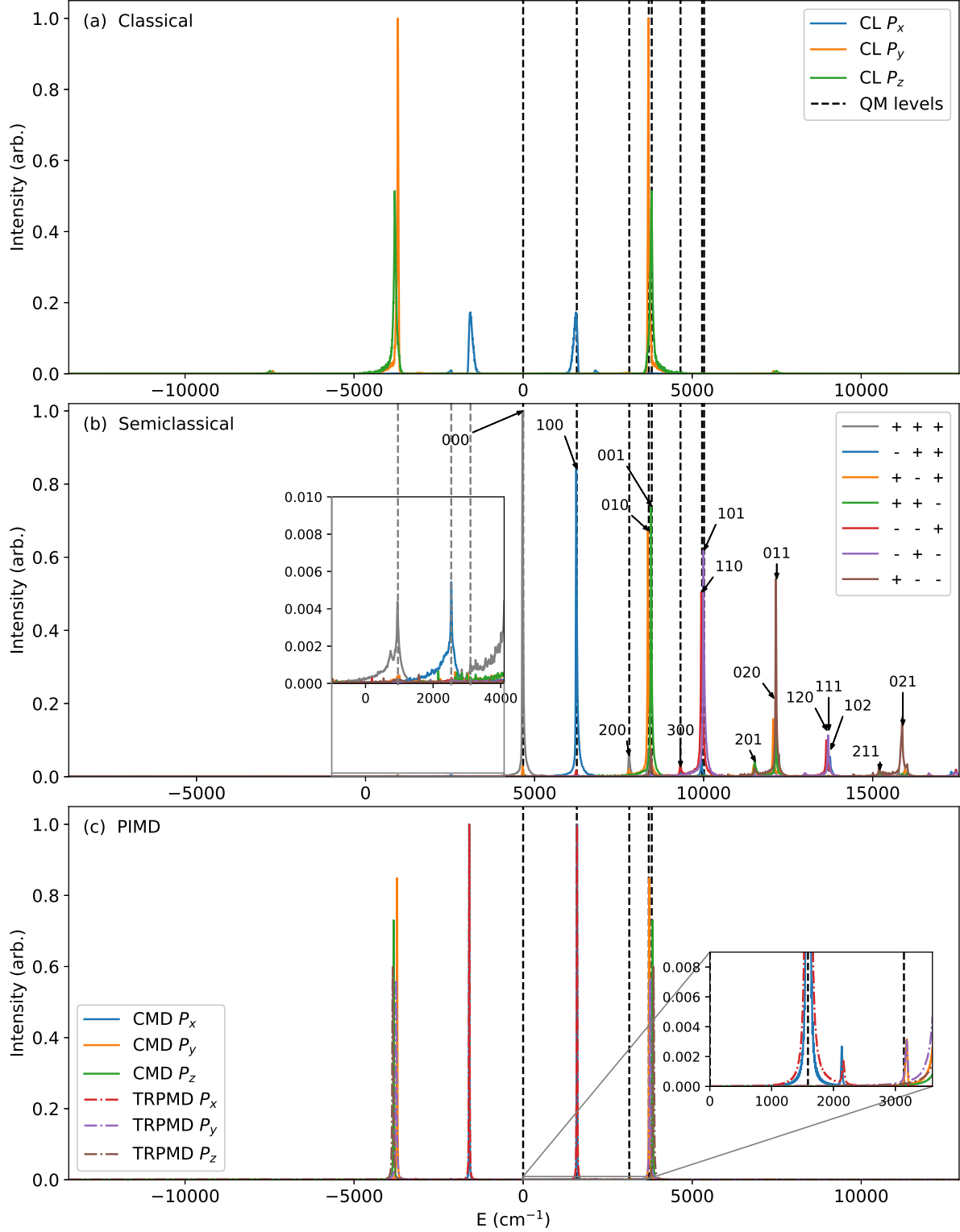


Figure 3. The vibrational power spectra of the isolated water molecule from (a) classical, (b) time-averaged MC-SCIVR and (c) CMD and TRPMD (generically labeled as PIMD) calculations. The legends are in the same convention as in Figure 2. The PIMD results are from simulations at 300K. The three vertical gray dashed lines in panel (b) mark the horizontal positions of the three corresponding peaks in panel (a).

benchmark.

$$\begin{aligned} \text{shifts} = & (\omega_{200} - 2\omega_1, \omega_{110} - \omega_1 - \omega_2, \omega_{101} - \omega_1 - \omega_3, \\ & \omega_{020} - 2\omega_2, \omega_{011} - \omega_2 - \omega_3, \omega_{002} - 2\omega_3) \end{aligned} \quad (15)$$

$$\text{MA shifts} = \frac{1}{6} \sum_i |\text{shifts}_i|$$

In Eq. (15), ω_{abc} refers to the calculated frequency associated with the state labeled as $1_a 2_b 3_c$, while ω_1 , ω_2 , and ω_3 are the fundamental frequencies. We notice that for PIMD methods the MA shifts value keeps small at $\sim 100\text{K}$ and grows towards the correct magnitude only beyond 1000K . However, at such high temperatures, the quantum correction on the potential typical of CMD becomes small and the results tend to the classical ones. So, even if the MA shifts value tends to the exact one, frequency values are not the exact ones but tend to the classical values found at the same temperature (the MAE is still large, pointing to an inaccurate calculation). There exists a competition between the gyration radius of the polymer (which increases at lower temperatures) and the kinetic energy of the centroid (which increases at higher temperatures). They both provide quantum features but are mutually exclusive, which makes it impossible to accurately describe the quantum anharmonicity. Considering the fact that the characteristic vibrational frequencies of most molecular systems are in the $\sim 1000\text{-}4000\text{ cm}^{-1}$ range, i.e. above 1400 K , the choice of a “physical” temperature like 300K falls into the low-temperature regime in which the centroid moves almost harmonically and the anharmonicity in the overtones and combination bands is lost. This can be verified by the extremely sharp peaks in Figure 3, where, for a direct comparison on this system between PIMD methods and the classical and semiclassical ones, the spectra from CL, time-averaged MC SCIVR, CMD and TRPMD are plotted. For the classical case (top panel (a)), individual trajectories contribute to the formation of the signal of each peak at different frequencies with different intensities, which sum up to spectra with some anharmonicity (and also widened peaks). We remark that the classical feature that a single classical trajectory provides spectroscopic signals at the algebraic sum of the corresponding classical fundamental frequencies still holds. However, when a number of classical trajectories is run, as we do here, another classical feature, i.e. the dependence of results on the trajectory energy, is present. Therefore, different trajectories lead to different classical estimates of the fundamental frequencies, so also to different sum-of-frequency signals. This explains the amount of anharmonicity in overtones and combination bands found in the calculations. Once again the classical spectra present the unphysical peaks at negative frequencies, and high-energy sum-of-frequency signals have too low intensities to be detected.

Conversely, the semiclassical time-averaged MC-SCIVR spectrum (middle panel (b)) faithfully reproduces, even when the signals are very close in frequency, the variegated quantum mechanical features of the water molecule vibrational dynamics, which is composed of a series of fundamentals, combination bands, and overtones. If one looked for classical reminiscences in panel (b) in correspondence of the classical negative frequency peaks of panel (a), they would need to zoom two orders of magnitude the intensity scale to see them, as highlighted in the inset. This definitely confirms the quantum genuineness of semiclassical dynamics, where the classical contribution is clearly negligible.

On the bottom panel the results of PIMD simulations (at 300K) are reported. The centroid potential within reach is almost harmonic, and the trajectories return peaks at the same frequencies, which stack up to a very sharp final result. Although the beads are exploring a range similar to the CL case, the centroid average wipes out the necessary information to recover the spectroscopic structure at higher energy than the fundamentals. Therefore, also in PIMD methods fundamental frequencies are combined algebraically, as in the classical case, with just small deviations due to the multi-trajectory simulation. The effect of the centroid average has been notably studied before²⁹, and it was pointed out that at low temperatures CMD and RPMD give insufficient intensity for the overtone and combination bands, while overestimating the difference bands, as shown in the inset in panel (c) of Figure 3. In the quantum spectra, the former are enhanced by ZPE and the latter is suppressed by the Boltzmann factor. Instead, in PIMD results all peaks behave classically. For example, the intensities of the two peaks in the inset, i.e. the stretching-bending difference band near 2100 cm^{-1} and the bending overtone at 3200 cm^{-1} are comparable, but only the last one is physical. This issue could be misleading when simulating and assigning larger molecules than water with PIMD.

Eventually, to provide a comprehensive picture of the simulations performed, we plot for comparison in Figure 4 the MAE of all these methods on the 3 fundamentals and the MAE on shifts on 6 combination bands and overtones according to the following equation

$$\text{MAE shifts}^j = \frac{1}{6} \sum_i \left| \text{shifts}_i^j - \text{shifts}_i^{\text{DVR}} \right|, \quad (16)$$

where j indicates the specific calculation to which the MAE shifts value is referred to.

The semiclassical methods have clearly lower errors than other methods in both aspects. The drastic reduction to a single classical trajectory slightly deteriorates this accuracy only for the combination and the overtone estimates. However, this is still overall more accurate than the

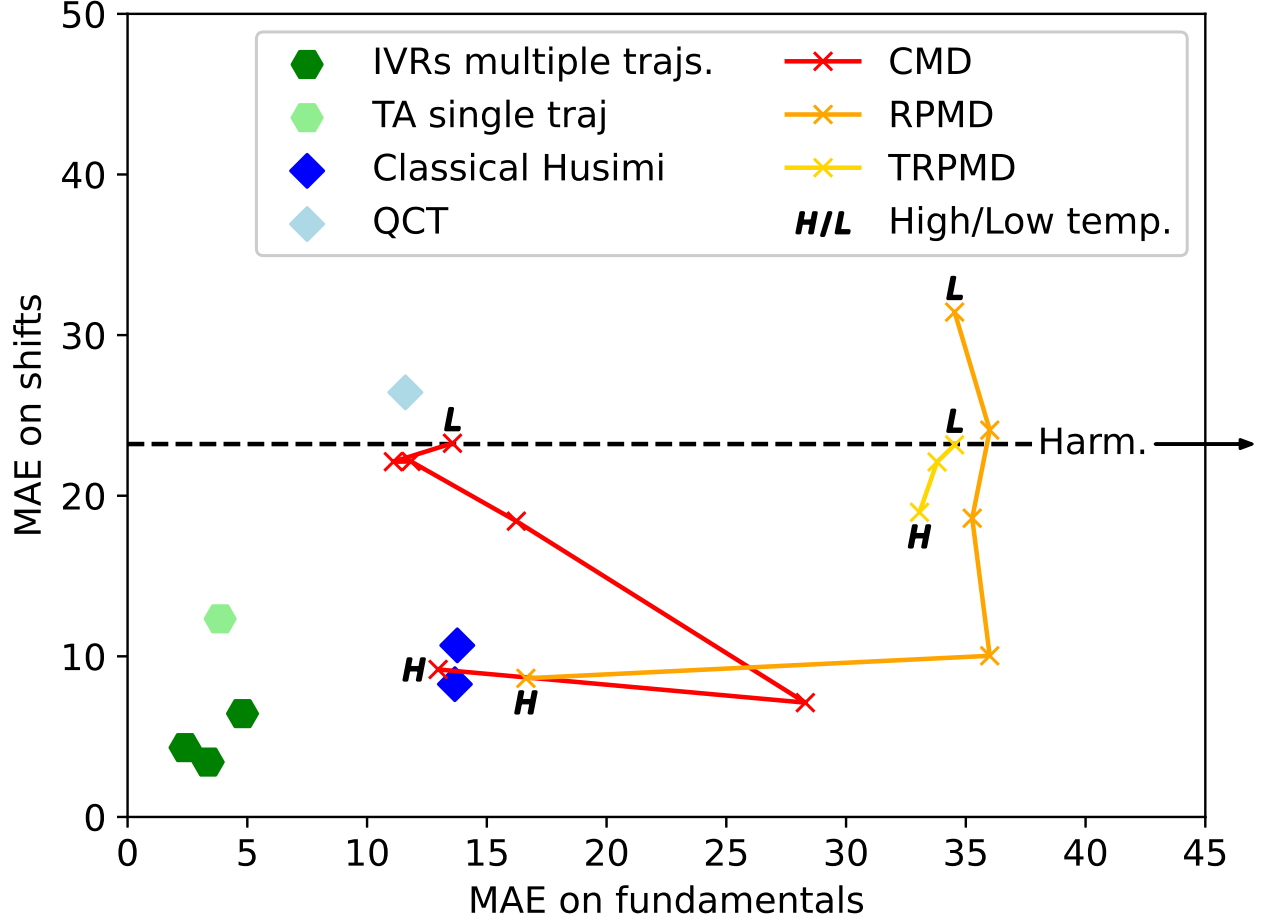


Figure 4. The mean absolute error of different methods on the 3 fundamental frequencies and the 6 shifts of overtones and combination bands. The harmonic approximation is at (105.6, 23.2) which is far away on the right. The arrow and the dashed line mark its vertical position. The PIMD data come from Table III and are connected by increasing temperature.

classical and PIMD simulations, with the QCT method is less accurate on the higher vibrational levels.

As far as PIMD methods are concerned, the errors tend to the classical ones at high temperatures, while at low temperatures they give different and less accurate estimates to the fundamentals and they all become harmonic for the higher levels. We conclude from this bidimensional plot that there does not exist some “optimal” temperature at which the PIMD methods behave better than the classical ones.

V. SUMMARY AND CONCLUSIONS

In this paper we have applied several different classical-trajectory-based methods to calculate the vibrational power spectra of a model system and the water molecule to test the quantum mechanical accuracy of each method. Classical simulations are known for returning energy-dependent frequencies and to provide signals at high frequency which are algebraic combinations of the fundamental frequencies,³⁸ as also detailed in a recent preprint.⁸⁶

Our results show that the methods based on the SC-IVR propagator give the most accurate results and capture the vast majority of the quantum features, while the classical and PIMD methods experience issues due to spurious peaks and lost anharmonicity. Judging from the accuracy and the structure of peaks, we conclude that the semiclassical methods have a quantum character, while PIMD ones are closer to classical methods. This is particularly striking when one considers the combination bands and the overtones. In this case, (PI)MD simulations at physical temperatures are unreliable and give nearly harmonic spectral features.

We notice that spectral features like combination bands and overtones are purely quantum ones. Therefore, while in the case of semiclassical IVR calculations these terms are properly adopted, we notice that, in our opinion, it is inappropriate to use them in the case of classical or PIMD-based simulations. These latter methods provide algebraic combinations of the fundamental frequencies with some small deviations due to the use of several trajectories. However, they miss most of the anharmonicity of overtones and combination bands, which is related to effects like real-time coherence and quantum interference. They would miss it also on fundamentals in the case of strong quantum effects. Among the methods explored in this paper, only SCIVR ones are able to reproduce these quantum effects, while QCT or PIMD approaches include just the anharmonicity related to the quantum statistics, for instance the anharmonicity due to the zero-point energy. Finally, we remark that the semiclassical propagators employed in this work are complete and not linearized. The linearized version of SCIVR cannot account for real-time coherences.

One criticism which is often moved against semiclassical methods is that they suffer from ZPE leakage during the time evolution. This has been demonstrated to be false in the case of a converged semiclassical calculation, i.e. based on many trajectories.⁸⁷ In the case of single-trajectory SC calculations, a certain amount of ZPE leakage is unavoidable but the issue is alleviated by the short propagation time. The results for single-trajectory SC methods presented here evidently support this claim.

One could notice that PIMD methods like those investigated here are able to account also for the absorption intensities providing a direct comparison to experimental IR spectra. Specifically, it has been shown that by means of appropriate corrections or sampling they can describe absorption intensities quite accurately.^{28,29} Furthermore, PIMD methods are often employed when dealing with solvated or condensed-phase systems. Non-linearized semiclassical approaches are able to provide accurate absorption intensities too, and they have been adopted to study large dimensional solvated systems.^{49,88} Several SC methods have been developed in our group to account for absorption intensities. In a first effort the IR spectrum was recollected upon determination of SC wavefunctions as linear combination of a vibrational harmonic basis set.⁵³ In a second method we demonstrated how to take advantage of the power spectrum lineshape to move to the absorption lineshape.⁵⁴ Finally, very recently, we developed a new SC approach able to provide accurate IR spectra based on the time average technique and capable, in principle, of application to systems of any dimensionality.^{55,56} All these methods, besides providing an accurate absorption intensity, preserve the quantum accuracy in frequency calculations demonstrated in this paper.

Clearly, we could not test all existing classical-trajectory-based methods here, and we limited ourselves to the most popular ones. However, we have pointed out some features that allows one to distinguish between a prevalently quantum approach and a classical one. These features can be employed to determine the quantum character of a newly developed method. In a quantum approach, combination bands and overtones are anharmonic and the MAE shifts metric can provide information about the quantum or classical nature of the method. Power spectra obtained from classical methods present spectral features also at negative frequencies and with intensities which poorly approximate those obtained from a quantum calculation. Furthermore, the presence of unphysical difference bands is typical of classical methods. The classical difference bands are sometimes used as a classical approximation (again missing anharmonicity) to the quantum hot bands. However, when one looks at a power spectrum, it is the vibrational density of states which is reproduced, and quantum mechanically there is generally no eigenvalue expected at the difference of two other eigenvalues (unless it happens by accident). So, the presence of difference bands in a power spectrum calculations is a clue of the classical character of the calculation.

We conclude by stating that semiclassical methods provide a safe, robust and accurately approximate quantum framework for vibrational spectral analysis. Accurate calculations of this type can be performed also on large dimensional systems.

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REFERENCES

- ¹M. Feit, J. Fleck Jr, and A. Steiger, *J. Comput. Phys.* **47**, 412 (1982).
- ²D. T. Colbert and W. H. Miller, *J. Chem. Phys.* **96**, 1982 (1992).
- ³V. Barone, M. Biczysko, J. Bloino, M. Borkowska-Panek, I. Carnimeo, and P. Panek, *Int. J. Quantum Chem.* **112**, 2185 (2011).
- ⁴S. Carter, J. M. Bowman, and A. R. Sharma, in *American Institute of Physics Conference Series*, Vol. 1504 (2012) pp. 465–466.
- ⁵J. M. Bowman, T. Carrington, and H.-D. Meyer, *Molecular Physics* **106**, 2145 (2008).
- ⁶H.-D. Meyer, U. Manthe, and L. S. Cederbaum, *Chem. Phys. Lett.* **165**, 73 (1990).
- ⁷Y. Wang and J. M. Bowman, *J. Chem. Phys.* **134**, 154510 (2011).
- ⁸H. Wang and M. Thoss, *J. Chem. Phys.* **119**, 1289 (2003).
- ⁹E. J. Heller, *Acc. Chem. Res.* **14**, 368 (1981).
- ¹⁰W. H. Miller, *J. Phys. Chem. A* **105**, 2942 (2001).
- ¹¹J. Cao and G. A. Voth, *J. Chem. Phys.* **104**, 273 (1996).
- ¹²I. R. Craig and D. E. Manolopoulos, *J. Chem. Phys.* **121**, 3368 (2004).
- ¹³J. Cao and G. A. Voth, *J. Chem. Phys.* **100**, 5093 (1994).
- ¹⁴M. Parrinello and A. Rahman, *J. Chem. Phys.* **80**, 860 (1984).
- ¹⁵J. Cao and G. A. Voth, *J. Chem. Phys.* **100**, 5106 (1994).
- ¹⁶A. Witt, S. D. Ivanov, M. Shiga, H. Forbert, and D. Marx, *J. Chem. Phys.* **130**, 194510 (2009).
- ¹⁷G. Trenins, M. J. Willatt, and S. C. Althorpe, *J. Chem. Phys.* **151** (2019).
- ¹⁸T. Fletcher, A. Zhu, J. E. Lawrence, and D. E. Manolopoulos, *J. Chem. Phys.* **155**, 231101 (2021).
- ¹⁹I. R. Craig and D. E. Manolopoulos, *J. Chem. Phys.* **123**, 034102 (2005).
- ²⁰M. Rossi, M. Ceriotti, and D. E. Manolopoulos, *J. Chem. Phys.* **140**, 234116 (2014).
- ²¹M. Rossi, V. Kapil, and M. Ceriotti, arXiv preprint arXiv:1704.05099 (2017).

- ²²F. Musil, I. Zaporozhets, F. Noé, C. Clementi, and V. Kapil, *The Journal of Chemical Physics* **157** (2022).
- ²³M. Shiga and A. Nakayama, *Chem. Phys. Lett.* **451**, 175 (2008).
- ²⁴A. Kaczmarek, M. Shiga, and D. Marx, *J. Phys. Chem. A* **113**, 1985 (2009).
- ²⁵M. Arandhara and S. G. Ramesh, *Phys. Chem. Chem. Phys.* **26**, 19529 (2024).
- ²⁶Q. Yu and J. M. Bowman, *J. Phys. Chem. A* **123**, 1399 (2019).
- ²⁷A. Nandi, R. Conte, P. Pandey, P. L. Houston, C. Qu, Q. Yu, and J. M. Bowman, *J. Chem. Theory Comput.* **21**, 5208 (2025).
- ²⁸S. C. Althorpe, *Annu. Rev. Phys. Chem.* **75**, 397 (2024).
- ²⁹T. Plé, S. Huppert, F. Finocchi, P. Depondt, and S. Bonella, *J. Chem. Phys.* **155**, 104108 (2021).
- ³⁰R. L. Benson and S. C. Althorpe, *J. Chem. Phys.* **155** (2021).
- ³¹T. E. Markland and M. Ceriotti, *Nat. Rev. Chem.* **2**, 0109 (2018).
- ³²E. A. Solovev, *Zh. Eksp. Teor. Fiz.* **75**, 1261 (1978).
- ³³L. Bonnet and J. Rayez, *Chem. Phys. Lett.* **277**, 183 (1997).
- ³⁴G. Amati, M. A. C. Saller, A. Kelly, and J. O. Richardson, *J. Chem. Phys.* **157**, 234103 (2022).
- ³⁵C. Qu and J. M. Bowman, *J. Phys. Chem. Lett.* **9**, 2604 (2018).
- ³⁶R. Conte, C. Aieta, G. Botti, M. Cazzaniga, M. Gandolfi, C. Lanzi, G. Mandelli, D. Moscato, and M. Ceotto, *Th. Chem. Acc.* **142**, 53 (2023).
- ³⁷D. Barbiero, G. Bertaina, M. Ceotto, and R. Conte, *J. Phys. Chem. A* **127**, 6213 (2023).
- ³⁸L. D. Landau and E. M. Lifshitz, *Mechanics* (Elsevier, 1982).
- ³⁹R. Conte, M. Gandolfi, D. Moscato, C. Aieta, S. Valtolina, and M. Ceotto, *J. Comput. Chem.* **46**, e70118 (2025).
- ⁴⁰F. Grossmann and A. L. Xavier, *Phys. Lett. A* **243**, 243 (1998).
- ⁴¹W. H. Miller, *Mol. Phys.* **100**, 397 (2002).
- ⁴²E. Pollak, “The Semiclassical Initial Value Series Representation of the Quantum Propagator,” in *Quantum Dynamics of Complex Molecular Systems* (Springer Berlin Heidelberg, Berlin, Heidelberg, 2007) pp. 259–271.
- ⁴³M. F. Herman and E. Kluk, *Chem. Phys.* **91**, 27 (1984).
- ⁴⁴A. L. Kaledin and W. H. Miller, *J. Chem. Phys.* **118**, 7174 (2003).
- ⁴⁵A. L. Kaledin and W. H. Miller, *J. Chem. Phys.* **119**, 3078 (2003).
- ⁴⁶M. Ceotto, S. Atahan, S. Shim, G. F. Tantardini, and A. Aspuru-Guzik, *Phys. Chem. Chem. Phys.* **11**, 3861 (2009).

- ⁴⁷J. Tatchen and E. Pollak, J. Chem. Phys. **130**, 041103 (2009).
- ⁴⁸M. Ceotto, G. Di Liberto, and R. Conte, Phys. Rev. Lett. **119**, 010401 (2017).
- ⁴⁹D. Moscato, G. Mandelli, M. Bondanza, F. Lipparini, R. Conte, B. Mennucci, and M. Ceotto, J. Am. Chem. Soc. **146**, 8179 (2024).
- ⁵⁰M. Wehrle, M. Sulc, and J. Vaníček, J. Chem. Phys. **140**, 244114 (2014).
- ⁵¹J. Vaníček and T. Begušić, “Ab initio semiclassical evaluation of vibrationally resolved electronic spectra with thawed gaussians,” in *Molecular Spectroscopy and Quantum Dynamics* (Elsevier, 2021) pp. 199–229.
- ⁵²D. Moscato, M. Gandolfi, and M. Ceotto, J. Chem. Phys. **162**, 234108 (2025).
- ⁵³M. Micciarelli, R. Conte, J. Suarez, and M. Ceotto, J. Chem. Phys. **149**, 064115 (2018).
- ⁵⁴M. Micciarelli, F. Gabas, R. Conte, and M. Ceotto, J. Chem. Phys. **150**, 184113 (2019).
- ⁵⁵C. Lanzi, C. Aieta, M. Ceotto, and R. Conte, J. Chem. Phys. **160**, 214107 (2024).
- ⁵⁶C. Lanzi, C. Aieta, M. Ceotto, and R. Conte, J. Chem. Phys. **163**, 024122 (2025).
- ⁵⁷C. Aieta, M. Micciarelli, G. Bertaina, and M. Ceotto, Nat. Comm. **11**, 4384 (2020).
- ⁵⁸C. Aieta, G. Bertaina, M. Micciarelli, and M. Ceotto, J. Chem. Phys. **153**, 214117 (2020).
- ⁵⁹J.-X. Zeng and X.-Z. Li, Comput. Mater. Today **6**, 100032 (2025).
- ⁶⁰J.-X. Zeng, S. Yang, Y.-C. Zhu, W. Fang, L. Jiang, E.-G. Wang, D. H. Zhang, and X.-Z. Li, J. Phys. Chem. A **127**, 2902 (2023).
- ⁶¹G. Mandelli, C. Aieta, and M. Ceotto, J. Chem. Theory Comput. **18**, 623 (2022).
- ⁶²F. Angiolari, G. Mandelli, S. Huppert, C. Aieta, and R. Spezia, Chem. Eur. J. **30**, e202401000 (2024).
- ⁶³T. Zimmermann and J. Vaníček, J. Chem. Phys. **141**, 134102 (2014).
- ⁶⁴G. Stock and M. Thoss, Phys. Rev. Lett. **78**, 578 (1997).
- ⁶⁵N. Ananth, C. Venkataraman, and W. H. Miller, J. Chem. Phys. **127**, 084114 (2007).
- ⁶⁶S. Malpathak, M. S. Church, and N. Ananth, J. Phys. Chem. A **126**, 6359 (2022).
- ⁶⁷M. S. Church and N. Ananth, J. Chem. Phys. **151**, 134109 (2019).
- ⁶⁸J.-X. Zeng and X.-Z. Li, AIP Advances **14**, 035023 (2024).
- ⁶⁹R. Conte, C. Aieta, M. Cazzaniga, and M. Ceotto, J. Phys. Chem. Lett. **15**, 7566 (2024).
- ⁷⁰R. Conte, G. Mandelli, G. Botti, D. Moscato, C. Lanzi, M. Cazzaniga, C. Aieta, and M. Ceotto, Chem. Sci. **16**, 20 (2025).
- ⁷¹A. Nandi, G. Laude, S. S. Khire, N. D. Gurav, C. Qu, R. Conte, Q. Yu, S. Li, P. L. Houston, S. R. Gadre, *et al.*, J. Am. Chem. Soc. **145**, 9655 (2023).

- ⁷²R. Conte, A. Aspuru-Guzik, and M. Ceotto, *J. Phys. Chem. Lett.* **4**, 3407 (2013).
- ⁷³Y.-C. Zhu, S. Yang, J.-X. Zeng, W. Fang, L. Jiang, D. H. Zhang, and X.-Z. Li, *J. Am. Chem. Soc.* **144**, 21356 (2022).
- ⁷⁴J. C. Light and T. Carrington Jr., “Discrete-variable representations and their utilization,” in *Adv. Chem. Phys.* (John Wiley & Sons, Ltd, 2000) pp. 263–310.
- ⁷⁵M. Ceotto, S. Atahan, G. F. Tantardini, and A. Aspuru-Guzik, *J. Chem. Phys.* **130**, 234113 (2009).
- ⁷⁶M. Ceotto, G. F. Tantardini, and A. Aspuru-Guzik, *J. Chem. Phys.* **135**, 214108 (2011).
- ⁷⁷D. Noid, M. Koszykowski, and R. Marcus, *J. Chem. Phys.* **67**, 404 (1977).
- ⁷⁸M. Koszykowski, D. Noid, and R. Marcus, *J. Phys. Chem.* **86**, 2113 (1982).
- ⁷⁹M. Buchholz, F. Grossmann, and M. Ceotto, *J. Chem. Phys.* **148**, 114107 (2018).
- ⁸⁰A. Rognoni, R. Conte, and M. Ceotto, *J. Chem. Phys.* **154**, 094106 (2021).
- ⁸¹G. A. Voth, “Path-integral centroid methods in quantum statistical mechanics and dynamics,” in *Adv. Chem. Phys.* (John Wiley & Sons, Ltd, 1996) pp. 135–218.
- ⁸²S. Jang and G. A. Voth, *J. Chem. Phys.* **111**, 2357 (1999).
- ⁸³Y. Litman, V. Kapil, Y. M. Y. Feldman, D. Tisi, T. Begušić, K. Fidanyan, G. Fraux, J. Higer, M. Kellner, T. E. Li, E. S. Pós, E. Stocco, G. Trenins, B. Hirshberg, M. Rossi, and M. Ceriotti, *J. Chem. Phys.* **161**, 062505 (2024).
- ⁸⁴R. Ramírez and T. López-Ciudad, *J. Chem. Phys.* **111**, 3339 (1999).
- ⁸⁵S. Dressler and W. Thiel, *Chem. Phys. Lett.* **273**, 71 (1997).
- ⁸⁶G. Botti, ChemRxiv (2025), 10.26434/chemrxiv-2025-zhckl.
- ⁸⁷M. Buchholz, E. Fallacara, F. Gottwald, M. Ceotto, F. Grossmann, and S. D. Ivanov, *Chem. Phys.* **515**, 231 (2018).
- ⁸⁸D. Moscato, F. Gabas, R. Conte, and M. Ceotto, *J. Biomol. Struct. Dyn.* **41**, 14248 (2023).