nature physics

Article

https://doi.org/10.1038/s41567-023-02308-9

Quantum-inspired classical algorithms for molecular vibronic spectra

Received: 25 February 2022

Accepted: 26 October 2023

Published online: 10 January 2024

Check for updates

Changhun Oh [1] ✉, Youngrong Lim [2], Yat Wong [1], Bill Fefferman [3] & Liang Jiang [1]

Plausible claims for quantum advantage have been made using sampling problems such as random circuit sampling in superconducting qubit devices, and Gaussian boson sampling in quantum optics experiments. Now, the major next step is to channel the potential quantum advantage to solve practical applications rather than proof-of-principle experiments. It has recently been proposed that a Gaussian boson sampler can efficiently generate molecular vibronic spectra, which are an important tool for analysing chemical components and studying molecular structures. The best-known classical algorithm for calculating the molecular spectra scales super-exponentially in the system size. Therefore, an efficient quantum algorithm could represent a computational advantage. However, here we propose an efficient quantum-inspired classical algorithm for molecular vibronic spectra with harmonic potentials. Using our method, the zero-temperature molecular vibronic spectra problems that correspond to Gaussian boson sampling can be exactly solved. Consequently, we demonstrate that those problems are not candidates for quantum advantage. We then provide a more general molecular vibronic spectra problem, which is also chemically well motivated, for which our method does not work and so might be able to take advantage of a boson sampler.

Quantum computers are believed to solve problems that cannot be efficiently solved using classical counterparts[1]. Ultimately, quantum computers need to be fault tolerant and scalable to solve various problems, such as integer factorization[2] and digital quantum simulation of the real-time dynamics of large quantum systems[3]. Although the theoretical study and experimental implementations of quantum error correction schemes are developing rapidly, quantum machines at hand are still noisy intermediate-scale quantum devices. Nevertheless, we have recently seen the first plausible quantum advantage demonstrations using noisy intermediate-scale quantum devices, such as a superconducting qubit system with random circuit sampling[4,5] and a quantum optical system with Gaussian boson sampling[6–8].

Since quantum advantages from sampling tasks are promising, there have been proposals for applications for which we can potentially exploit the advantages. One such example is the generation of so-called molecular vibronic spectra[9]. Due to its importance in chemistry, its classical algorithm has been extensively studied, whereas the best-known algorithm still scales combinatorially in system size[10]. Recently, it has been proposed to employ a quantum simulator, which is a Gaussian boson sampler[11], to efficiently generate the spectra[9]. Gaussian boson sampling is a task that is believed to be hard for classical computers under plausible computational complexity assumptions and that has been exploited for a quantum advantage demonstration[11–13]. Therefore, the molecular vibronic spectra problem has been treated as a candidate for applications of quantum simulators[14]. Indeed, many experiments have been conducted to generate spectra using a Gaussian boson sampler[15–17]. Also, many classical algorithms to simulate Gaussian boson sampling have been proposed[18–22], but the cost is exponential, in general, in the system size. Thus, resolving the molecular vibronic spectra problem by simulating Gaussian boson sampling takes exponential costs.

[1]Pritzker School of Molecular Engineering, University of Chicago, Chicago, IL, USA. [2]School of Computational Sciences, Korea Institute for Advanced Study, Seoul, Korea. [3]Department of Computer Science, University of Chicago, Chicago, IL, USA. ✉e-mail: changhun0218@gmail.com

Meanwhile, the proposed quantum algorithms might also inspire us to develop efficient classical algorithms[23]. For example, the D-Wave device has inspired efficient algorithms[24,25]. Some quantum machine learning algorithms also inspired novel polynomial-scaled classical algorithms[26,27]. More recently, it was claimed that there is an efficient approximate classical algorithm for molecular vibronic spectra, although details have not been given[28].

In this work, by using the framework of boson sampling, we establish the complexity of the molecular vibronic spectra problem. We first consider the problem corresponding to Fock-state boson sampling and show that the exact computation of the spectra is computationally hard (#P-hard). However, even running a boson sampler entails a sampling error, which indicates that an additive error, instead of exact computation, is the correct target for classical algorithms. To achieve the target accuracy as efficient as a boson sampler, we devise an approximate classical algorithm using Fourier transformation. In particular, we generalize Gurvits's algorithm to approximate the Fourier components of general Fock-state molecular vibronic spectra that include multiphoton input states; furthermore, by using Parseval's relation, we show that the generalized Gurvits's algorithm and the inverse Fourier transformation achieve the same accuracy as a boson sampler in an efficient way. We then generalize the method to an actual molecular vibronic spectra problem corresponding to Gaussian boson sampling and show that we can even exactly compute the Fourier components and spectra efficiently. Consequently, we demonstrate that the molecular vibronic spectra problem corresponding to Fock-state boson sampling or Gaussian boson sampling does not provide a quantum advantage. By providing a more general type of molecular vibronic spectra problem, we then show that there exists a chemically well motivated problem that the proposed method does not solve as precisely as running a corresponding boson sampler. Thus, it suggests that we might be able to take advantage of boson sampling to solve such a classically hard problem.

Results

Grouped probability of boson sampling

Before we present our main results for the molecular vibronic spectra problem, let us first discuss how to potentially exploit a boson sampling for estimating a computational hard quantity, which provides a more general sense of the molecular vibronic problem. One naive way of using a boson sampler is to estimate a permanent, which is a hard graph-theoretical quantity, because the output probability of boson sampling can be expressed as a permanent. A caveat is that in the hardness regime, the probability—or the corresponding permanent—is exponentially small so that we still need exponentially many samples to achieve a reasonable accuracy due to the nature of sampling, even without considering experimental imperfections. Such a caveat suggests that if we want to estimate a quantity using a boson sampler, it needs to be sufficiently large that the required number of samples is at most polynomially many. One way to construct such problems is to group the output probabilities and estimate their sum, instead of estimating individual probabilities, so the quantity becomes sufficiently large. The molecular vibronic spectra problem is exactly such kind of a problem, which will be elaborated in the following section.

Molecular vibronic spectra

Let us first define the problem using the framework of Fock-state boson sampling and then generalize the problem to the one corresponding to Gaussian boson sampling, which describes the actual molecular vibronic spectra (we define the problem from the chemical perspective[29] and elaborate on the relation in Methods). Consider an M-mode Fock-state boson sampling with input state $|\psi_{\text{in}}\rangle = |\mathbf{n}\rangle$, where $\mathbf{n} \equiv (n_1, \ldots, n_M) \in \mathbb{Z}^M_{\geq 0}$, and an M-mode linear-optical circuit $\hat{U}$, characterized by an $M \times M$ unitary matrix U. The probability of measuring the output photon configuration $|\mathbf{m}\rangle$ is then written as

$$p(\mathbf{m}) = \frac{|\mathrm{Per} U_{\mathbf{n},\mathbf{m}}|^2}{\mathbf{n}!\mathbf{m}!}, \tag{1}$$

where $U_{\mathbf{n},\mathbf{m}}$ is obtained by repeating the ith row of U by n_i times and the jth column of U by m_j times. We then introduce two more parameters that define groups of probabilities: a weight vector $\boldsymbol{\omega} \in \mathbb{Z}^M_{\geq 0}$ with each element at most polynomially large, that is, $\omega_i \leq O(\mathrm{poly}(M))$ for all $i \in [M]$, and a set of numbers $\Omega \in \{0, \ldots, \Omega_{\max}\}$, which represents each group of outcomes (the polynomial-size integer weight vector corresponds to the polynomially accurate harmonic angular frequency in spectroscopy). Methods provides a more detailed discussion on the weight vector. We lift this assumption below. Using these parameters, we group the output probabilities in a way that we sum them if the inner product $\boldsymbol{\omega} \cdot \mathbf{m}$ is equal, that is,

$$G(\Omega) \equiv \sum_{\mathbf{m}=\mathbf{0}}^{\infty} p(\mathbf{m}) \delta(\Omega - \boldsymbol{\omega} \cdot \mathbf{m}) = \sum_{\mathbf{m} \in \mathcal{G}(\Omega)} p(\mathbf{m}), \tag{2}$$

where we defined sets $\mathcal{G}(\Omega) \equiv \{\mathbf{m} \in \mathbb{Z}^M_{\geq 0} : \boldsymbol{\omega} \cdot \mathbf{m} = \Omega\}$ for $\Omega \in \{0, \ldots, \Omega_{\max}\}$. We will call such a grouped probability $G(\Omega)$ as the molecular vibronic spectra in a more general sense. Intuitively, computing the spectra seems difficult because the probability $p(\mathbf{m})$ is hard to compute; furthermore, for each Ω, we need to sum $p(\mathbf{m})$ over exponentially many outcomes. Even if we are able to approximate the individual probabilities with a reasonable error, it is non-trivial to approximate the grouped probabilities by suppressing the error because the number of outcomes are exponentially large.

Meanwhile, a boson sampler enables us to straightforwardly estimate the spectra by collecting the samples and counting the number of samples that give Ω after the inner product (Fig. 1). Since the number of distinct groups is $\Omega_{\max} + 1 \leq O(\mathrm{poly}(M))$, each grouped probability's magnitude $|G(\Omega)|$ becomes $O(1/\mathrm{poly}(M))$; thus, a reasonable target error becomes $O(1/\mathrm{poly}(M))$ as well. By the Chernoff bound, the running time to achieve the target error ϵ with high probability $1 - \delta$ is $T = O(\mathrm{poly}(M, 1/\varepsilon, \log \delta^{-1}))$, that is, at most polynomial in the system size and the target accuracy is $1/\epsilon$. We emphasize that in contrast to estimating each probability, which is exponentially small, grouping the probabilities into polynomially many groups allows the sampling error $O(1/\mathrm{poly}(M))$ obtained with polynomially many samples to become still reasonable.

Fourier components of molecular vibronic spectra

As evident from the definition of the spectra in equation (2), a direct computation or even an approximation does not seem trivial. The key idea of our algorithm to circumvent the direct computation of exponentially many probabilities is to consider its Fourier components. First, we derive the Fourier components of the molecular vibronic spectra (Methods provides the derivation):

$$\tilde{G}(k) \equiv \left\langle \bigotimes_{i=1}^{M} \left(\sum_{m_i=0}^{\infty} |m_i\rangle\langle m_i|_i \mathrm{e}^{-\mathrm{i}k\theta m_i \omega_i} \right) \right\rangle = \left\langle \mathrm{e}^{-\mathrm{i}k\theta \hat{\mathbf{n}} \cdot \boldsymbol{\omega}} \right\rangle, \tag{3}$$

$$G(\Omega) = \frac{1}{\Omega_{\max} + 1} \sum_{k=0}^{\Omega_{\max}} \tilde{G}(k) \mathrm{e}^{\mathrm{i}k\theta\Omega} = \sum_{\mathbf{m}=\mathbf{0}}^{\infty} p(\mathbf{m}) \delta(\Omega - \boldsymbol{\omega} \cdot \mathbf{m}), \tag{4}$$

where $\theta \equiv 2\pi/(\Omega_{\max} + 1)$, $k \in \{0, \ldots, \Omega_{\max}\}$, and $|m_i\rangle\langle m_i|_i$ is the projector on the m_i photon state for the ith mode. Note that we did not assume Fock-state boson sampling, that is, the relation is applicable to any circuit. Hence, in general, the Fourier component is the overlap between an output state $|\psi_{\text{out}}\rangle$ and a phase-shifted state $\mathrm{e}^{-\mathrm{i}k\theta\hat{\mathbf{n}}\cdot\boldsymbol{\omega}} |\psi_{\text{out}}\rangle$, and once we can efficiently compute the overlap, we obtain the Fourier components and recover the spectra by the inverse Fourier transformation (Fig. 1). Note that the Fourier components depend only on input photons $\mathbf{n}$ and not on output configurations $\mathbf{m}$.

https://doi.org/10.1038/s41567-023-02308-9

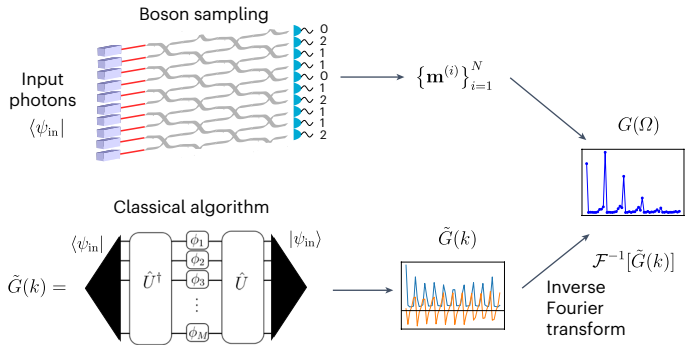

Fig. 1 | Molecular vibronic spectra generation using boson sampling and the proposed classical algorithm by computing the Fourier components of the spectra. The Fourier components are described by a circuit diagram whose expression is given in equation (3) by defining $\phi_i = -k\theta\omega_i$. The operation for each ϕ_i is the phase-shifting operator $e^{i\phi_i \hat{n}_i}$.

For Fock-state boson sampling, the Fourier components can be written as

$$\tilde{G}(k) = \langle \mathbf{n}|\, \hat{U}^\dagger e^{-ik\theta \hat{\mathbf{n}}\cdot\boldsymbol{\omega}} \hat{U}\, |\mathbf{n}\rangle \equiv \langle \mathbf{n}|\, \hat{V}\, |\mathbf{n}\rangle = \frac{\mathrm{Per}(V_{\mathbf{n},\mathbf{n}})}{\mathbf{n}!}, \tag{5}$$

where we defined a unitary operator $\hat{V} \equiv \hat{U}^\dagger e^{-ik\hat{\mathbf{n}}\cdot\boldsymbol{\omega}\theta}\hat{U}$, consisting of $\hat{U}$ and a phase-shift operator $e^{-ik\hat{\mathbf{n}}\cdot\boldsymbol{\omega}\theta}$ and $\hat{U}^\dagger$. Thus, it is a linear-optical circuit characterized by a unitary matrix $V = U^\dagger D U$, where $D \equiv \mathrm{diag}(e^{-ik\theta\omega_1}, \ldots, e^{-ik\theta\omega_M})$ characterizing the phase-shift operator. Here such a diagonal form suggests that V is a general form of a unitary matrix. Together with this fact, since computing the permanent of an arbitrary matrix in multiplicative error is #P-hard and one can embed an arbitrary complex matrix into a submatrix of a unitary matrix by normalizing the matrix[12], computing its Fourier component in multiplicative error is also #P-hard. Therefore, it shows that computing the Fourier components in multiplicative error is a #P-hard problem, and consequently, it proves that the exact computation of the spectra is also a #P-hard problem.

In fact, we again emphasize that even if we run a boson sampling experiment using a quantum device and reproduce the spectra from the sampling outcomes, the resultant spectra has an additive sampling error. Therefore, reproducing the spectra within a multiplicative error is not expected to be achievable by running a boson sampling circuit with polynomially many samples; thus, an additive error is a relevant target using a classical simulation to compare with a quantum device. Interestingly, there exists a classical algorithm, the so-called Gurvits's algorithm, which can efficiently approximate the permanent of a matrix within an additive error[12,30]. However, this algorithm and its slightly generalized version[31] are insufficient for general Fock-state boson sampling cases where the input and output photons n_i contain more than a single photon for some i values because the error can increase exponentially in system size in that case (Supplementary Section 1). We further generalize Gurvits's algorithm from another work[30] using a similar technique in ref. 12 to estimate the spectra, which includes multiple photons $\mathbf{n}$ using the following equality (Supplementary Section 1 provides the derivation):

$$\frac{\mathrm{Per}(V_{\mathbf{n},\mathbf{n}})}{\mathbf{n}!} = \mathbb{E}_{\mathbf{x}\in\mathcal{X}}\left[\prod_{i=1}^{M}\left(\frac{\bar{y}_i(Vy)_i}{n_i}\right)^{n_i}\right], \tag{6}$$

where $y_i \equiv \sqrt{n_i}x_i$, $\mathbf{x} \in \mathcal{X} \equiv \mathcal{R}[n_1+1]\times\cdots\times\mathcal{R}[n_M+1]$, where $\mathcal{R}[j]$ is the set of jth roots of unity. Thus, by sampling the random variable with uniform $\mathbf{x} \in \mathcal{X}$, the randomized algorithm gives an estimate μ of permanent of an $n\times n$ matrix such that

$$\left|\frac{\mathrm{Per}(V_{\mathbf{n},\mathbf{n}})}{\mathbf{n}!} - \mu\right| < \epsilon \,\|\, V\|^n \tag{7}$$

with high probability $1-\delta$ and running time $T = O(\mathrm{poly}(n, 1/\varepsilon, \log\delta^{-1}))$. Here $\|V\|$ is the spectral norm of the matrix V, which is always 1 for our case because V is a unitary matrix. Thus, the generalized Gurvits's algorithm enables us to efficiently approximate the Fourier components within a reasonable additive error even though the computation of the Fourier components in a multiplicative error is hard (#P-hard). Note that although a generalized Gurvits's algorithm might be used to approximate the individual probabilities in equation (4), it is non-trivial to approximate the sum of exponentially many probabilities, which is enabled by approximating Fourier components instead of probabilities.

The remaining challenge is the error propagation of Fourier coefficients to that of the spectra through the inverse Fourier transformation. Using Parseval's relation, we prove that as long as we estimate the Fourier coefficients with a small error ϵ, the transformed spectra's error is also small as ϵ (Methods provides the proof):

$$\sum_{\Omega=0}^{\Omega_{\max}} |\Delta G(\Omega)|^2 = \frac{1}{\Omega_{\max}+1}\sum_{k=0}^{\Omega_{\max}} |\Delta\tilde{G}(k)|^2 \le \epsilon^2, \tag{8}$$

which proves that $|\Delta G(\Omega)| \le \epsilon$ for any Ω, where ΔG and $\Delta\tilde{G}$ represent the error of spectra and Fourier component estimation, respectively. Hence, if there is an efficient algorithm that approximates the Fourier components within an error ϵ in a running time $T = O(\mathrm{poly}(M, 1/\varepsilon, \log\delta^{-1}))$, the algorithm enables us to achieve the same accuracy as running a boson sampling. For the Fock-state boson sampling case, the generalized Gurvits's algorithm is such an algorithm estimating the Fourier components. Consequently, we have shown that the molecular vibronic spectra problem corresponding to Fock-state boson sampling can be efficiently solved by a classical computer as accurately as by running a boson sampler, which indicates that there is no quantum advantage from this problem.

Finally, we lift the assumption that the weight vector is at most polynomially large. In this case, since $\Omega_{\max} = \omega(\mathrm{poly}(M))$, the standard Fourier transformation costs superpolynomial time. However, notice that even for the boson sampling case, it costs superpolynomial time to estimate all the quantities in a superpolynomial number of bins. Thus, let us focus on estimating the largest $t = O(\mathrm{poly}(M))$ elements of $G(\Omega)$, namely, peaks as large as $\Omega(1/\mathrm{poly}(M))$ guaranteeing that a boson sampler can provide a reasonable estimate. In this case, we show that by using the sparse fast Fourier transformation[32], we can efficiently approximate the peaks in $O(\mathrm{poly}(M, 1/\epsilon))$ with high probability (Supplementary Section 2). Specifically, we show that such a procedure with approximated Fourier components by the generalized Gurvits's algorithm still enables us to achieve an accuracy as good as running a boson sampler (Methods and Supplementary Section 2).

Exact computation of actual molecular vibronic spectra

As mentioned before and in Methods, actual molecular vibronic spectra problems at zero temperature under harmonic potential approximation correspond to Gaussian boson sampling. For this case where the input state is a product Gaussian state $|\psi_{\rm in}\rangle = \hat{D}(\boldsymbol{\alpha})\hat{S}(\mathbf{r})\,|\mathbf{0}\rangle$ and the circuit is again a linear-optical circuit $\hat{U}$, the Fourier components can be written as

$$\tilde{G}(k) = \langle\psi_{\rm in}|\, \hat{U}^\dagger e^{-ik\theta\hat{\mathbf{n}}\cdot\boldsymbol{\omega}}\hat{U}\,|\psi_{\rm in}\rangle\,. \tag{9}$$

Since only a Gaussian state and Gaussian operations are involved in Fourier components, one can easily compute them using the standard technique of quantum optics without needing Gurvits's approximate algorithm. More explicitly, we use the positive P representation[33] for equation (3), motivated by another work[34].

Using the positive P representation of single-mode Gaussian states[35] and the relation for a normal-ordered operator such as $e^{-\gamma\hat{n}} =: e^{\hat{n}(e^{-\gamma}-1)} :$ (ref. 36), we can rewrite the Fourier components in equation (3) as (Supplementary Section 3)

$$\tilde{G}(k) = \int_{\mathbb{R}^{2M}} d\mathbf{x}d\mathbf{y} P_{\text{in}}(\mathbf{x},\mathbf{y}) \exp\left[\sum_{i=1}^{M} x_i' y_i' (e^{-ik\theta\omega_i} - 1)\right], \tag{10}$$

where $P_{\text{in}}(\mathbf{x},\mathbf{y})$ is the positive P representation of an input squeezed state. Here $: \hat{O} :$ is the normal-ordered form of an operator $\hat{O}$ (ref. 37), and $(\mathbf{x}',\mathbf{y}') = (U\mathbf{x}, U^*\mathbf{y})$ accounts for the linear-optical unitary operation. More specifically, when a coherent state goes through an M-mode linear-optical circuit $\hat{U}$, it transforms as $\hat{U}|\mathbf{x}\rangle = |U\mathbf{x}\rangle$, where U is the corresponding $M \times M$ unitary matrix for the circuit. Since $\tilde{G}(k)$ is now written as a Gaussian integral, it can be analytically obtained as

$$\tilde{G}(k) = \mathcal{N}\frac{(2\pi)^M}{\sqrt{\det(Q)}} \exp\left(\frac{1}{2}\mathbf{c}^{\mathrm{T}} Q^{-1}\mathbf{c} + c_0\right), \tag{11}$$

where $\phi_j \equiv -k\theta\omega_j$,

$$Q \equiv \begin{pmatrix} 2\Gamma^{-1} + \mathbb{1}_M & -U^{\mathrm{T}}\mathrm{diag}(e^{i\phi_j})_{j=1}^{M} U^* \\ -U^{\dagger}\mathrm{diag}(e^{i\phi_j})_{j=1}^{M} U & 2\Gamma^{-1} + \mathbb{1}_M \end{pmatrix} \tag{12}$$

and

$$\begin{aligned} &\mathcal{N} \equiv \prod_{i=1}^{M} \frac{\sqrt{1+\gamma_i}}{\pi\gamma_i},\ \Gamma \equiv \mathrm{diag}(\gamma_i)_{i=1}^{M},\ \Phi = \mathrm{diag}(e^{i\phi_j} - 1)_{j=1}^{M}, \\ &\mathbf{c} \equiv (\mathbf{a}^{\mathrm{T}}, \mathbf{b}^{\mathrm{T}})^{\mathrm{T}},\ \mathbf{a} \equiv \frac{U^{\mathrm{T}}\Phi\boldsymbol{\delta}^*}{\sqrt{2}},\ \mathbf{b} \equiv \frac{U^{\dagger}\Phi\boldsymbol{\delta}}{\sqrt{2}},\ c_0 \equiv \frac{\boldsymbol{\delta}^{\mathrm{T}}\Phi\boldsymbol{\delta}^*}{2}. \end{aligned} \tag{13}$$

Here $\boldsymbol{\delta}/\sqrt{2}$ is a displacement vector of the final state $\hat{U}|\psi_{\text{in}}\rangle$. Note that Q is a complex symmetric matrix and $\mathrm{Re}(Q)$ is positive definite, which guarantees that the Gaussian integral converges. Supplementary Section 5 provides more details of the derivation and convergence of the integral. It implies that the molecular vibronic spectra's Fourier components at zero temperature have an analytic solution, so we can obtain the spectra by simply taking the inverse Fourier transform; thus, we do not need a quantum simulator to generate the spectra (Fig. 2). Using the technique from another work[38], such an approach can also solve the molecular vibronic spectra problem at a finite temperature (Supplementary Section 6). In contrast to the Fock-state boson sampling case, one interesting feature is that although the spectra is still the sum of probabilities that are hard to compute (hafnian), the spectra itself can be efficiently computed by using the provided method even without approximation.

We emphasize that a similar method that provides an analytical expression for vacuum or thermal input states, corresponding to Gaussian boson sampling, has already been proposed elsewhere[39], whereas our method using a positive P representation allows to consider a more general case such as operations mixing position and momentum operators, that is, a complex unitary operation. Furthermore, the method shown in the other work[39] overlaps only with the Gaussian boson sampling cases and cannot recover more general cases that we consider, such as the Fock-state boson sampling case, which requires a more complicated method.

Potential quantum advantage from molecular vibronic spectra

So far, we have shown that the molecular vibronic spectra problem corresponding to Fock-state or Gaussian boson sampling is efficiently solvable using a classical algorithm as accurately as running boson samplers. The key property we exploit to solve the problem is that the Fourier coefficients are efficiently approximable using generalized Gurvits's algorithm or exactly computable.

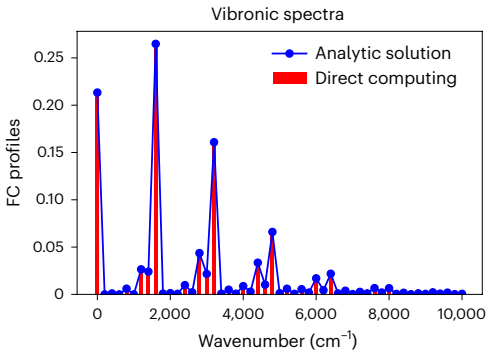

Fig. 2 | Molecular vibronic spectra of formic acid (CH_2O_2, $1^1A' \rightarrow 1^2A'$) generated by directly computing all the probabilities and by the solution obtained using an equation in the main text. The resolution for the spectra is set to be 200 cm^{-1}. We first compute the Fourier components using equation (11) and take the inverse Fourier transform to obtain the spectra. The corresponding transformation is obtained from another work[9].

We finally consider a more general case, which might potentially provide a quantum advantage. Here we set the initial state to be a displaced squeezed Fock state $\hat{D}(\boldsymbol{\alpha})\hat{S}(\mathbf{r}_0)|\mathbf{n}\rangle$, which can be thought of as a hybrid state of the two previous cases. We emphasize that such a problem is well motivated in chemistry in that it is required when a spectrum from specific vibronic levels needs to be analysed, instead of a thermal distribution or a ground state[40], for example, optical processes including the single-vibronic-level fluorescence and the resonance Raman scattering[41,42]. Indeed, a quantum simulation of such a process has also been experimentally implemented for various photoelectron processes such as the photodetachment of ozone anion[17]. In this case, its Fourier components are written as

$$\begin{aligned} \tilde{G}(k) &= \langle\mathbf{n}|\hat{S}^{\dagger}(\mathbf{r}_0)\hat{D}^{\dagger}(\boldsymbol{\alpha})\hat{U}^{\dagger} e^{-ik\theta\hat{\mathbf{n}}\cdot\boldsymbol{\omega}}\hat{U}\hat{D}(\boldsymbol{\alpha})\hat{S}(\mathbf{r}_0)|\mathbf{n}\rangle \\ &\equiv \langle\mathbf{n}|\hat{W}|\mathbf{n}\rangle, \end{aligned} \tag{14}$$

where $\hat{W} \equiv \hat{S}^{\dagger}(\mathbf{r}_0)\hat{D}^{\dagger}(\boldsymbol{\alpha})\hat{U}^{\dagger} e^{-ik\theta\hat{\mathbf{n}}\cdot\boldsymbol{\omega}}\hat{U}\hat{D}(\boldsymbol{\alpha})\hat{S}(\mathbf{r}_0)$ is a general Gaussian unitary operation including squeezing, instead of a linear-optical operation, which is different from the Fock-state boson sampling case. Using Bloch–Messiah decomposition[43], we can decompose the Gaussian unitary operation as $\hat{W} = \hat{D}(\boldsymbol{\xi})\hat{U}_{\text{lin2}}\hat{S}(\mathbf{r})\hat{U}_{\text{lin1}}$, where $\hat{U}_{\text{lin1}}$ and $\hat{U}_{\text{lin2}}$ represent linear-optical circuits, which are characterized by $M \times M$ unitary matrices U_{lin1} and U_{lin2}, respectively.

In Supplementary Section 8, we show that the Fourier components can be written as a loop hafnian of a matrix[44] as

$$\tilde{G}(k) = \frac{\mathrm{lhaf}(\Sigma_{\mathbf{n}})}{\mathbf{n}!Z}, \tag{15}$$

where

$$\Sigma \equiv \begin{pmatrix} U_{\text{lin2}}\tanh\mathbf{r}U_{\text{lin2}}^{\mathrm{T}} & U_{\text{lin2}}\,\mathrm{sech}\mathbf{r}U_{\text{lin1}} \\ U_{\text{lin1}}^{\mathrm{T}}\,\mathrm{sech}\mathbf{r}U_{\text{lin2}}^{\mathrm{T}} & -U_{\text{lin1}}^{\mathrm{T}}\tanh\mathbf{r}U_{\text{lin1}} \end{pmatrix} \tag{16}$$

is a $2M \times 2M$ complex symmetric matrix,

$$\boldsymbol{\zeta} \equiv \begin{pmatrix} -U_{\text{lin2}}\tanh\mathbf{r}U_{\text{lin2}}^{\mathrm{T}}\cdot\boldsymbol{\xi}^* + \boldsymbol{\xi} \\ -U_{\text{lin1}}^{\mathrm{T}}\,\mathrm{sech}\,\mathbf{r}U_{\text{lin2}}^{\mathrm{T}}\cdot\boldsymbol{\xi}^* \end{pmatrix} \tag{17}$$

is a $2M$-dimensional vector and

https://doi.org/10.1038/s41567-023-02308-9

Table 1 | Computational complexity of exactly computing Fourier components of molecular vibronic spectra and approximability within an 1/poly(*n*) additive error for different setups

	Vacuum or thermal input with squeezing	Fock state	Fock state with squeezing	Fock state with squeezing and displacement
Related quantity	Gaussian integral*	Permanent*	Hafnian*	Loop hafnian*
Complexity	P*	#P-hard[12]	#P-hard[12,47]	#P-hard[12,47]
Approximability	Exactly computable*	Approximable* (generalized Gurvits)	Approximable for large squeezing*	Not known

*Derived in the present work. Specifically, in the present work, we find that the Fourier components of the molecular vibronic spectra are related to the Gaussian integral, permanent, hafnian and loop hafnian for different cases, and show that the Fock-state cases can be solved by a generalized Gurvits's algorithm and Fock state with squeezing by another generalized Gurvits's algorithm (hafnian) for some regime.

$$Z^{-1} \equiv \langle 0|\hat{V}|0\rangle = \frac{\mathrm{e}^{\frac{1}{2}\boldsymbol{\xi}^{\mathrm{T}}\cdot(U_{\mathrm{lin2}}\tanh \mathbf{r} U_{\mathrm{lin2}}^{\mathrm{T}})\cdot\boldsymbol{\xi}}}{\sqrt{\prod_{i=1}^{M}\cosh r_i}} \tag{18}$$

is the normalization factor, which is the same as the Fourier components of the molecular vibronic spectra at zero temperature. Here $\tilde{\Sigma}_{\mathbf{n}}$ is obtained by first replacing the diagonal elements of Σ by $\boldsymbol{\zeta}$ to obtain $\tilde{\Sigma}$ and repeating the ith row and column of each block matrix of $\tilde{\Sigma}$ n_i times; thus, it is an $n \times n$ matrix with $n \equiv \sum_{i=1}^{M} n_i$. Therefore, computing the Fourier components reduces to computing the loop hafnians of $n \times n$ complex symmetric matrices.

The loop hafnian is a quantity related to the perfect matchings of a graph including loops (hafnian does not allow loops)[44]. The best-known algorithm's computational cost of computing a loop hafnian is $O(n^3 2^{n/2})$ (ref. 44), where n is the matrix size. Thus, if one tries to directly compute the probability of each outcome $\mathbf{m}$ in equation (2), which is written as a loop hafnian of a matrix whose size is $n+m$ ($m \equiv \sum_{i=1}^{M} m_i$) (ref. 45) and then obtain the spectra, the complexity of computing a single probability already costs exponential in $(n+m)/2$. On the other hand, the complexity of computing the Fourier components relies on the input photons $\mathbf{n}$ and not on the output photons $\mathbf{m}$ and the system size, that is, the proposed method is efficient as long as n is small enough. Furthermore, we prove that the redundancy of rows and columns for $n_i \geq 2$ does not increase the complexity of computing a loop hafnian as a hafnian[20,44,46] because it does not increase the rank of the matrix (Supplementary Section 7). Thus, the important factor for complexity is the number of non-zero elements of $\mathbf{n}$.

Meanwhile, since the loop hafnian is more general than the permanent (Supplementary Section 8), computing the loop hafnian is also #P-hard[12,47]. It implies that computing the Fourier components of general molecular vibronic spectra with Fock-state inputs and squeezing is also #P-hard. Noting that the Fourier components reduce to a hafnian and permanent when there is no displacement or squeezing, respectively, we summarize the complexity in Table 1.

Again, for our purpose, it suffices to find an efficient classical algorithm to additively approximate the Fourier components, which are loop hafnian, to determine if we can efficiently approximate the spectra as accurately as a boson sampler. In fact, in contrast to the permanent, there is no known efficient classical algorithm that approximates the loop hafnian as accurately as Gurvits's algorithm, to the best of our knowledge. Thus, one obvious step is to generalize Gurvits's algorithm to be applicable to a loop hafnian. For simplicity, let us assume that the displacement is zero; the loop hafnian in equation (15) then reduces to a hafnian. Similar to Gurvits's algorithm, we construct a randomized algorithm to estimate a hafnian of an $n \times n$ complex symmetric matrix Σ using Kan's formula[48]

$$\mathrm{haf}(\Sigma) = \mathbb{E}_{\mathbf{v}\in\{0,1\}^n}\left[(-1)^{\sum_{i=1}^{n} v_i}\frac{2^{n/2}}{(n/2)!}(h^{\mathrm{T}}\Sigma h)^{n/2}\right], \tag{19}$$

where $\mathbb{E}_{\mathbf{v}}[\cdot]$ is the average over $\mathbf{v} \in \{0,1\}^n$ with uniform distribution, $h = (1/2 - v_1, \ldots, 1/2 - v_M)^{\mathrm{T}}$ and n is even (otherwise, the hafnian is zero). Therefore, by uniformly sampling $\mathbf{v} \in \{0,1\}^n$ and averaging over the samples, we estimate the hafnian. Together with the fact that $\|\Sigma\| = 1$ from equation (16), the bound of error for estimate q of a Fourier component is given by

$$\Pr\left[\left|q - \frac{\mathrm{haf}(\Sigma_{\mathbf{n}})}{Z\mathbf{n}!}\right| \gtrsim \epsilon\frac{\mathrm{e}^{n/2}}{\sqrt{\pi n}Z}\right] \leq 2\mathrm{e}^{-N\epsilon^2/2}, \tag{20}$$

where $Z = \sqrt{\prod_{i=1}^{n}\cosh r_i}$ and N is the number of samples. Thus, if $\prod_{i=1}^{n}\cosh r_i > \mathrm{e}^n$, the estimation error is smaller than ϵ with an exponentially small failure probability if we choose the number of samples as $N = O(1/\epsilon^2)$. Therefore, it suggests that if the condition is satisfied, classically estimating the Fourier components and taking the inverse Fourier transformation efficiently renders the same scaling of precision as a boson sampler.

However, when the condition is not satisfied, the estimation error of the proposed classical algorithm with the generalized Gurvits's algorithm grows exponentially due to the factor $e^{n/2}$. Therefore, if we cannot find a classical algorithm to approximate the hafnian, for example, which approximates

$$\Pr\left[\left|q - \frac{\mathrm{haf}(\Sigma_{\mathbf{n}})}{Z\mathbf{n}!}\right| \geq \epsilon\right] \leq \delta \tag{21}$$

in running time $T = \mathrm{poly}(n, 1/\varepsilon, \log\delta^{-1})$, a boson sampler might provide a potential advantage for solving this molecular vibronic spectra and give evidence of the quantum advantage of a boson sampler for practical problems. If we find such an algorithm, it can eventually solve the problem as accurately as a boson sampler.

For non-zero displacement and loop hafnian, although there is a similar equality as in equation (19), the resultant error bound is more complicated than a hafnian (Supplementary Section 9). Although we did not find a regime where the approximation error is sufficiently small, it would be an important future work to identify the regime to characterize parameters for which running a boson sampling circuit may be advantageous than the classical algorithm. We summarize the well-known or derived complexity of the approximation of the molecular vibronic spectra's Fourier components in Table 1.

Discussion

Although we have recently seen the first plausible quantum advantage demonstration experiments using sampling tasks[4–8], the present work leaves an open question to find a practically useful task of quantum sampling problems. Our results imply that although grouping the probabilities and estimating the grouped probability would be a natural and potential way of exploiting a boson sampler, an efficient classical counterpart might exist due to coarse graining. In particular, our results suggest that the molecular vibronic spectra corresponding to the Fock-state or Gaussian boson sampling may not be the candidate for which the power of a quantum sampler can boost the computational performance beyond classical means. We also note that our method can be easily generalized to certain non-Condon effects[49], coherent

driving of molecular vibronic spectra generation[50] and dynamics of the vibrational state of molecules[51].

On the other hand, we have presented a molecular vibronic spectra problem that might provide a potential quantum advantage and is chemically well motivated. For this problem, to the best of our knowledge, the performance of a classical algorithm computing the spectra by approximating its Fourier components is not as sufficiently accurate as running a boson sampler. It leaves an interesting open question of finding a classical algorithm to solve this problem or proving the hardness to identify the potential quantum advantage. We also note that the way we group the probabilities is based on the simple inner product between the outcome and a given weight vector, which is translated as phase shifters in Fourier basis. Thus, generalizing the way of grouping the probabilities, which makes the Fourier component to contain a non-trivial nonlinear operation, and establishing the complexity would be an important open question to find the power or limitation of the present method.

Finally, since we assume the harmonic potential for our results, incorporating the anharmonicity of potentials[52–54] into our results is an important future work. In Supplementary Section 10, we present a way in which we can embed a bounded-error quantum polynomial-time-complete problem, which is essentially equivalent to simulating a universal quantum computing circuit, into a molecular vibronic spectra problem containing nonlinear effects beyond Gaussian operations, which might be necessary to incorporate the anharmonicity. Thus, the molecular vibronic spectra problem including nonlinear effects can be difficult to efficiently simulate using classical computers even in an additive approximation.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41567-023-02308-9.

References

1. Nielsen, M. A. & Chuang, I. *Quantum Computation and Quantum Information* (Cambridge Univ. Press, 2002).
2. Shor, P. W. Algorithms for quantum computation: discrete logarithms and factoring. In *Proc. 35th Annual Symposium on Foundations of Computer Science* 124–134 (IEEE, 1994).
3. Lloyd, S. Universal quantum simulators. *Science* **273**, 1073–1078 (1996).
4. Arute, F. et al. Quantum supremacy using a programmable superconducting processor. *Nature* **574**, 505–510 (2019).
5. Wu, Y. et al. Strong quantum computational advantage using a superconducting quantum processor. *Phys. Rev. Lett.* **127**, 180501 (2021).
6. Zhong, H.-S. et al. Quantum computational advantage using photons. *Science* **370**, 1460–1463 (2020).
7. Zhong, H.-S. et al. Phase-programmable Gaussian boson sampling using stimulated squeezed light. *Phys. Rev. Lett.* **127**, 180502 (2021).
8. Madsen, L. S. et al. Quantum computational advantage with a programmable photonic processor. *Nature* **606**, 75–81 (2022).
9. Huh, J., Guerreschi, G. G., Peropadre, B., McClean, J. R. & Aspuru-Guzik, A. Boson sampling for molecular vibronic spectra. *Nat. Photon.* **9**, 615–620 (2015).
10. Barone, V., Bloino, J. & Biczysko, M. Vibrationally-resolved electronic spectra in Gaussian 09. *Rev. A* **02**, 1 (2009).
11. Hamilton, C. S. et al. Gaussian boson sampling. *Phys. Rev. Lett.* **119**, 170501 (2017).
12. Aaronson, S. & Arkhipov, A. The computational complexity of linear optics. In *Proc. Forty-Third Annual ACM Symposium on Theory of Computing* 333–342 (ACM, 2011).
13. Deshpande, A. et al. Quantum computational advantage via high-dimensional Gaussian boson sampling. *Sci. Adv.* **8**, eabi7894 (2022).
14. Arrazola, J. et al. Quantum circuits with many photons on a programmable nanophotonic chip. *Nature* **591**, 54–60 (2021).
15. Shen, Y. et al. Quantum optical emulation of molecular vibronic spectroscopy using a trapped-ion device. *Chem. Sci.* **9**, 836–840 (2018).
16. Paesani, S. et al. Generation and sampling of quantum states of light in a silicon chip. *Nat. Phys.* **15**, 925–929 (2019).
17. Wang, C. S. et al. Efficient multiphoton sampling of molecular vibronic spectra on a superconducting bosonic processor. *Phys. Rev. X* **10**, 021060 (2020).
18. Quesada, N. & Arrazola, J. M. Exact simulation of Gaussian boson sampling in polynomial space and exponential time. *Phys. Rev. Research* **2**, 023005 (2020).
19. Wu, B. et al. Speedup in classical simulation of Gaussian boson sampling. *Sci. Bull.* **65**, 832–841 (2020).
20. Bulmer, J. F. F. et al. The boundary for quantum advantage in Gaussian boson sampling. *Sci. Adv.* **8**, eabl9236 (2022).
21. Quesada, N. et al. Quadratic speed-up for simulating Gaussian boson sampling. *PRX Quantum* **3**, 010306 (2022).
22. Oh, C., Lim, Y., Fefferman, B. & Jiang, L. Classical simulation of boson sampling based on graph structure. *Phys. Rev. Lett.* **128**, 190501 (2022).
23. Drucker, A. & de Wolf, R. Quantum proofs for classical theorems. *Theory Comput. Grad. Surv.* **2**, 1–54 (2011).
24. Shin, S. W., Smith, G., Smolin, J. A. & Vazirani, U. How 'quantum' is the D-Wave machine? Preprint at https://arxiv.org/abs/1401.7087 (2014).
25. Heim, B., Rønnow, T. F., Isakov, S. V. & Troyer, M. Quantum versus classical annealing of Ising spin glasses. *Science* **348**, 215–217 (2015).
26. Tang, E. A quantum-inspired classical algorithm for recommendation systems. In *Proc. 51st Annual ACM SIGACT Symposium on Theory of Computing* 217–228 (ACM, 2019).
27. Gilyén, A., Lloyd, S. & Tang, E. Quantum-inspired low-rank stochastic regression with logarithmic dependence on the dimension. Preprint at https://arxiv.org/abs/1811.04909 (2018).
28. Aaronson, S. Chinese BosonSampling experiment: the gloves are off. https://scottaaronson.blog/?p=5159 (2020).
29. Doktorov, E., Malkin, I. & Man'Ko, V. Dynamical symmetry of vibronic transitions in polyatomic molecules and the Franck-Condon principle. *J. Mol. Spectrosc.* **64**, 302–326 (1977).
30. Gurvits, L. On the complexity of mixed discriminants and related problems. In *International Symposium on Mathematical Foundations of Computer Science* 447–458 (Springer, 2005).
31. Aaronson, S. & Hance, T. Generalizing and derandomizing Gurvits's approximation algorithm for the permanent. *Quantum Inf. Comput.* **14**, 541–559 (2014).
32. Hassanieh, H., Indyk, P., Katabi, D. & Price, E. Nearly optimal sparse Fourier transform. In *Proc. Forty-Fourth Annual ACM Symposium on Theory of Computing* 563–578 (ACM, 2012).
33. Drummond, P. & Gardiner, C. Generalised *p*-representations in quantum optics. *J. Phys. A: Math. Gen.* **13**, 2353 (1980).
34. Drummond, P. D., Opanchuk, B., Dellios, A. & Reid, M. D. Simulating complex networks in phase space: Gaussian boson sampling. *Phys. Rev. A* **105**, 012427 (2022).
35. Janszky, J. & Vinogradov, A. V. Squeezing via one-dimensional distribution of coherent states. *Phys. Rev. Lett.* **64**, 2771 (1990).
36. Vargas-Martínez, J., Moya-Cessa, H. & Fernández Guasti, M. Normal and anti-normal ordered expressions for annihilation and creation operators. *Rev. Mex. Fis. E* **52**, 13 (2006).
37. Walls, D. F. & Milburn, G. J. *Quantum Optics* (Springer Science & Business Media, 2007).

38. Huh, J. & Yung, M.-H. Vibronic boson sampling: generalized Gaussian boson sampling for molecular vibronic spectra at finite temperature. *Sci. Rep.* **7**, 7462 (2017).
39. Baiardi, A., Bloino, J. & Barone, V. General time dependent approach to vibronic spectroscopy including Franck-Condon, Herzberg-Teller, and Duschinsky effects. *J. Chem. Theory Comput.* **9**, 4097–4115 (2013).
40. Huh, J. & Berger, R. Coherent state-based generating function approach for Franck–Condon transitions and beyond. In *Journal of Physics: Conference Series* **380**, 012019 (IOP Publishing, 2012).
41. Hollas, J. M. *High Resolution Spectroscopy* (Butterworth-Heinemann, 2013).
42. Hollas, J. M. *Modern Spectroscopy* (John Wiley & Sons, 2004).
43. Braunstein, S. L. Squeezing as an irreducible resource. *Phys. Rev. A* **71**, 055801 (2005).
44. Björklund, A., Gupt, B. & Quesada, N. A faster hafnian formula for complex matrices and its benchmarking on a supercomputer. *ACM J. Exp. Algorithmics* **24**, 1–17 (2019).
45. Quesada, N. Franck-Condon factors by counting perfect matchings of graphs with loops. *J. Chem. Phys.* **150**, 164113 (2019).
46. Barvinok, A. I. Two algorithmic results for the traveling salesman problem. *Math. Oper. Res.* **21**, 65–84 (1996).
47. Barvinok, A. *Combinatorics and Complexity of Partition Functions* Vol. 9 (Springer, 2016).
48. Kan, R. From moments of sum to moments of product. *J. Multivar. Anal.* **99**, 542–554 (2008).
49. Jnane, H. et al. Analog quantum simulation of non-Condon effects in molecular spectroscopy. *ACS Photonics* **8**, 2007 (2021).
50. Jahangiri, S., Arrazola, J. M., Quesada, N. & Delgado, A. Quantum algorithm for simulating molecular vibrational excitations. *Phys. Chem. Chem. Phys.* **22**, 25528 (2020).
51. Sparrow, C. et al. Simulating the vibrational quantum dynamics of molecules using photonics. *Nature* **557**, 660–667 (2018).
52. McArdle, S., Mayorov, A., Shan, X., Benjamin, S. & Yuan, X. Digital quantum simulation of molecular vibrations. *Chem. Sci.* **10**, 5725–5735 (2019).
53. Sawaya, N. P. & Huh, J. Quantum algorithm for calculating molecular vibronic spectra. *J. Phys. Chem. Lett.* **10**, 3586–3591 (2019).
54. Sawaya, N. P., Paesani, F. & Tabor, D. P. Near- and long-term quantum algorithmic approaches for vibrational spectroscopy. *Phys. Rev. A* **104**, 062419 (2021).

Methods

Molecular vibronic spectra problem

In this section, we define the molecular vibronic spectra problem from a chemical perspective and show its equivalence to the presented definition from a boson sampling perspective in the main text. The molecular vibronic spectra is a fundamental property of molecules, which allows us to extract molecular structural changes. An electronic transition of a molecule changes the nuclei configuration, which introduces a new set of vibronic modes. Specifically, the transition probability between an initial vibronic mode and a certain final vibronic mode is called the Franck–Condon (FC) factor. One may obtain the FC profiles by computing many FC factors corresponding to a given vibrational transition frequency (Ω). The FC factor is obtained with the initial vibrational state $|\psi_{\text{in}}\rangle$ as

$$\text{FCP}(\Omega) = \sum_{\mathbf{m}=\mathbf{0}}^{\infty} |\langle \mathbf{m}| \hat{U}_{\text{Dok}} |\psi_{\text{in}}\rangle|^2 \delta\left(\Omega - \boldsymbol{\omega}^{\text{f}} \cdot \mathbf{m}\right), \tag{22}$$

where the Doktorov transformation $\hat{U}_{\text{Dok}}$ is given by[29]

$$\hat{U}_{\text{Dok}} = \hat{D}(\boldsymbol{\delta}/\sqrt{2})\hat{S}^{\dagger}(\Omega^{\text{f}})\hat{U}_R\hat{S}(\Omega^{\text{i}}), \tag{23}$$

where $\delta(\cdot)$ is the delta function and $\mathbf{m} = (m_1, \ldots, m_M)$ is the final vibrational modes' excitation vector. Here $\boldsymbol{\Omega}^{\text{i}}$ and $\boldsymbol{\Omega}^{\text{f}}$ are given by

$$\boldsymbol{\Omega}^{\text{i}} \equiv \text{diag}(\sqrt{\omega_1^{\text{i}}}, \ldots, \sqrt{\omega_M^{\text{i}}}),\ \boldsymbol{\Omega}^{\text{f}} \equiv \text{diag}(\sqrt{\omega_1^{\text{f}}}, \ldots, \sqrt{\omega_M^{\text{f}}}), \tag{24}$$

where $\boldsymbol{\omega}^{\text{i}} \equiv (\omega_1^{\text{i}}, \ldots, \omega_M^{\text{i}})$ and $\boldsymbol{\omega}^{\text{f}} \equiv (\omega_1^{\text{f}}, \ldots, \omega_M^{\text{f}})$ account for the initial and final harmonic angular frequencies, respectively.

In particular, the FC factor at zero temperature is obtained with the initial vacuum state $|\psi_{\text{in}}\rangle = |\mathbf{0}\rangle$. In this case, using the Bloch–Messiah decomposition, we can rewrite the Doktorov transformation as

$$\hat{U}_{\text{Dok}} = \hat{U}_2\hat{D}(\boldsymbol{\alpha})\hat{S}(\boldsymbol{\Omega}'')\hat{U}_1, \tag{25}$$

where $\hat{U}_1$ and $\hat{U}_2$ are rotations, that is, described by linear-optical circuits. Since $\hat{U}_1|\mathbf{0}\rangle = |\mathbf{0}\rangle$, the final state after the Doktorov transformation is given by

$$\hat{U}_{\text{Dok}}|\mathbf{0}\rangle = \hat{U}_2\hat{D}(\boldsymbol{\alpha})\hat{S}(\boldsymbol{\Omega}'')|\mathbf{0}\rangle, \tag{26}$$

which is exactly the same as the output state of Gaussian boson sampling with arbitrary pure product Gaussian states. It shows the direct relation between the molecular vibronic spectra at zero temperature and Gaussian boson sampling.

In the main text, we also study the molecular vibronic spectra from a single vibronic level, where the input state is no longer a vacuum state but a Fock state $|\mathbf{n}\rangle$. In this case, the output state is given by $\hat{U}_{\text{Dok}}|\mathbf{n}\rangle$. Especially when we consider the molecular vibronic spectra problem corresponding to Fock-state boson sampling, the Doktorov transformation is simply a rotation without any squeezing and displacement.

Let us further discuss the relation between the frequency vector and weight vector $\boldsymbol{\omega}$. First, since we only consider a Fock-state or a vacuum-state input, the initial energy is always fixed; thus, it is merely an offset, which we can omit. Hence, the relation is between the final frequency vector $\boldsymbol{\omega}^{\text{f}}$ and $\boldsymbol{\omega}$. Although the frequency vector $\boldsymbol{\omega}$ does not necessarily have to be an integer vector, the resolution of $\boldsymbol{\omega}^{\text{f}}$ is limited in practical molecular vibronic spectra problems. Hence, practically, the frequency vector can be written as floating-point numbers up to the resolution. Therefore, by multiplying a sufficiently large number, we can transform the actual frequency into a weight vector that is an integer vector. Here the magnitude of the final weight vector depends on the resolution of the frequencies. For example, if we have a polynomial resolution on the frequencies, we only need to multiply a polynomially large number to transform the vector into an integer weight vector. If we have an exponential resolution on the frequencies, we need to multiply an exponentially large number. Therefore, assuming the weight vector to be an integer does not lose generality.

We note that throughout the work, we assume the harmonic potential for vibrational modes, whereas we emphasize that the effect of anharmonicity is important for more general cases[52–54].

Derivation of Fourier coefficient

Here we derive the expression of Fourier coefficients $\tilde{G}(k)$ of the spectra $G(\Omega)$ in equation (3).

$$\tilde{G}(k) \equiv \sum_{\Omega=0}^{\Omega_{\max}} G(\Omega)\mathrm{e}^{-\mathrm{i}k\theta\Omega} \tag{27}$$

$$= \sum_{\Omega=0}^{\Omega_{\max}} \sum_{\mathbf{m}=0}^{\infty} p(\mathbf{m})\delta(\Omega - \boldsymbol{\omega}\cdot\mathbf{m})\mathrm{e}^{-\mathrm{i}k\theta\Omega} \tag{28}$$

$$= \frac{1}{\Omega_{\max}+1} \sum_{\Omega=0}^{\Omega_{\max}} \sum_{\mathbf{m}=0}^{\infty} p(\mathbf{m}) \sum_{l=0}^{\Omega_{\max}} \mathrm{e}^{\mathrm{i}l\theta(\Omega-\boldsymbol{\omega}\cdot\mathbf{m})-\mathrm{i}k\theta\Omega} \tag{29}$$

$$= \frac{1}{\Omega_{\max}+1} \sum_{l=0}^{\Omega_{\max}} \sum_{\mathbf{m}=0}^{\infty} p(\mathbf{m})\mathrm{e}^{-\mathrm{i}l\theta\boldsymbol{\omega}\cdot\mathbf{m}} \sum_{\Omega=0}^{\Omega_{\max}} \mathrm{e}^{\mathrm{i}\theta\Omega(l-k)} \tag{30}$$

$$= \sum_{\mathbf{m}=0}^{\infty} p(\mathbf{m})\mathrm{e}^{-\mathrm{i}k\theta\boldsymbol{\omega}\cdot\mathbf{m}} \tag{31}$$

$$= \sum_{\mathbf{m}=0}^{\infty} \langle\psi_{\text{out}}|\mathbf{m}\rangle\langle\mathbf{m}|\psi_{\text{out}}\rangle\,\mathrm{e}^{-\mathrm{i}k\theta\boldsymbol{\omega}\cdot\mathbf{m}} \tag{32}$$

$$= \left\langle \bigotimes_{i=1}^{M} \left(\sum_{m_i=0}^{\infty} |m_i\rangle\langle m_i|\,\mathrm{e}^{-\mathrm{i}k\theta\omega_i m_i} \right) \right\rangle \tag{33}$$

$$= \langle \mathrm{e}^{-\mathrm{i}k\theta\boldsymbol{\omega}\cdot\hat{\mathbf{n}}} \rangle. \tag{34}$$

Also, the Fourier relation implies that

$$G(\Omega) = \frac{1}{\Omega_{\max}+1} \sum_{k=0}^{\Omega_{\max}} \tilde{G}(k)\mathrm{e}^{\mathrm{i}k\theta\Omega}, \tag{35}$$

which is equation (4).

Error propagation from inverse Fourier transformation

We present the relation between the approximation error in Fourier basis and the one in spectra using Parseval's relation. Let us assume that we have obtained the Fourier components $\tilde{G}(k)$ within an error ϵ, that is, $|\Delta\tilde{G}(k)| \leq \epsilon$. After taking the inverse Fourier transform $\mathcal{F}^{-1}$, we obtain $G(\Omega)$ with an error $\Delta G(\Omega)$:

$$G(\Omega) + \Delta G(\Omega) = \mathcal{F}^{-1}[\tilde{G}(k) + \Delta\tilde{G}(k)] \tag{36}$$

and

$$|\Delta G(\Omega)| = |\mathcal{F}^{-1}[\Delta\tilde{G}(k)]|. \tag{37}$$

Using Parseval's relation, we have

$$\sum_{\Omega} |\Delta G(\Omega)|^2 = \frac{1}{K+1} \sum_{k} |\Delta\tilde{G}(k)|^2 \leq \epsilon^2, \tag{38}$$

which shows $|\Delta G(\Omega)| \leq \epsilon$ for all Ω. Therefore, if we estimate the Fourier components within an error ϵ for each, then the error for the spectra is smaller than ϵ.

Sparse fast Fourier transformation

As stated in the main text, we exploit the sparse fast Fourier transformation[32] for the case where the weight vectors are superpolynomially large, so that the total number of bins is $\Omega_{\max}+1=\omega(\mathrm{poly}(n))$, and show how it enables us to classically efficiently solve the problem.

The sparse fast Fourier transformation runs as follows (more details are available elsewhere[32]). (1) By randomly permuting the bins and hashing the bins, obtain a smaller number of bins, each of which contains at most a single peak from the initial distribution with high probability. (2) Locate the peaks from the hashed bins. (3) Estimate a large constant fraction of the peaks with good precision and high probability. (4) Subtract the obtained estimates, which makes the distribution sparser. (5) Iterate the procedure from (1) to (4). The algorithm takes running time $O(t/\varepsilon\log(\Omega_{\max}/t)\log(\Omega_{\max}/\delta))$ and succeeds with high probability, where ϵ and δ determine the error.

The sparse fast Fourier transformation is already sufficient to solve the molecular vibronic spectra problem corresponding to Gaussian boson sampling. For the problem corresponding to Fock-state boson sampling, we need to be more careful because we can only approximate the Fourier coefficients. In Supplementary Section 2, we show that the approximation error does not change the position of the peaks, that is, it does not delete or produce peaks, with high probability, which guarantees that the sparse fast Fourier transformation with the generalized Gurvits's algorithm efficiently solves the problem.

Generalized and positive *P* representation

The generalized *P* representation of an *M*-mode quantum optical state is one of the quasi-probability distributions of a bosonic state[33,37] (Supplementary Section 3):

$$\hat{\rho}=\int_{\mathbb{C}^{2M}}P(\boldsymbol{\alpha},\boldsymbol{\beta})\hat{\Lambda}(\boldsymbol{\alpha},\boldsymbol{\beta})\mathrm{d}\boldsymbol{\alpha}\mathrm{d}\boldsymbol{\beta},\quad \hat{\Lambda}(\boldsymbol{\alpha},\boldsymbol{\beta})\equiv\frac{|\boldsymbol{\alpha}\rangle\langle\boldsymbol{\beta}^{*}|}{\langle\boldsymbol{\beta}^{*}|\boldsymbol{\alpha}\rangle},\tag{39}$$

where $|\boldsymbol{\alpha}\rangle=|\alpha_1\rangle\otimes\cdots\otimes|\alpha_M\rangle$ is an *M*-mode coherent state. An important property of the generalized *P* representation is that the distribution $P(\boldsymbol{\alpha},\boldsymbol{\beta})$ can always be chosen to be non-negative (we call this a positive *P* representation), and the expectation value of a normal-ordered operator can be readily computed[33]. Especially, the positive *P* representation for a single-mode squeezed state can be chosen as[33–35] (Supplementary Section 4)

$$P(x,y)=\frac{\sqrt{1+\gamma}}{\pi\gamma}\mathrm{e}^{-(x^2+y^2)(\gamma^{-1}+1/2)+xy},\tag{40}$$

where *x* and *y* are real numbers (not complex numbers as general cases in equation (39)) and $\gamma\equiv\mathrm{e}^{2r}-1$ for a squeezing parameter $r>0$.

Data availability

Source data are provided with this paper.

Acknowledgements

We thank N. Quesada, J. Huh, S. Irani, B. O'Gorman, J. Whitfield and N. Sawaya for interesting and fruitful discussions. B.F. acknowledges support from AFOSR (YIP nos. FA9550-18-1-0148 and FA9550-21-1-0008). This material is based on work partially supported by the National Science Foundation (NSF) under Grant CCF-2044923 (CAREER) and by the US Department of Energy (DOE), Office of Science, National Quantum Information Science Research Centers, as well as by DOE QuantISED grant DE-SC0020360. We acknowledge support from the ARO (W911NF-18-1-0020 and W911NF-18-1-0212), ARO MURI (W911NF-16-1-0349 and W911NF-21-1-0325), AFOSR MURI (FA9550-19-1-0399 and FA9550-21-1-0209), AFRL (FA8649-21-P-0781), DOE Q-NEXT, NSF (EFMA-1640959, OMA-1936118, EEC-1941583, OMA-2137642), NTT Research and the Packard Foundation (2020-71479). This research was supported in part by the NSF under PHY-1748958. Y.L. acknowledges the National Research Foundation of Korea for a grant funded by the Ministry of Science and ICT (NRF-2020M3E4A1077861) and KIAS Individual Grant (CG073301) at the Korea Institute for Advanced Study. We also acknowledge the University of Chicago's Research Computing Center for their support of this work.

Author contributions

C.O., Y.L. and Y.W. developed the theory, and C.O. wrote the paper. B.F. and L.J. directed the research and developed the theory. All authors edited the paper.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41567-023-02308-9.

Correspondence and requests for materials should be addressed to Changhun Oh.

Peer review information *Nature Physics* thanks Alexandra Moylett and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.