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Two-Dimensional Raman (2D Raman) Correlation Spectroscopy Study of Non-oxidative Photodegradation of β -Carotene[†]

Isao Noda^{*,‡} and Curtis Marcott[§]

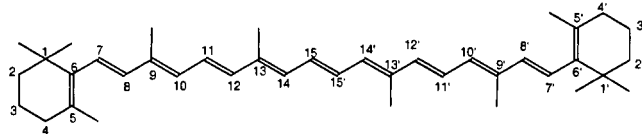
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Photoinduced decomposition reaction of *all-trans*- β -carotene in the absence of oxygen was studied by 2D Raman correlation spectroscopy. Generalized two-dimensional correlation analysis, coupled with NIR-excited Raman scattering measurements, reveals the presence of both simultaneous and sequential changes of Raman intensities associated with the decomposing β -carotene and the creation of photoreaction products. The largest intensity increase occurs for the Raman band at 1537 cm^{-1} , which is likely due to the formation of a photoisomerization product containing one or more *cis* C=C groups. The formation of this product occurs at an earlier stage of the reaction than the steady decrease of band intensities associated with *all-trans*- β -carotene at 1522 and 1520 cm^{-1} . Smaller intensity increases at 1133, 1569, and 1284 cm^{-1} occur synchronously with the growth of the 1537 cm^{-1} band and prior to the overall decrease in the *all-trans*- β -carotene bands. Thus, the decomposition product associated with the Raman bands at 1133, 1569, and 1284 cm^{-1} are either due to the same decomposition product as that represented by the 1537 cm^{-1} band, or different products formed at the same rate. The intensities of Raman bands at 1005 and 1000 cm^{-1} decrease in intensity, but this decrease lags behind that observed in the main 1520 and 1520 cm^{-1} *all-trans*- β -carotene bands. These bands may represent spectral contributions from different decomposition products overlapped with the dominant β -carotene contribution as well as a toluene solvent band.

Introduction

β -Carotene is known for the rapid degradation induced by the exposure to light or oxygen.¹ It is speculated that this sensitivity of β -carotene to light and oxygen may actually serve as a beneficial biological protective mechanism against photo-induced tissue injury. For example, singlet oxygen and free radicals produced during a photosensitized oxidative reaction can cause cellular damage by reacting with DNA and proteins or by inducing lipid peroxidation.² By effectively scavenging free radicals and quenching singlet oxygen, β -carotene may minimize such tissue damage.³ It is also known that β -carotene undergoes extensive degradation reactions, even in the absence of oxygen. Thus, a sample of β -carotene, while carefully stored in a well-sealed substantially oxygen-free bottle, may become contaminated by the photodegradation products, if it is unprotected from even a mild light source, such as room ceiling fluorescent light. This non-oxidative photodegradation of β -carotene is the focus of the current study. Shown below is the basic structure of *all-trans*- β -carotene.



Raman spectroscopy has been used extensively for the study of β -carotene and related compounds.^{4–12} One of the practical

reasons behind the immense popularity of β -carotene in the field of Raman spectroscopy stems from the simple fact that β -carotene is an exceptionally strong Raman scatterer. Raman signals obtained from β -carotene are so strong that the even subtle changes in spectral features induced by various external factors, including the onset of minor chemical reactions, can be unambiguously captured with excellent signal-to-noise ratio. Near-infrared induced Raman scattering, e.g., using the excitation at 752 nm, is of special interest in the study of the photodecomposition chemistry of β -carotene, as the sample can be excited well outside the main absorption bands of β -carotene located between 380 and 520 nm.^{16,12} The selection of the excitation wavelength is effective in minimizing the unwanted side reactions of the probe-induced decomposition during the measurement of Raman spectra of β -carotene.

The fundamental concept of the *generalized two-dimensional (2D) correlation spectroscopy* was introduced during the first AIRS meeting in Tokyo organized by Tasumi et al. in 1993.¹³ The 2D correlation is a powerful, model-free spectroscopic tool to clarify and sort out complex variations in spectral features detected during the observation of a system under some external physical influences.^{14–16} A pairwise cross-correlation analysis of spectral intensity variations generates the 2D correlation spectra useful for the determination of not-so-apparent correlated behavior of various spectral features. Because of the broad and robust applicability of this technique, 2D correlation analysis has been successfully utilized in numerous areas of spectroscopy, including IR, Raman, fluorescence, NIR, X-ray, etc.^{16–23}

The first application of 2D correlation analysis to Raman spectroscopy was reported during the same AIRS meeting.^{24,25} A set of nanosecond time-resolved resonance Raman spectra

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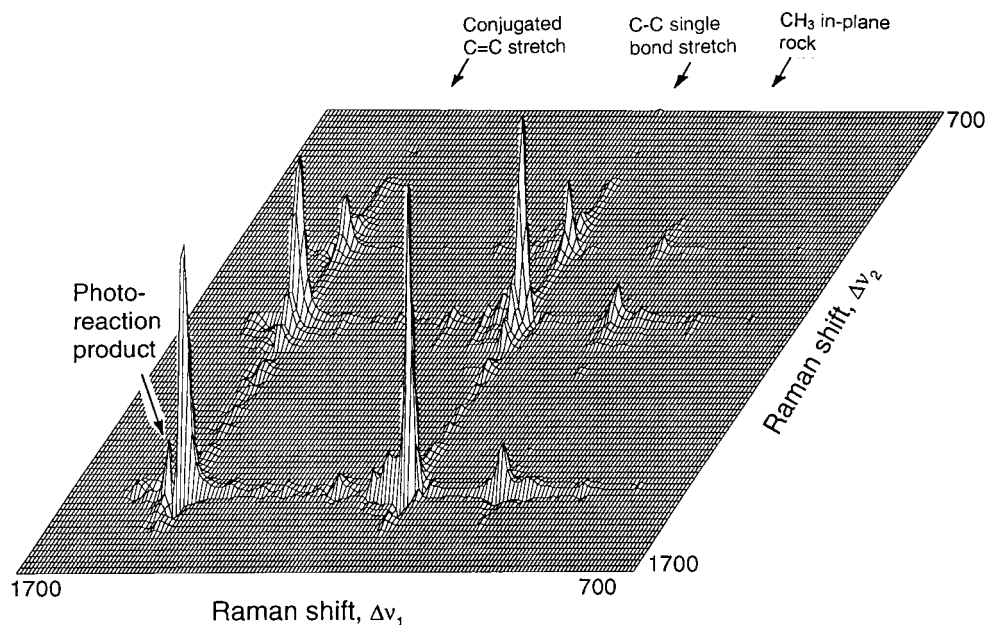


Figure 1. Fishnet (3D) representation of the synchronous 2D Raman correlation spectrum of the photoinduced decomposition of β -carotene.

of benzil radical anions in a solvent measured during a pump–probe experiment was analyzed by the 2D correlation method to generate the first 2D Raman spectra. By taking advantage of the distinct transient waveform signature of Raman intensity signals, the 2D Raman study successfully separated the spectral contributions arising from radical anions and those from solvent background.²⁵ Gustafson et al. later applied the 2D correlation analysis to the picosecond transient Raman study of solvent/solute interactions for *trans*-4,4'-diphenylstilbene in methylene chloride to accentuate the subtle effect observed in the course of a pump–probe experiment.²⁶ A rheo-optical study of polymers using 2D correlation coupled with time-resolved Raman measurement was reported by Fuller and co-workers.²⁷ Submolecular segmental dynamics of polymer chains was elucidated by the 2D Raman technique. Around the same time, the temperature-dependent variation of Raman spectra of *N*-methylacetamide in the pure liquid state was analyzed by the generalized 2D correlation technique by Ozaki and co-workers.²⁸ The state of hydrogen bonding interactions of this highly associated compound was probed with both 2D Raman and IR-Raman heterospectral correlation analysis.

In 2D Raman correlation spectroscopy,^{25–28} the cross-correlation intensities of dynamic variations of Raman scattering signals, arising from the physicochemical changes imposed onto the system of interest, such as those created by a photoinduced chemical reaction, are plotted on two independent Raman shift axes. Figure 1 shows an example of the synchronous 2D Raman correlation spectrum, where the correlated changes of Raman intensities are plotted using a two-dimensional spectral plane defined by orthogonal Raman shift axes. The important feature of such 2D correlation spectra is that the similarity or dissimilarity of the overall time-dependent spectral signal variations can be identified by the presence of correlation peaks appearing at a point on the appropriate coordinates of the 2D spectral plane. The appearance of these peaks indicates the coordinated variational nature of specific Raman spectral features.

In this study of β -carotene, we coupled the transient measurement of NIR-excited Raman scattering with the generalized two-dimensional correlation analysis to probe the complex time-dependent photochemical degradation of β -carotene in the

absence of oxygen. It will be shown that 2D Raman correlation analysis is especially suited for highlighting the sequential order of multiple spectral events occurring during a complex process like photodegradation of β -carotene.

Background

Since the basic theory of 2D correlation spectroscopy has already been covered extensively elsewhere, only a very brief description of 2D Raman correlation analysis pertinent to the current study is provided here. For more detailed discussion on 2D Raman spectroscopy and related subjects, readers are directed to the pertinent literature.^{14,15}

From the time-dependent Raman scattering intensity $I(\Delta\nu, t)$ observed during the photochemical reaction of β -carotene as a function of not only Raman shift $\Delta\nu$, but also reaction time t , one obtains the mean-centered *dynamic spectral intensity variations*

$$\tilde{I}(\Delta\nu, t) = I(\Delta\nu, t) - \bar{I}(\Delta\nu) \quad (1)$$

The dynamic intensity may be regarded as the difference or deviation spectrum of the individual time-dependent Raman spectrum $I(\Delta\nu, t)$ with respect to the time-averaged reference spectrum $\bar{I}(\Delta\nu)$ obtained for the observed reaction period T .

$$\bar{I}(\Delta\nu) = \int_0^T I(\Delta\nu, t) dt / T \quad (2)$$

The synchronous and asynchronous 2D Raman correlation spectrum, $\Phi(\Delta\nu_1, \Delta\nu_2)$ and $\Psi(\Delta\nu_1, \Delta\nu_2)$, which correspond to the real and imaginary parts of the complex cross-correlation function of the dynamic Raman spectral intensity variations,¹⁴ are given by

$$\Phi(\Delta\nu_1, \Delta\nu_2) = \frac{1}{T} \int_0^T \tilde{I}(\Delta\nu_1, t) \cdot \tilde{I}(\Delta\nu_2, t) dt \quad (3)$$

$$\Psi(\Delta\nu_1, \Delta\nu_2) = \frac{1}{T} \int_0^T \tilde{I}(\Delta\nu_1, t) \cdot \tilde{J}(\Delta\nu_2, t) dt \quad (4)$$

where $\tilde{J}(\Delta\nu_2, t)$ is the time-domain Hilbert transform of $\tilde{I}(\Delta\nu_2, t)$,

which can be obtained by taking the principal value of the integration below:²⁹

$$\tilde{J}(\Delta\nu_2, t) = \frac{1}{\pi} p\nu \int_0^T \frac{\tilde{I}(\Delta\nu_2, t')}{t' - t} dt' \quad (5)$$

The synchronous correlation intensity $\Phi(\Delta\nu_1, \Delta\nu_2)$ represents the coincidental or simultaneous changes of Raman spectral intensities measured at $\Delta\nu_1$ and $\Delta\nu_2$ during the photoinduced decomposition reaction of β -carotene. A synchronous 2D Raman spectrum is a symmetric spectrum with respect to a diagonal line corresponding to coordinates $\Delta\nu_1 = \Delta\nu_2$. Correlation peaks appear at both diagonal and off-diagonal positions. The peaks located at diagonal positions are referred to as autopeaks. The magnitude of an autopeak, which corresponds to the autocorrelation function of spectral intensity variations, represents the overall change in the Raman scattering intensity of the sample observed at a given Raman shift during the photoinduced decomposition.

Cross-peaks located at the off-diagonal positions of a synchronous 2D Raman spectrum represent simultaneous or coincidental changes of spectral intensities observed at two different Raman shifts, $\Delta\nu_1$ and $\Delta\nu_2$. Such a synchronized change, in turn, suggests the possible existence of a coupled or related origin of the Raman intensity variations. While the sign of autopeaks is always positive, the sign of cross-peaks can be either positive or negative. The sign of a synchronous cross-peak becomes positive if the spectral intensities at the two Raman shifts corresponding to the coordinates of the cross-peak are either increasing or decreasing together as functions of time during the reaction. On the other hand, a negatively signed cross-peak indicates one of the Raman intensities is increasing, while the other is decreasing.

An asynchronous 2D Raman spectrum $\Psi(\Delta\nu_1, \Delta\nu_2)$, or the imaginary part of the cross-correlation function, is antisymmetric with respect to the diagonal line. The asynchronous spectrum has no autopeaks and consists exclusively of cross-peaks located at off-diagonal positions. An asynchronous cross-peak develops only if the intensities of two Raman intensities change out of phase (i.e., delayed or accelerated) with each other. This feature is especially useful in differentiating overlapped bands arising from Raman signals of different origins. For example, different spectral intensity contributions from individual components of a complex reaction mixture may be effectively discriminated. Even if bands are located relatively close to each other, as long as the signature or the pattern of time-dependent variations of Raman intensities are substantially different, asynchronous cross-peaks will develop between their spectral coordinates. The sign of asynchronous 2D Raman cross-peaks can be either negative or positive. The sign of an asynchronous cross-peak becomes positive if the intensity change at $\Delta\nu_1$ occurs predominantly before $\Delta\nu_2$. It becomes negative, on the other hand, if the change occurs after $\Delta\nu_2$. This rule, however, is reversed if $\Phi(\Delta\nu_1, \Delta\nu_2) < 0$.

Experimental Section

The β -carotene obtained from Fluka (higher than 97% purity) was recrystallized three times from deoxygenated toluene prior to the preparation of a 1.0% solution in deoxygenated toluene. HPLC measurements show that this recrystallized β -carotene has significantly higher purity compared to the original Fluka sample. The solution was sealed in a vial and exposed to fluorescent room light in our laboratory 24 h a day. The sample was excited with 80–100 mW of 752-nm radiation from an

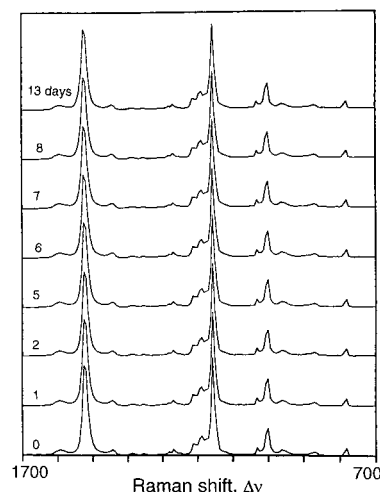


Figure 2. A series of time-resolved Raman spectra representing the photoinduced decomposition of β -carotene in the absence of oxygen. Spectra were collected after 0, 1, 2, 5, 6, 7, 8, and 13 days of exposure to fluorescent room light.

argon-ion-pumped Ti-sapphire laser. An EIC NIR-775 CCD Echelle spectrograph was used to collect data. The use of a fiber optic probe enabled the measurements to be conducted through the glass vial. Two 3-s exposures were coadded after sequence filtering to eliminate cosmic events. The initial spectrum was recorded within 30 min after the sample had been prepared. Subsequent spectra were obtained after 1, 2, 5, 6, 7, 8, and 13 days.

Transient NIR-excited Raman spectra, representing the non-oxidative photoinduced decomposition reaction of β -carotene thus collected were first normalized to the intensity of the 785 cm^{-1} toluene solvent band. The toluene internal standard has no major features in the pertinent regions. The set of normalized time-resolved Raman data are then converted to the synchronous and asynchronous 2D Raman correlation spectra by using the relationships given in eqs 1–5. The discrete numerical Hilbert transform method²⁹ was used for the efficient computation of 2D Raman correlation spectra. The uneven sampling of spectral data with respect to the reaction time was compensated by the numerical third order polynomial interpolation of raw transient Raman data along the time axis to generate an evenly spaced data set containing the equivalent transient information. Due to the exceptionally high intensity of β -carotene Raman signals, no data pretreatment such as smoothing of noise was necessary.

Results and Discussion

Figure 2 shows the eight consecutive time-resolved transient NIR-excited Raman spectra of β -carotene, which was exposed continuously to the room fluorescent light in the absence of oxygen in the spectral region from 1700 to 700 cm^{-1} . Pronounced Raman scattering peaks corresponding to the conjugated C=C stretching mode around 1520 cm^{-1} , the C–C single bond stretching mode around 1150 cm^{-1} , and also the CH_3 in-plane rocking mode around 1000 cm^{-1} are all clearly observable in these 1D Raman spectra of β -carotene undergoing photoinduced decomposition. In general, however, it is rather difficult to identify from such a simple stack of Raman spectra the subtle changes of spectral features, such as the development of shoulders and peak position shifts, and their complex relationships with respect to reaction time, i.e., the sequential order of intensity changes.

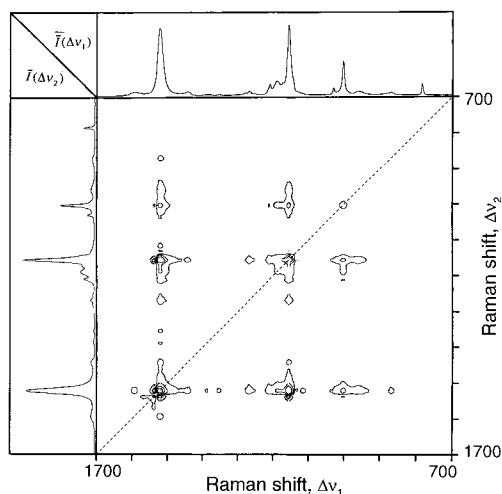


Figure 3. A synchronous 2D Raman correlation spectrum of the photoinduced decomposition of β -carotene in the absence of oxygen.

Figure 1 shown earlier is the synchronous 2D Raman correlation spectrum of the β -carotene corresponding to the spectral data given in Figure 2. This 2D Raman spectrum (Figure 1) is represented in the so-called fishnet or three-dimensional stacked-trace plot. The features corresponding to the conjugated C=C stretching mode, the C—C single bond stretching, and the CH₃ in-plane rocking mode are all well represented by the 2D Raman correlation spectrum. While a fishnet plot provides the most visually recognizable way to represent the relative magnitudes of 2D correlation intensities, it is usually much easier to analyze the detailed feature of a 2D correlation spectrum by plotting it in the form of a contour map.

Figure 3 shows the corresponding contour map representation of the same 2D Raman spectrum shown in Figure 1. Numerous autopeaks and cross-peaks are observed, indicating the presence of spectral intensity changes induced by the photodegradation of β -carotene into contaminant products even in the absence of oxygen. For example, while relatively small in the magnitude, the independent autopeak assignable to the photoinduced degradation product of β -carotene located at 1537 cm⁻¹ near the major 1520 cm⁻¹ peak is clearly observable in the 2D spectrum represented by either Figure 1 or Figure 3.

Figure 4 is a close-up view of the stack of transient Raman spectra of photodecomposing β -carotene in the Raman region of conjugated C=C stretching mode from 1550 to 1500 cm⁻¹. Even though the gradual decrease of Raman intensities around the major overlapped peaks at 1520 and 1522, accompanied by the slight increase of a shoulder centered around 1537 cm⁻¹, may be observed by trained keen eyes, the detailed features of these subtle changes are difficult to capture with the conventional 1D Raman plots.

At present, the identity of the decomposition product assignable to this 1537-cm⁻¹ band is not fully known, but a Raman band at this wavenumber has been reported for several *cis* isomers of β -carotene. It is, however, interesting to point out that the similar decomposition study carried out for a β -carotene sample in the presence of oxygen³⁰ does not result in the marked increase in the Raman intensity of the band at 1537 cm⁻¹. This band is strictly due to some photoinduced reaction product. Although the appearance of a band at 1537 cm⁻¹ is consistent with a reduction in the number of conjugated C=C groups,^{4,6,11} it seems more likely to be due to the production of one or more *cis* isomers of β -carotene. The decomposition of β -carotene in the case of oxidation without light will produce exclusively other types of products, not represented by the 1537-cm⁻¹ band, such

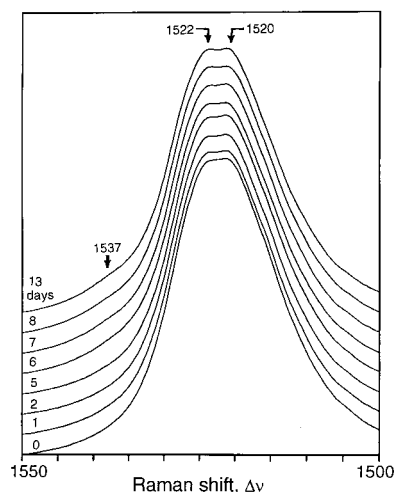


Figure 4. A close-up view of the time-resolved Raman spectra representing the photoinduced decomposition of β -carotene in the absence of oxygen in the spectral region from 1550 to 1500 cm⁻¹ corresponding to the conjugated C=C stretching modes.

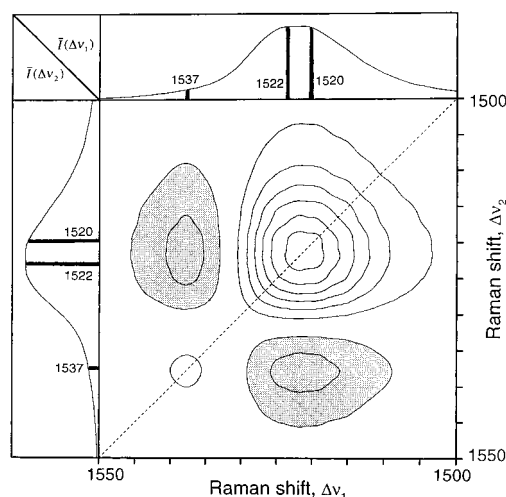


Figure 5. A synchronous 2D Raman correlation spectrum of photo-degradation of β -carotene in the spectral region from 1550 to 1500 cm⁻¹. Shaded areas represent the negative correlation intensity.

as those containing carbonyl moieties, not easily detected by Raman scattering but easily identified by IR spectroscopy.

Figure 5 shows the corresponding synchronous 2D Raman correlation spectrum of the same region. It is now possible to determine from the presence of autopeaks and cross-peaks that there exist detectable Raman intensity changes around the Raman shifts of 1520 and 1537 cm⁻¹. From the sign of the cross-peaks, it is quite straightforward to determine that the decrease in Raman intensities at 1520 and 1522 cm⁻¹ is negatively correlated (indicated by the shading) with the increase in the Raman intensity at 1537 cm⁻¹. The result is consistent with the fact that observed Raman bands at 1520 and 1522 cm⁻¹ are assignable to the conjugated stretching modes of β -carotene, which are decreasing in intensity due to photoinduced decomposition, while that at 1537 cm⁻¹ assignable to the photoreaction product is increasing.

The asynchronous 2D Raman correlation spectrum of the same spectral region (Figure 6) reveals even more intriguing results. The presence of asynchronous 2D Raman cross-peaks indicates that there are strong asynchronous relationships between the disappearance of β -carotene and appearance of the decomposition product. In other words, the consumption of

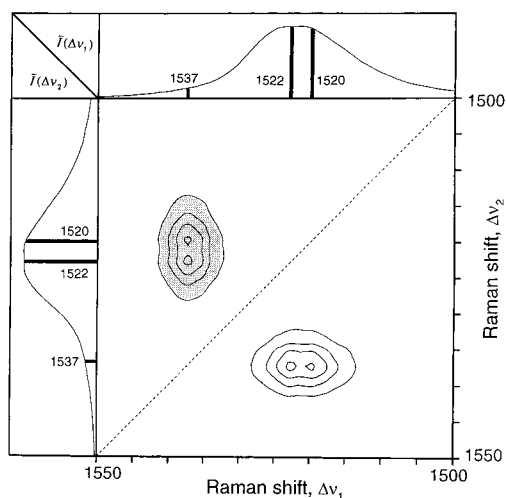


Figure 6. An asynchronous 2D Raman correlation spectrum of photodegradation of β -carotene in the spectral region from 1550 to 1500 cm^{-1} . Shaded areas represent the negative correlation intensity.

β -carotene is not strictly coupled quantitatively with the production of this particular decomposition product. Thus, a rather simplistic view that all β -carotene which is decomposed under the influence of light will automatically produce a single product represented by the band at 1537 cm^{-1} clearly does not hold.

The analysis of the signs of cross-peaks found in the asynchronous Raman spectrum of β -carotene photodecomposition is even more interesting. The asynchronous cross-peak intensities at the spectral coordinates (1537, 1522) and (1537, 1520) are both negative, indicated by the shading of the peaks. The peak signs of the synchronous spectrum at the corresponding spectral coordinates are all negative. According to the sign rules of the 2D correlation spectra,^{14,15} the result indicates that the appearance of the 1537 cm^{-1} band occurs before the overall disappearance of band intensities at 1522 and 1520 cm^{-1} . Apparently, the major part of the production of the compound represented by the 1537 cm^{-1} band is completed much earlier, while the decomposition of β -carotene at 1522 and 1520 cm^{-1} continues to produce something else, not related to the compound of 1537 cm^{-1} band.

The generation of other decomposition products is indicated by the appearance of appropriate 2D Raman cross-peaks at different spectral coordinates. The increase in Raman scattering intensity arising from the production of a new species should be negatively correlated with the weakening Raman intensity at 1522 cm^{-1} for the disappearance of β -carotene. Therefore, by simply looking for the appearance of a negative (shaded) synchronous cross-peak along the coordinate 1522 cm^{-1} , one should be able to find a band for a decomposition product.

For example, a close-up view of the synchronous spectrum (Figure 7) shows that, near the strong Raman band around 1156 cm^{-1} , which is associated with the C—C single bond stretching mode, a small but distinct negative cross-peak is observed at the coordinate (1522 \pm 10, 1133). This 1133- cm^{-1} band is only a small shoulder in the 1D Raman spectrum, barely observable unless specifically looked for. A small positive cross-peak is also observed at (1537, 1133), once more indicating the 1133- cm^{-1} band is associated with a decomposition product, like the 1537- cm^{-1} species which increases in the population as the photodegradation reaction continues. The fact that there is no significant corresponding asynchronous cross-peaks (not shown) located at the same spectral coordinates as these synchronous

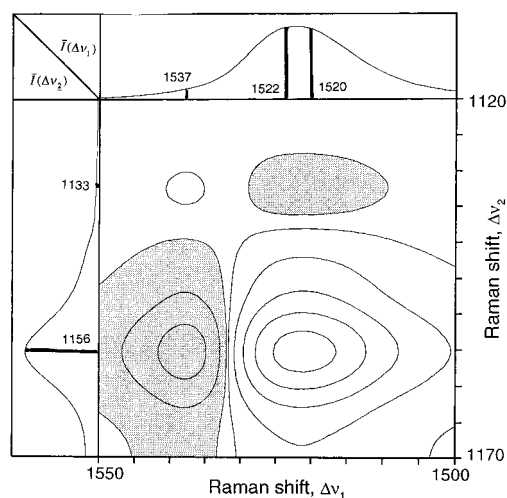


Figure 7. A synchronous 2D Raman correlation spectrum comparing spectral variations in the region from 1550 to 1500 cm^{-1} and from 1170 to 1120 cm^{-1} .

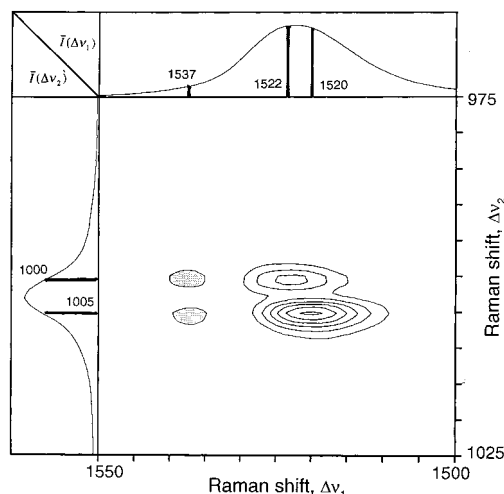


Figure 8. An asynchronous 2D Raman correlation spectrum comparing variations in the spectral region from 1550 to 1500 cm^{-1} and from 1025 to 975 cm^{-1} .

peaks indicates that the appearance of 1133- cm^{-1} species occurs at the same time as the appearance of 1537- cm^{-1} species.

Other areas of the 2D Raman spectrum also indicate the presence of various decomposition products. Figure 8 shows a close-up view of the asynchronous 2D Raman spectrum, comparing the time-dependent behavior of Raman intensity changes between the C=C stretching and CH_3 in-plane rocking regions. Two distinct positive asynchronous cross-peaks are observed at (1522, 1000 \pm 5) and (1520, 1005 \pm 10), as well as two small negative cross-peaks at 1537- cm^{-1} region. The signs of the asynchronous cross-peaks, combined with those of the synchronous peaks observed in Figure 3, reveal the following. The overall Raman intensities of bands associated with the CH_3 in-plane rocking modes are decreasing. The majority of the decrease, on the other hand, occurs at a much later stage as compared to the increase in the 1537- cm^{-1} band from a decomposition product or the overall decrease in the 1522 and 1520 cm^{-1} doublet arising from the β -carotene decomposition.

The above result is consistent with a view that some level of compensation of Raman intensities is taking place by the decomposition product having a Raman band located in this spectral region. Because of the heavy spectral overlap with the

dominant β -carotene band, as well as a toluene solvent band, the presence of the decomposition product contributing to the Raman intensity around 1005 cm^{-1} did not produce a clearly observable negative synchronous peak, as in the case of (1522, 1133). However, the appearance of asynchronous peaks suggests the small latent intensity increase due to a decomposition product is giving the appearance of slowed Raman intensity decrease in this spectral region compared to isolated β -carotene bands. Because of the considerable spectral overlap in this region, it is possible that the decomposition product band developing in near 1000 cm^{-1} is in fact synchronous with and, as a result, due to the same decomposition product(s) as those represented by the bands at 1537 and 1133 cm^{-1} .

A closer examination of the 2D Raman maps (not shown) reveals two additional weak bands appearing (at 1569 and 1284 cm^{-1}) as a function of exposure to room light in the absence of oxygen. The lack of asynchronous cross-peaks with the bands at 1537 and 1133 cm^{-1} suggests that these bands are likely due to the same decomposition product, or possibly, additional decomposition products formed at the same rate. All four of these bands (1569, 1537, 1284 and 1133 cm^{-1} , as well as the band at 1000 cm^{-1}) are consistent with strong Raman bands in known cis isomers of β -carotene.²⁹ The most likely decomposition products being formed include 15-*cis*- β -carotene, 9-*cis*- β -carotene, 13-*cis*- β -carotene, or 9,13-di-*cis*- β -carotene.⁹

Conclusions

Generalized two-dimensional correlation analysis, coupled with NIR-excited Raman scattering measurements, yields a very interesting result on the photodecomposition reaction of β -carotene in the absence of oxygen. The synchronous and asynchronous 2D Raman correlation spectra reveal the presence of both simultaneous and sequential changes of Raman intensities associated with β -carotene and the photoinduced reaction products.

The intensity increase of the Raman band at 1537 cm^{-1} , which is likely due to the formation of a photoisomerization product containing one or more cis C=C groups, occurs at an earlier stage of the reaction, while the steady decrease of band intensities associated with β -carotene at 1522 and 1520 cm^{-1} continues to a later stage producing other photoreaction products. Smaller intensity increases at 1133, 1569, and 1284 cm^{-1} occur synchronously with the growth of the 1537 cm^{-1} band prior to the overall decrease of *all-trans*- β -carotene. Thus, the decomposition product(s) associated with the Raman bands at 1133, 1569, and 1284 cm^{-1} are either due to the same decomposition product as that represented by the band at 1537 cm^{-1} , or different products formed at the same rate. The intensities of Raman bands at 1005 and 1000 cm^{-1} may contain spectral contributions from different decomposition products, but the situation is complicated due to overlap with the dominant *all-*

trans- β -carotene contribution, as well as a toluene solvent band. All of the new bands observed are consistent with β -carotene isomers containing one or more cis C=C groups.

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References and Notes

- (1) Stratton, S. P.; Schaefer, W. H.; Liebler, D. C. *Chem. Res. Toxicol.* **1993**, *6*, 542.
- (2) Krinsky, N. L. *Free Radical Biol. Med.* **1989**, *7*, 617.
- (3) Krinsky, N. L. *Pure Appl. Chem.* **1979**, *51*, 649.
- (4) Rimai, L.; Kilponen, R. G.; Gill, D. J. *Am. Chem. Soc.* **1970**, *92*, 3824.
- (5) Rimai, L.; Heyde, M. E.; Gill, D. J. *Am. Chem. Soc.* **1973**, *95*, 4493.
- (6) Inagaki, F.; Tasumi, M.; Miyazawa, T. *J. Mol. Spectrosc.* **1974**, *50*, 286.
- (7) Harada, I.; Furukawa, Y.; Tasumi, M.; Shirakawa, H.; Ikeda, S. *J. Chem. Phys.* **1980**, *73*, 4746.
- (8) Saito, S.; Tasumi, M.; Eugster, C. H. *J. Raman Spectrosc.* **1983**, *14*, 299.
- (9) Saito, S.; Tasumi, M. *J. Raman Spectrosc.* **1983**, *14*, 310.
- (10) Fujiwara, M.; Hamaguchi, H.; Tasumi, M. *Appl. Spectrosc.* **1986**, *40*, 137.
- (11) Castiglioni, C.; Zoppo, M. D.; Zerbi, G. *J. Raman Spectrosc.* **1993**, *24*, 485.
- (12) Parker, S. F.; Tavender, S. M.; Dixon, N. M.; Herman, H.; Williams, K. P. J.; Maddams, W. F. *Appl. Spectrosc.* **1999**, *53*, 86.
- (13) Noda, I. International Symposium on Advanced Infrared Spectroscopy (AIRS), The University of Tokyo, Tokyo, Japan, March 24, 1993.
- (14) Noda, I. *Appl. Spectrosc.* **1993**, *47*, 1329.
- (15) Noda, I.; Dowrey, A. E.; Marcott, C.; Story, G. M.; Ozaki, Y. *Appl. Spectrosc.* **2000**, *54*, 236A.
- (16) Ozaki, Y.; Noda, I. *Two-Dimensional Correlation Spectroscopy. AIP Conference Proceedings*, 2000; Vol. 53.
- (17) Nakano, T.; Shimada, S.; Saitoh, R.; Noda, I. *Appl. Spectrosc.* **1993**, *47*, 1337.
- (18) Ozaki, Y.; Liu, Y.; Noda, I. *Appl. Spectrosc.* **1997**, *51*, 526.
- (19) Sefara, N. L.; Magtoto, N. P.; Richardson, H. H. *Appl. Spectrosc.* **1997**, *51*, 536.
- (20) Czarniecki, M. A.; Maeda, H.; Ozaki, Y.; Suzuki, M.; Iwahashi, M. *Appl. Spectrosc.* **1998**, *52*, 994.
- (21) Magtoto, N. P.; Sefara, N. L.; Richardson, H. H. *Appl. Spectrosc.* **1999**, *53*, 178.
- (22) Smeller, L.; Heremans, K. *Vibrat. Spectrosc.* **1999**, *19*, 375.
- (23) Noda, I.; Story, G. M.; Marcott, C. *Vibrat. Spectrosc.* **1999**, *19*, 461.
- (24) Ebihara, K.; Takahashi, H.; Noda, I. International Symposium on Advanced Infrared Spectroscopy (AIRS), The University of Tokyo, Tokyo, Japan, March 24, 1993.
- (25) Ebihara, K.; Takahashi, H.; Noda, I. *Appl. Spectrosc.* **1993**, *47*, 1343.
- (26) Gustafson, T. L.; Morris, D. L.; Huston, L. A.; Butler, R. M.; Noda, I. *Time-Resolved Vibrational Spectroscopy, VI, Springer Proceedings in Physics*, **1994**, *74*, 131.
- (27) Huang, K.; Archer, L. A.; Fuller, G. G. *Macromolecules* **1996**, *29*, 966.
- (28) Noda, I.; Liu, Y.; Ozaki, Y. *J. Phys. Chem.* **1996**, *100*, 8674.
- (29) Noda, I. *Appl. Spectrosc.* **2000**, *54*, 994.
- (30) Reeder, R. C.; Marcott, C. *Proc. ICORS XV*, Asher, S. A., Stein, P., Eds.; Wiley: New York, 1996; p 1102.