Bayesian spectroscopy in solid-state photo-physics

Ichiro Akai¹, Kazunori Iwamitsu², Masato Okada³, Masato Okada³

¹Institute of Pulsed Power Science, Kumamoto University, 2-39-1 Kurokami Chuo-ku, Kumamoto 860-8555, Japan.
²Faculty of Science, Kumamoto University, 2-39-1 Kurokami Chuo-ku, Kumamoto 860-8555, Japan.
³Department of Complexity Science and Engineering, The University of Tokyo, 5-1-5 Kashiwanohasha Kashiwa, Chiba 277-8561, Japan.
⁴Research and Service Division of Materials Data and Integrated System, National Institute for Material Science, 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047, Japan.

E-mail: iakai@kumamoto-u.ac.jp

Abstract. We propose Bayesian spectroscopy (BS) both for the spectral analyses of optical spectra and for normal mode analyses of coherent phonon (CP) signals in solid-state materials. In optical spectra due to elementary electronic excitations, multiple excitonic absorption peaks appear and are overlapped with other background optical transitions, which makes their spectral decomposition difficult. We demonstrate that BS can be used to estimate the band gap and the excitonic binding energies with high accuracies by the introduction of physical laws related with the excitonic transitions. For normal mode analyses of CP signals, we show that BS can estimate the frequency and initial vibrating phase of the normal mode with high accuracies. In contrast to the Fourier transform spectrum which has a broad spectral width on account of the damping behaviors of the CP signals, BS with a physical model of a damped oscillation improves the estimation accuracy of the normal mode frequency by two orders of magnitude compared to the Fourier transform method. These results indicate the significant advantages of BS over conventional methodologies such as the least-squares and Fourier transform methods.

1. Introduction

Optical spectroscopy is a powerful method to investigate various physical properties of materials because electrons and related elementary excitations interact with the incident light. Any substances absorb and/or emit light of specific wavelengths; therefore, optical spectra can be measured that includes various information related to their physical properties. Recent advances in spectroscopic and ultrashort pulsed laser technologies have led to improvements in spectroscopic energy resolution and time resolution of temporal measurements, and have contributed significantly to frontier research in photo-physics.

The least-squares method [1] has typically been used for spectral analyses. The method is based on causal determinism, and it considers that the measured data will be scattered due to random noise. However, the spectral parameters that represent the physical properties are nonlinearly included in the spectral functions that represent the causality of the optical spectra; therefore, analyses by the least-squares method frequently encounter difficulties. The difficulties increase, particularly in solid-state materials, because the optical spectra become complicated due to overlapping of several types of discrete and continuous optical transitions. In such
complicated spectra, it cannot be guaranteed that the analysis results are correct, and the estimation accuracies of the spectral parameters cannot be discussed with statistical confidence.

Recently, a Bayesian methodology to decompose such complicated spectra has been developed. Nagata et al. have succeeded in the deconvolution of X-ray photoelectron and optical absorption spectra that include multi-spectral components, and have statistically evaluated the probability distributions of their spectral parameters [2]. More recently, a virtual measurement analysis (VMA) methodology based on the Bayesian inference has also been proposed [3], which has enabled evaluation of the detection limits and optimization of the experimental setups.

In this paper, we propose Bayesian spectroscopy for solid-state photo-physics, which has significant advantages over the conventional least-squares method. In Sec. 2, we survey the fundamental methodology of the Bayesian inference. In Sec. 3, Bayesian spectroscopy of an optical spectrum of elementary electronic excitations is described. From the absorption spectrum of a CuO thin crystal, we demonstrate that the band gap energy $E_g$, can be estimated with extremely high accuracy by the introduction of physical laws of excitonic transitions [4]. In addition, a VMA is performed to evaluate the variation of the estimation accuracy for $E_g$ with respect to the spectral widths of exciton transitions. Bayesian spectroscopy has significant advantages, not only for such spectral decomposition, but also in normal mode analyses for coherent phonon (CP) signals. In solid-state substances, we can coherently excite phonons by femtosecond (fs) laser pulses. To resolve normal modes from such coherently-excited phonon signals, Fourier and wavelet transformations have been employed to date. In Sec. 4, we demonstrate that Bayesian spectroscopy can be used to estimate the normal mode frequency and initial vibrating phase with high accuracy beyond such conventional methods. In the final sub-sections of Secs. 3 and 4, we summarize the future prospects of such Bayesian spectroscopy.

2. Bayesian inference

In Bayesian spectroscopy, we attempt to fit a measured data set $D(y_i; x_i) \ (i = 1, \cdots, N)$ by an appropriate model function $G(x_i; \theta)$ specified by a parameter set $\theta$. However, noise $n_i$ is randomly superposed during measurements. Therefore, $y_i$ is expressed as $y_i = G(x_i; \theta) + n_i$ and the mean square error function $E(\theta)$ of the model function is defined as:

$$E(\theta) = \frac{1}{2N} \sum_{i=1}^{N} [y_i - G(x_i; \theta)]^2 . \tag{1}$$

A joint probability $P(D, \theta)$ for $D$ and $\theta$ is equivalent to $P(D|\theta)P(\theta)$, where the $P(D|\theta)$ and $P(\theta)$ are a conditional probability of $D$ under $\theta$ given and a prior probability of $\theta$, respectively. By Bayes’ theorem [5], the $P(D, \theta)$ is also written as $P(\theta|D)P(D)$, where $P(\theta|D)$ is a conditional probability of $\theta$ under the measured data $D$ given, which is what must be evaluated. When noise $n_i$ is dispersed by a normal distribution with a standard deviation $\sigma_{\text{noise}}$, and a mean value of zero, the noise distribution $P\{n_i\}$ is the same as $P(D|\theta)$ and it is proportional to $\exp\left[-NE(\theta)/\sigma_{\text{noise}}^2\right]$. Consequently, the posterior probability distribution $P(\theta|D)$ can be evaluated using Eq. (2) [2].

$$P(\theta|D) = \frac{P(D|\theta)P(\theta)}{P(D)} \propto \exp \left[-\frac{N}{\sigma_{\text{noise}}^2}E(\theta)\right] P(\theta), \tag{2}$$

where $P(D)$ becomes constant after measurement of the data set $D$. When $P(\theta)$ is a continuous uniform distribution, $P(\theta|D)$ is proportional to $\exp\left[-NE(\theta)/\sigma_{\text{noise}}^2\right]$. Consequently, the respective values in $\theta$ will be distributed nearby the minimum point of $E(\theta)$ in the parameter space, according to the $\sigma_{\text{noise}}$ of the noise.

Markov chain Monte Carlo (MCMC) methods [2, 6] have been employed to efficiently obtain the distributions of $P(\theta|D)$. In this paper, the parameters in $\theta$ were updated and recorded.
using a Metropolis algorithm [7, 8] after sufficient burn-in [6] phases. To perform Bayesian spectroscopy appropriately, the Metropolis samplings were conducted repeatedly with changing $\sigma_{\text{noise}}$ and the value of $\sigma_{\text{noise}}$ was determined based on a criterion that the root mean squared error of $\{G(x_i; \Theta)\}$ obtained from the data set $D$ is balanced with $\sigma_{\text{noise}}$.

3. Bayesian spectroscopy for elementary electronic excitations
In solid-state materials, dipole-allowed excitonic transitions [9, 10] play important roles in properties such as optical nonlinearity [11, 12] and luminescence [13, 14]. In contrast, dipole-forbidden excitonic states have also attracted much attention from a recent experimental result [15]. Such excitonic states are important candidates for the realization of excitonic Bose-Einstein condensation [16] (X-BEC) because of their long lifetimes. Investigations of X-BEC have been conducted intensively on Cu$_2$O crystals due to the finding of unusual and ballistic exciton transport [17]. However, a valid manifestation of X-BEC has only recently been reported [15] at sub-Kelvin temperatures. In addition, the optical responses (e.g., absorption and luminescence) of such excitonic states are very weak because of the dipole-forbidden transitions. Therefore, we encounter difficulties in their spectral analyses, even though we can detect such signals.

The conventional approach to decompose such complicated and weak optical spectra is the least-squares method. After decomposition, the properties of such excitonic state are investigated for each spectral component. However, it is difficult to evaluate the accuracies of the respective spectral parameters because such parameters are included nonlinearly in each spectral function. To overcome such a limitation, we have recently employed Bayesian spectroscopy to decompose an excitonic absorption spectrum in a Cu$_2$O thin crystal sandwiched by paired MgO substrates [4].

3.1. Excitonic absorption spectrum in the Cu$_2$O thin crystal
The open circles in Fig. 1(a) shows an absorption spectrum measured for a Cu$_2$O thin crystal [4]. The absorption intensity is quite weak, as shown in the ordinate scale, due to the thinness (ca. 2.8 $\mu$m [18]) of the crystal; therefore, this spectrum is obtained through wavelength integration of a wavelength modulated absorption spectrum [18, 19]. To realize X-BEC in such thin crystals, spatial accumulation of excitons beyond the critical density and suppression of spatial diffusion of excitons are essential. To achieve this goal, we must therefore confirm the formation of a shallow potential to trap excitons. Therefore, it is important to quantitatively evaluate the differences in the band gap energy $E_g$, and the excitonic Rydberg constant $R_y$, between single and thin Cu$_2$O crystals.

The absorption spectrum in Fig. 1(a) includes spectral components of excitonic resonance transitions for the yellow exciton series $X_n$ ($n = 2, 3, \ldots, \infty$), excitonic continuous and band-to-band absorption bands. The spectral functions of $X_n$ are asymmetric Lorentzian functions [20] in Eq. (3) for the resonance energy $E_n$ of the $n$-th exciton state, and they have three spectral parameters of absorption strength $f_n$, asymmetric degree $A_n$, and homogeneous broadening width, $\Gamma_n$.

$$X_n(E; E_n) = f_n \times \frac{1}{\pi} \frac{\Gamma_n + 2A_n(E - E_n)}{(E - E_n)^2 + \Gamma_n^2}.$$  (3)

Spectral functions $X_C(E; E_g)$ and $B(E; E_g)$ for the excitonic continuous and band-to-band absorption bands have been described in [4]. For analysis of the measured absorption spectrum, it is necessary to convolve inhomogeneous broadenings in the respective spectral components $g(E; E_0)$ as expressed in Eq. (4), because of the spectral resolution and sample inhomogeneity.

$$G\left(g(E; E_0)\right) = \int g(E; E_0 + d\varepsilon) \exp \left(-\ln \frac{2\varepsilon^2}{\gamma_g^2}\right) d\varepsilon / \int \exp \left(-\ln \frac{2\varepsilon^2}{\gamma_g^2}\right) d\varepsilon.$$  (4)
3.2. Physical laws for excitonic transitions

In our recent work [4], we have claimed that even if each spectral component has broad spectral width, it is possible to estimate spectral parameters with high accuracy by the introduction of appropriate physical laws between these spectral parameters. For the absorption spectrum in Fig. 1(a), a physical law was introduced in Eq. (5) among the excitonic resonance energies $E_n$, the band gap energy $E_g$, and the excitonic Rydberg constant $R_y$ [9].

$$E_n = E_g - \frac{R_y}{n^2}, \quad (n = 2, 3, \ldots, n_\infty). \quad (5)$$

In addition, a physical law was also introduced in Eq. (6) for the absorption intensities of the dipole-forbidden direct $n$–th excitonic resonances [21].

$$f_n = f_0 \left( \frac{n^2 - 1}{n^5} \right), \quad (n = 2, 5, \ldots, n_\infty), \quad (6)$$

where $f_3$ and $f_4$ do not obey this physical law, as reported in [18], so that they are dealt with as independent spectral parameters. $n_\infty$ in Eqs. (5) and (6) is the number of excitonic excited states to be considered and this is set to 20 because $f_{20}/f_2$ becomes sufficiently small.

3.3. Bayesian spectroscopy of excitonic absorption spectrum

The parameter set $\Theta$ for our Bayesian spectroscopy is expressed in Eq. (7).

$$\Theta = \{ E_g, R_y, A_2, A_3, f_0, f_3, f_4, \gamma_X, \Gamma_2, \Gamma_X \}, \quad (7)$$

where it was assumed that all excitonic resonances $X_n$ ($n = 2, \ldots, 20$), have the same inhomogeneous broadening factor $\gamma_X$. $\Gamma_2$ and $\Gamma_X$ are homogeneous broadening factors for the excitonic resonance peaks, where $\Gamma_2$ for the broad absorption peak of $X_2$ was implemented separately from the other peaks $X_n$ ($n = 3, \ldots, 20$). Asymmetric factors of the excitonic resonances higher than $X_4$ are neglected because their absorption strengths become weak at large $n$. We have successfully obtained posterior probability distributions $P(\Theta|D)$, through 2.5 million samplings after a sufficient burn-in phase. Using the mean values $\hat{\Theta}$ of $P(\Theta|D)$, we can reproduce the measured absorption spectrum well, as depicted by the solid line in Fig. 1(a).
For the Cu$_2$O thin crystal sandwiched by paired MgO plates, a small lattice mismatch between Cu$_2$O and MgO induces two-dimensional stresses at the epitaxial interface between Cu$_2$O and MgO [22]. It is thus expected that the transition energies of the excitonic resonance are changed by such stresses. Therefore, we evaluate both energy shifts $\Delta E_g$ and $\Delta R_y$ in the band gap energy and the effective Rydberg constant and the effective energy of the exciton, becomes small [4].

3.4. Virtual measurement analysis of excitonic absorption spectrum

The dashed-line spectrum overlapped on the measured spectrum in Fig. 1(a) indicates the background spectrum of the excitonic resonance transitions. The background comes from $X_C$ and $B$, and has only a gentle slope rising to the higher energy side. Therefore, the spectral profiles $X_C(E; \tilde{E}_g)$ and $B(E; \tilde{E}_g)$ [4] do not change significantly with a small change of $\tilde{E}_g$ and do not have a significant contribution to the estimation of $\tilde{E}_g$. In contrast, the excitonic resonance transitions $X_2$, $X_3$ and $X_4$ provide clear peaks and a shoulder structure on the measured spectrum in Fig. 1(a). Consequently, these transitions make it possible to estimate $\tilde{E}_g$ and $\tilde{R}_y$ with high precision because of the strong constraint among the transition energies $E_n$, in Eq. (5).

![Figure 2](image-url)  

**Figure 2.** (a) Synthesized spectra (○) with the $\gamma_X$=1.9, 3.0, 4.8, and 7.6 meV, in which the parameters of $\tilde{E}_g$ = 2.171392 eV, $\tilde{R}_y$ = 93.6 meV, $A_2$ = −0.201, $A_3$ = −0.34, $f_0$ = 8.8 $\times$ 10$^{-8}$ O.D., $f_3$ = 0.355 $\times$ 10$^{-8}$ O.D., $f_4$ = 0.179 $\times$ 10$^{-8}$ O.D., $\tilde{f}_2$ = 2.37 meV and $\tilde{f}_X$ = 1.6 meV are used. The dashed and solid lines represent the background component $(X_C + B)$ in the synthesized spectra and the reproduced spectra obtained from Bayesian spectroscopy. (b) Spectral profiles of the excitonic resonances with the respective $\gamma_X$.

To verify how the introduction of the physical law in Eq. (5) is effective for Bayesian spectroscopy, a VMA [3] was performed to evaluate the estimation accuracies of $E_g$ and $R_y$ from the synthesized data, which were made with different inhomogeneous broadening factors $\gamma_X$ in Eq. (7). Spectra plotted by open circles in Fig. 2(a) are synthesized absorption spectra with the respective $\gamma_X$. The mean values $\tilde{\Theta}$ of $P(\Theta|D)$ are used for other spectral parameters as they are.
Figure 2(b) shows the variation of the spectral profiles of $X_2$, $X_3$, $X_4$ and $X_{5\sim 20}$. The standard deviation of noise in the synthesized spectra is the same as that in the measured spectrum of Fig. 1(a). The higher excitonic resonance peaks $X_n$ ($n \geq 3$) fade away with increasing $\gamma_X$ and the lowest $X_2$ peak only shows a shoulder structure at the largest $\gamma_X$ (=7.6 meV).

![Figure 3](image-url)

Figure 3. (a-c) Variations of the mean values $\hat{E}_g$, $\hat{R}_y$ and $\hat{\gamma}_X$ with the change in $\gamma_X$, which were obtained by Bayesian spectroscopy using the synthesized spectra in Fig. 2. $\gamma_X$ are denoted in the logarithmic abscissa scale. The ordinate for $\hat{\gamma}_X$ is also a logarithmic scale. Error bars indicate the standard deviations $\sigma_{E_g}$, $\sigma_{R_y}$ and $\sigma_{\gamma_X}$ of $P(E_g|D)$, $P(R_y|D)$ and $P(\gamma_X|D)$. Dashed lines indicate the true values of the respective parameters. The horizontal dot-dashed line in (c) shows the true value of $\hat{I}_2$. (d-f) Variations of $\sigma_{E_g}$, $\sigma_{R_y}$ and $\sigma_{\gamma_X}$ with the change in $\gamma_X$, where the abscissa and ordinate axes are logarithmic scales.

The variations of the mean values $\hat{E}_g$, $\hat{R}_y$ and $\hat{\gamma}_X$, and the distribution widths of the respective $P(\Theta|D)$ are plotted by closed circles and error bars in Figs. 3(a), (b) and (c), respectively, which were obtained in the same manner as the measured spectrum. It should be noted that $\hat{E}_g$ and $\hat{R}_y$ can be estimated with high accuracy for $\gamma_X < 3$ meV. Figures 3(a) and (b) show that $\hat{E}_g$ and $\hat{R}_y$ do not significantly deviate from their true values (horizontal dashed lines), and $\sigma_{E_g}(\gamma_X)$ and $\sigma_{R_y}(\gamma_X)$ do not noticeably increase, as shown in Figs. 3(d) and (e). In the measured spectrum of Fig. 1, $\gamma_X$ was estimated to be $1.2 \pm 0.1$ meV [4]. Therefore, the accuracies of the estimated $\hat{E}_g$ and $\hat{R}_y$ depicted in Figs. 1(c) and (d) are sufficiently guaranteed.

In contrast to the cases with $\gamma_X < 3$ meV, $\hat{E}_g$ and $\hat{R}_y$ suddenly change with $\gamma_X \geq 3$ meV, and $\sigma_{E_g}(\gamma_X)$ and $\sigma_{R_y}(\gamma_X)$ begin to increase, as shown in Fig. 3. It is considered that such a change at the boundary of $\gamma_X \sim 3$ meV is due to the change in the spectral profiles of the synthesized spectra in Fig. 2. In the synthesized spectra with $\gamma_X \geq 3$ meV, the intensity of the second excitonic resonance peak $X_3$ becomes weak and its peak structure fades into the higher energy tail of the $X_2$ peak, and the absorption bands of $X_{5\sim 20}$ and the background ($X_C$ and $B$).

3.5. Future prospects in Bayesian spectroscopy of elementary electronic excitations

As noted in Sec. 3.1, measured optical spectra always include inhomogeneous broadenings in addition to homogeneous broadenings that represent physical properties such as lifetimes of the elementary electronic excitations. Although the inhomogeneous broadenings are convoluted into the optical spectra by Eq. (4), decomposition of the inhomogeneous and homogeneous
broadenings is generally a difficult problem. However, it is strongly considered that Bayesian spectroscopy will exhibit good performance for such decomposition. The closed and open circles in Fig. 3(c) show the variations of the inhomogeneous ($\gamma_X$) and homogeneous ($\hat{\gamma}_2$) broadening factors with the change in the inhomogeneous $\gamma_X$. Below the crossing point between these broadening factors, the decomposition is fully succeeded. The open circles for $\hat{\gamma}_2$ lie on the horizontal dot-dashed line that represents the true value of $\hat{\gamma}_2$. On the other hand, $\gamma_X$ increases linearly; therefore, under the conditions where the spectrum has sufficient data-point numbers, Bayesian spectroscopy can appropriately distinguish the difference between the Lorentzian and Gaussian spectral functions, and can thus decompose the spectral width into the homogeneous and inhomogeneous broadening factors.

Dipole-forbidden excitonic transitions were analyzed in the previous sections however, Bayesian spectroscopy is also effective for other spectral analyses. Spatially indirect excitons in semiconductor quantum wells and their related elementary electronic excitations in the high density regime have recently attracted much attention in the field of condensed matter physics [24] due to controversy regarding the existence of a stable electron-hole liquid phase [25]. In such quantum well systems, photoluminescence bands of the excitons, excitonic molecules, electron-hole droplets and their phonon-side bands are overlapped under high-density excitation conditions. These spectral components must be decomposed using several types of physical laws for the spectral parameters based on the established data; however, the potential of Bayesian spectroscopy for the spectral decomposition of such complicated spectra is high [26].

4. Bayesian spectroscopy for normal modes in coherent phonons

The spectroscopy of phonon normal modes is also an important issue in solid-state physics. Such normal mode spectroscopy has been performed with Raman [27] and infrared (IR) absorption [28] spectroscopy measurements. The Bayesian spectroscopy described in Sec. 3 is also useful for the spectral decomposition of such Raman and IR spectra.

4.1. Coherent phonon spectroscopy

Recent developments of fs-laser technologies have been remarkable [29], and measurements of CP signals [30, 31] using fs-laser pulses have opened a new frontier for normal mode spectroscopy. CP signals are detected as time-series intensity variations of weak probe-pulses after illumination with intense pumping pulses. At the time-origin, phonons in solid-state substances can be excited coherently by intense fs-pumping pulses and subsequent phonon vibrations periodically change the reflectivity and/or transmittance of substances, which can then be detected as CP signals using the delayed probe-pulses from the time origin.

To analyze normal modes and their dynamics from CP signals, Fourier [32] and wavelet [33] transformations have been universally employed. However, the oscillating amplitude of CP signals varies dynamically with time for such damped oscillations. When the decay time constant of the damped oscillation is $\tau$, the normal mode peak in the Fourier spectrum has spectral width uncertainty of ca. $1/\tau$. In addition, it is difficult to extract important information such as the initial vibrating phase by such conventional methods. In contrast, Bayesian spectroscopy can solve these problems through the use of an appropriate physical model that represents CP signals, and can thus significantly improve the accuracy of physical parameter estimation [34].

4.2. Bayesian spectroscopy of coherent phonons in a bismuth thin film

The dashed line in Fig. 4(a) shows the CP signal for a bismuth thin film evaporated on a Si (100) substrate [34]. The data set $D \equiv \{(t_1, y_1), \ldots, (t_N, y_N)\}$ of this CP signal can be explained by a model function $g(t; \Theta)$ in Eq. (8) with a parameter set $\Theta \equiv \{A, f, \phi, \tau, \tau_d\}$, in which $A$, $f$, $\phi$, $\tau$, and $\tau_d$ are the time-integrated intensity, vibration frequency, initial vibrating phase, the
Figure 4. (a) CP signal in a bismuth thin film and reproduced data by Bayesian inference, which were reported in [34]. Dashed and solid lines represent the measured and reproduced data, respectively. (b) Magnitude spectrum of the CP signal in (a) obtained by the DFT method and the posterior probability distribution $P(f|D)$, of the normal mode frequency obtained by Bayesian spectroscopy. The solid line shows the DFT magnitude spectrum. Solid squares with lines represent $P(f|D)$.

The most impressive results of Bayesian spectroscopy for CP signals are that the $P(f|D)$ of the normal mode frequency has an extremely narrow distribution and the initial vibrating phase $\phi$, can also be estimated with high accuracy. The $P(f|D)$ is plotted by solid squares in Fig. 4(b) and has a distribution width of 0.93 GHz in the probable error criterion. The solid line in Fig. 4(b) shows a magnitude spectrum calculated by discrete Fourier transformation (DFT), which has a bandwidth of ca. 160 GHz. The noise intensity included in the measured data corresponds to a signal-to-noise (S/N) ratio of 16 dB compared with the maximum amplitude of the $g(t; \hat{\Theta})$. As shown by the measured data in Fig. 4(a), even if the S/N ratio is not good (16 dB), the estimation accuracy of the normal mode frequency can be improved by more than two orders of magnitude compared with that for the Fourier transform. The reason for such improvement is to introduce the causality of the appropriate physical model in Eq. (8). In addition, this is the specialty of Bayesian spectroscopy for vibrational wave form analyses.

4.3. VMA of coherent phonon spectroscopy

A VMA [3] was performed to study the noise immunity of such high accuracy estimation ability of Bayesian spectroscopy for CP signals. Synthesized CP signals were prepared, as shown in Fig. 5(a), with variation of the noise intensity. In the synthesized data, the mean values $\hat{\Theta}$ obtained in Sec. 4.2 are used as true values. In the case of $-0.95$ dB, the oscillatory waveform is buried in noise; therefore, it is difficult to resolve a clear normal mode peak in the conventional Fourier and wavelet transformations.

$$g(t; \Theta) = \frac{A}{\tau_d - \tau_r} \left[ \exp \left( -\frac{t}{\tau_d} \right) - \exp \left( -\frac{t}{\tau_r} \right) \right] \sin{(2\pi ft + \phi)}, \quad (t \geq 0).$$ (8)
Figures 5(b) and (c) show the variations of $P(f|D; \sigma_{\text{noise}})$ with respect to $\sigma_{\text{noise}}$, where the noise intensities are denoted as S/N ratios in the legends. The ordinates are given as logarithmic scales. A DFT magnitude spectrum of the synthesized data at +19.0 dB is superimposed by the solid line in Fig. 5(b) with the same logarithmic scale. As reported in [34], $P(f|D; \sigma_{\text{noise}})$ at +19.0 dB was confirmed to have a predominantly narrow distribution width compared to the bandwidth of the DFT spectrum, as shown in Fig. 5(b). With further decrease in the noise intensity, the estimation accuracy of $f$, i.e., the distribution width of $P(f|D; \sigma_{\text{noise}})$, was improved, as shown in Fig. 5(c). In addition, even when the S/N ratio becomes negative (S/N = -0.95 dB), the distribution width of $P(f|D; \sigma_{\text{noise}})$ is sufficiently smaller than the bandwidth of the DFT magnitude spectrum, as shown in Fig. 5(b). $P(f|D; \sigma_{\text{noise}})$ also includes the true value of $f$, which is indicated by the vertical dashed line in Figs. 5(b) and (c). In experimental measurements, the amplitude of the oscillatory waveform is frequently rather small and buried in noise. However, this result implies that Bayesian spectroscopy can estimate the normal mode frequencies correctly in such rigorous situations.

The noise immunity of Bayesian spectroscopy for the CP signals is summarized in Fig. 6. Closed circles and error bars in Figs. 6(a)-(e) represent the variations of the mean values $\Theta$, and the standard deviations $\sigma_{\Theta}$ of the respective $P(\Theta|D)$ for the parameters in Eq. (8). Horizontal dashed lines show the true values of the corresponding parameters used in the synthesized CP signals. Here, attention should be paid to the ordinate ranges of the respective parameters. In these figures, the ranges indicated by double-arrowed vertical lines are given as percentages of the respective true values. It should be first noted that the estimations of the normal mode frequency $f$ and the initial vibrating phase $\phi$ have strong noise immunity, as shown in Figs. 6(b).
and (c), respectively. Even at the right end of these figures, where the oscillatory amplitude is buried in noise, the estimated values of $\hat{f}$ and $\hat{\phi}$ are confined within the range of $\pm 5\%$ from their true values, and it is understood that sufficient precision required in experiments is satisfied even with the worst case ($S/N = -0.95$ dB). In contrast, the amplitude $A$ and the time constants of $\tau_f$ and $\tau_d$ deviate significantly from the corresponding true values at $S/N$ ratios of less than 10 dB, as shown in Figs. 6(a), (d) and (e), respectively. Such differences in the noise immunity among these parameters are discussed in the next paragraph.

Although the optical spectrum discussed in Sec. 3 contains multiple spectral components, these components generally appear at different abscissa positions and their superposition describes the entire spectrum. In the case of the CP signals, the signal intensity change vibrationally in a successive time series. As a result, even small deviations of $f$ and $\phi$ give large residuals on $g(t; \Theta)$ at all data points where the oscillatory amplitude remains. The large residuals significantly increase the fitting error $E(f, \phi; \hat{A}, \hat{\tau}_f, \hat{\tau}_d)$ in Eq. (1). Therefore, $E(f, \phi; \hat{A}, \hat{\tau}_f, \hat{\tau}_d)$ will have a deep and steep valley at the minimum point $(\Theta = \hat{\Theta})$ in the parameter space of $\Theta$, so that $f$ and $\phi$ can be estimated correctly with significantly narrow distributions of $P(f|D)$ and $P(\phi|D)$. In the parameters $A$, $\tau_f$ and $\tau_d$, the behavior that these small deviations contribute to $E(f, \phi; \hat{A}, \hat{\tau}_f, \hat{\tau}_d)$ are different from those of $f$ and $\phi$ because these parameters only change the envelope (temporal) profile of the oscillatory waveform. Therefore, these parameters will be strongly disturbed by an increase in the noise intensity.

The effect of the noise immunity on $f$ and $\phi$ is confirmed by the variations of the distribution widths of $P(f|D)$ and $P(\phi|D)$ with respect to the noise intensity. The results are plotted in Figs. 6(f) and (g), respectively, where their distribution widths are expressed by the standard deviations $\sigma_f$ and $\sigma_\phi$, of the distributions. As shown in these figures, $\sigma_f$ and $\sigma_\phi$ are proportional

![Figure 6](image-url)
to the noise intensity, as expected.

4.4. Future prospects in Bayesian spectroscopy for coherent phonons

As described in Secs. 4.2 and 4.3, Bayesian spectroscopy for CP signals has significant advantages for estimation of the normal mode frequency $f$ and the initial vibrating phase $\phi$. Regardless of the superiority of frequency estimation, the advantage of Bayesian spectroscopy is the high accuracy for the estimation of $\phi$ for the CP signal analyses. In the conventional methods, information on $\phi$ obtained by Fourier transformation has been mostly discarded. However, the initial vibrating phase $\phi$ provides insight with respect to the mechanism for the excitation of coherent phonons because the initial phases are different depending on the excitation mechanisms [35, 36, 37]. In the case of the impulsive stimulated Raman scattering (ISRS) mechanism, atoms located at the equilibrium points in the unit cells start to vibrate from the equilibrium points by impulsive light irradiations. Therefore, the CP signals excited by the ISRS mechanism have temporal profiles of the sine function [35, 36]. On the other hand, in the mechanism for the displacive excitation of coherent phonons (DECP), the CP signals change according to cosine functions with time [37].

On the other hand, from the perspective of experimental research, it is necessary to improve the measurement accuracy of the time-origin to make full use of this Bayesian spectroscopy performance. The initial vibrating phase can also be estimated with a high accuracy of 0.012 radian [34] from the measured CP signal in Fig. 4(a). This accuracy of $\phi$ corresponds to a time-origin accuracy of ca. 0.65 fs in this normal mode. It is generally difficult to determine the time-origin with such high accuracy in experimental setups of the pump-probe methods. Therefore, when the determination of an absolute value of $\phi$ with high accuracy is required, it is necessary to improve the experimental setup.

5. Conclusion

We have proposed Bayesian spectroscopy for both spectral analyses of optical spectra and for normal mode analyses of CP signals in solid-state materials.

In the optical absorption spectrum of excitonic series in a Cu$_2$O thin crystal sandwiched by paired MgO substrates, it is an important issue to elucidate small changes of the band gap energy $E_g$ and the binding energy of the excitons $R_y$ due to stress effects from the small mismatch of the lattice constants between Cu$_2$O and MgO. Although such highly accurate estimation is strongly desired, it has been impossible by conventional analysis that decomposes the entire excitonic absorption spectrum into individual excitonic absorption peaks of $X_2$, $X_3$ and $X_4$, · · · because of the broad spectral widths of the absorption peaks. For highly accurate estimation beyond this limitation, Bayesian spectroscopy was performed by introducing physical laws with respect to the transition energies and transition strengths of the excitonic series in Cu$_2$O. It has been confirmed that the changes of $E_g$ and $R_y$ by the stress effect have very sharp posterior probability distributions, and $E_g$ and $R_y$ are significantly reduced compared with that for stress-free single crystals. In VMA for spectral analysis of the excitonic absorption, the effectiveness of Bayesian spectroscopy has been examined with synthesized spectra by changing the inhomogeneous broadening factor $\gamma_X$. As a result, the clear appearance of the excitonic $X_2$ and $X_3$ absorption peaks is necessary for high accurate estimation of $E_g$ and $R_y$. Furthermore, when the inhomogeneous broadening factor $\gamma_X$ is smaller than the homogeneous broadening factor $I_X$, it has been clearly shown that the inhomogeneous and homogeneous broadening factors can be distinguished and both $\gamma_X$ and $I_X$ can be estimated with high accuracy. These results demonstrate the potential of Bayesian spectroscopy and it is strongly expected that Bayesian spectroscopy will be employed to decompose complicated optical spectra and to estimate material parameters with high accuracy.
For the analysis of time series data in CP signals, the Fourier transform method has been traditionally used to decompose the normal mode with CP signals and to estimate the vibrating frequency $f$. In the Fourier transformation, continuous plane wave functions (sine and cosine functions) are employed as expanding basis functions. In contrast, the amplitude of CP signals changes with time and the normal mode vibrations can be modeled by damped oscillating waveforms. As a result, the normal mode has broad peaks in the magnitude spectrum obtained by Fourier transformation. In addition, the damped oscillating waveforms are expanded by inappropriate basis functions (continuous plane wave functions); therefore, the initial vibrating phase $\phi$ cannot be estimated by the Fourier transform method. Such limitations of the Fourier transform method can be overcome by Bayesian spectroscopy, in which the temporal variation of the oscillating amplitude has been modeled appropriately by exponential functions with rising $\tau_r$ and decaying $\tau_d$ time constants. In the CP signal of a bismuth thin film with an S/N ratio of 16 dB, Bayesian spectroscopy can be used to estimate the normal mode frequency with a posterior probability distribution width of 0.93 GHz, which is two orders of magnitude smaller than the bandwidth of the normal mode in the Fourier magnitude spectrum. In VMA for CP signal analysis, the noise immunity of the highly accurate estimation has been examined by changing the noise intensity. Although the estimation accuracy for the intensity $A$, and for $\tau_r$ and $\tau_d$ degrades with an increase in the noise intensity, Bayesian spectroscopy can correctly estimate both the vibrating frequency $f$ and the initial phase $\phi$ within 5% deviations from the respective true values, even when the S/N ratio is negative ($-0.95$ dB) and where the normal mode vibration is buried by the noise. Through such advantages of Bayesian spectroscopy, it will become possible to elucidate the excitation mechanism of CPs by the initial phase, and both detection and analysis of extremely weak CP signals will be possible.

The advantages of Bayesian spectroscopy clearly demonstrated here are expected to be applied to realize significant progress in solid-state physics.

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