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Determination of Chemical Decay Mechanisms of Parylene-C during X-ray Irradiation using Two-Dimensional Correlation FTIR

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Abstract:

Parylene (poly-p-xylylene), and its family of halogenated variants, have a long history for application as protective coatings and dielectric barriers. Among them, Parylene-C is the most popular due to its high impermeability to moisture, resistance to corrosive environments, and its vapor deposition polymerization, which is self-initiated and unterminated creating an extremely pure polymer coating. In order to apply these advantageous material characteristics in an environment containing ionizing radiation the effects of irradiation on the chemical stability of the polymer throughout the lifetime of the material needs to be further understood.

In this work, Fourier-transform infrared (FTIR) and two-dimensional correlation (2D-COS) spectroscopies were used to monitor the structural changes in a ~25μm freestanding film of Parylene-C after subjection to X-ray irradiation. Samples were exposed to X-ray doses up to 100,000 Gy in atmospheric conditions, and IR spectra were measured after each 500Gy dose. Using 2D-COS it was possible to gain insight into the chemical stability and temporal mechanisms of the chemical reactions accompanying X-ray radiation of Parylene-C. Oxidation was observed by the production of a new species absorbing in the IR at 1697 and 1740 cm^{-1}. Additionally, skeletal stretching of the aliphatic back bone were positively correlated to C-O oxidation products found in the region of 1425-1100 cm^{-1}. The present work is confirmation that

Parylene-C does experience chemical degradation from x-ray dose caused by oxidation of the polymer structure.

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Keywords: 2D-COS, FTIR, Parylene-C

Introduction

Parylene-C is the generic name of a chlorinated member of the poly-para-xylylene family of thermoplastic, semi-crystalline polymers. It is a vapor deposited polymer created by the vacuum pyrolysis of di-para-xylylene via the Gorham process.[1] By heating di-para-xylylene above 550 °C at pressures less than 1 torr, the dimer is cleaved into two monomers which are adsorbed onto a surface at room temperature. The monomers then polymerize, forming a high molecular weight, linear polymer thin film. Aromatic chlorination of the standard poly-para-xylylene gives rise to Parylene-C with one chlorine atom on average per repeat unit. The chemical structure of Parylene-C can be seen in Figure 1. The polymers of the Parylene family have been used extensively as protective coatings in the electronics and medical industries due to their chemical inertness, excellent moisture barrier properties, and ease of creating thick, pinhole free coatings.[2,3,4,5] Parylene is vapor deposited and requires no additional materials for initiation or termination, resulting in films that are extremely pure and of high quality. Among the members of the Parylene polymer group, Parylene-C is the most resistant to moisture.[6] Both oxidative degradation[7,8,9] and degradation caused by photooxidation[10,11,12,13,14] have been studied extensively in the literature. The proposed oxidative mechanisum is that external stimulus such as UV light causes chain session at a chain C-H site, leaving a radical capable of interation with atmospheric molecular oxygen. This oxidation process first forms aldehydes at low doses of light

exposure and, as dose is increased the formation of carboxylic acids is observed within the thin films of the polymer. However, little has been published on the radiolytic degradation of the polymer when exposed to X-ray in amibiant air.

In this work Two-Dimensional Infrared Spectroscopy (2D-IR) was applied to study the radiolytic chemical decay in Parylene-C. 2D-IR was originally proposed by Isao Noda in 1986, as a novel technique to increase the resolution and clarity of a series of infrared spectra by spreading the information over a second independent wavenumber axis.[15] This was later generalized (2D-COS) by Noda to include any time-dependent variable, not just an oscillating mechanical disturbance, that can generate change in the intensity, location, or shape of IR peaks.[16] This technique eliminates many problems encountered in traditional spectroscopy such as overlapping bands and, weak signal-to-noise ratios by increasing the spectral resolution by distributing the data over a second wavenumber axis. The objective of this work was to determine the effectiveness of 2D-COS as a characterization method for understanding the chemical degradation that occurs within a sample of Parylene-C as it is exposed to ionizing radiation. Determination of the different oxidation products created by exposure to x-ray in an air atmosphere, as well as the nature of chain scission products, are of prime importance as these factors will effect the material's mechanical properties and service life. In this work, Parylene-C films were exposed to X-ray radiation and FTIR spectra were collected between dose applications. 2D-COS was then applied to analyze the new chemical structures being formed as a result of the X-ray dose applied.

Materials and Methods

Material and Irradiation

The Parylene-C dimer was purchased from Specialty Coasting Systems and vapor deposited via the Gorham process onto a glass substrate to a thickness of ~25 μm based on the deposition rate.[1] The films were removed from the substrate by submerging in water for 30 minutes and peeling the Parylene free from the glass, while still submerged and without distorting the material. This resulted in ~25 μm free standing films that were allowed to dry in air for 24 hours before further use. Each film was installed into an IR card with a 9.5mm aperture for ease of handling. Samples were irradiated, in the IR card, using a PANalytical PW3830 X-ray generator at a dose rate of 2 Gy/s under atmospheric conditions. The Parylene-C film was additively dosed with 500 Gy between spectra collection to a maximum dose of 100,000 Gy. After each dose the sample was removed from the X-ray generator and installed into the Bruker Vertex 80v spectrometer to performed IR analysis before being reinstalled into the X-ray generator for additional dose applications.

Infrared Spectroscopy and Data Preprocessing

All spectra for the Parylene samples were collected under vacuum in transmission mode using a Bruker Vertex 80v spectrometer with a liquid nitrogen cooled MCT D316 detector. Data was collected between 400 and 4000 wavenumbers (cm^{-1}) at a resolution of 2 cm^{-1} and a total of 200 scans per spectra. An inital background spectra was taken for all samples which was ultimately subtracted from the collected spectra. All 201 collected spectra were baselined using OMNIC software (Thermo Fisher Scientific).

In order to normalize the data, the selective and non-selective effects within the data set must be understood. A selective effect is defined as a change in the spectra created by a perturbation variable that directly and selectively modifies an area of the IR spectra. An example of a

selective effect is the increase in concentration of a new chemical species as a result of radiolytic dose application. Alternatively, a non-selective effect is a change that modifies all features within an IR spectra, such as a decrease in total intensity caused by the application of a perturbation variable. If not corrected, non-selective effects will cause erroneous features in the two-dimensional correlation spectra.[17] If possible, non-selective effects are eliminated from the data set by normalizing the spectra relative to an internal IR band not affected by the perturbation variable. In the case of Parylene-C, a doublet is observed at 1608 and 1557 cm^{-1} representing the asymmetric, C-C stretching of the substituted aromatic ring found within the polymer backbone.[18] It was determined that these skeletal ring vibrations are the least sensitive to X-ray dose and the medium strength peak at 1557 cm^{-1} was selected to normalize the spectra. This peak was selected based on the fact that the radical site formed which interacts with molecular oxygen due to photolytic scission is most likely a chain C-H bond, according to Pruden et al.[14] Therefor, the spectra were normalized using OMNIC software to the skeletal ring vibration peak at 1557 cm^{-1} to correct for non-selective effects found in the data set due to the fact that oxidation was least likely to occure at these sites.

2D Correlation Analysis

After all spectra were baseline corrected and normalized to remove non-selective effects, 2D correlation analysis was performed using the methodology developed by Noda. Dynamic spectra were generated using the Biodata toolbox for MATLAB, a free toolbox developed by De Gussem used to store and process large spectral libraries.[19] The dynamic spectra where then used to generate the synchronous and asynchronous correlation spectra contour maps using the discrete Hilbert transform algorithm.[20] The Synchronous contour map shows the coherence of dynamic fluctuations. Correlation squares can be created by connecting on diagonal autopeaks to

off diagonal peaks to show whether the autopeaks are changing in the same (positive off diagonal peaks) or opposite direction (negative off diagonal peaks). The Asynchronous contour map shows the independent fluctuation in the dynamic spectra. This map is read by generating correlation squares by connecting off diagonal peaks to the center diagonal of the plot. Both the synchronous and asynchronous correlation spectra use red to indicate positive values and blue to indicate negative values of autopeaks and cross peaks.

Results and Discussion

Fingerprint Region of Untreated Parylene-C

The fingerprint region of the IR spectra for Parylene-C has been well documented in the literature.[6, 18, 21] All spectral band assignments are based on the repeat unit of Parylene-C shown in Figure 1 with an average of one Chlorine atom per repeat unit. A typical experimental FTIR spectrum of the fingerprint region for Parylene-C can be seen in Figure 2. Notable bands within this region are presented in Table 1. It is important to note the absence of an absorption band in the region of ~1700 cm^{-1} indicating that there are no carbonyl or carboxylic bonds in the as-deposited film.

The IR spectra of X-ray Irradiated Parylene C

Figure 3 shows the entire collected spectral region, while Figure 4 shows the fingerprint region of X-ray irradiated Parylene-C. Formation of a new band at 1697 cm^{-1} and a general intensity increase in the 1100-1425 cm^{-1} region was observed as the polymer yellowed during X-ray irradiation. These changes were attributed to the formation of new aldehyde and carboxylic acid groups.[14] Atmosphereic O_2 is thought to bond to radicals created via aliphatic chain scission triggered by X-ray interaction. Additionally, an intensity decrease at both 827 and 1051 cm^{-1} was

observed. This indicates a decrease in the movement of single hydrogen atoms bonded to an aromatic ring with neighboring chlorine and ethyl groups (827 cm^{-1}) as well as a decrease in the movement of chlorine atoms bonded to the aromatic backbone of the polymer. While the high frequency region of the spectra, Figure 3, specifically around 3100 cm^{-1} is useful in the determination of the formation of carboxylic acid as a decay product, this band is broad in nature and is characteristic of the existance of O-H bonds. The low intensity and broad nature of this area of the spectra resulted in it being excluded from the final 2D correlation analysis. Due to the fact that peaks accociated with water are also found in the high frequency region of the spectra that can obscure the data in this region making it difficult to interpret. The IR peaks needed to draw the conclusion that carboxylic acid groups form is a degradation product of the radiolitic decay are included in the region analyized; a new peak at 1696 cm-1 (C=O group) and a new peak at 1266 cm-1 in the region of the characteristic (C-O) bond.[14]

2D Correlation Analysis of Irradiated Parylene-C films

When generalized 2D correlation analysis is applied to the IR data set , both synchronous and asynchronous correlation spectra are generated. The synchronous spectra gives information pertaining to how similar the response in the spectra is to the applied perturbation, in this case radiation dose. The asynchronous spectra gives information pertaining to alteration in the spectra which are not synchronous correlated, meaning changes occurring at different dose application levels. The 2D correlation spectra for the entire fingerprint region can be seen in Figure 5. The fingerprint region is subsequently divided into three wavenumber regions for ease of analysis. The 2D correlation maps of the irradiated Parylene-C in the region of 1800-1450 cm^{-1} are shown in Figure 6. In the synchronous spectrum (Fig. 5a) autopeaks and cross peaks can be observed at 1697, 1607, and 1495 cm^{-1}. The peak at 1697 cm^{-1} is assigned to newly formed C=O bonds

caused by X-ray exposure. The growth of the peak at 1607 cm^{-1} is correlated with the growing peak at 1697 cm^{-1} with positive cross peaks, meaning that they are both increasing with increasing dose. In the case of the peak at 1495 cm^{-1}, it was found that there is a negative correlation between both the 1697 and 1607 cm^{-1} peaks, meaning that the 1495 cm^{-1} peak is decreasing in intensity with increasing radiation exposure. As the peak at 1495 cm^{-1} has been previously associated with C-C stretching in an aromatic ring, it can be concluded that as new oxidation products are forming the stretching mode intensitity decreases, possibily indicating aromatic groups being cleaved by irradiation or, more likely, added oxygen containing groups being added to the chain sections of the polymer dampening this stretching mode. It can be seen in the asynchronous spectra for this same region (Figure 6b) that there are positive cross peaks correlating the bands at (1697 cm^{-1}, 1513 cm^{-1}) and (1697 cm^{-1}, 1595 cm^{-1}). It can be seen that there are negative cross peaks correlation the bands at (1697 cm^{-1}, 1495 cm^{-1}), (1595 cm^{-1}, 1495 cm^{-1}), (1697 cm^{-1}, 1607 cm^{-1}), (1718 cm^{-1}, 1697 cm^{-1}), and (1740 cm^{-1}, 1697 cm^{-1}). Applying Noda's rules to regions of the 2D asynchronous correlation spectra it is possible to determine the order of damaging events through the comparison of increasing versus decreasing intensity of the bands of interest that occur during X-ray irradiation of the sample film[15]. However, this analysis is outside of the scope of the current work.

The 2D correlation maps for the irradiated films in the region of 1500-1000 cm^{-1} can be seen in Figure 7. In this region (Figure 7a) autopeaks and cross peaks can be observed at 1421, 1266, 1209, 1190, and 1051 cm^{-1}. As stated previously, the peak at 1051 cm^{-1} is representative of chlorine bonded to an aromatic ring. It is observed that this peak is negatively correlated with all other peaks in this region of the correlation spectrum, meaning that it decreases in intensity with respect to the other bands. Intensity decreases in this peak show that there is a decrease in the

mobility of the stretching mode assigned to the chlorine atoms bonded to aromatic rings. Therefore, the stretching mode associated with this bond is apparently being hindered by the newly observed oxidation products. All other autopeaks found in this region are positively correlated and appear in the area of C-O stretch and C-O-H bend vibrations, suggesting the formation of carboxylic acids, esters and alcohols.[11] The asynchronous plot for this region (Fig. 7b) shows positive cross peaks correlating the bands at (1421 cm^{-1}, 1048 cm^{-1}) and (1266 cm^{-1}, 1048 cm^{-1}). Additionally, Negative cross peaks can be observed correlating bands at (1421 cm^{-1}, 1051 cm^{-1}), (1375 cm^{-1}, 1051 cm^{-1}), and (1266 cm^{-1}, 1051 cm^{-1}).

The 1100-600 cm^{-1} region of the 2D correlation spectra can be seen in Figure 8. Autopeaks in this region (Fig. 8a) are related to the C-H out-of-plane vibrations of aromatic compounds. Autopeaks in this region for mono-substituted benzene are negatively correlated while peaks representative of new benzene species are positively correlated. In the asynchronous spectra (Figure 8b), negative cross peaks can be seen correlating to bands at (1051 cm^{-1}, 877 cm^{-1}), (1051 cm^{-1}, 827 cm^{-1}), and (1051 cm^{-1}, 688 cm^{-1}).

Conclusions

It is evident that X-ray irradiation up to 100,000 Gy causes oxidation and molecular changes in Parylene-C thin films. A new peak at 1697 cm^{-1} in the region of C=O stretching was observed, correlating to changes in the skeletal stretching of the aromatic back bone as well as other positive synchronous correlations to C-O oxidation products found in the 1425-1000 cm^{-1} region. This is evidence that the primary oxidation occurs after a chain scission event forming a terminal carboxylic acid. Parylene-C, in air, is expected to suffer the same oxidative degradation, formation of initial aldehyde degradation products and formation of carboylic acids at higher

exposure doses, in a radiolictic environment as it would when exposed to UV light as previously studied in the literature.[13] In short, X-ray irradiation of Parylene-C in air has been shown to cause both chemical and conformational changes within the thin film.

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Table 1 Notable spectral bands based on the repeat unit of Parylene-C with an average of one Chlorine atom per repeat unit[6, 8, 21]

Assignment	Wavenumber (cm^{-1})
Two neighboring H atoms bonded to aromatic ring vibrations	827
Cl bonded to aromoatic ring vibrations	877
Cl bonded to aromoatic ring vibrations	1051
In-plane deformation of C-H bond in aromatic ring vibrations	1200-1000
CH3 symmetric bending vibrations	1340
C-C deformation vibrations	1403
CH2 rocking vibrations	1452
C-C ring stretching vibrations	1495
Skeletal aromatic C-C vibrations	1557
Skeletal aromatic C-C vibrations	1607

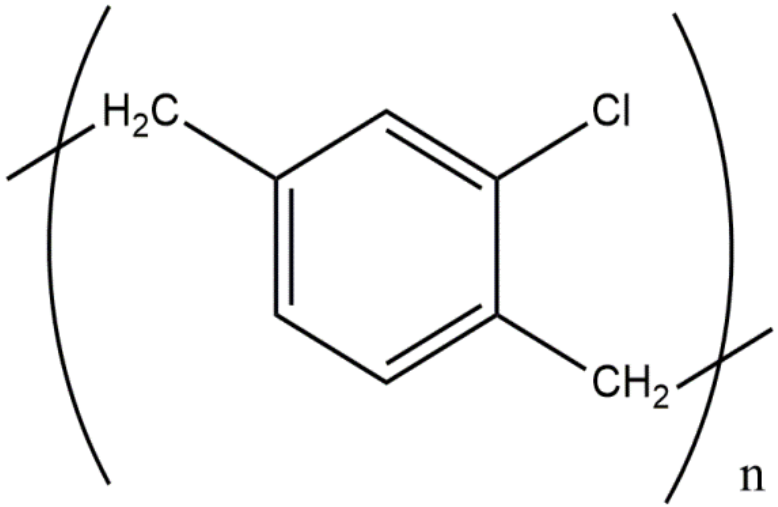

Figure 1 Chemical Structure of Parylene-C Polymer

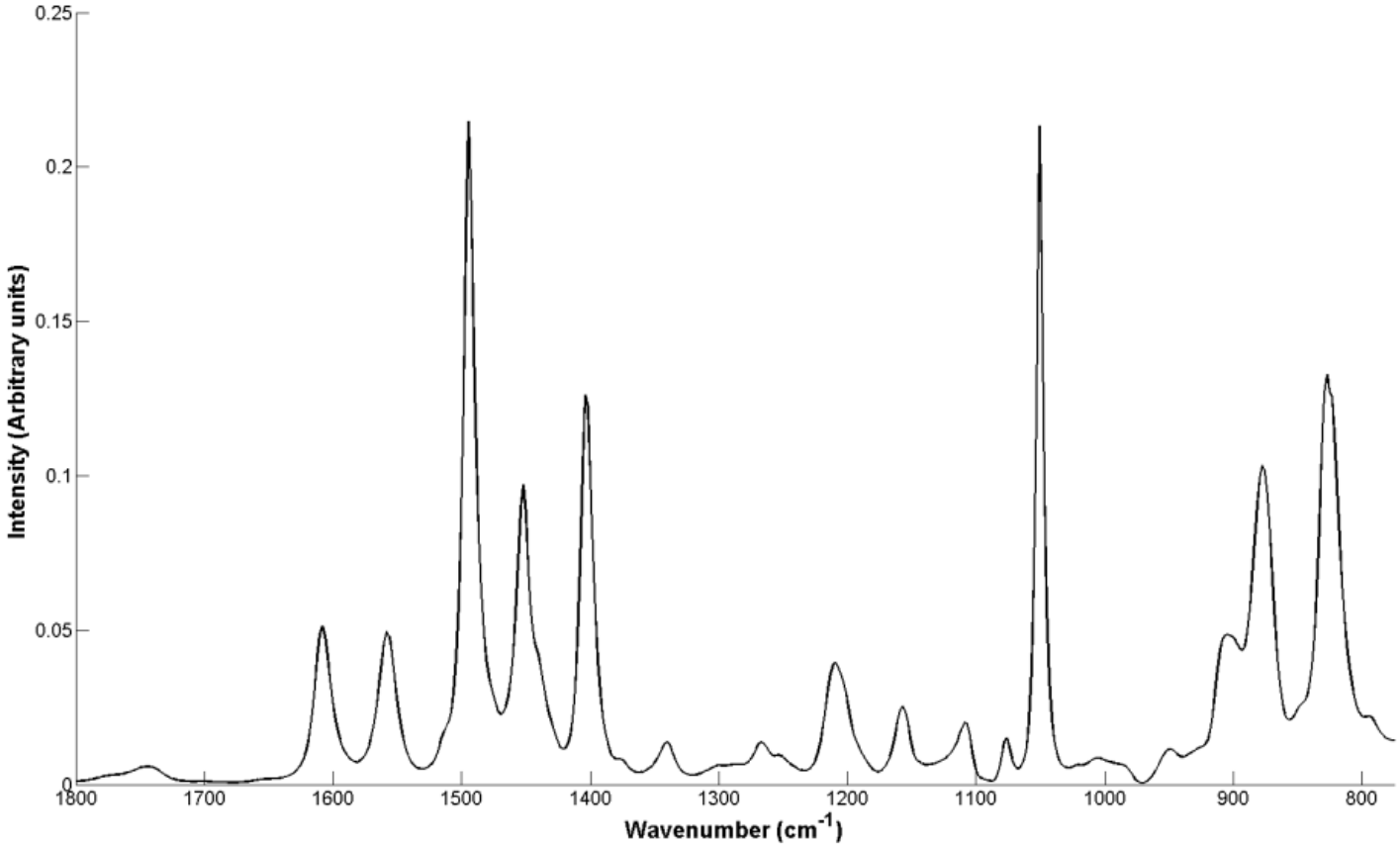

Figure 2 Finger print region of untreated Parylene-C film

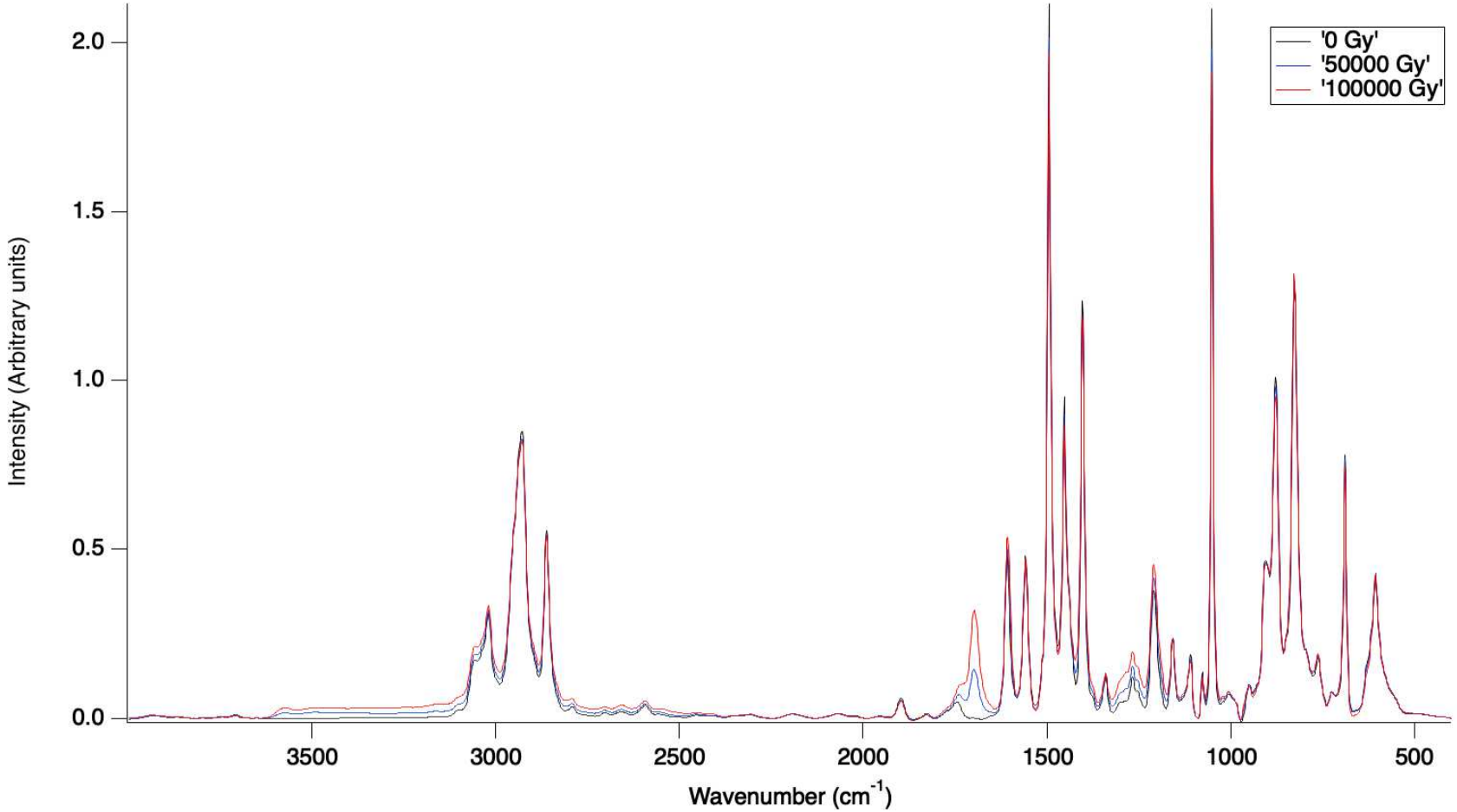

Figure 3 Entire collected spectral region of X-ray irradiated Parylene-C film

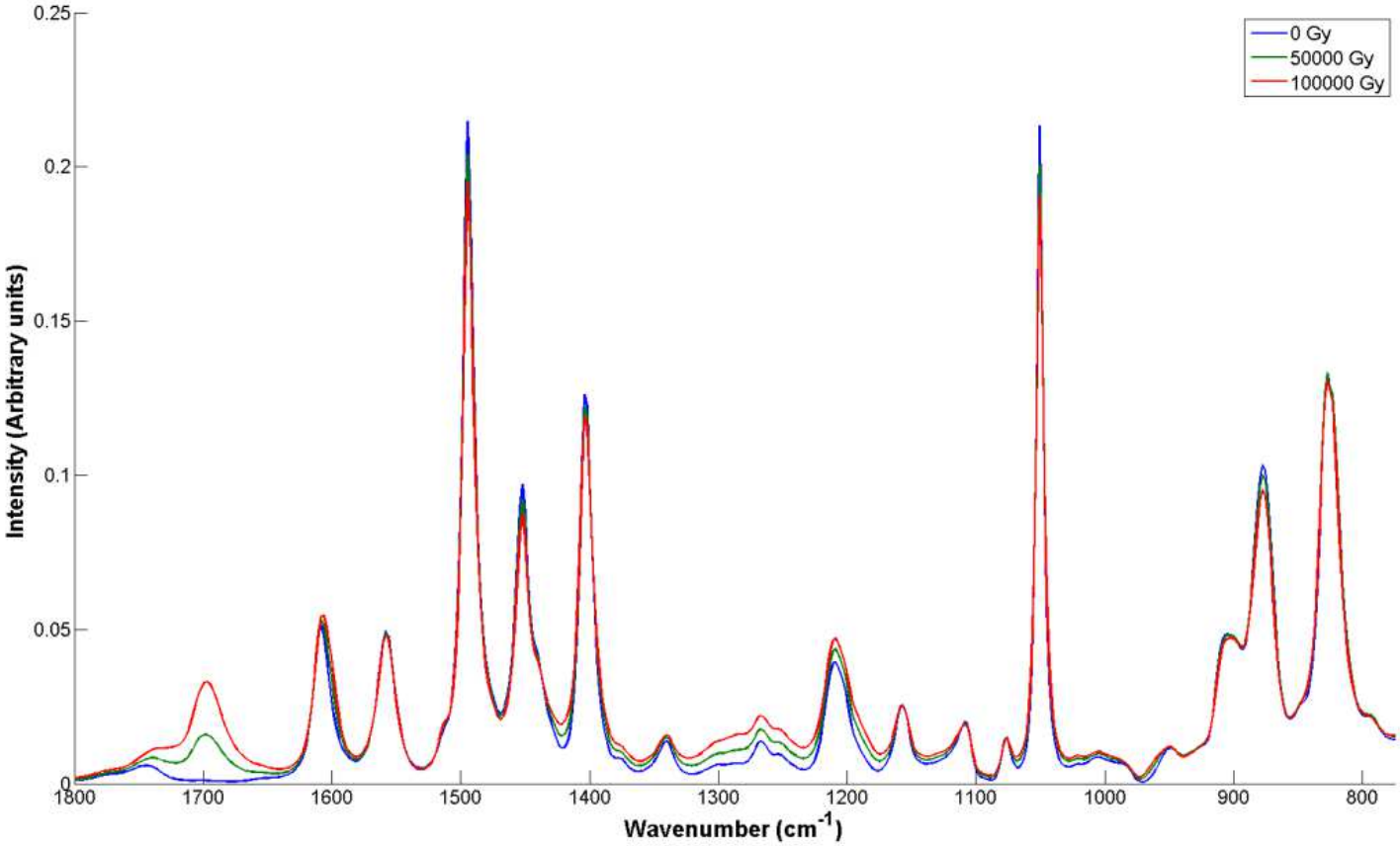

Figure 4 Finger print region of X-ray irradiated Parylene-C

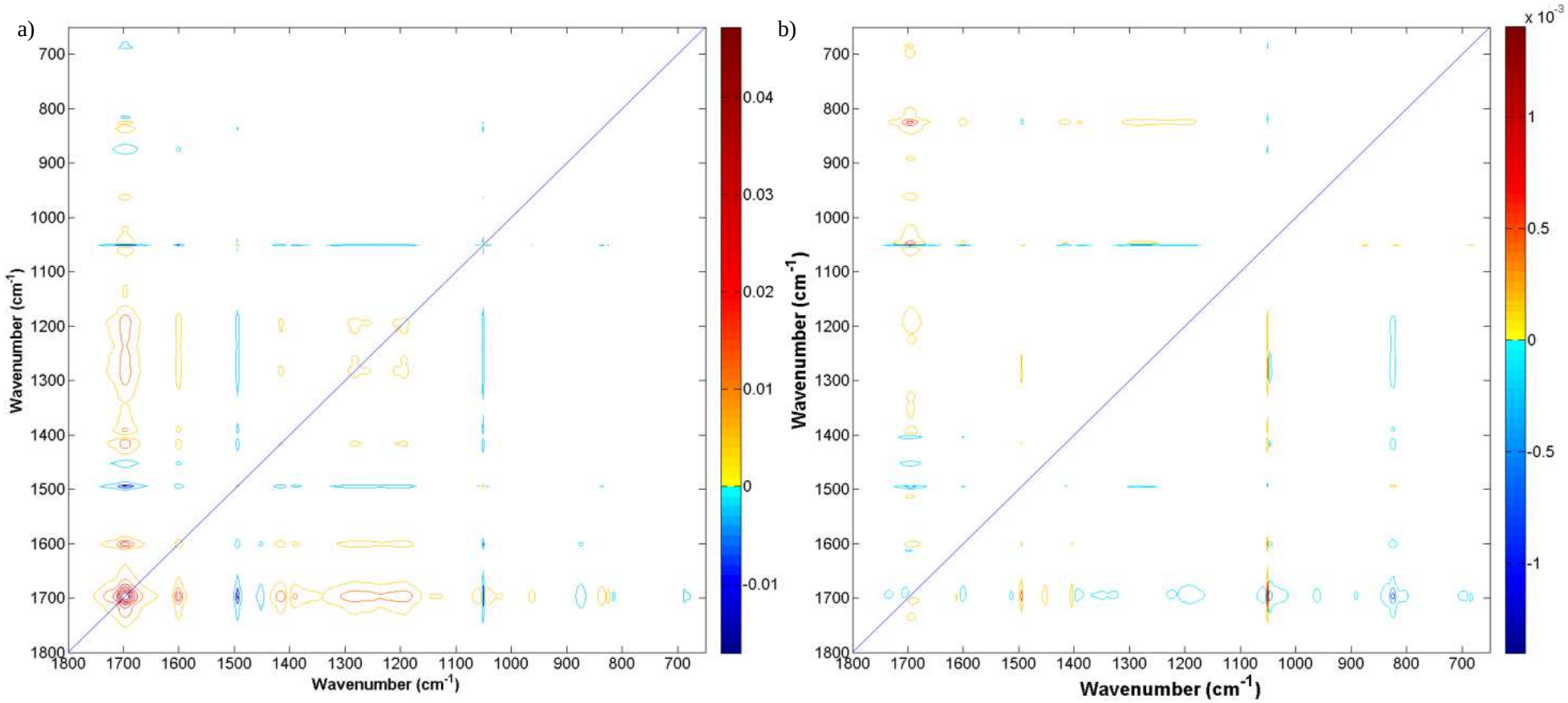

Figure 5 2D correlation spectra of X-ray irradiatied Parylene-C in the finger print region a) Synchronous spectra b) Asynchronous spectra

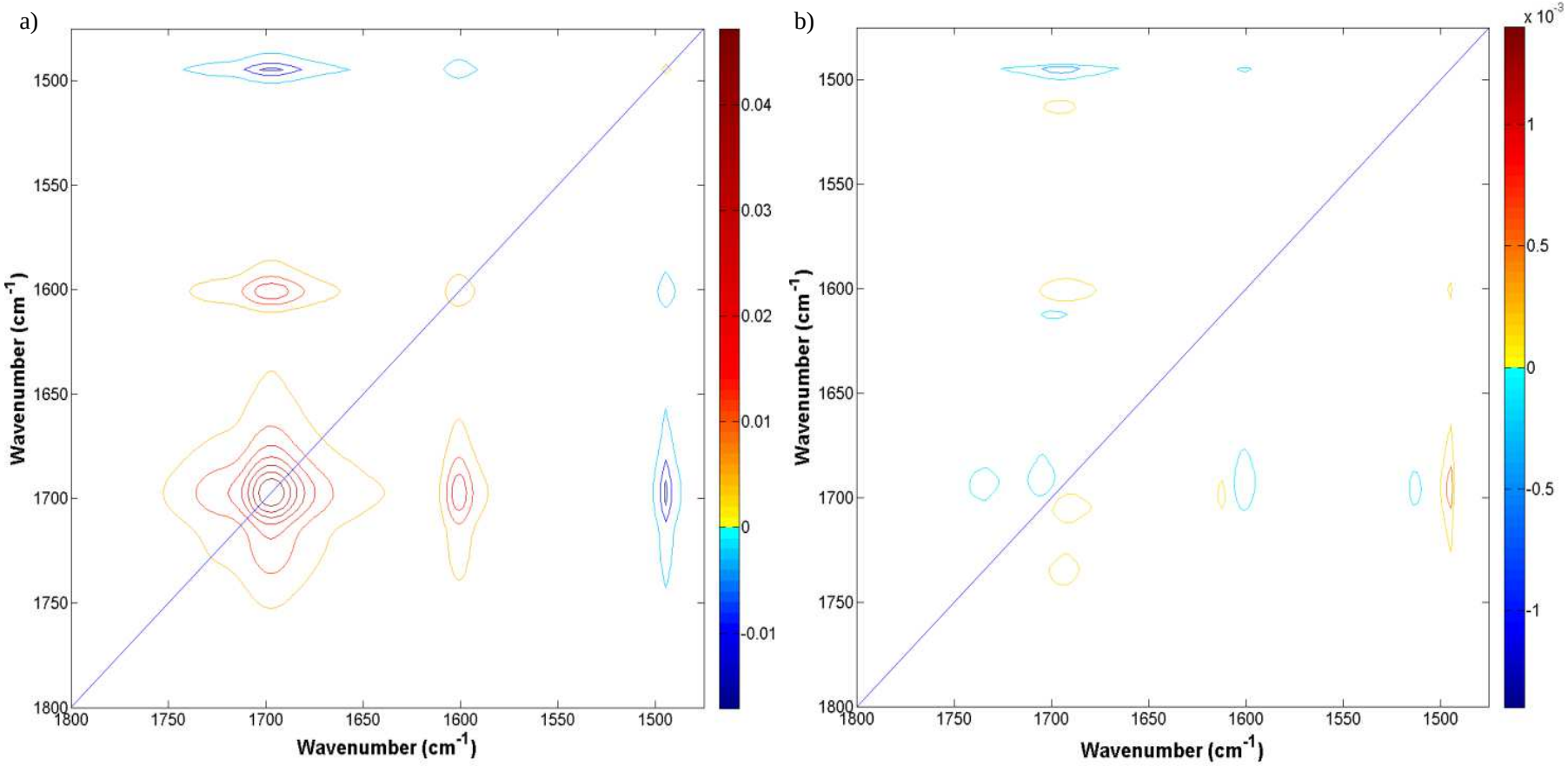

Figure 6 2D correlation spectra of X-ray irradiated Parylene-C in the range of 1800-1450 cm^{-1} a) Synchronous spectra b) Asynchronous spectra

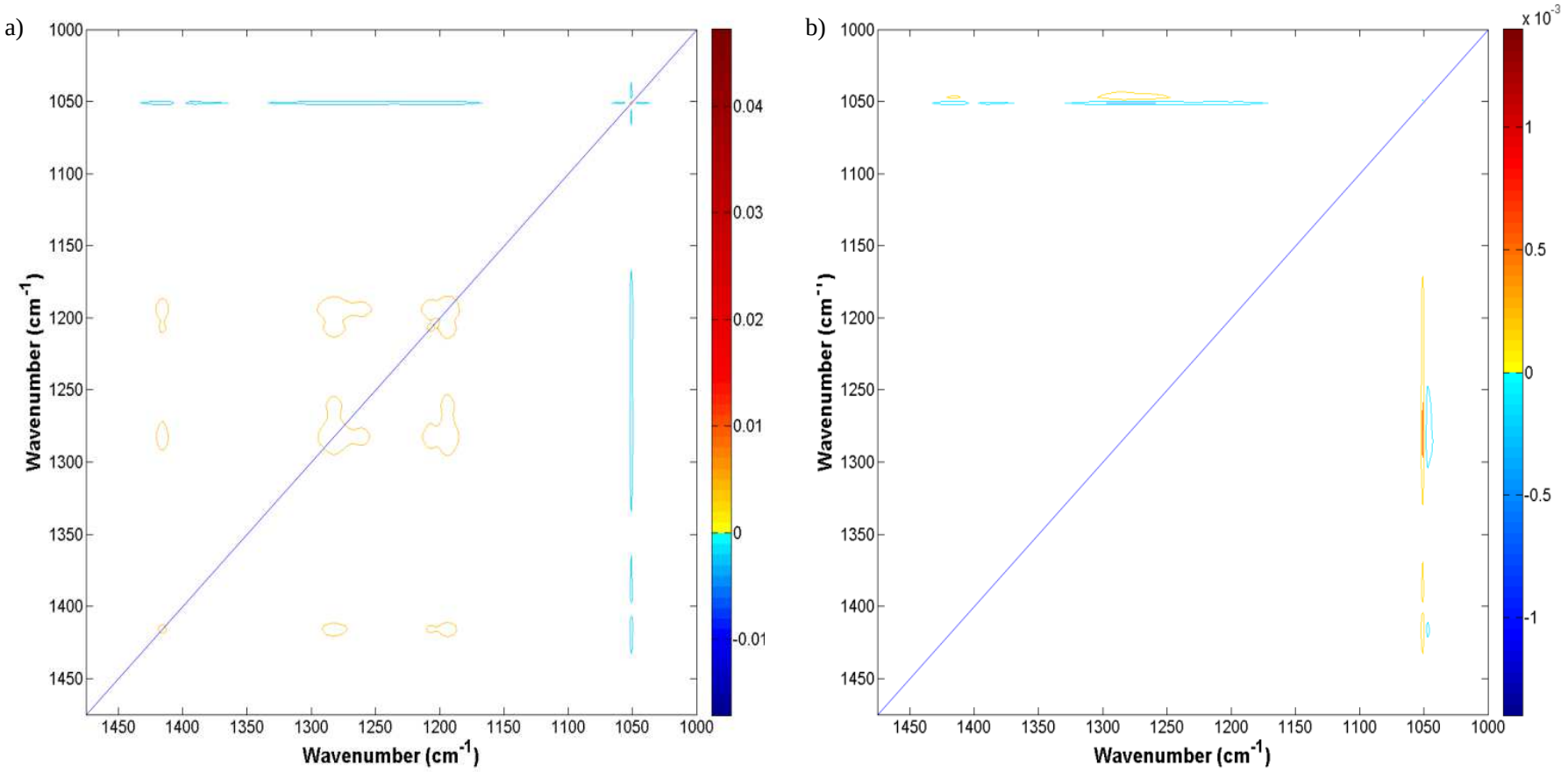

Figure 7 2D correlation spectra of X-ray irradiated Parylene-C in the range of 1500-1000 cm^{-1} a) Synchronous spectra b) Asynchronous spectra

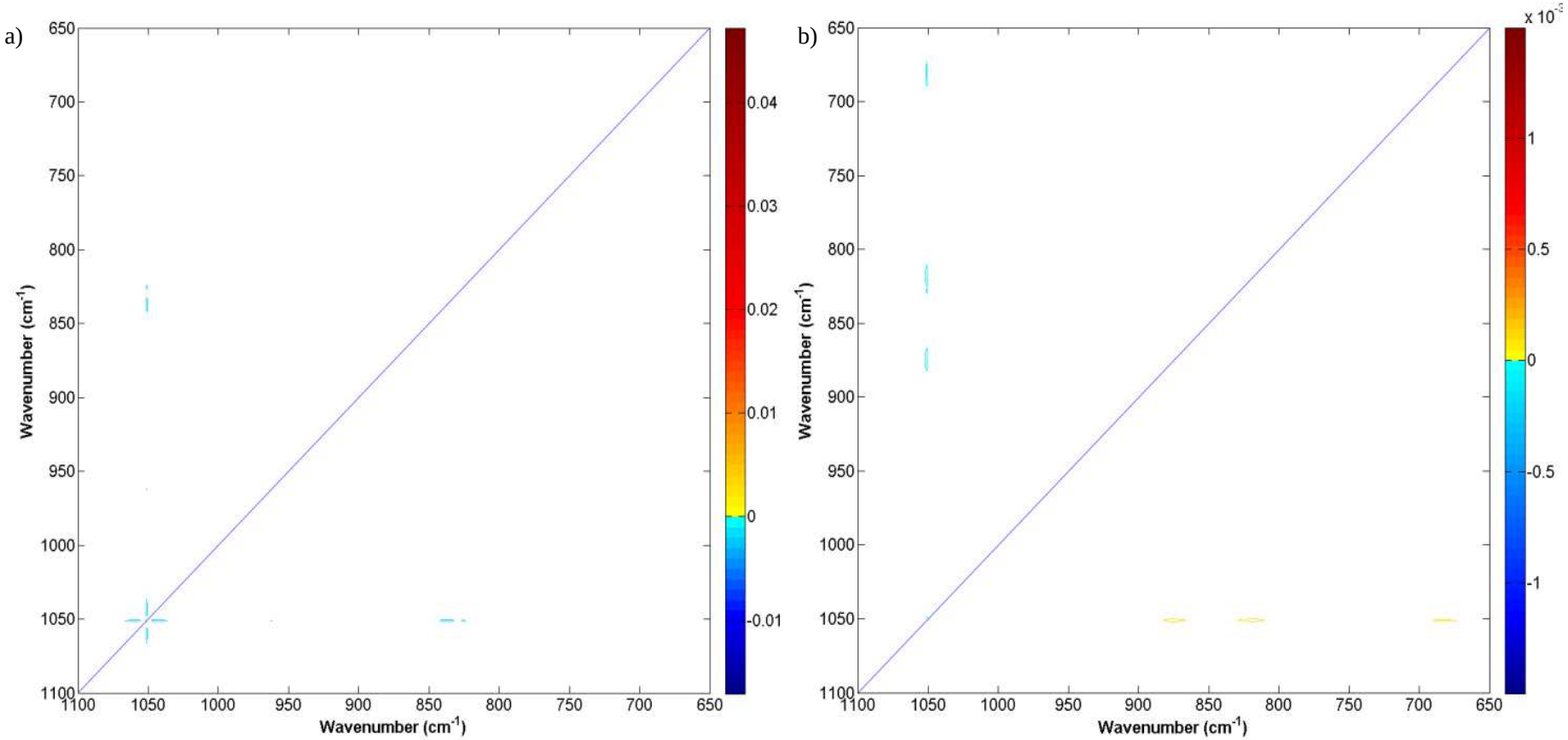

Figure 8 2D correlation spectra of X-ray irradiated Parylene-C in the range of 1500-1000 cm^{-1} a) Synchronous spectra b) Asynchronous spectra

Determination of Chemical Decay Mechanisms of Parylene-C during X-ray Irradiation using Two-Dimensional Correlation FTIR

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Highlights:

- X-ray irradiation of Parylene-C thin films results in oxidative degradation
- 2D correlation provides insight into the temporal nature of degradation
- FTIR spectra can be better understood applying 2D correlation technique

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: