Simulations of Two-Dimensional Electronic Correlation Spectra

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Two-dimensional (2D) correlation method, which generates the synchronous and the asynchronous 2D spectrum by complex cross correlation of the Fourier transformed spectra, is an analysis method for the changes of the sample spectrum induced by various perturbations. In the present work, the 2D electronic correlation spectra have been simulated for the cases where the sample spectrum composed of two gaussian bands changes linearly. When only the band amplitudes of the sample spectrum change, the synchronous spectrum shows strong peaks at the band centers of the sample spectrum, but the asynchronous spectrum does not make peaks. When the sample spectrum shifts without changing intensity and width, the synchronous spectrum shows peaks around the initial and final positions of the band maximum and the asynchronous spectrum shows long peaks spanning the shifting range. The band width change produces the complex 2D correlation spectra. When the sample spectrum shifts with band broadening, the width change by 50% of full width at half maximum (FWHM) does not give so large an effect on the correlation spectrum as the spectral shift by one half of FWHM of the sample spectrum.

Keywords : Two-dimensional correlation, Electronic spectra.

Introduction

Recent studies use two-dimensional (2D) correlation spectroscopy to observe the characteristics of the vibrational spectrum of different molecular systems. Obviously the 2D spectrum, which plots the spectral intensity in the space of two independent spectral variables, provides more information about complex systems than a one-dimensional spectrum. Researchers have studied temperature dependent liquid phase dynamics[1,2] and reaction dynamics in liquid[3] using 2D correlation spectroscopy. 2D correlation spectroscopy is useful in the study of complicated topics of polymer science, such as the secondary structure of polymers,[4] the conformational changes of polymer blends[5] and the crystallization process of polymers.[6] Phase transition of liquid crystalline materials[7] and monolayer films[8] is another complex example studied with the 2D correlation method. Investigations on the denaturation[9,10] and structural changes[11-13] of proteins using 2D correlation spectroscopy are reported.

2D correlation spectroscopy is different from 2D spectroscopy, which uses mutiple-pulse excitations, such as the 2D NMR spectroscopy. The vibrational version of 2D NMR spectroscopy is regarded as having the potential to provide information about molecular geometry and vibrational energy dynamics,[14] and many experiments on nonlinear 2D vibrational spectroscopy have been carried out by several research groups.[15-20] The vibrational analog of 2D NMR spectroscopy is sometimes called nonlinear 2D vibrational spectroscopy since the vibrational nonlinearities are involved. 2D vibrational correlation spectroscopy does not provide direct information about interactions between the vibrational modes, as the nonlinear 2D vibrational spectroscopy does. However, 2D correlation spectroscopy is effective in analyzing complex spectra and understanding the effects of various perturbations causing spectral modifications, such as time, concentration, temperature, pressure, etc.

The 2D correlation method has been applied mostly to the analysis of the vibrational spectrum, and some simulation studies of the 2D vibrational correlation spectrum are reported.[21-23] Studies show that the effects of random noise and baseline fluctuation can be eliminated by 2D correlation analysis.[21] The effects of changes of band position, width and amplitude on the 2D vibrational correlation spectrum are also studied by simulation.[22] However, the changes of vibrational spectra by perturbations is not very significant. The vibrational band shift is 10 cm^{-1} more or less and the relative intensity change is only a few percent under most perturbations. The fundamental spectral shape of the vibrational band hardly changes in many cases. So relatively small changes of spectral parameters are investigated in the simulation studies of the 2D vibrational correlation spectrum.

The 2D correlation method is not limited by the spectral range of the sample spectrum. Even the heterocorrelation between different spectroscopic regions is possible,[24] however, 2D electronic correlation spectra have not been reported, to our knowledge. Since the electronic spectrum is composed of many vibrational bands, 2D electronic correlation spectroscopy may provide much information that the 2D vibrational correlation spectroscopy does not have. Band intensity, position, and width of electronic spectra are modified by perturbations such as concentration, temperature, pressure, solvents, etc. The solvent effect on the electronic spectrum has been studied at length[25] and the solvation dynamics, which requires ultrafast spectroscopic techniques, has been one of the main research topics in physical

chemistry.[26] Analysis of the electronic spectrum with the 2D correlation method may give valuable information about the details of the potential energy surface for the electronic states. In the present work, the 2D electronic correlation spectra are generated from the sample spectra, which are composed of two gaussian bands. The linear variations of positions, amplitudes, and/or widths of the gaussian bands are studied with the 2D correlation spectrum.

Calculation of 2D Correlation Spectra

The mathematical background for the 2D correlation has been described elsewhere in detail.[26-28] Many properties of the 2D correlation spectrum have also been investigated. A brief outline of the 2D correlation method is given here. The dynamic spectrum $y(\nu, \tau)$ is obtained by subtracting the average spectrum $s(\nu)$ from each sample spectrum $s(\nu, \tau)$, where ν is a spectral frequency.

$$y(\nu, \tau) = s(\nu, \tau) - s(\nu), \quad (1)$$

where $s(\nu)$ is equal to $(1/n) \sum_{\tau} s(g, \tau)$, n is the total number of spectra produced by perturbations, and τ is the index for the spectrum, that is, τ changes from 1 to n. Discrete Fourier transform of the dynamic spectra, $Y(\nu, g)$ has both real and imaginary components.

$$Y(\nu, g) = (1/n) \sum_{\tau} y(\nu, \tau)\, e^{-i2\pi g(\tau/n)}, \quad (2)$$

where g=1, 2, ..., n is a running index in the Fourier space. The complex cross correlation between the Fourier transformed spectra at ν_1 and ν_2 gives the synchronous and asynchronous spectrum, $\Phi(\nu_1,\nu_2)$ and $\Psi(\nu_1,\nu_2)$.

$$\Phi(\nu_1,\nu_2) + i\Psi(\nu_1,\nu_2) = (2/\pi n) \sum_{g} Y^*(\nu_1,g)Y(\nu_2,g) \quad (3)$$

The synchronous spectrum is composed of autopeaks at the diagonal line corresponding to $\nu_1 = \nu_2$ and cross peaks for the bands which have the correlated dynamic relation in the sample spectrum. The autopeaks have only positive intensity. The asynchronous spectrum has only cross peaks at (ν_1,ν_2) where the intensities at ν_1 and ν_2 change out of phase in the sample spectrum. The cross peaks at (ν_1,ν_2) and (ν_2,ν_1) of the asynchronous spectrum have the same amplitude but different sign. The synchronous spectrum generally shows much greater peak intensity than the conjugate asynchronous spectrum as given in Table 1-4.

If the intensities of two positions of the sample spectrum increase or decrease together, the corresponding cross peak of the synchronous spectrum has a positive sign. If the intensity of one position of the sample spectrum increases but the intensity of the coupled position decreases, the corresponding cross peak of the synchronous spectrum has a negative sign. The cross peak appears in the asynchronous spectrum only when the intensity change of two positions is delayed or accelerated simultaneously. The peak of the asynchronous spectrum depends on the phase of the intensity change in the sample spectrum. When the intensities of the sample spectrum change synchronously, the asynchronous correlation spectrum have no peaks. The asynchronous spectrum does not develop peaks even with the synchronous intensity change where one band grows and the other band diminishes. The sign of the asynchronous peak depends on the sign of the phase difference so that the asynchronous spectrum is anti-symmetric to the diagonal line. If the intensity of a specific region of the sample spectrum does not change at all, no peaks appear in the corresponding region of the correlation spectrum.

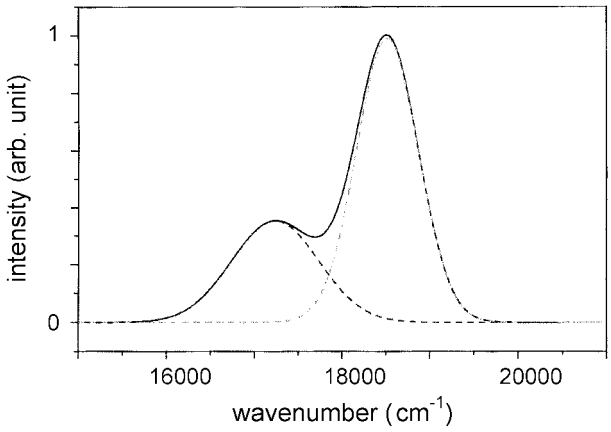

Figure 1. The sample spectrum before spectral change. Two constituent bands (dashed line) are gaussian and the intensity ratio is 2.

The sample electronic spectrum for the simulation of the 2D correlation spectrum is shown in Figure 1. The spectrum is composed of two gaussian bands, one band with FWHM of 1200 cm^{-1} at 17240 cm^{-1} and the other larger band with FWHM of 800 cm^{-1} at 18520 cm^{-1}. The intensity ratio of the two bands is 2 before the spectral changes. This spectrum is similar to the spectrum of organic dye molecules. Eleven sample spectra corresponding to $s(\nu,\tau)$ of Eq. (1) were obtained by changing linearly band intensity, width, and/or center of the two gaussian bands and processed to determine the correlation spectrum. The number of the sample spectrum used in the 2D correlation does not affect the resulting correlation spectra to a great event as long as the overall spectral change is equivalent. The gaussian shape of each band of the sample spectrum is kept during the variation of the spectral parameters but different variation of each band distorts the overall shape of the sample spectrum. The program for the 2D correlation used in this work is obtained from Ozaki group.[30]

Results

Figure 2 shows the synchronous spectra for the cases in which only the amplitudes of the two bands of the sample spectrum were varied. All the 2D correlation spectra of the present work were normalized with the peak maximum intensity. When the amplitudes of both bands increased or decreased together, the synchronous spectrum did not have any negative peaks as the spectrum of Figure 2(a). When one band grew and the other band was diminished, the synchronous spectrum had negative peaks as shown in the spectrum

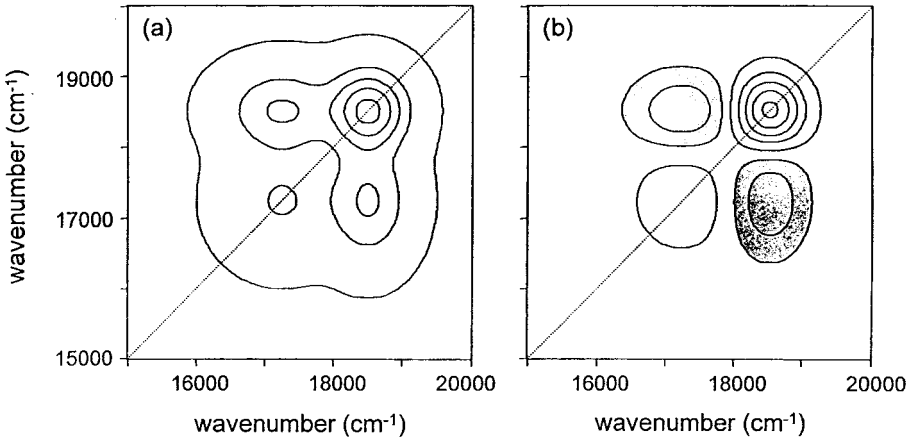

Figure 2. The synchronous spectra when only the amplitudes of the two bands of the sample spectrum change. The shadowed part of the spectrum represents the area of negative intensity and the same notation is used in all of the correlation spectra. All the 2D correlation spectra of this work are normalized with the peak maximum intensity. The peak maximum intensities are given in Table 1-2. (a) The amplitudes of both bands decrease by 50%. (b) The amplitude of the red side band of the sample spectrum increases by 50% while the amplitude of the blue side band decreases by 50%. The conjugate asynchronous spectra of (a) and (b) do not have peaks.

of Figure 2(b). If only the amplitude of each band of the sample spectrum changed, the asynchronous spectrum did not develop peaks at all, that is, the asynchronous spectrum was not generated. The peak maximum intensities of the synchronous spectrum for several cases of the band amplitude change are given in Table 1.

Figure 3 shows the correlation spectra when the sample spectrum shifted without changing width and amplitude of each band. In case of the overall shift of the sample spectrum, the synchronous spectrum had the autopeaks around the initial and final band maximum. The small autopeaks due to the shift of the smaller red side band were not clearly shown in the normalized spectrum. The band shift made the long peaks along the diagonal in the asynchronous spectra. When the bands shift in different directions, the asynchronous spectrum has some peaks in the region between the two bands as shown in Figures 3(f) and 3(h). The peak maximum intensities of the correlation spectrum for the different shift cases are given in Table 2.

The 2D correlation spectra for the cases in which the band width varied without band shift and band area change are shown in Figure 4. The synchronous spectra had strong autopeaks around the band centers of the sample spectrum. Positive and negative peaks appeared alternatively at the off-diagonal region of the synchronous spectrum. The asynchronous spectra showed L-shape or complicated peaks. As given in Table 3, the peak maximum intensity of the correlation spectrum is greater in case of the band narrowing than in case of the broadening.

Figure 5 shows the 2D correlation spectra for the cases in which the sample spectrum shifted and broadened simultaneously. The band width increased by 50% but the shift was different in three cases. The peak maximum intensity of the correlation spectrum decreased with the lesser shift as given in Table 4. As the spectra of Figure 5 are the normalized spectrum, the spectra for the shift of 100 cm^{-1} and 300 cm^{-1} showed peaks which did not appear in the spectrum for the shift of 500 cm^{-1}.

Discussion

Band Amplitude Change. When only the band amplitudes increased or decreased simultaneously without change in the band width and the position in the sample spectrum, the synchronous spectrum had only positive peaks, as seen in the Results section. Even when the amplitude change rates of the two bands were different, no negative peaks were generated in the synchronous spectrum.

The 2D correlation spectrum was not sensitive to changes in the relatively small bands of the sample spectrum. The peaks due to the change of the smaller band of the sample spectrum were not clear in the normalized correlation spectrum. As the sample spectrum had a larger band at the blue side, the synchronous spectrum had a larger peak at the blue side. The peak intensity of the correlation spectrum is not related to the relative change of the sample spectrum. The larger change in the absolute intensity of the sample spectrum created the greater peaks in the correlation spectrum. The synchronous spectrum in the case of the band amplitude increase by 50% is almost identical with the spectrum of

Table 1. The peak maximum intensity of the synchronous spectrum when only the amplitudes of the bands change

change(%)*	(–10, –10)	(–30, –30)	(–50, –50)	(50, –50)	(–50, 50)	(50, 50)
intensity**	40	350	970	900	900	930

*The numbers in the parenthesis indicate the changing ratio of the red side band and the blue side band of the sample spectrum respectively. **The intensity of the same scale is used for the data of Table 1-4.

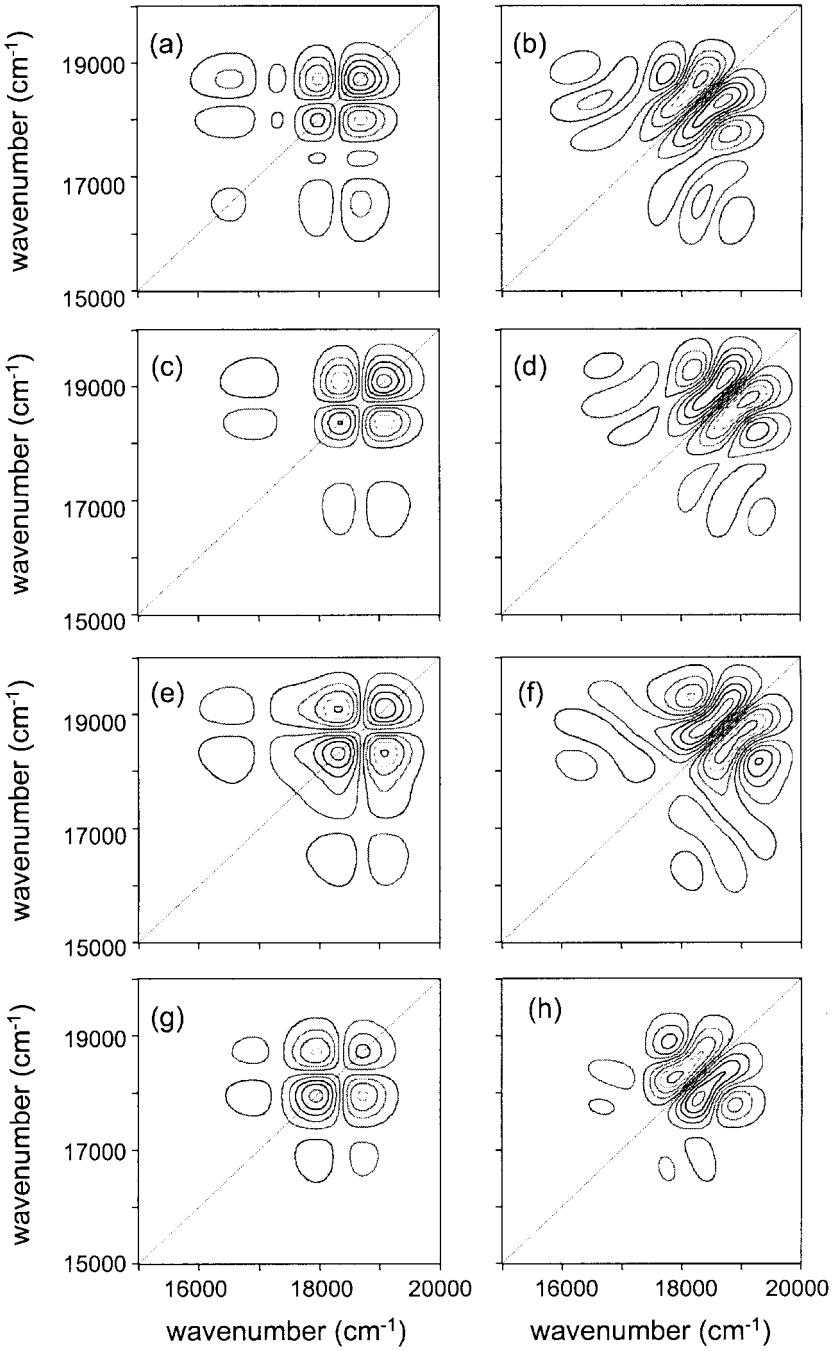

Figure 3. The correlation spectra for the cases where the bands of the sample spectrum shift. (a) The synchronous spectrum when two bands shift to red by 500 cm^{-1}. (b) The conjugate asynchronous spectrum of (a). (c) The synchronous spectrum when two bands shift to blue by 500 cm^{-1}. (d) The conjugate asynchronous spectrum of (c). (e) The synchronous spectrum when the bands are separating by shifting by 500 cm^{-1} respectively. (f) The conjugate asynchronous spectrum of (e). (g) The synchronous spectrum when the bands are merging by shifting by 500 cm^{-1} respectively. (h) The conjugate asynchronous spectrum of (g).

Figure 2(a).

The off-diagonal cross peaks of Figure 2(b) were negative because one band grew and the other band was diminished in the sample spectrum. It can be shown with the Fourier transform relation for the 2D correlation that the asynchronous correlation spectrum has no peaks if only the amplitudes of the constituent bands change. When the change in the sample spectrum is expressed by a linear combination of the given bands, the Fourier transform for the asynchronous spectrum vanishes.

Band Shift. The direction of the spectrum shift does not make significant differences in the correlation spectrum as shown in Figures 3(a)-3(d). The synchronous spectra for the red shift [Figure 3(a)] and the blue shift [Figure 3(c)] had the same pattern, except for the peak positions, which depend on the initial and final position of the bands in the sample

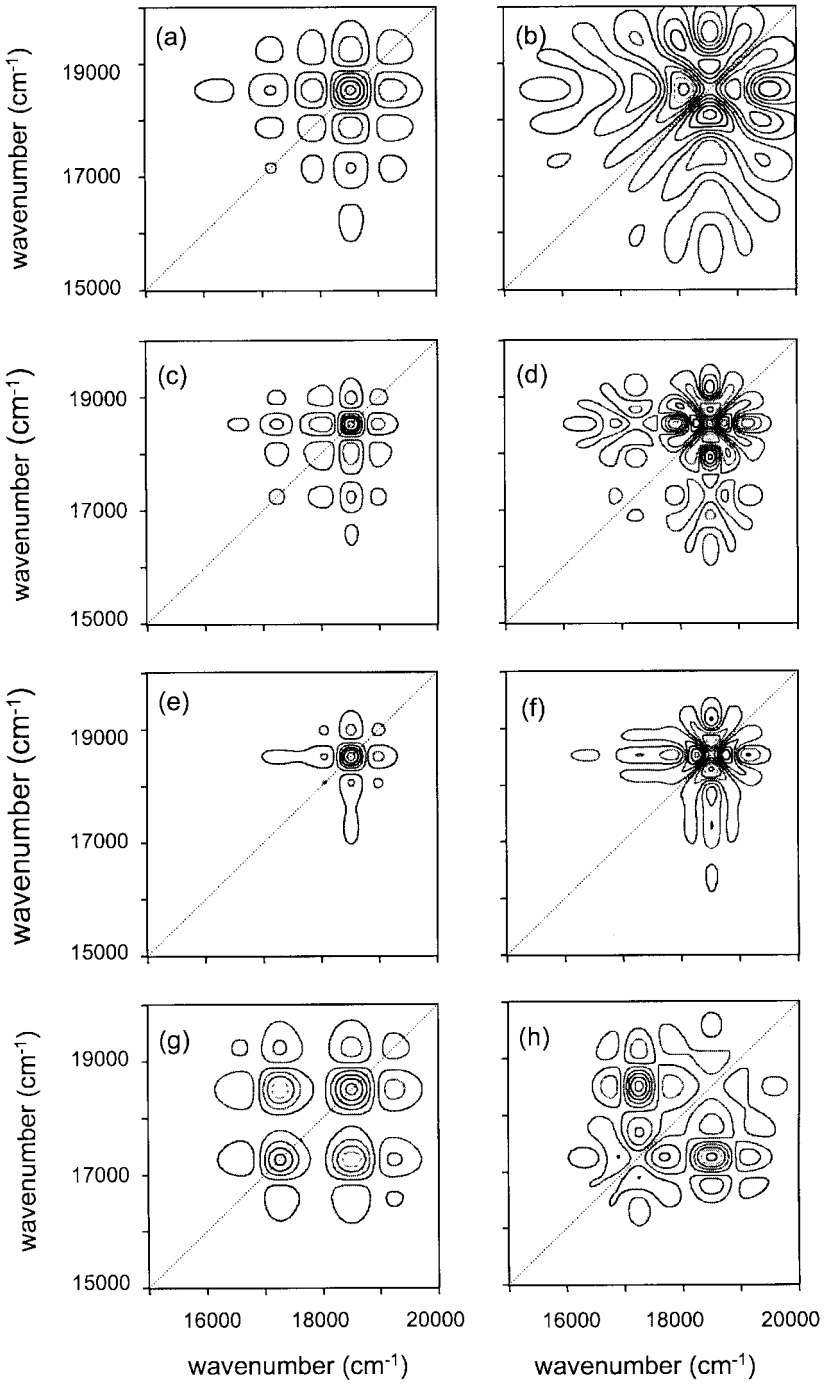

Figure 4. The correlation spectra for the cases where the band width of the sample spectrum changes without the band area change. (a) The synchronous spectrum when the width of two bands increases by 50%. (b) The conjugate asynchronous spectrum of (a). (c) The synchronous spectrum when the width of two bands decreases by 50%. (d) The conjugate asynchronous spectrum of (c). (e) The synchronous spectrum when the width of the red side band increases by 50% and the width of the blue side band decreases by 50%. (f) The conjugate asynchronous spectrum of (e). (g) The synchronous spectrum when the width of the red side band decreases by 50% and the width of the blue side band increases by 50%. (h) The conjugate asynchronous spectrum of (g).

spectrum. The 2D correlation spectra reflect the correlation of the spectral intensity at γ_1 and γ_2. When a band maximum shifts from γ_1 to γ_2, the spectral intensity at γ_1 decreased and the spectral intensity at γ_2 increased. The synchronous spectrum for the spectral shift shows a similar pattern as the synchronous spectrum for the amplitude change shown in Figure 2(b). The peaks from the shift of the smaller band at 17240 cm^{-1} of the sample spectrum are not shown in the normalized correlation spectra of Figure 3.

When two bands of the sample spectrum shift in different directions [Figures 3(e)-3(h)], the synchronous spectrum has the strongest autopeak at the overlapped region of the two

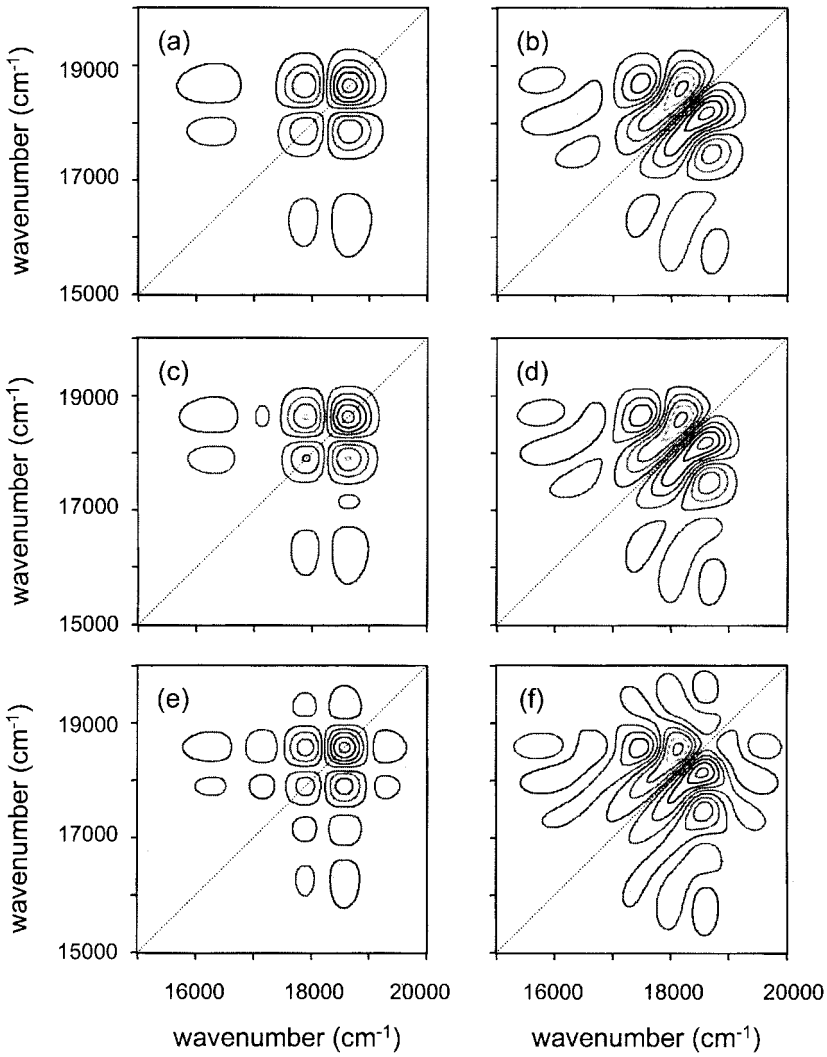

Figure 5. The correlation spectra for the cases where the bands of the sample spectrum shift and broaden simultaneously. The band area is kept constant during the spectral change as in Figure 4. (a) The synchronous spectrum when two bands shift to red by 500 cm^{-1} and broaden by 50% simultaneously. (b) The conjugate asynchronous spectrum of (a). (c) The synchronous spectrum when two bands shift to red by 300 cm^{-1} and broaden by 50% simultaneously. (d) The conjugate asynchronous spectrum of (c). (e) The synchronous spectrum when two bands shift to red by 100 cm^{-1} and broaden by 50% simultaneously. (f) The conjugate asynchronous spectrum of (e).

bands in the sample spectrum, where the spectral intensity changed greatest. The maximum autopeak in the overlapped region of the sample spectrum was not observed in the synchronous spectra of Figures 2, 3(a) and 3(c). In the case of the 500 cm^{-1} shift, the intensity change in the sample spectrum was greater for the band merging than separating so that the peak maximum intensity was greater for the merging bands, as given in Table 2.

The correlation of the red and the blue edge of the sample spectrum appears in the upper-left and lower-right region of the correlation spectrum. The signs of these cross peaks of the synchronous spectrum are related with the pattern of the intensity change in the sample spectrum. The negative sign of the cross peak of the synchronous spectrum indicates that the intensity of one position increases and the intensity of the coupled position decreases in the sample spectrum. In the case in which the whole spectrum shifted, the intensities of the red and blue edge of the sample spectrum displayed

Table 2. The peak maximum intensity of the correlation spectrum when the two bands shift

shift (cm^{-1})*	(100, 100)	(300, 300)	(500, 500)	(–500, 500)	(500, –500)	(–500, –500)
intensity**	(115, 3)	(950, 70)	(2250, 270)	(3500, 330)	(2400, 290)	(2200, 270)

*The numbers in the parenthesis indicate the shift of the red side and the blue side band of the sample spectrum respectively. The positive and negative values represent the red and blue shift respectively. **The numbers of the parenthesis correspond to the synchronous and asynchronous spectrum respectively.

opposite change. The cross peak between the red and blue edge has a negative sign. In the case in which the two bands of the sample spectrum shifted in different directions, the intensities of the edges of the sample spectrum changed in the same direction, that is, they increased or decreased together. The cross peak between the edge has a positive sign in the synchronous spectrum.

The difference in the intensity change sequence generated peaks in theasynchronous spectrum. The peaks of Figures 3(b) and 3(d) have different signs because the spectrum shifted in different directions. The long peak along the diagonal of the asynchronous spectrum due to the shift is also reported in the simulation with the vibrational correlation spectrum.[21] The asynchronous spectrum in the case of the band separating shown in Figure 3(f) has the L shape peak. The relatively long peak in the direction perpendicular to the diagonal is attributed to the intensity difference of the two bands of the sample spectrum. The correlation spectrum for the case of the band merging has the peaks in the smaller region compared with the case of the band separating because the main intensity change occurred in the smaller region of the sample spectrum in the case of the band merging. The asynchronous spectra of Figure 3 show mainly the effect of the larger band of the sample spectrum, which can be confirmed from the distribution of the peak sign in the asynchronous spectrum of Figure 3. Figures 3(b) and 3(h) indicate that the larger band shifts to red, whereas Figures 3(d) and 3(f) indicate that the larger band shifts to blue. When the sample spectrum shift was less than 500 cm^{-1}, the peak intensities of the correlation spectrum were reduced as given in Table 2, but the patterns of the correlation spectra are very similar.

Band Width Change. In the case in which the two bands of the sample spectrum became broader or narrower without the band area change, the correlation spectra show similar patterns in the different ranges, as the spectra of Figure 4(a)-4(d). The band narrowing (broadening) without the band area change made the intensity at the band center increase (decrease), and the intensity of the band edge decrease (increase). Therefore, the synchronous spectrum shows three autopeaks, the strongest one at the middle. When the width of one band changed without change of its band area, the synchronous spectrum produced three cross peaks. One was positive and the others were negative. In the case of the band narrowing, the intensity change occurred in the smaller region of the sample spectrum and the correlation spectrum produced the peaks in the smaller region. The situation is similar, as in case of the band merging and separating. The absolute intensity change of the sample spectrum was greater in the case of the band narrowing than the band broadening. Therefore, the band narrowing in the sample spectrum made the greater peak maximum in the correlation spectrum, as given in Table 3. The narrowing effect of the larger band is overwhelming in Figure 4(e). The peaks due to the change in the smaller band were not clear in the normalized spectrum. The peak signs are inversed for the case of band narrowing and broadening.

When one band broadens and the other band narrows, the asynchronous spectrum show a complicated pattern as the spectrum of Figures 4(f) and 4(h). While the asynchronous spectrum has much smaller peak intensity than the synchronous spectrum, the asynchronous spectrum is more sensitive to the changes of the sample spectrum than the synchronous spectrum. However, the small peak intensities of the asynchronous spectrum for the case of the band broadening, as given in Table 3, suggest that the band width effect might be difficult to investigate with the 2D correlation method.

Simultaneous Shift and Broadening. Perturbations of a molecular system usually cause the spectrum to shift and broaden. The band maximum intensity decreases with broadening if the band area does not change. Sometimes the band area itself varies by perturbations. The change in the spectral intensity can be monitored easily by integrating the spectrum. If the sample spectra are normalized before analyzing with the 2D correlation method, the effect of intensity change is separated and the effects of the other spectral parameters can be studied through the 2D correlation analysis. In this work, the spectral area change of the sample spectrum is not considered, except in Figure 2.

The 2D correlation spectra for the case in which the sample spectrum shifts to red by 500 cm^{-1} and broadens by 50% of FWHM, are similar to the spectra for the case of the shift only as shown in Figures 3 and 5. The effect of the band shift of 500 cm^{-1}, which is close to one half of FWHM, is

Table 4. The peak maximum intensity of the correlation spectrum when the shift and the broadening occur simultaneously. The shift and the broadening ratio are the same for the two bands of the sample spectrum*

shift (cm^{-1}) / width (%)	0	100	300	500
0	(0, 0)	(115, 3)	(950, 70)	(2250, 270)
10	(30, 0.2)	(125, 4)	(850, 60)	(2050, 230)
30	(190, 4)	(265, 10)	(850, 60)	(1800, 185)
50	(400, 13)	(500, 20)	(950, 65)	(1700, 170)

*The numbers of the parenthesis correspond to the synchronous and asynchronous spectrum respectively.

Table 3. The peak maximum intensity of the correlation spectrum when the band width changes

change (%)*	(10, 10)	(30, 30)	(50, 50)	(–50, 50)	(50, –50)	(–50, –50)
intensity**	(30, 0.2)	(190, 4)	(400, 13)	(550, 60)	(3050, 165)	(2650, 135)

*The numbers in the parenthesis indicate the changing ratio of the red side and the blue side band of the sample spectrum respectively. The positive and negative values represent the ratio of broadening and narrowing respectively. **The numbers of the parenthesis correspond to the synchronous and asynchronous spectrum respectively.

dominant in the correlation spectrum for the case that the shift and the broadening are mixed in the sample spectrum. The shift by 100 cm^{-1}, corresponding to about 10% of FWHM of the bands, does not have great impact on the 2D correlation spectrum. The correlation spectrum for the case of the 100 cm^{-1} shift and 50% broadening, is similar to the correlation spectrum for the case of the 50% broadening only. The relative importance of the shift and the broadening in the correlation spectrum seems to be determined by the size of the absolute intensity change of the sample spectrum.

The intensity of the blue side of the sample spectrum decreases at the greatest rate in the case of the red shift since the larger band is located in the blue side. The synchronous spectrum for the red shift of the sample spectrum has the maximum intensity in the blue region. When the sample spectrum becomes broader, the intensity around the band maximum decreases, but the intensity of the edge increases. The effects of the shift and the broadening are combined in complicated manners as seen in Table 4. The width dependence of the peak maximum intensity is not simple. The width dependence changes with the amount of shift. More extensive study is required to understand the peak intensity of the correlation spectrum quantitatively.

Summary

The 2D correlation method was applied to simulate the electronic correlation spectrum. The wide electronic spectrum is affected much more by the usual perturbations than the vibrational spectrum. When only the band intensity changes, the synchronous spectrum has peaks at the band centers of the sample spectrum, but the asynchronous spectrum has no peaks. When a band of the sample spectrum shifts, the synchronous spectrum has autopeaks around the initial and final band center of the sample spectrum, and the asynchronous spectrum has long peaks along the diagonal spanning the shifting range in the sample spectrum. The spectral width change in the sample spectrum develops complex patterns of the 2D correlation spectra. The band narrowing of the sample spectrum makes larger peaks in the correlation spectrum than the band broadening because the absolute intensity change of the sample spectrum is greater in the case of the band narrowing. The complicated correlation spectra attributed to the absolute intensity change of the sample spectrum are produced when the sample spectrum broadens and shifts simultaneously.

The spectral changes of the electronic spectrum simulated in this work may be encountered in many experiments. As examples, the electronic spectrum of molecules changes at high pressures and the spectrum of probe molecules varies with the structural relaxation of biomolecules. One of advantages of electronic spectroscopy over vibrational spectroscopy is that both the absorption and emission spectra can be obtained easily. Meanwhile, the same ground and excited state are involved in the absorption and emission; both absorption and emission spectrum have different information. The absorption spectrum provides detailed information about the excited state while the emission spectrum is related to the structure of ground electronic state. If the 2D correlation analysis method is applied to both the absorption and emission spectrum of a system being perturbed by the various parameters, the detailed information about the potential energy surface of the excited and ground electronic states can be obtained. It would be interesting to investigate the difference in the response of the ground and excited electronic state to perturbations. The molecular systems that give well resolved vibronic bands such as anthracene, would be a good model system for the 2D electronic correlation analysis.

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