

Boson Sampling for Molecular Vibronic Spectra

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I. BOSON SAMPLING AND VIBRATIONAL OVERLAPS

The transition amplitude $\langle \mathbf{m} | \hat{R}_U | \mathbf{n} \rangle$ can be computed in, at least, two distinct ways: The first way involves taking partial derivatives [1]:

$$\langle \mathbf{m} | \hat{R}_U | \mathbf{n} \rangle = \left(\prod_{k=1}^M \frac{\partial_{\alpha_k}^{n_k} \partial_{\gamma_k^*}^{m_k}}{\sqrt{n_k! m_k!}} \right) \exp(\gamma^\dagger \mathbf{U}^* \alpha) \Big|_{\alpha, \gamma^* = \mathbf{0}}, \quad (1)$$

where $\partial_a^b = \frac{\partial^b}{\partial a^b}$, while the second approach involves computing matrix permanents (Per) of submatrices of \mathbf{U} [2, 3] as described by

$$\langle \mathbf{m} | \hat{R}_U | \mathbf{n} \rangle = \left(\prod_{k=1}^M \sqrt{n_k! m_k!} \right)^{-1} (\text{Per}([\mathbf{U}]_{\mathbf{n}, \mathbf{m}}))^*, \quad (2)$$

with $[\mathbf{U}]_{\mathbf{n}, \mathbf{m}}$ being a $N \times N$ submatrix of \mathbf{U} obtained by repeating the k -th column of \mathbf{U} n_k times and copying the l -th row of the column of the resulting matrix m_l times [3]. The transition probability measured in boson sampling setups, which is proportional to $|\langle \mathbf{m} | \hat{R}_U | \mathbf{n} \rangle|^2$, can be considered a calculation of the permanent of the matrix described above through the relation [2, 3],

$$|\text{Per}([\mathbf{U}]_{\mathbf{n}, \mathbf{m}})|^2 = \left(\prod_{k=1}^M n_k! m_k! \right) |\langle \mathbf{m} | \hat{R}_U | \mathbf{n} \rangle|^2. \quad (3)$$

From this, it is clear that the output of boson sampling devices can be related to both the permanent of submatrices of \mathbf{U} as well as to the partial derivatives of $\exp(\gamma^\dagger \mathbf{U}^* \alpha)$.

According to the formalism usually adopted by the vibronic spectroscopy community, the transition amplitude in the Duschinsky relation can be obtained from the partial derivatives of $\exp(\frac{1}{2}(|\gamma|^2 + |\alpha|^2)) \langle \gamma | \hat{U}_{\text{Dok}} | \alpha \rangle$, *i.e.*

$$\langle \mathbf{m} | \hat{U}_{\text{Dok}} | \mathbf{n} \rangle = \langle \mathbf{0} | \hat{U}_{\text{Dok}} | \mathbf{0} \rangle \left(\prod_{k=1}^N \frac{\partial_{\alpha_k}^{n_k} \partial_{\gamma_k^*}^{m_k}}{\sqrt{n_k! m_k!}} \right) e^{-\frac{1}{2}(\alpha^\dagger \gamma^\dagger) \mathbf{W} \begin{pmatrix} \alpha \\ \gamma^* \end{pmatrix} + \mathbf{r}^\dagger \begin{pmatrix} \alpha \\ \gamma^* \end{pmatrix}} \Big|_{\alpha, \gamma^* = \mathbf{0}}. \quad (4)$$

Here γ and α are M -dimensional complex (column) vectors defining the coherent states, while \mathbf{W} is a self-inverse $2M \times 2M$ matrix and \mathbf{r} is a $2M$ -dimensional vector, which are defined as follows,

$$\mathbf{W} = \begin{pmatrix} \mathbf{I} - 2\mathbf{Q} & -2\mathbf{R} \\ -2\mathbf{R}^\dagger & \mathbf{I} - 2\mathbf{P} \end{pmatrix}, \quad \mathbf{r} = \sqrt{2} \begin{pmatrix} -\mathbf{R}\delta \\ (\mathbf{I} - \mathbf{P})\delta \end{pmatrix}, \quad (5)$$

where \mathbf{I} is a M -dimensional identity matrix, $\mathbf{Q} = (\mathbf{I} + \mathbf{J}^\dagger \mathbf{J})^{-1}$, $\mathbf{P} = \mathbf{J} \mathbf{Q} \mathbf{J}^\dagger$ and $\mathbf{R} = \mathbf{Q} \mathbf{J}^\dagger$.

II. FORMIC ACID

Franck-Condon factors (≥ 0.01) are listed in Table I. The photoelectron spectrum of formic acid ($1^1A' \rightarrow$

Frequency (ω_{vib})/ cm^{-1} Franck-Condon factor

Frequency (ω_{vib})/ cm^{-1}	Franck-Condon factor
0	0.2152
ω'_3	0.2717
$2\omega'_3$	0.1649
$3\omega'_3$	0.0640
$4\omega'_3$	0.0178
$\omega'_3 + \omega'_4$	0.0211
$\omega'_3 + \omega'_5$	0.0281
$\omega'_3 + \omega'_6$	0.0145
$2\omega'_3 + \omega'_5$	0.0237
$3\omega'_3 + \omega'_5$	0.0123
ω'_4	0.0242
ω'_5	0.0153
ω'_6	0.0112

TABLE I. Franck-Condon factors (≥ 0.01) in Fig. 3

$1^2A'$) can be found in Leach *et al.* [4]. Formic acid has a C_s point group symmetry, which is composed of two irreducible representations a' and a'' . As a result the Duschinsky rotation matrix for formic acid is in a block diagonal form with the blocks corresponding to the irreducible representations. The overall spectral shape is dominated by the contribution from the totally symmetric block a' while the non-totally symmetric block a'' only provides a minor correction to the spectral shape due to its lack of the structural displacements. Therefore,

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here we give the characteristic matrices and vectors for the symmetry block a' , which is composed of 7 quantum harmonic oscillators for a simple boson sampling experiment.

Below, we provide the characteristic parameters for formic acid for its symmetric block a' as

$$\mathbf{U} = \begin{pmatrix} 0.9934 & 0.0144 & 0.0153 & 0.0286 & 0.0638 & 0.0751 & -0.0428 \\ -0.0149 & 0.9931 & 0.0742 & 0.0769 & -0.0361 & -0.0025 & 0.0173 \\ -0.0119 & -0.0916 & 0.8423 & 0.1799 & -0.3857 & 0.3074 & 0.0801 \\ 0.0381 & 0.0409 & -0.3403 & -0.5231 & -0.6679 & 0.3848 & 0.1142 \\ -0.0413 & -0.0342 & -0.4004 & 0.7636 & -0.1036 & 0.4838 & 0.0941 \\ 0.0908 & -0.0418 & -0.0907 & 0.3151 & -0.5900 & -0.7193 & 0.1304 \\ -0.0325 & 0.0050 & -0.0206 & 0.0694 & -0.2018 & 0.0173 & -0.9759 \end{pmatrix}, \quad (6)$$

$$\boldsymbol{\omega} = \begin{pmatrix} 3765.2386 \\ 3088.1826 \\ 1825.1799 \\ 1416.9512 \\ 1326.4684 \\ 1137.0490 \\ 629.7144 \end{pmatrix}, \quad \boldsymbol{\omega}' = \begin{pmatrix} 3629.9472 \\ 3064.9143 \\ 1566.4602 \\ 1399.6554 \\ 1215.3421 \\ 1190.9077 \\ 496.2845 \end{pmatrix}, \quad \boldsymbol{\delta} = \begin{pmatrix} 0.2254 \\ 0.1469 \\ 1.5599 \\ -0.3784 \\ 0.4553 \\ -0.3439 \\ 0.0618 \end{pmatrix} \quad (7)$$

where the vibrational frequencies are in cm^{-1} , while the other quantities are dimensionless.

The corresponding boson sampling parameters, can be obtained by singular value decomposition of the \mathbf{J} matrix, *i.e.* $\mathbf{J} = \mathbf{C}_L \boldsymbol{\Sigma} \mathbf{C}_R^t$

$$\mathbf{C}_L = \begin{pmatrix} -0.0786 & 0.6624 & -0.1910 & 0.0194 & -0.7022 & 0.1170 & 0.1069 \\ 0.1918 & -0.1188 & -0.8128 & -0.5265 & 0.0841 & 0.0637 & 0.0039 \\ 0.6084 & 0.0851 & -0.1492 & 0.3436 & -0.0404 & -0.6888 & 0.0792 \\ 0.6373 & -0.0386 & 0.4649 & -0.4920 & -0.2417 & 0.2050 & -0.1839 \\ 0.3455 & 0.2308 & -0.1980 & 0.4883 & 0.2781 & 0.5577 & -0.4017 \\ -0.0348 & -0.6595 & -0.1588 & 0.2914 & -0.6007 & 0.0687 & -0.2968 \\ -0.2454 & 0.2240 & 0.0069 & -0.1973 & 0.0396 & -0.3874 & -0.8361 \end{pmatrix}, \quad (8)$$

$$\boldsymbol{\Sigma} = \begin{pmatrix} 1.1020 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1.0728 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1.0214 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.9420 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.9276 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0.8941 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0.8296 \end{pmatrix}, \quad (9)$$

$$\mathbf{C}_R = \begin{pmatrix} -0.0691 & 0.5634 & -0.1635 & 0.0188 & -0.7859 & 0.1322 & 0.1248 \\ 0.1446 & -0.0943 & -0.7600 & -0.6104 & 0.0841 & 0.1129 & 0.0120 \\ 0.1759 & 0.0478 & -0.2556 & 0.1972 & -0.0150 & -0.8645 & 0.3390 \\ 0.0237 & 0.0326 & -0.5446 & 0.7256 & 0.1295 & 0.1946 & -0.3474 \\ -0.6311 & 0.3592 & -0.1218 & 0.0398 & 0.4392 & 0.1241 & 0.4979 \\ 0.6132 & 0.6591 & 0.1373 & -0.0571 & 0.3982 & 0.0877 & -0.0333 \\ 0.4104 & -0.3268 & -0.0111 & 0.2383 & -0.0825 & 0.4017 & 0.7069 \end{pmatrix}. \quad (10)$$

Stochastic simulation

In Fig. 1, we simulate the results of what one would expect, accordingly, in a boson sampling simulation of Formic acid. This is done by stochastic sampling (equation (14)) on the known probability distributions for the output modes and analysed according to equation (8). The results from this simulation indicate relatively few samples are needed from the device to resolve the over-

all shape of the spectrum, supporting the experimental feasibility of the approach.

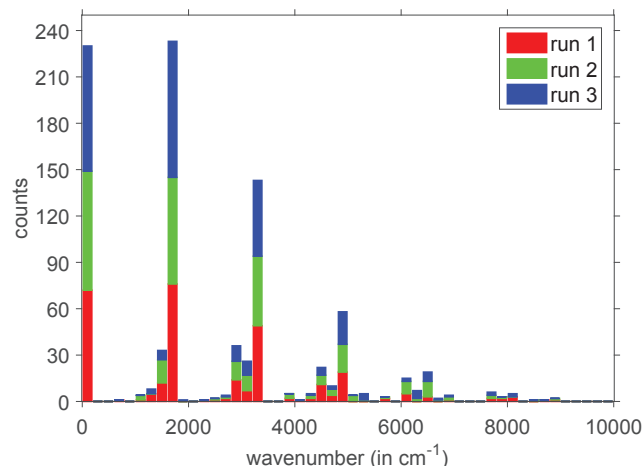


FIG. 1. We report the results from a stochastic simulation of the Franck-Condon profile of formic acid according to equation (14) (without normalization). The colors correspond to subsequent runs of 300 independent samples each of the modified boson sampling experiment. This plot demonstrates how few samples one may require from the boson sampling device to resolve a spectra. The bin size in this simulation is set to $\Delta_{\text{vib}} = 200 \text{ cm}^{-1}$.

III. THYMINE

The computed vibronic spectrum in Ref. [5] is in a good agreement with the experimental one. Thymine also belongs to the C_s point group. As a consequence, The Duschinsky rotation matrix is also in a block diagonal form. There are 26 and 13 vibrational degrees of freedom for the irreducible representations a' and a'' , respectively. In Fig. 4 we show the reproduced Franck-Condon profile based on information from Ref. [5] with **hotFCHT** [5–7]. The characteristic matrices and vectors of each irreducible representation can be provided on the request. The full spectrum in Fig. 4 can be obtained by convoluting the two Franck-Condon profiles from each irreducible representation. For the boson sampling experiments, the full spectrum can be obtained either by performing experiments on the full system in a block diagonal form or by convoluting the results from each blocks.

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