Quantum algorithm for calculating molecular vibronic spectra

Nicolas P. D. Sawaya*1 and Joonsuk Huh12,3

1Intel Labs, Santa Clara, California, USA
2Department of Chemistry, Sungkyunkwan University, Republic of Korea
3SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Republic of Korea

Abstract

We present a quantum algorithm for efficiently calculating the molecular vibronic spectrum of a molecule, using the quantum circuit model. Both zero- and finite-temperature algorithms are described. The algorithm outputs the Franck-Condon profile with the inclusion of Duschinsky effects, a common chemical problem that scales combinatorially on a classical computer. Previous quantum computation proposals for simulating the same problem have focused on the use of a boson sampling device, while ours instead is based partly on the quantum phase estimation (QPE) algorithm. Our approach provides several potential advantages over previous quantum-based proposals for this problem: after measuring the transition energy, the quantum state is preserved for further analysis; vibrational anharmonicity (which is classically very difficult to simulate) is naturally taken into account with polynomial overhead; we potentially circumvent the difficulty of accurately detecting large photon numbers in boson sampling devices; and known error correction methods are applicable. Future quantum computers running this algorithm will be able to accelerate the characterization and design of molecules and materials with specific light-absorption and energy transfer properties, and our algorithmic strategy for calculating full spectra will be applicable to other problems of interest in chemistry and condensed matter physics.

1 Introduction

Calculating the absorption spectrum of molecules is a common and important problem in theoretical chemistry, as it aids both the interpretation of experimental spectra and the a priori design of molecules with particular optical properties prior to performing a costly laboratory synthesis. Theoretical studies on vibronic structures are equally important for fundamental scientific studies on interactions between electronic and vibrational degrees of freedom [1]. An accurate absorption spectrum calculation in the visible/ultraviolet region involves the calculation of Franck-Condon factors between a molecule’s ground and excited electronic potential energy surfaces (PESs), while also modeling the change of coordinates between the two PESs. The widespread use of mature software that estimates vibronic spectra is one indication of this problem’s importance in chemistry [2, 3, 4, 5].

In this work, we propose an efficient quantum algorithm for calculating molecular vibronic spectra, within the standard quantum circuit model. A quantum algorithm to solve this problem, for implementation on a boson sampling machine [6, 7], was previously proposed and demonstrated experimentally [8, 9], but to our knowledge no one has previously developed a distinct algorithm for the universal circuit model of quantum computation, nor one that can efficiently include vibrational anharmonic effects. We are also aware of unpublished work that studies the connection between quantum phase estimation and sampling problems [10]. We note that, because it is used to efficiently converge a spectral function and not to draw samples from an exponentially large

*nicolas.sawaya@intel.com
†joonsukhuh@gmail.com
space, we do not classify the algorithm of this work as a sampling algorithm. Below, we discuss
the several possible advantages of our approach over the bosonic approach.

Other related previous work includes quantum algorithms for calculating single Franck-Condon
factors \[11, 12\] or low-lying vibrational states \[13\], algorithms for simulating vibrational dynamics
\[12, 14\], and a experimental photonics implementation \[14\] that simulated several processes related
to molecular vibrations in molecules. Though these four works simulate vibrational effects, they
do not address the problem of efficiently solving the full vibronic spectrum despite the presence of
an exponential number of relevant vibrational states, which is the focus of this work.

Many quantum algorithms have been proposed for practical problems in chemistry, chiefly for
solving the fermionic problem of determining the lowest-energy configuration of \(N_e\) electrons, given
the presence of a set of clamped atomic nuclei \[15, 15, 17, 18, 20, 21, 22, 23\]. However, for
many chemical problems of practical interest, solving the ground-state electronic structure problem
is insufficient. To calculate exact vibronic spectra, for instance, an often combinatorially scaling
classical algorithm must be implemented after the electronic structure problem has been solved
for many nuclear positions \[24, 25, 26, 27, 28, 6\].

We note that calculating the vibronic spectrum is also distinct from solving for the low-level
excited-state electronic spectrum of a molecule, which is sometimes referred to as calculating
the molecule’s spectrum, and for which several quantum algorithmic approaches have been proposed
\[29, 30, 31, 32\]. This electronic-only spectrum involves calculating excited states for clamped nuclei.
On the other hand, a vibronic spectrum resolves the structure arising from the vibrational quanta,
leading to the correct light absorption spectrum of a molecule. A sufficiently accurate photon
absorption spectrum can rarely be calculated without including vibrational effects. As noted,
another conceptual difference is that, while just a few (expensive to calculate) low-lying excited
states are relevant in electronic spectra, calculations of vibronic spectra can involve appreciable
contributions from a exponentially large number of eigenstates.

2 Theory

2.1 Problem description

In this work we consider high accuracy calculations of the vibronic spectrum between two molecular
electronic states, each represented by a PES that is a function of the nuclear coordinates. One needs
to account for the fact that the shapes of the two hyper-surfaces may be stretched, rotated, and
shifted arbitrarily. For many molecules, the hypersurfaces may be anharmonic. In this approach,
for now assuming that the two PESs are harmonic (i.e. parabolic along all normal coordinates),
the relationship between the two PES is determined by the Duschinsky transformation \[33\],

\[
\vec{q}' = S\vec{q} + \vec{d}
\]

where \(\vec{q}'\) and \(\vec{q}\) are the vibrational normal coordinates for the ground and excited states, re-
spectively, the Duschinsky matrix \(S\) is unitary, and \(\vec{d}\) is a displacement vector. The number of
vibrational modes \(M\) is equal to \(3N_{\text{atoms}} - 6(5)\) in nonlinear (linear) molecules, where \(N_{\text{atoms}}\) is
the number of atoms in the molecule.

A vibronic spectrum calculation consists of determining the Franck-Condon profile, defined as

\[
\text{FCP}(\omega) = \sum_{\{f_i\}} |\langle 0 | f_i \rangle |^2 \delta(\omega - \omega_i),
\]

where \(\omega\) is the transition energy, \(0\) is the vibrational vacuum state of the initial PES (i.e. of
the initial electronic state), and \(|f_i\rangle\) is the \(i\)th eigenstate of the final PES with energy \(\omega_i\). In
practice, the function is desired to some precision \(\Delta\omega\), such that the \(\delta\) function can be replaced
with a finite-width “energy bin.” For a given transition, the quantity \(|\langle 0 | f_i \rangle|^2\) is referred to as that
transition’s Franck-Condon factor (FCF). In the finite-temperature case, instead of just \(0\), we
would consider thermally weighted contributions from all appreciably populated initial vibrational
states.

Fig. \[1\] gives a one-dimensional schematic of the vibronic problem, where the two parabolas
denote PESs of different electronic states. The vertical arrows denote the transitions, and the
FCFs are determined by the overlaps of the vibrational wavefunctions shown. For the general
Figure 1: A schematic of the vibronic problem. (a) The one-dimensional case, corresponding to a diatomic molecule, for which the only vibrational degree of freedom is the distance between the two atoms. The lower and upper parabolas represent the potential energy surfaces (PESs) of the ground and first excited electronic states, respectively. The vibronic spectrum problem consists of calculating overlaps, called Franck-Condon factors (FCFs), between vibrational wavefunctions, producing a plot of intensity versus energy. In the zero-temperature case shown here, the initial state is $|0\rangle$, the ground vibrational state of the ground electronic PES. The thickness of the transition arrows vary because the FCF factors for those transitions differ.

(b) The multidimensional analogue, where the normal mode coordinates of each PES are used. In the harmonic case, the relationship between the two hypersurfaces can be described by a transformation that includes displacement, squeezing, and rotation operations. For many molecules, the vibronic problem is computationally hard on a classical computer, partly because spectral contributions from exponentially many vibrational Fock states can be present.

In principle there can be spectral contributions from exponentially many overlaps $\langle 0000...|n_1 n_2 n_3 n_4...\rangle_B$, where $|n_1 n_2 n_3 n_4...\rangle_B$ can take on any combination of values ($A$ and $B$ denote the two PESs). And though in real molecules a subset of the transitions will have negligible intensity, it is not possible to know a priori which these are. In practice there is an upper limit to the value of each integer particle number eigenvalue $n_i$ [25], as the intensity of each mode’s sequence of intensities follows the rapidly decaying Poisson distribution as $n_i$ increases [34].

### 2.2 Vibrational Hamiltonians

In the photonics-based vibronic boson sampling (VBS) algorithm [6], a change of basis is used to transform between the two PESs. This is done with the help of the Doktorov transformation [35], which splits the procedure performed on the initial state into a four-Gaussian-operation process of displacement, squeezing, rotation, and a second squeezing.

Instead of this direct basis change approach, our work is based on constructing a Hamiltonian that encodes the relationship between the two PESs. This provides multiple advantages, outlined in Section 3.

We denote dimensionless position and momentum operators as $\hat{q}_{sk}$ and $\hat{p}_{sk}$ respectively, where $s$ labels the potential energy surface ($s \in \{A, B\}$ in this work) and $k$ labels the vibrational mode. These follow standard definitions $\hat{q}_{sk} = (\hat{a}_{sk} + \hat{a}_{sk}^\dagger)/\sqrt{2}$ and $\hat{p}_{sk} = (\hat{a}_{sk} - \hat{a}_{sk}^\dagger)/i\sqrt{2}$, where $a_{sk}^\dagger$ and $a_{sk}$ are vibrational creation and annihilations operators. We use the notation $\vec{\cdot}$ to denote standard vectors as well as vectors of operators, such that e.g. $\vec{q}_A = [\hat{q}_{A0}, ..., \hat{q}_{AM}]^T$.

The purpose of our classical pre-processing procedure is to express the vibrational Hamiltonian for PES $B$ in terms of $\{q_{sk}, p_{sk}\}$, by making the following transformations: $\{\vec{q}_A, \vec{p}_A\} \rightarrow \{\vec{Q}_A, \vec{P}_A\}$.
\[
\{\vec{Q}_s, \vec{P}_s\} \rightarrow \{\vec{q}_s, \vec{p}_s\}, \text{ where } \vec{Q}_s \text{ and } \vec{P}_s \text{ are respectively the mass-weighted position and momentum operators of PES } s. \text{ The full transformations are}
\]

\[
\vec{q}_s = \Omega_s \mathbf{S} \Omega_A^{-1} \vec{q}_A + \Omega_B \vec{d}
\]

(3)

\[
\vec{p}_s = \Omega_s^{-1} \mathbf{S} \Omega_A \vec{p}_A,
\]

(4)

where

\[
\Omega_s = \text{diag}(\omega_{s1}, ..., \omega_{sM})^{1/2}
\]

(5)

and \{\omega_{sk}\} are the scalar harmonic oscillator frequencies of PES \(s\). A more pedagogical explanation as well as an alternate formulation are given in Appendix A. In some works \cite{36, 28, 6} a displacement parameter vector denoted \(\delta\) is given instead of \(d\), with the relationship \(\delta_{sk} = d_{sk} \sqrt{\omega_{sk}/\hbar}\).

Finally, the vibrational Hamiltonian of PES \(B\) is expressed in a standard form as

\[
H_B = \frac{1}{2} \sum_k \omega_{Bk}(\vec{q}_{Bk}^2 + \vec{p}_{Bk}^2).
\]

(6)

As it is important for the finite temperature procedure, we also write down the vibrational Hamiltonians for PES \(A\) and \(B\) respectively in standard form as:

\[
H_A = \sum_i \omega_{Ai}(\hat{a}^\dagger_i \hat{a}_i + \frac{1}{2})
\]

(7)

and

\[
H_B = \sum_i \omega_{Bi}(\hat{b}^\dagger_i \hat{b}_i + \frac{1}{2})
\]

(8)

where \{\hat{a}^\dagger_i\} and \{\hat{b}^\dagger_i\} are respectively creation operators for QHO states of PES \(A\) and \(B\). Hence the high-level building block of our algorithm is a truncated creation operator,

\[
\hat{a}^\dagger_i = \sum_{l=1}^{l_{max}} \sqrt{l} |l - 1\rangle
\]

(9)

where \(l\) denotes a vibrational energy level and the imposed cutoff \(l_{max}\) denotes the maximum level. Mappings to qubits (including integer-to-bit encodings) are discussed in Appendix B and errors are analyzed in Section 4.

Though this work primarily considers the harmonic case in order to introduce the methodology, it the largest quantum advantage will arise from modeling anharmonic effects. Such effects are especially relevant in molecules of insufficient rigidity or for electronic transitions that cause substantial structural rearrangement. FCF profiles from anharmonicity are vastly more costly to approximate than the harmonic case using classical algorithms \cite{37, 26, 38, 28}; we are not aware of molecules larger than \(\sim 10\) atoms that have been simulated. We emphasize that arbitrary anharmonicity can be straightforwardly included in the quantum algorithm by adding higher-order potential energy terms to the unperturbed (e.g. Eq. 6) vibrational Hamiltonian \(H_0\):

\[
H = H_0 + \lambda_{ijk} \vec{q}_i \vec{q}_j \vec{q}_k + ...
\]

(10)

The ease with which one includes anharmonic effects is an advantage over the VBS algorithm \cite{6, 7}.

3 Algorithm description

3.1 Zero temperature

Now that we have outlined the required classical steps, we describe our quantum algorithm for determining the Franck-Condon profile. Unlike most quantum computational approaches to Hamiltonian simulation \cite{39, 40, 41, 21}, which aim to find the energy of a particular quantum state, the purpose of our algorithm is to construct a histogram from many measurements.
As the procedure makes use of the quantum phase estimation (QPE) algorithm \cite{42,43,44}, we use two quantum registers. The first register $S$ stores a representation of the vibrational state, and the second register $E$ is used to read out the energy (strictly speaking, it outputs the phase, from which the energy is trivially obtained). First, all qubits in register $S$ are initialized to $|0\rangle^{\otimes N_q} \equiv |0\rangle$, where $N_q$ is the number of qubits in the register. $|0\rangle$ denotes the ground state of $H_A$. A simple but key observation is that $|0\rangle$ can be written in the eigenbasis of $H_B$, such that

$$|0\rangle = \sum_i c_i |\psi_i\rangle$$

(11)

where $\{|\psi_i\rangle\}$ are eigenstates of $H_B$ and coefficients $c_i$ are not a priori known.

One then runs QPE using the Hamiltonian $H_B$ (i.e. implementing $U = e^{-i\tau H_B}$ for arbitrary $\tau$), with register $E$ storing the eigenvalues. Many quantum algorithms have been developed for Hamiltonian simulation \cite{39,45,46,47,48,49,50,51,52}, any of which can be used in conjunction with the algorithm’s QPE step. Convincing numerical evidence suggests that Trotterization \cite{39,45} is likely to be the most viable option for early quantum devices \cite{51}. Computational scaling is discussed in Appendix D.

We define $\epsilon_i$ as the eigenenergy of $|\psi_i\rangle$, and $\tilde{\epsilon}_i$ as its approximation, where an arbitrarily high precision can be achieved by increasing the number of qubits in register $E$. Degeneracies in $\tilde{\epsilon}$ will be ubiquitous, and we define the subspace of states with approximate energy $\tilde{\epsilon}_j$ as $D_j = \{|\psi_{j1}\rangle,...,|\psi_{jK_j}\rangle\}$, where $K_j$ is the degeneracy in $\tilde{\epsilon}_j$. Measuring register $E$ yields $\tilde{\epsilon}_j$ with probability $\sum_{k \in D_j} |c_k|^2$. Hence—and this is the key insight—values $\tilde{\epsilon}_j$ are outputted with a probability exactly in proportion to the Franck-Condon factors of Eq. 2. The measurements then produce a histogram that yields the vibronic spectrum. The procedure is depicted in Fig. 2, where for the zero-temperature case one may disregard register $I$ and gate $\bar{V}(\beta)$. See Appendix C for a step-by-step outline of the algorithm.

We note four potential benefits of this algorithm over the VBS algorithm \cite{5,7}. First, the quantum state in register $S$ is preserved for further analysis, while in VBS the final state is destroyed. After measurement, the state stored in $S$ is a superposition of many states with approximate energy $\tilde{\epsilon}_j$. One possibility is to use a SWAP test \cite{53} between register $S$’s state and a state stored in an ancilla register, which determines the overlap between the two states. One could also use the state in register $S$ to estimate the expectation value with respect to an arbitrary operator of interest, or estimate the transition intensity from that particular state to yet another electronic state’s PES (e.g. to study excited-state absorption).

The second potential benefit is that, as stated above, anharmonic effects are easily included in our framework. Third, accurate photon number detection for higher photon counts is a major difficulty in experimental quantum optics \cite{8,9}; it may be that a scaled-up universal quantum computer is built before quantum optical detectors improve satisfactorily, though this is difficult to predict and the opposite may end up happening. Fourth, while there are error correction methods for universal quantum computers, we do not know of such methods for boson sampling devices.

### 3.2 Finite temperature

Even at room temperature, the spectrum of a molecule is substantially different from its zero temperature spectrum \cite{54}, necessitating methods for including finite temperature effects. These effects can be included by appending additional steps before and after the zero temperature algorithm, following the work of Huh and Yung \cite{7}. The idea is to begin with a purification of the second register $S$ in $\text{PES}$, it is necessary to introduce the scalar function $E_A(n)$, defined as the energy of a Fock state in $\text{PES}$ $A$:

$$E_A(n) = E_A([n_0,...,n_M]) = \sum_i \omega_i (n_i + \frac{1}{2})$$

(12)

where $n_i$ is the occupation number of the $i$th mode.

First we add an additional register, $I$ (for ‘initial state’), of ancilla qubits. Registers $I$ and $S$ must have the same size, and we prepare a pure state $|\Psi_{IS}\rangle = \sum |\phi\rangle_I |\psi\rangle_S$ such that $\rho_B = Tr_I(|\Psi_{IS}\rangle \langle \Psi_{IS}|)$ is the desired Gibbs thermal state in the initial $\text{PES}$. Before running the QPE
In the zero-temperature case, only registers $S$ and $E$ are used, with gate $\hat{V}(\beta)$ ignored. Register $S$, which encodes the vibrational state, is initialized to $\ket{0} \otimes N_0$, the vibrational ground state of the ground electronic PES. Running the quantum phase estimation (QPE) algorithm with registers $S$ and $E$ yields quantum state $\sum_i c_i \ket{\psi_i}_S \ket{\tilde{\varepsilon}_i}_E$, where a key insight is that $|c_i|^2$ are proportional to the Franck-Condon Factors (FCFs) for each eigenstate $i$ of vibrational Hamiltonian $H_B$. $\text{QFT}^{-1}$ denotes the inverse quantum Fourier transform, $U$ is a unitary exponential of $H_B$, and $H$ is the Hadamard gate. A measurement on register $E$ then yields some value $\tilde{\varepsilon}_j$, proportional to the measured phase. $\tilde{\varepsilon}_j$ is the energy of the transition to an arbitrary precision. One then produces a histogram from many runs of the quantum circuit. Note that the quantum state $A_j \sum_{k \in D_j} c_k \ket{\psi_k}$ is preserved in register $S$ for further analysis. In the finite temperature case, a register $I$ (encoding the initial state) is added, and the constant-depth operation $\hat{V}(\beta)$ is implemented. After QPE, one then measures both registers $E$ and $I$, with the contribution to the histogram being $\tilde{\varepsilon}_j$ minus the energy of the initial Fock state $\ket{n_I}$.

Routine, we need the pure state
\begin{equation}
\ket{\Psi_{IS}} = \sum_n \kappa_n \ket{n}_I \otimes \ket{n}_S = \sum_n \sqrt{\kappa_n \rho_{th}} \ket{n}_I \otimes \ket{n}_S
\end{equation}

where $\ket{n} = |n_0, ..., n_M\rangle$. To prepare $\ket{\Psi_{IS}} = \hat{V}(\beta)\ket{0}_I \ket{0}_S$, one implements the unitary operator
\begin{equation}
\hat{V}(\beta) = \bigotimes_i^M \exp(i (\alpha_i^\dagger a_i^\dagger - \alpha_i a_i)/2)
\end{equation}

where $a_i^\dagger$ and $a_i$ are ladder operators for the $i$th vibrational mode of register $I$. The inverse temperature is $\beta = 1/k_BT$, where $k_B$ is the Boltzman constant and $T$ is temperature. Angle $\theta_i$ is defined by $\tanh(\theta_i/2) = \exp(-\beta \hbar \omega_i/2) = \sqrt{\pi_i/(\pi_i + 1)}$ and $\pi_i$ is the mean quantum number for mode $i$ [53 7].

After this initial state preparation step, the remainder of the algorithm proceeds as before, but with the following additional elements. After the QPE circuit is applied using registers $S$ and $E$ as before, registers $I$ and $E$ are both measured. The measured state $\ket{n_I}$ in register $I$ effectively acts as a label, indicating the vibrational eigenstate (Fock state) in the initial PES from which the measured transition occurred. Finally, the contribution to the vibronic spectrum is $\tilde{\varepsilon}_i - E_A(\ket{n_I})$, instead of just $\varepsilon_i$, because the measured transition “began” in vibrational state $\ket{n_I}$ in the $A$ basis.

An outline of the procedure is given in Appendix C and a quantum circuit diagram is shown in Fig. 2.

### 4 Truncation errors

The least-studied source of error in our algorithm is due to an insufficiently large QHO cutoff $L_{max}$, i.e. the highest allowed vibrational level in the encoding. It is especially important to study this source of error, both qualitatively and quantitatively, because the standard classical algorithms for calculating FCFs [24 26 3 28] do not directly simulate the vibrational Hamiltonian in the basis of PES $A$, and hence do not suffer from this type of truncation error. As stated previously, one of several possible advantages of our algorithm over VBS may be that an error-corrected quantum
Figure 3: Theoretically exact (solid) and approximate (dotted) vibronic spectra for SO$_2$, H$_2$O, D$_2$O, and NO$_2$. After histogram construction, each peak was broadened by a Gaussian of arbitrary width 100 cm$^{-1}$. Inaccuracies in the approximate spectra are due to an insufficiently large cutoff $L_{\text{max}}$ when representing the larger-$\delta$ vibrational mode, where $L_{\text{max}}$ is the highest energy level in the truncated ladder operator used to represent the mode. The approximate spectra are included in order to show the main qualitative effect of the truncation error, namely that lower energy peaks converge rapidly, while higher energy peaks are blue-shifted. Insight into this type of error is valuable because such truncation errors are not present in standard classical vibronic algorithms.

In the approximate data, the L$_1$ errors and cutoffs $L_{\text{max}}$ are {0.208, 0.231, 0.228, 0.241} and {10, 45, 57, 61} respectively for SO$_2$, H$_2$O, D$_2$O, and NO$_2$. 
computer could be developed before hardware issues associated with multi-photon detection in quantum optical devices can be perfected; this is another justification for focusing on the effects of cutoff errors. We note that an analysis of Suzuki-Trotter errors will be dependent on the QHO mapping chosen and is left to future work.

We chose four three-atom molecules—sulfur dioxide (SO$_2$), water (H$_2$O), deuterated water (D$_2$O; D ≡ $^2$H), and nitrogen dioxide (NO$_2$)—and simulated their vibronic spectra using one electronic transition from each. For the former three molecules, we are effectively calculating the photoelectron spectrum, as we are considering an ionization process. The latter three were chosen explicitly because they have unusually high phonon occupation numbers for a vibronic transition, making them good candidates for a study on $L_{\text{max}}$ requirements. Additionally, because of the experimental difficulty in photon counting for higher occupation numbers, in the future it is possible that these molecules might be more easily simulated on a universal quantum computer than a photonic device [8, 9]. The electronic transitions are SO$_2 ^{-} \rightarrow$SO$_2 ^{+}$e$^-$ [56], H$_2$O(D$_2$O)$\rightarrow$H$_2$O$^+(D_2O^+) + e^-$ [57], and NO$_2$’s ground to excited state transition $^2$B$_2 ^1 \rightarrow ^2$A$_1 ^1$ [58].

Fig. 3 shows both the theoretically exact vibronic spectra (solid line) and an approximate spectrum (dotted line) for each molecule. Simulation details are given in Appendix F. These plots show the qualitative behavior of truncation errors. The approximate spectra were arbitrarily chosen such that the $L_{1}$ error (ε$_{L_{1}}$) lies between 0.2 and 0.25.

Qualitatively, the effect of a too-low cutoff number is to preferentially blue shift the higher energy peaks. This numerical artifact results from the fact that the $L_{\text{max}}$ cutoff effectively introduces anharmonicity to the problem; operators constructed from exact (infinite) ladder operators will not have the same spectrum as those constructed from truncated operators. As $L_{\text{max}}$ is increased, the low energy peaks are converged much sooner than the high energy peaks are. For instance, in the approximate H$_2$O spectrum shown, there is an effectively perfect match below $\sim 15,000$ cm$^{-1}$, but the blue-shift errors become even larger than $\sim 100$ cm$^{-1}$ for eigenvalues above $\sim 23,000$ cm$^{-1}$.

Being aware of this consistent qualitative error behavior can provide guidance when interpreting results from an implementation of our quantum algorithm. Additional results on convergence with increasing $L_{\text{max}}$ are shown in Appendix F.

This truncation error does not appear in the standard classical methods for calculating FCFs [24, 26, 3, 28], since for those methods a ladder operator hamiltonian is not directly simulated. When using a future large-scale quantum computer, one would need to run the algorithm with increasing $L_{\text{max}}$ until the spectrum is converged.

5 Conclusions

We introduced a quantum algorithm for calculating the vibronic spectrum of a molecule to arbitrary precision. We highlight four potential advantages over the previously proposed vibronic boson sampling (VBS) algorithm. First, measuring the eigenenergy in our algorithm leaves the quantum state preserved, allowing for further analysis that would not be possible in VBS. Second, anharmonic effects (whose inclusion is very costly classically but often chemically relevant) can be easily included in our approach. Third, our use of a universal quantum computer might circumvent the challenge of detecting large photon numbers in quantum optics. Fourth, while error correction algorithms are well-developed in universal quantum computers, error correction methods are not known for boson sampling devices. We expect the most significant quantum advantage over classical algorithms to be seen when including anharmonic effects, which are notoriously difficult to calculate in classical vibronic algorithms. The algorithm can be extended in the future to include non-Condon effects, vibronic simulations in molecular aggregates and clusters, and simulations of crystalline vibrational processes in frequency space. Further, complex dynamical phenomena could be studied, including resonance Raman scattering, internal conversion, and intersystem crossing. This work’s general strategy, of calculating the energy distribution outputted from quantum phase estimation to arbitrary precision, may be applied to other spectral problems in chemistry and condensed matter physics.

Acknowledgements

J.H. acknowledges support by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF-
2015R1A6A3A04059773). The authors thank Gian Giacomo Guerreschi for helpful suggestions on
the manuscript.

References

[1] Gad Fischer. *Vibronic Coupling: The Interaction Between the Electronic and Nuclear Motions*. Academic Press, London, 1984.

[2] R. Berger, C. Fischer, and M. Klessinger. Calculation of the vibronic fine structure in electronic spectra at higher temperatures. 1. Benzene and pyrazine. *The Journal of Physical Chemistry A*, 102(36):7157–7167, Sep 1998.

[3] Vincenzo Barone, Julüen Bloino, Malgorzata Biczysko, and Fabrizio Santoro. Fully integrated approach to compute vibrationally resolved optical spectra: From small molecules to macrosystems. *Journal of Chemical Theory and Computation*, 5(3):540–554, Mar 2009.

[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and J. D. Fox. Gaussian 16 Revision B.01, 2016. Gaussian Inc. Wallingford CT.

[5] H.-J. Werner, P. J. Knowles, G. Kuizia, F. R. Manby, M. Schütz, P. Celani, W. Gyoerffy, D. Kats, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamansdar, T. B. Adler, R. D. Amos, S. J. Bennie, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbiny, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, S. J. R. Lee, Y. Liu, A. W. Lloyd, Q. Ma, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, T. F. Miller III, M. E. Mura, A. Nicklass, D. P. O’Neill, P. Palmieri, D. Peng, K. Pfüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, and M. Welborn. Molpro, Version 2018.2, A package of ab initio programs, 2018.

[6] Joonsuk Huh, Gian Giacomo Guerreschi, Borja Peropadre, Jarrod R. Mcclean, and Alán Aspuru-Guzik. Boson sampling for molecular vibronic spectra. *Nature Photonics*, 9(9):615–620, 2015.

[7] Joonsuk Huh and Man-Hong Yung. Vibronic boson sampling: Generalized gaussian boson sampling for molecular vibronic spectra at finite temperature. *Scientific Reports*, 7(1), Aug 2017.

[8] William R Clements, Jelmer J Renema, Andreas Eckstein, Antonio A Valido, Adriana Lita, Thomas Gerrits, Sae Woo Nam, W Steven Koltzhammer, Joonsuk Huh, and Ian A Walmsley. Approximating vibronic spectroscopy with imperfect quantum optics. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 51(24):245503, Nov 2018.

[9] Yangchao Shen, Yao Lu, Kuan Zhang, Junhua Zhang, Shuining Zhang, Joonsuk Huh, and Kihwan Kim. Quantum optical emulation of molecular vibronic spectroscopy using a trapped-ion device. *Chemical Science*, 9(4):836–840, 2018.

[10] Raul Garcia-Patron. Personal communication, 2018.

[11] Sharad Joshi, Abhishek Shukla, Hemant Katiyar, Anirban Hazra, and T. S. Mahesh. Estimating Franck-Condon factors using an NMR quantum processor. *Phys. Rev. A*, 90:022303, Aug 2014.
[12] Sam McArdle, Alex Mayorov, Xiao Shan, Simon Benjamin, and Xiao Yuan. Quantum computation of molecular vibrations, 2018. arXiv:1811.04069.

[13] Alexander Tepelkin, Brian K. Kendrick, and Dmitri Babikov. Calculation of molecular vibrational spectra on a quantum annealer, 2018. arXiv:1812.05211.

[14] Chris Sparrow, Enrique Martín-López, Nicola Maraviglia, Alex Neville, Christopher Harrold, Jacques Carolan, Yogesh N. Joglekar, Toshihiko Hashimoto, Nobuyuki Matsuda, Jeremy L. O’Brien, David P. Tew, and Anthony Laing. Simulating the vibrational quantum dynamics of molecules using photonics. Nature, 557(7707):660–667, May 2018.

[15] Jonathan Olson, Yudong Cao, Jonathan Romero, Peter Johnson, Pierre-Luc Dallaire-Demers, Nicolas Sawaya, Prineha Narang, Ian Kivlichan, Michael Wasielewski, and Alán Aspuru-Guzik. Quantum information and computation for chemistry (NSF workshop report), 2017. arXiv:1706.05413.

[16] Yudong Cao, Jonathan Romero, Jonathan P. Olson, Matthias Degroote, Peter D. Johnson, Mária Kieferová, Ian D. Kivlichan, Tim Menke, Borja Peropadre, Nicolas P. D. Sawaya, Sukin Sim, Libor Veis, and Alán Aspuru-Guzik. Quantum chemistry in the age of quantum computing, 2018. arXiv:1812.09976.

[17] Sabre Kais (Editor). Quantum Information and Computation for Chemistry (Advances in Chemical Physics). Wiley, 2014.

[18] Alan Aspuru-Guzik, Anthony D. Dutoi, Peter J. Love, and Martin Head-Gordon. Simulated quantum computation of molecular energies. Science, 309(5741):1704–1707, Sep 2005.

[19] James D. Whitfield, Jacob Biamonte, and Alán Aspuru-Guzik. Simulation of electronic structure Hamiltonians using quantum computers. Molecular Physics, 109(5):735–750, Mar 2011.

[20] Alberto Peruzzo, Jarrod McClean, Peter Shadbolt, Man-Hong Yung, Xiao-Qi Zhou, Peter J. Love, Alán Aspuru-Guzik, and Jeremy L. O’Brien. A variational eigenvalue solver on a photonic quantum processor. Nature Communications, 5(1), Jul 2014.

[21] Jarrod R McClean, Jonathan Romero, Ryan Babbush, and Alán Aspuru-Guzik. The theory of variational hybrid quantum-classical algorithms. New Journal of Physics, 18(2):023023, 2016.

[22] Ryan Babbush, Nathan Wiebe, Jarrod McClean, James McClain, Hartmut Neven, and Garnet Kin-Lic Chan. Low-depth quantum simulation of materials. Phys. Rev. X, 8:011044, Mar 2018.

[23] Markus Reiher, Nathan Wiebe, Krysta M. Svore, Dave Wecker, and Matthias Troyer. Elucidating reaction mechanisms on quantum computers. Proceedings of the National Academy of Sciences, 114(29):7555–7560, Jul 2017.

[24] Peder Thusgaard Ruhoff and Mark A. Ratner. Algorithms for computing Franck–Condon overlap integrals. International Journal of Quantum Chemistry, 77(1):383–392, 2000.

[25] Raymond Kan. From moments of sum to moments of product. Journal of Multivariate Analysis, 99(3):542–554, Mar 2008.

[26] H.-C. Jankowiak, J. L. Stuber, and R. Berger. Vibronic transitions in large molecular systems: Rigorous prescreening conditions for Franck-Condon factors. The Journal of Chemical Physics, 127(23):234101, Dec 2007.

[27] Fabrizio Santoro, Alessandro Lami, Roberto Improta, and Vincenzo Barone. Effective method to compute vibrationally resolved optical spectra of large molecules at finite temperature in the gas phase and in solution. The Journal of Chemical Physics, 126(18):184102, May 2007.

[28] Joonsuk Huh. Unified Description of Vibronic Transitions with Coherent States. PhD thesis, Goethe Univ. Frankfurt, 2011.

[29] Hefeng Wang, Sabre Kais, Alán Aspuru-Guzik, and Mark R. Hoffmann. Quantum algorithm for obtaining the energy spectrum of molecular systems. Physical Chemistry Chemical Physics, 10(35):5388, 2008.
[30] Jarrod R. McClean, Mollie E. Kimchi-Schwartz, Jonathan Carter, and Wibe A. de Jong. Hybrid quantum-classical hierarchy for mitigation of decoherence and determination of excited states. Physical Review A, 95(4), Apr 2017.

[31] R. Santagati, J. Wang, A.A. Gentile, S. Paesani, N. Wiebe, J. McClean, D. Bonneau, J.W. Silverstone, S. Morley-Short, P.J. Shadbolt, D.P. Tew, X. Zhou, J. L. O’Brien, and M. G. Thompson. Finding excited states of physical Hamiltonians on a silicon quantum photonic device. In Frontiers in Optics 2017. OSA, 2017.

[32] J.I. Colless, V. V. Ramasesh, D. Dahlen, M. S. Blok, M. E. Kimchi-Schwartz, J. R. McClean, J. Carter, W. A. de Jong, and I. Siddiqi. Computation of molecular spectra on a quantum processor with an error-resilient algorithm. Physical Review X, 8(1), Feb 2018.

[33] F. Duschinsky. The importance of the electron spectrum in multiatomic molecules. concerning the Franck–Condon principle. Acta Physicochim. URSS., 7:551–566, 1937.

[34] Volkhard May and Oliver Kuhn. Charge and Energy Transfer Dynamics in Molecular Systems. John Wiley and Sons, 2008.

[35] E.V. Doktorov, I.A. Malkin, and V.I. Manko. Dynamical symmetry of vibronic transitions in polyatomic molecules and the Franck-Condon principle. Journal of Molecular Spectroscopy, 64(2):302–326, Feb 1977.

[36] Per-Åke Malmqvist and Niclas Forsberg. Franck-Condon factors for multidimensional harmonic oscillators. Chemical Physics, 228(1-3):227–240, Mar 1998.

[37] Josep M. Luis, Bernard Kirtman, and Ove Christiansen. A variational approach for calculating Franck-Condon factors including mode-mode anharmonic coupling. The Journal of Chemical Physics, 125(15):154114, Oct 2006.

[38] Joonsuk Huh, Michael Neff, Guntram Rauhut, and Robert Berger. Franck-Condon profiles in photodetachment-photoelectron spectra of and based on vibrational configuration interaction wavefunctions. Molecular Physics, 108(3-4):409–423, Feb 2010.

[39] S. Lloyd. Universal quantum simulators. Science, 273(5278):1073–1078, Aug 1996.

[40] R. Somma, G. Ortiz, J. E. Gubernatis, E. Knill, and R. Laflamme. Simulating physical phenomena by quantum networks. Physical Review A, 65(4), Apr 2002.

[41] Rolando D. Somma, Gerardo Ortiz, Emanuel H. Knill, and James Gubernatis. Quantum simulations of physics problems, 2003.

[42] A. Kitaev. Quantum computations: algorithms and error correction. Russian Mathematical Surveys, 52(6):1191–1249, Dec 1997.

[43] Daniel S. Abrams and Seth Lloyd. Simulation of many-body fermi systems on a universal quantum computer. Phys. Rev. Lett., 79:2586–2589, Sep 1997.

[44] Dominic W. Berry, Graeme Ahokas, Richard Cleve, and Barry C. Sanders. Quantum algorithm providing exponential speed increase for finding eigenvalues and eigenvectors. Phys. Rev. Lett., 83:5162–5165, Dec 1999.

[45] Dominic W. Berry, Andrew M. Childs. Black-box Hamiltonian simulation and unitary implementation. Quantum Info. Comput., 12(1-2):29–62, January 2012.

[46] Dominic W. Berry, Andrew M. Childs, Richard Cleve, Robin Kothari, and Rolando D. Somma. Exponential improvement in precision for simulating sparse Hamiltonians. In Proceedings of the 46th Annual ACM Symposium on Theory of Computing - STOC 14. ACM Press, 2014.

[47] Dominic W. Berry, Andrew M. Childs, Richard Cleve, Robin Kothari, and Rolando D. Somma. Simulating Hamiltonian dynamics with a truncated Taylor series. Physical Review Letters, 114(9), Mar 2015.
A Hamiltonian construction

Here we give a more pedagogical summary of the Hamiltonian construction summarized in Section 2.2. The procedure involves these three transformations: \( \{ \vec{q}_A, \vec{p}_A \} \rightarrow \{ \vec{Q}_A, \vec{P}_A \} \rightarrow \{ \vec{Q}_B, \vec{P}_B \} \rightarrow \{ \vec{q}_B, \vec{p}_B \} \). Mass-weighted position and moment operators, \( \vec{Q}_s \) and \( \vec{P}_s \) respectively, are

\[
\vec{Q}_s = \Omega_s^{-1} \vec{q}_s
\]

\[
\vec{P}_s = \Omega_s \vec{p}_s
\]

with the \( M \times M \) matrix...
\[ \Omega_s = \text{diag}([\omega_{s1}, ..., \omega_{sM}]) \]  

where \{\omega_{sk}\} are the scalar harmonic oscillator frequencies of normal mode \( k \) on PES \( s \).

Because the Duschinsky transformation is not dimensionless, its direct application is inappropriate only to the vector of mass-weighted position and momentum operators:

\[ \tilde{Q}_B = S\tilde{Q}_A + d \]  
\[ \tilde{P}_B = S\tilde{P}_A. \]

Then the following are used to obtain the final dimensionless operators:

\[ \tilde{q}_B = \Omega_B\tilde{Q}_B \]  
\[ \tilde{p}_B = \Omega_B^{-1}\tilde{P}_B. \]

Combining these steps leads to equations \( 3 \) and \( 4 \).

An alternative route for expressing \( H_B \) in terms of the operators of PES \( A \) (the one taken in references \( 36, 6 \)) first transforms the ladder operators directly using the transformation

\[ \tilde{b}^\dagger = \frac{1}{2}(J - (J^t)^{-1})\tilde{a}^\dagger + \frac{1}{2}(J + (J^t)^{-1})\tilde{a}^\dagger + \frac{1}{\sqrt{2}}\delta \]

where \{\tilde{a}^\dagger\} and \{\tilde{b}^\dagger\} are respectively creation operators for states of PES \( A \) and \( B \), and \( J = \Omega_B\Omega_A^{-1} \). Eq. \( 22 \) is then used to construct Eq. \( \ref{eq:qcircuit} \).

It is important to note that there are oftentimes only one or a few electronic transitions that are relevant for a chemist, often the transition between the ground and first excited state. The potential energy surface (PES) of two electronic states must be calculated beforehand, with one of several electronic structure algorithms. For most organic molecules, density functional theory calculations (which roughly speaking often have cubic scaling in the number of electrons) typically provide electronic PESs that are accurate enough to produce vibronic spectra that match experiment. For other classes of molecules, substantially more expensive methods may be required for obtaining the PES \( 59 \).

### B QHO to qubit mappings

To implement the algorithm within the standard quantum circuit model, one requires a mapping of quantum harmonic oscillators to a set of qubits. Several mappings from bosonic DOFs to qubits have been proposed in the past \( 60, 61, 62, 12 \). Here, we outline what are perhaps the two most straightforward mappings for the QHO, which in this work we will call the standard binary and unary mappings. It is worth mentioning that we would not expect an approach based on the Holstein-Primakoff transformation \( 63 \) to be particularly promising, since it would require first mapping a bosonic system to a spin-\( s \)-system, after which one would need the additional step of mapping to spin-half qubits using Clebsch-Gordan coefficients.

Here we summarize how one would convert the operators of \( H_B \) into quantum gates of the standard circuit model. The mappings are used to represent operators \( \tilde{a}_i^\dagger \) and \( \tilde{a}_i \) in qubits.

The **standard binary** mapping represents each level as a binary number such that any integer \( n \) is represented as \( \sum_{p=0}^{p_{\text{max}}-1} x_p 2^p \), where \( p \) is the qubit id. The state \([0], |1\rangle, |2\rangle, |3\rangle, |4\rangle, \ldots \rangle^T \) is isomorphic to \([|000\rangle, |001\rangle, |010\rangle, |011\rangle, |100\rangle, \ldots \rangle^T \), where a mapping to 3 qubits was used in this example. Hence each QHO eigenlevel \( \ell \) is a string of 0s and 1s. Any single-mode operator used in constructing Hamiltonian \( H_B \) can be expressed in terms of elements \([|l\rangle \langle l'|angle^T \), where \( l \) and \( l' \) denote two vibrational levels. In qubit space this leads to operators of the form \([x_0 \ldots x_{p_{\text{max}}}] \langle x_0' \ldots x_{p_{\text{max}}}'| \) where each \( x_p \) is a binary value and \( p_{\text{max}} \) is the number of qubits used in the mapping for a particular mode. As \([x_0 \ldots x_{p_{\text{max}}}] \langle x_0' \ldots x_{p_{\text{max}}}'| \) is equivalent to \([x_0] \langle x_0' \rangle \otimes \ldots \otimes [x_{p_{\text{max}}}] \langle x_{p_{\text{max}}}'| \) in the latter expression one of four operators is substituted for each single-qubit operator:

\[ |0\rangle \langle 1| = \frac{1}{2}(X + iY) = \sigma^- \]  

(23)
The quantum circuit model requires us to set a finite cutoff for the maximum occupation number of each QHO. For vibronic transitions in real molecules, the number $l_j$ of vibrational quanta in the $j$th mode does not exceed some maximum value $L_{\text{max},j}$ (assuming some finite precision) \cite{26}. In practice, on a future real-world quantum computer, the simplest solution is to increase $L_{\text{max},j}$ values for all modes until convergence is reached.

C Outline of Algorithms

What follows is an outline of the zero- and finite-temperature algorithms for calculating molecular vibronic spectra.

**Zero-temperature algorithm:**

1. Initialize state $|0\rangle_S |0\rangle_E$.
2. Run QPE using Hamiltonian $H_B$, expressed in the $A$ basis: $|0\rangle_S |0\rangle_E \rightarrow \sum_i c_i |\psi_i\rangle |\tilde{\epsilon}_i\rangle$.
3. Measure register $E$ to obtain eigenenergy $\tilde{\epsilon}_i$: $\sum_i c_i |\psi_i\rangle |\tilde{\epsilon}_i\rangle \rightarrow A_j \sum_{k \in D_j} c_k |\psi_k\rangle |\tilde{\epsilon}_j\rangle$, where $A_j$ is a renormalization constant.
4. If desired, perform additional analysis on the preserved state $A_j \sum_{k \in D_j} c_k |\psi_k\rangle$ in register $S$, as discussed in Section 3.1. For example, perform a SWAP test with another state, or resolve one of the Fock states in $D_j$.
5. Repeat these steps to obtain a histogram of $\tilde{\epsilon}_i$ values.

**Finite-temperature algorithm:**

1. Initialize state $|0\rangle_I |0\rangle_S |0\rangle_E$.
2. Prepare the thermal state by acting on registers $I$ and $S$: $\hat{V}(\beta) |0\rangle_I |0\rangle_S |0\rangle_E \rightarrow \sum_n \kappa_n |n\rangle_S |n\rangle_I |0\rangle_E$.
3. Apply QPE with $H_B$, on registers $S$ and $E$: $\sum_n \kappa_n |n\rangle_S |0\rangle_E \rightarrow \sum_n \kappa_n |n\rangle_S \sum_i (c_{n,i}|\psi_i\rangle |\tilde{\epsilon}_i\rangle)$.
4. Measure both registers $E$ and $I$: $\rightarrow |n_I\rangle (A_{j,n_I} \sum_{k \in D_j} c_{n_I,k} |\psi_k\rangle |\tilde{\epsilon}_j\rangle)$.
5. Perform optional analysis on register $S$, as previously mentioned.
6. The contribution to the histogram is then $\tilde{\epsilon}_j - E_A(n_I)$. (Contrast this with the zero-temperature case, where $E_A(n_I)$ is omitted.)
D Computational Scaling

Below we assume the parameters $S$, $\delta$, $\Omega_A$, and $\Omega_B$ are given. Setting aside more advanced linear algebra approaches, both the $q$-$p$ method (equation 8) and the ladder operator method (equation 8) require $O(M^2)$ classical preparation steps, since all transformations involve only matrix-vector multiplications or diagonal-dense matrix multiplications. For comparison, VBS requires $O(M^3)$ classical steps because it uses the singular value decomposition. As described in Section 3, one element of our algorithm uses Hamiltonian simulation to implement $H_B$ for use in the quantum phase estimation (QPE) algorithm. An essential consideration, especially for near- and mid-term hardware, is the computational cost of implementing one Trotter step of the Hamiltonian’s propagator.

Each operator $b_i$ is a linear combination of terms in $\{a_i^\dagger\}$ and $\{a_i\}$. The operator $H_B$, after summing the number operators in $\{b_i^\dagger b_i\}$ and grouping terms, is a linear combination of terms in $\{a_i a_j\}, \{a_i^\dagger a_j\}, \{a_i a_j^\dagger\}$, and $\{a_i^\dagger a_j^\dagger\}$. Hence in the worst case, the number of terms in $H_B$ scales as $O(M^2)$, meaning the number of operations in a Trotter step is $O(M^2)$ as well.

The circuit depth of a Trotter step scales as $O(M)$, i.e. linear-depth. To see this, consider placing two-boson operators (each corresponding to an interaction term such as $a_i^\dagger a_j$) on all boson pairs $i,j$ that satisfy $(i-j) = w \mod N_q$, where $w \in \{1,2,\ldots,N_q-1\}$. For a single value of $w$, this gate placement has constant depth. Iterating through all values of $w$ yields a circuit with linear depth $O(M)$, and single-boson terms do not change this scaling. The same argument applies to the method based on $q$ and $p$ operators. Note that the finite-temperature algorithm scales no worse than the zero-temperature procedure, since the state preparation takes $O(M)$ operations with $O(1)$ depth.

When anharmonic effects are included, the complexity of implementing a Trotter step will be $O(M^k)$, where $k$ is the highest-order term in the Taylor expansion of Eq. 10. It is possible that there will be methods for reducing this complexity in the anharmonic case, for example by using other other classes of functions in the expansion, e.g. the Morse potential.

E Molecular data

The four simulated molecules, all of the $C_2$ point group, have three vibrational modes: a bending mode, a symmetric stretch, and an anti-symmetric stretch. Due to symmetry, the first two modes are decoupled from the anti-symmetric mode. We consider only the two coupled modes in these analyses.

The following parameters were used, taken from the literature. $S$ and $\delta$ are dimensionless; energies of $\bar{\omega}$ are in wavenumbers, cm$^{-1}$.

$SO_2^- \rightarrow SO_2 + e^-$ [50]:

$$
\begin{align*}
S_{SO_2} &= \begin{bmatrix} 0.9979 & 0.0646 \\ -0.0646 & 0.9979 \end{bmatrix}; \\
\delta_{SO_2} &= \begin{bmatrix} -1.8830 \\ 0.4551 \end{bmatrix}; \\
\bar{\omega}_{SO_2} &= \begin{bmatrix} 943.3 \\ 464.7 \end{bmatrix}; \\
\bar{\omega}_{SO_2} &= \begin{bmatrix} 1178.1 \\ 518.8 \end{bmatrix}
\end{align*}
$$

(27)

$H_2O \rightarrow H_2O^+ + e^-$ [51]:

$$
\begin{align*}
S_{H_2O} &= \begin{bmatrix} 0.9884 & -0.1523 \\ 0.1523 & 0.9884 \end{bmatrix}; \\
\delta_{H_2O} &= \begin{bmatrix} 0.5453 \\ 4.2388 \end{bmatrix}; \\
\bar{\omega}_{H_2O} &= \begin{bmatrix} 3862 \\ 1649 \end{bmatrix}; \\
\bar{\omega}_{H_2O} &= \begin{bmatrix} 2633 \\ 1620 \end{bmatrix}
\end{align*}
$$

(28)

$D_2O \rightarrow D_2O^+ + e^-$ [51]:

$$
\begin{align*}
S_{D_2O} &= \begin{bmatrix} 0.9848 & -0.1737 \\ 0.1737 & 0.9848 \end{bmatrix}; \\
\delta_{D_2O} &= \begin{bmatrix} 0.7175 \\ 4.8987 \end{bmatrix}; \\
\bar{\omega}_{D_2O} &= \begin{bmatrix} 2785 \\ 1207 \end{bmatrix}; \\
\bar{\omega}_{D_2O} &= \begin{bmatrix} 1915 \\ 1175 \end{bmatrix}
\end{align*}
$$

(29)

$NO_2(2B_2 \rightarrow 2A_1)$ [53]:

$$
\begin{align*}
S_{NO_2} &= \begin{bmatrix} 0.938 & -0.346 \\ -0.346 & 0.938 \end{bmatrix}; \\
\delta_{NO_2} &= \begin{bmatrix} -4.0419 \\ 5.3185 \end{bmatrix}; \\
\bar{\omega}_{NO_2(gr)} &= \begin{bmatrix} 1358 \\ 737 \end{bmatrix}; \\
\bar{\omega}_{NO_2(ex)} &= \begin{bmatrix} 1461 \\ 739 \end{bmatrix}
\end{align*}
$$

(30)

F Error Analysis

We studied truncation errors, i.e. those due to insufficiently large $L_{max}$, primarily because this type of error is not present in standard classical vibronic simulations, which are not based on
Figure 4: $L_1$-norm errors between exact and approximate vibronic spectra, for molecules $SO_2$, $H_2O$, $D_2O$, and $NO_2$ (where $D$ is deuterium), where each eigenvalue was broadened with a Gaussian of width 100 cm$^{-1}$ to make error analysis possible (broadening is performed after the histogram is constructed). $H_2O$, $D_2O$, and $NO_2$ were chosen because they have particularly high phonon occupation numbers, necessitating a large QHO cutoff $L_{\text{max}}$. In general a larger displacement $\delta$ leads to a larger required cutoff. In this simulation, the mode with a smaller $\delta$ was assigned a converged $L_{\text{max}}$; hence we isolated the effects of the variable of the more significant (larger $\delta$) mode by varying its $L_{\text{max}}$.

diagonalizing $H_B$ \cite{24, 26, 3, 28}. All results are obtained by creating $H_B$ with truncated ladder operators, diagonalizing the Hamiltonian, calculating FCFs, and binning the results in bins of width 1 cm$^{-1}$.

To make our error analysis method possible, the spectra in this work were broadened with a Gaussian of width 100 cm$^{-1}$, a width that represents $\lesssim$ 1% of the spectral range for these four molecules. The broadening is a distinct separate step, and is performed after formation of the histogram. Errors were calculated using the $L_1$ norm between the exact and approximate spectra (both broadened),

$$\epsilon_{L_1} = \int |\text{FCP}_{\text{exact}}(\omega) - \text{FCP}_{\text{approx}}(\omega)| d\omega.$$

(31)

Because FCF profiles have unit norm, the worst case of two spectra with zero overlap yields $\epsilon_{L_1} = 2$.

The exact and approximate Hamiltonians were constructed using equations 22 and 8, varying ladder operator size to reflect $L_{\text{max}}$. The numerically exact results were considered converged when the $L_1$ norm between two subsequent $L_{\text{max}}$ values was below $10^{-4}$. We validated our method's numerically exact results by demonstrating that our results for $SO_2$ were identical to those produced by the software program hotFCHT \cite{2}, which uses an entirely different algorithmic approach based on recurrence formulas.

For all simulations, the mode that required a smaller cutoff was set to a high converged value, so that we isolated the effect of $L_{\text{max}}$ for the mode requiring a larger cutoff. This is the mode that is more shifted, i.e. the one with larger $|\delta|$. Hence for $SO_2$ we varied the cutoff for the first mode, while for the other three molecules we varied the cutoff for the second mode. We plotted the approximate spectra (dotted lines, Fig. 3) in order to demonstrate the qualitative effect of an insufficient cutoff. The approximate spectra in Fig. 3 were arbitrarily chosen such that $\epsilon_{L_1}$ lies between 0.2 and 0.25. For these illustrative approximate spectra, $\epsilon_{L_1}$ and $L_{\text{max}}$ are \{0.208, 0.231, 0.228, 0.241\} and \{10, 45, 57, 61\} for $SO_2$, $H_2O$, $D_2O$, and $NO_2$, respectively.

Fig. 4 shows $\epsilon_{L_1}$ as a function of $L_{\text{max}}$, again for the mode with larger $\delta$. The approximate $L_{\text{max}}$ cutoffs at which the error can be considered converged are \{12, 51, 64, 69\} respectively for $SO_2$, $H_2O$, $D_2O$, and $NO_2$. For this small set, the $L_{\text{max}}$ order matches the order of increasing $\delta$, which is the expected approximate trend. Using the standard binary mapping for QHO levels (which requires $\lfloor \log_2 L_{\text{max}} \rfloor$ for a given mode) would mean that the number of qubits required for
the larger-$\delta$ mode are 4, 6, 6, and 7 qubits, respectively.

Counter-intuitively, $L_{\text{max}}$ must be substantially larger than the highest QHO level at which appreciable intensity exists. For example, one may naively expect that $L_{\text{max}}=8$ would be sufficient for SO$_2$, since the FC factor $\sum_{n_0'} |\langle 0 | n_0' \rangle|^2$ is a near-negligible value of $\sim 1.6 \times 10^{-3}$ (just 0.6% of the largest FCF). But $L_{\text{max}}=13$ is required for eigenvalue positions and the $L_1$-norm error to converge. This is despite the fact that transitions to levels 12 and 13 are very small, with $\sum_{n_0'} |\langle 0 | n_0' = 12 \rangle|^2 \approx 5.2 \times 10^{-5}$ and $\sum_{n_0'} |\langle 0 | n_0' = 13 \rangle|^2 \approx 1.5 \times 10^{-5}$.

The truncation values are not expected to depend explicitly on $M$ because the intensities of a given mode’s vibronic progression is known to approximately follow the rapidly-decaying Poisson distribution [34].