

Investigation of the photolysis of molybdenum hexacarbonyl in cyclohexane solution by two-dimensional correlation and singular value decomposition analysis of time-resolved infrared spectra using infrared linear array spectrometer.

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In partial fulfillment
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Doctor of Philosophy

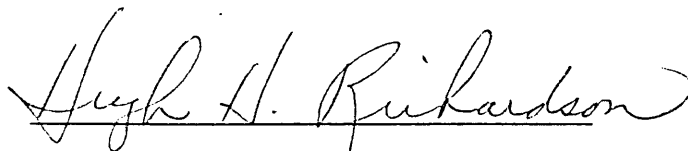
Sadeq Mahdi Alawi
March 1997

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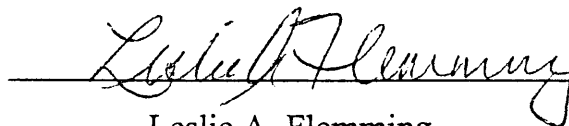
Sadeq Mahdi Alawi

This dissertation has been approved
for the Department of Chemistry
and the College of Arts and Sciences by

A handwritten signature in cursive script, reading "Hugh H. Richardson", written over a horizontal line.

Hugh H. Richardson

Associate Professor of Chemistry

A handwritten signature in cursive script, reading "Leslie A. Flemming", written over a horizontal line.

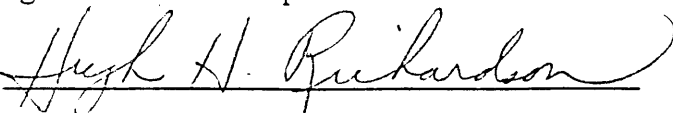
Leslie A. Flemming

Dean, College of Arts and Sciences

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An infrared spectrometer has been constructed that uses a dispersive monochromator and a 32 element InSb linear array detector. Infrared spectral data have been recorded using this linear array spectrometer at short time intervals following the photolysis of molybdenum hexacarbonyl in cyclohexane containing CO. These spectra illustrate rapid formation of a primary reaction intermediate that is assigned to be a solvent complex, $\text{Mo}(\text{CO})_5\text{S}$. For the first time, production of a dimer, $\text{Mo}_2(\text{CO})_{11}$ in solution is observed. The solvent complex has a band at 1970 cm^{-1} , and the dimer has a band at 2010 cm^{-1} . These species were observed to decay in the order of microseconds to form other products. One product was $\text{Mo}(\text{CO})_5$ complexing with a contaminant, $\text{Mo}(\text{CO})_5\text{X}$. The reformation of the parent molecule was also observed. The dynamical spectra are converted into two-dimensional (2D) correlation spectra. Infrared bands that change together in time show up as either positive or negative band intensities in the synchronous 2D correlation spectrum. Infrared bands that have much different decay characteristics give rise to band intensities in the disrelational 2D correlation spectrum. The disrelational 2D correlation spectrum shows two unique components; one has a band at $\sim 1970\text{ cm}^{-1}$ and the other has a band at $\sim 1950\text{ cm}^{-1}$.

The band at 1970 cm^{-1} is assigned to the solvent complex, $\text{Mo(CO)}_5\text{S}$, while the band at 1950 cm^{-1} is assigned to the contaminant complex, $\text{Mo(CO)}_5\text{X}$. The data are also analyzed by the singular value decomposition (SVD) method. This method yields orthogonal basis vectors that change with respect to time. The SVD method provides the means to determine the number of independent components involved in the time-resolved spectra after proper rotation. This method showed that there are two independent components were generated after the photolysis of the Mo(CO)_6 in cyclohexane system. One of them is the solvent complex, $\text{Mo(CO)}_5\text{S}$, which relaxes with a time constant of $17\text{ }\mu\text{s}$. The other species is the contaminant complex, $\text{Mo(CO)}_5\text{X}$, which decays very slowly with half life of 3 ms. The solution photolysis of Mo(CO)_6 was also performed in the presence of benzene and acetone with different concentrations. The life time and intensity of the transient bands were increased with increase in ligand concentration. The SVD results showed that benzene complexes with Mo(CO)_5 . Two mechanisms that describe the data were tested. The rate constants obtained in this work were in reasonable agreement with the published values.

Approved 
Associate Professor of Chemistry

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Chapter 1

Introduction

One of the major objectives in the field of infrared spectroscopy is fast spectral acquisition. Traditional IR methods cannot provide information concerning the exact chemical composition of the system when the system changes on a time scale of microseconds or nanoseconds. Many analysts hope to obtain information about transient species, the kinetics of an experiment or other mechanistic information which slower IR method can not provide. Therefore, finding and improving upon time-resolved infrared (TRIR) techniques are of great importance.

1.1. Historical background on the development of TRIR:

One of the first pioneers in the field of TRIR spectroscopy was George Bethke who published his work on a simple rapid-scanning infrared spectrometer in 1960.¹ He modified a commercial monochromator to achieve fast timing of scans. The instrument consisted of a prism for dispersion and scanned the infrared spectrum of a sample by the lateral movement of the entrance slit. This spectrometer used an InSb fast response detector and was capable of obtaining 20,000 scans per seconds. However, this instrument could not detect transients with half-lives less than milliseconds.

Herr and Pimental, a few years later, also used a dispersive prism in their studies, but obtained fast scanning with a high speed rotating mirror and ZnGe detector. They measured the infrared spectrum following photolysis of chloroformic acid in the spectral region between $650\text{-}5000\text{ cm}^{-1}$. Scan rates of 1000 cm^{-1} per $100\text{ }\mu\text{s}$ were reported by Herr and Pimental.²

With the development of Fourier-transform infrared (FTIR) spectrometers, an effort to obtain time-resolved spectra using interferometers was started. There are two basic methods used to study time dependent phenomena using Fourier-transform methodologies: step scanning and rapid scanning interferometry.

In step scan interferometry, the mirror of the interferometer is held stationary at each point while the entire time-evolution of the data is recorded. The data are sorted and Fourier-transformed to give infrared spectra at each measurement interval. However, a reproducible event must be initiated and sampled for each mirror position to yield time-resolved spectral information.³

An effort to study the vibrational relaxation of CO_2 and CO by step scan interferometry was initiated by Murphy and Sakai in the early 1970's.⁴ The reaction was carried out in a flow cell. The excitation was initiated with a pulsed electron gun. Time-resolved data were produced by repeating this cycle for each mirror position. Murphy and Sakai were able to achieve temporal resolution of

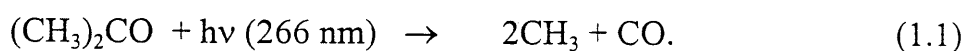
100 μs with a spectral resolution of 2 cm^{-1} . This group continued their research in this area, and in 1978, achieved significant improvements in spectral (0.1 cm^{-1}) and time resolution ($1\text{ }\mu\text{s}$).⁵

In 1989, Palmer and his group modified an FT-IR spectrometer for step-scan operation and collected near infrared spectra with 100 cm^{-1} spectral resolution and ms time resolution.⁶ They extended their work to the mid infrared with an increase in spectral resolution.⁷ They collaborated with Noda to merge step-scan interferometry with two dimensional correlation methodologies.⁸⁻¹⁰

In 1991, time-resolved step-scan FTIR absorption spectroscopy was implemented with a commercial interferometer by Seibert's group.¹¹ They performed time-resolved experiments on photobiological samples and showed that spectral changes smaller than 10^{-2} absorbance units can be detected with a time resolution of $20\text{ }\mu\text{s}$ and spectral resolution of 4 cm^{-1} .

In the second method, rapid-scanning FTIR spectroscopy, time-resolved data are obtained by synchronizing the initiation of data acquisition with the mirror movement.³ Donaldson and Leone have used this method to study gas phase photolysis reactions.¹² The time interval between laser pulse and data collection was carefully controlled. They could achieve better than 0.1 cm^{-1} spectral resolution in the microsecond range by cycling through the experiment many

thousands of time. There are so many other groups who performed work in both step-scan and rapid scan FTIR during the last decade and can be found in literature.¹³ As may be noted at this stage, both step-scanning and rapid-scanning FTIR techniques require reversible, and easily reproducible reactions in order to obtain time-resolved data. This requires effective control on experimental conditions otherwise spectral artifacts could result. This problem is clearly observed by Mantz and, later, by Garrison.^{14,15} Mantz reported TRIR data acquired using a rapid-scanning interferometer. He was studying the photolysis of acetone, and expecting to see an evidence of the well known reaction:



He reported that no CH_3 spectral features were observed, however a spectral band at 3138 cm^{-1} was observed and identified as due to ketene absorption. This had never before been seen as a product of this reaction. It was shown in later work done by Garrison and his co-workers that the results of the time resolved experiments performed by Mantz had been misinterpreted owing to the production of spectroscopic artifacts. These artifacts were due to fluctuations during data acquisition and were not related to transient species. The supposed ketene peak was actually displaced CO_2 .

Moore and his co-workers applied FTIR methods to fast time-resolved spectroscopy.¹⁶ They reported that all FTIR-TRS techniques suffer the problem of large amounts of noise. They concluded that “FTIR-TRS has not yet reached the point of being a routine method for the examination of systems where no independent measurement of the time-resolved spectroscopy is possible.” They also added, when comparing different TRS techniques, that the IR flash-kinetic method appears more favorable when accurate kinetic information is required. Furthermore, another group applied time-resolved rapid-scan FTIR spectroscopy in their dynamic gas phase $\text{Cl}_2/\text{C}_2\text{H}_6/\text{N}_2$ system.¹⁷ The time resolution of the rapid-scan FTIR spectrometer has been limited to 20 ms. Rapid-scan FTIR spectroscopy requires quick, stable, and accurate scanning of the movable mirror, which is difficult to achieve. Although, multichannel technique has a history of more than a decade, it was only recently that the real potential of this technique became fully appreciated as an alternative to step-scanning and rapid-scanning FTIR spectroscopy.¹⁸ In multichannel systems, the spectral information from more than one spectral element is acquired simultaneously and independently.¹⁹ Also, the wavenumber accuracy is high because of the freedom from the error arising from the spectrometer scanning. This is especially important when adding, averaging, and subtracting the spectra. Winefordner and his group compared signal-to-noise

ratios for multiplex methods vs. multichannel methods in optical spectroscopy.²⁰

They reported that for the same spectral source, and the same detector, the multichannel approach is the best. Most recently, McCreery showed, in comparison between multiplex and multichannel methods, that the intensity is not affected by the fluctuation of the laser power in multichannel methods, and therefore making the measurement of relative intensities and band shapes highly reliable.²¹ The only disadvantage of multichannel technique lies in the fact that the spectral region measured at one time is limited by the active area of the detectors.¹⁸

The advantages of multichannel system led Richardson and his coworkers to construct an infrared spectrometer employing a multichannel detector to collect time-resolved infrared data on the time scale of microseconds.²² This spectrometer uses a dispersion grating with an InSb linear array detector consisting of 32 detector elements. The spectrometer was characterized in terms of the spectral resolution, and the S/N ratio.²³ The spectral resolution of the spectrometer was found by measuring the FWHM of a peak and comparing that with the FWHM of the same sample taken with an FTIR at a known resolution. It was found that the natural bandwidth of the absorbing species is always narrower than the instrumental resolution of the infrared linear array, IRLA, spectrometer. This observation was confirmed with the FT-IR spectrometer.²³ The noise reduction in

IRLA followed a $1/\sqrt{N}$ dependence where N is the number of spectra averaged together. A detail description of IRLA spectrometer and its components are presented in chapter 3.

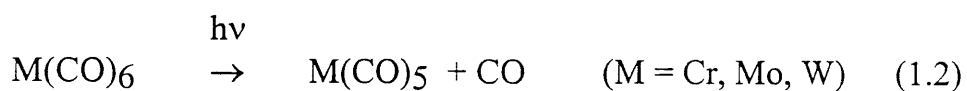
The research work on IRLA spectrometer is started by collecting IR spectra on the UV photolysis of Mo(CO)_6 in cyclohexane solution. There are several reasons for selecting the Mo(CO)_6 in cyclohexane solution as the system of study. First of all, the CO stretch from the metal carbonyl was in a spectral range that is easily followed with the IRLA spectrometer. Second, some preliminary work has already been done on the photolysis of metal carbonyl in solution. Third, a new contribution in explaining the kinetics and mechanism of this important system can be made with the IRLA spectrometer.

1.2. Background on the photolysis of metal carbonyl:

The importance of metal carbonyl is based on the photoproducts as a result of the photolysis which have shown to play an important role as catalysts.²⁴⁻²⁷ Unsaturated metal carbonyls, M(CO)_n (where $\text{M}=\text{Fe}$, Cr , and Mo), have been reported to catalyze reactions such as the geometric isomerization and the hydrogenation of olefins.²⁸ Such catalytic activity has been observed in the gas phase as well as in solution. Flash photolytic methods have proven to be an effective means for generating unsaturated organometallic complexes. However,

the photodissociation pathways and photoproducts have not been fully explored in solution, and our knowledge of the identity, structure, and reactivity of their reaction intermediates in solution is still very limited. On the other hand, there has been a great deal of effort in the last two decades directed toward the identification and characterization of such coordinatively unsaturated metal carbonyl compounds in low temperature matrices.

Thompson and Garratt proposed, as early as 1934, that the primary photochemical step for metal carbonyls was the loss of a molecule of carbon monoxide as in the following equation.²⁹



In general, every metal carbonyl can undergo loss of one CO as a result of the photolysis to generate a reactive intermediate.

Graham and his co-workers studied the photolysis of metal carbonyls in inert matrices at 15 K.³⁰ M(CO)_6 -argon gas mixture was sprayed onto a window at 15 K and photolysed with the soda-filtered mercury lamp ($\lambda > 330 \text{ nm}$). The IR bands of the metal pentacarbonyl as a product of the photolysis was assigned to a

structure with C_{4v} symmetry. The bands and assignments for the C_{4v} molybdenum pentacarbonyl, $Mo(CO)_5$, are shown in Table 1.1.

Bands (cm^{-1})	Assignment
2098 vw	A_1
1972 s	E
1932 m	A_1

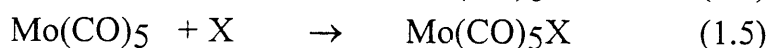
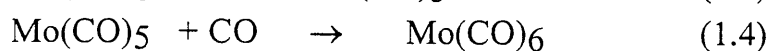
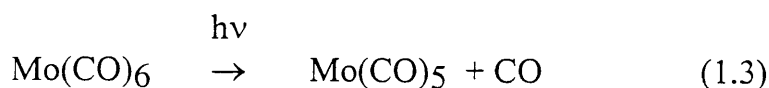
Table 1.1. The bands and assignments for molybdenum pentacarbonyl, $Mo(CO)_5$, observed in inert matrices at 15 K as a C_{4v} structure.

This group then made some preliminary observations on the photolysis of hexacarbonyls in solution. Approximately 8.0×10^{-3} M solution of the $Mo(CO)_6$ in cyclohexane was photolysed at room temperature using an unfiltered mercury lamp. The oxygen in the solution was removed by bubbling nitrogen through the solution for fifteen minutes. They could not observe any change in the solution following photolysis for a solution saturated with CO. On the other hand, a pale yellow color was observed following photolysis when the solution was saturated

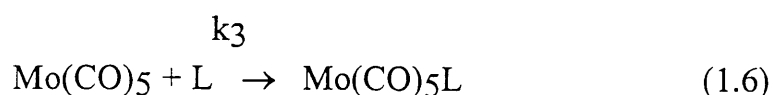
with N_2 or H_2 . The pale yellow color observed faded slowly in the absence of CO eventually depositing a film of metal on the sides of the container. They concluded that bubbling nitrogen or hydrogen through the solution removes the CO and reduces the possibility of recombination.

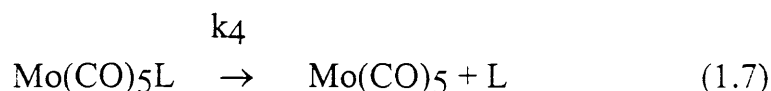
Nasielski at some other times performed a flash photolysis experiment on chromium hexacarbonyl in cyclohexane solution.³¹ They claimed that absorption spectrum of the first transient $\text{Cr}(\text{CO})_5\text{S}$ recorded by monitoring the decay at various wavelengths, showed a broad band with a maximum around 483 nm. The disappearance followed unimolecular kinetics, with an average rate constant of 170 s^{-1} . The absorption did not drop to zero, because a second species absorbed slightly at this wavelength. They could not determine accurately the rate constant of this second compound due to technical difficulties but they reported an average pseudo-unimolecular rate constant of 2.7 s^{-1} . The group reported that The first species at λ_{max} 483 nm did not react with CO, but instead formed the second (λ_{max} 445nm) which slowly recombined with CO with a half life of 25 s. These species were assigned to the C_{4v} and D_{3h} forms of $\text{Cr}(\text{CO})_5$. They also obtained similar results with $\text{Mo}(\text{CO})_6$ but these were rejected by Gustrof, who examined this system ($\text{Mo}(\text{CO})_6$ in cyclohexane) using a flash photolysis apparatus with a higher time resolution and more purified solvent.³² Under these conditions, this group

observed a species immediately after the photolysis. This species showed a broad band in the visible absorption spectrum at 503 nm. This species reacted with CO to reform Mo(CO)_6 with a half life of 25 μs . In addition, they reported that small quantity of other product was simultaneously formed. This group proposed the following mechanism:



However, this mechanism was rejected by many other groups including Gustrof and his group themselves at a later time, because the final product, $\text{Mo(CO)}_5\text{X}$, was not stable. They related this contaminant to the presence of water in their solutions, but the kinetics and mechanism of these reactions, due to their complexity, have not been resolved, and therefore not very well understood. Kelly and Gustrof anticipated that, in the presence of a ligand (L), the following reactions (1.6 and 1.7) would occur after the photochemical generation of Mo(CO)_5 .³³

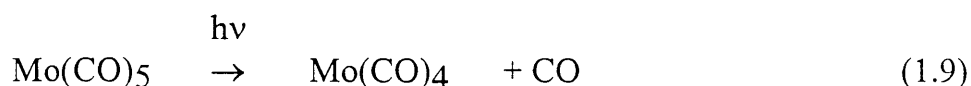
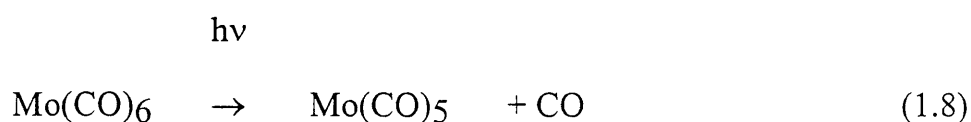




Herman and his group worked on the photochemistry of Mo(CO)_6 in 1982 after they designed a flash photolysis system with infrared detection which permitted the recording of IR absorption point by point every 0.005 μm and kinetics of transients of $\geq 5 \mu\text{s}$ lifetimes in solution.³⁴ They reported that Mo(CO)_5 as a result of the photolysis combines with the solvent at a rate that is nearly diffusion-controlled to form $\text{Mo(CO)}_5\text{S}$. This formation was too fast to be detected by their IR technique, but its disappearance at 1968 cm^{-1} was synchronously observed with the building up of another transient with two maxima at 1952 and 1918 cm^{-1} , which they called a contaminant complex, $\text{Mo(CO)}_5\text{X}$. This group failed to identify the contaminant X.

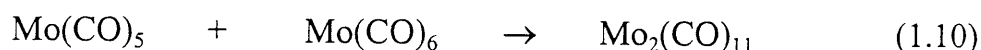
At a later time, with the development of picosecond absorption spectroscopy, Simon and Xie examined the dynamics of formation of $\text{Cr(CO)}_5(\text{solvent})$ generated by photolysis of Cr(CO)_6 in cyclohexane solution using time-resolved picosecond absorption spectroscopy.³⁵ However, in order to collect a single absorbance value, approximately 400 laser shots were used. They monitored the kinetics at the absorption maximum of $\text{Cr(CO)}_5\text{S}$, $500 \pm 5 \text{ nm}$ for cyclohexane. They observed a rise time of 0.8 ps.

Recently, It was reported by Heilweil and Dougherty that flash photolysis of Mo(CO)_6 in hexane solution using a transient broadband IR absorption technique with 390 fs time resolution gives a highly reactive species with C_{4v} symmetry.³⁶ The absorption of the photoproduct's E and A_1 symmetry modes are observed at 1952 and 1910 cm^{-1} respectively. Both of these absorptions were observed to decay on a similar timescale. However, an additional feature was observed at 1941 cm^{-1} . This absorption feature was not expected and has not been seen with other d6 metal carbonyls. They did not assign this band but suggested that Mo(CO)_5 as a result of the photolysis, loses another CO to form Mo(CO)_4 as shown in the following equations.



However, CH_4 matrix of Mo(CO)_4 studies reported that there should be a second IR absorption at 1887 cm^{-1} for Mo(CO)_4 .^{30, 37} Therefore this suggestion is inconsistent with low temperature matrices, and further explanation is required.

On the other hand, photolysis of group 6 metal carbonyls, in the gas phase, show trends in photofragmentation. Seder observed a strong dependence of the degree of fragmentation on the observed photon energy.³⁸ In 1989, Jane and his group reported results of the photochemistry of Mo(CO)_6 in the gas phase.³⁹ They monitored the vibrational spectroscopy and life times of Mo(CO)_5 , Mo(CO)_4 , and Mo(CO)_3 formed upon photolysis at 351, 308, and 248 nm respectively. They concluded that all three unsaturated species undergo rapid association reactions with Mo(CO)_6 to form dimers. A year later, Yoichi Ishikawa and his coworkers studied in more detail the excimer laser photolysis of Mo(CO)_6 in the gas phase with laser-based time-resolved infrared absorption spectroscopy.⁴⁰ They observed bands growing in at around 1990 and 2010 cm^{-1} with 2 μs time resolution. They assigned these bands to the formation of a dimer as shown in the following equation:



In our lab, IR spectra between 2060 cm^{-1} and 1880 cm^{-1} were collected during UV pulsed excitation of a solution of Mo(CO)_6 . Broad band transients with many overlapping bands are observed that decay with time. Details of the experiments and the discussions of the results are explained in chapters 3 and 4.

1.3. Goals of this work:

The first goal of this research is to show the ability of our novel IRLA spectrometer to collect time-resolved IR data. The second goal is to analyze the collected data with known chemometric techniques: Two-dimensional infrared (2D-IR) correlation and single value decomposition (SVD). Finally, to test these chemometric techniques for strength and weaknesses and applicability to analyze the IR data collected with the IRLA spectrometer. We start our analysis by converting the time-resolved IR spectra into a 2D-IR correlation spectrum. In this case, the Mo(CO)_6 solution changes with time following UV pulse excitation and spectral features that are synchronously or asynchronously correlated with time are plotted on a 2D grid. The 2D-IR correlation spectrum gives us a qualitative idea of the principal components and mechanistic information of the kinetic problem. For a quantitative analysis of the kinetic problem we turn to SVD. SVD of the time-resolved spectra yields orthogonal basis vectors that change with respect to time. The basis vectors with the largest variance are selected, then the pure components are determined after rotating them with an appropriate factor. Finally, kinetic models that accurately describe the time trace of the pure components are found.

1.4. The outline of the dissertation:

This dissertation is organized as follows: the next chapter provides the reader with an overview on the methods used in the data analysis. It includes the theoretical background of 2D-IR correlation and SVD analysis. It also describes the numerical recipe for doing both of these analysis. Experimental principals will be presented in chapter 3. The IRLA spectrometer with the data acquisition and all the related components will be described in detail. The optical design of the IRLA spectrometer with the excimer laser will also be presented. All the purification methods for the Mo(CO)_6 sample and the solvent, cyclohexane, will be explained including the type of sample cell used, and the technique used in transferring the sample into the cell. The process in which the data collected and signal averaging procedure before the analysis is performed will be discussed in a step by step. A clear picture of the 2D-IR correlation and SVD analysis along with a detailed procedure on converting the time-resolved IR data for 2D-IR correlation and SVD analysis will be given. Chapter 4 will focus on the results and discussion of the data analysis of the photolysis of Mo(CO)_6 in cyclohexane saturated with CO. In this chapter, the results of various data acquisition techniques with different time resolutions will be presented. The ability of collecting time-resolved data with several acquisition methods adds another advantage to the IRLA spectrometer. The results obtained from 2-D correlation and SVD will be

discussed thoroughly and several possible postulated mechanisms will be tested kinetically that accurately describe the time trace of the pure components.

Chapters 5 and 6 will extend the mechanism of the photolysis, of $\text{Mo}(\text{CO})_6$ in cyclohexane saturated with CO, by introducing known ligand concentrations into the original system. The ligands used are benzene and acetone in chapters 5 and 6 respectively. The time-resolved data collected in these two chapters are also analyzed by 2D correlation and SVD methods. Finally, summary and suggestions possible for future work are highlighted in chapter 7.

Chapter 2

Data Processing Methodologies

2.1 Two-dimensional infrared, 2D-IR, correlation:

2.1.a. Historical background:

Two-dimensional infrared (2D-IR) correlation is an analytical method based on time-resolved detection of IR signals to study molecular interaction.⁴¹ 2D-IR correlation has the advantage of showing the infrared bands that change together in time as either positive or negative band intensities in the synchronous 2-D correlation, while the infrared bands that have much different decay characteristics give rise to band intensities in the disrelational 2-D correlation spectrum. 2D-IR was originally applied to systems with overlapped spectral features by making perturbations to the sample environment in order to enhance the resolution.⁴² Examples of perturbations applied to the sample in order to enhance the information content of IR spectra are changes in temperature, concentration, and mechanical strain. This technique was first presented by I. Noda in 1986.⁴³ When a perturbation is applied to the system, various chemical species of the system are excited. The excitation and subsequent relaxation toward the equilibrium can be probed with IR. In IR spectroscopy, typical changes observed in time-resolved

spectra are the variation of intensities, and wavenumber shift of absorption bands.⁴³

2D-IR correlation has gained great interest among scientists since the development of this concept in 1986. The first system studied in detail by 2D-IR spectroscopy was a solution of polystyrene whose IR bands are very well known.⁴¹ In this study, all the synchronous and asynchronous peaks were identified and matched very well to the IR absorbance spectra. Another successful study for 2D-IR studies was on methyl methacrylate.⁴⁴ Its IR absorbance spectra showed some overlapped peaks between α -methyl groups and ester methyl group. The 2D-IR analysis managed to differentiate and separate these overlapped bands. Tatsuhiko and his group applied 2-D correlation into their time-resolved spectra.⁴⁵ They reported results of a study of reorientation dynamics of liquid crystals under the influence of an external electric field. They discovered a new absorption band which was not seen in a conventional IR spectrum. They proposed a possible assignment for this band on the basis of the results of 2-D correlation analysis. Most recently, Sefara et al. applied 2-D correlation analysis to both the mid and near IR regions in order to examine changes in the secondary structures of β -lactoglobulin in D₂O.⁴⁶ This group used bromoethanol as a perturber to disrupt the β -structure of the protein. They proposed a mechanism for converting β -

lactoglobulin from the β -sheet to an α -helical structure based on the results obtained by 2D-IR spectroscopy. There are many other groups found in the literature who applied 2-D correlation in various system.⁴⁷⁻⁵²

As pointed out by the above studies, the effect of each perturbation is uniquely associated with the specific mechanism that relates the stimulus with the corresponding response of individual constituent of the system. In our study, the UV light source with wavelength of 249 nm is used as a perturber to the system, Mo(CO)_6 in cyclohexane. The effect of the UV light is to remove one CO from Mo(CO)_6 and produce various components in the presence of the solvent or a contaminant. Each of these new components behave differently and show up at different wavenumbers. The rates at which the concentrations of these species change can be observed by time-resolved IR spectrometry.

2.1.b. Theory:

Basically, in order to obtain two-dimensional correlation spectra, it was necessary to Fourier transform the dynamic spectra into the frequency domain first.⁵³ The forward Fourier transform $Y_1(\omega)$ of the dynamic spectral intensity $y(\nu_1, t)$ observed at a wavenumber, ν_1 is given by:

$$\begin{aligned} Y_1(\omega) &= \int_{-\infty}^{\infty} y(\nu_1, t) e^{-i\omega t} dt \\ &= Y_1^{re}(\omega) + iY_1^{im}(\omega) \end{aligned} \quad (2.1)$$

where $Y_1^{re}(\omega)$ and $Y_1^{im}(\omega)$ are the real and the imaginary components of the complex Fourier transform of $y(v_1, t)$. The Fourier frequency ω represents the individual frequency component of the time-dependent variation of $y(v_1, t)$.

Likewise, the conjugate of the Fourier transform $Y_2^*(\omega)$ of dynamic spectral intensity $y(v_2, t)$ observed at spectral variable v_2 is given by

$$\begin{aligned} Y_2^*(\omega) &= \int_{-\infty}^{\infty} y(v_2, t) e^{+i\omega t} dt \\ &= Y_2^{re}(\omega) - i Y_2^{im}(\omega) \end{aligned} \quad (2.2)$$

Given the Fourier transforms, $Y_1(\omega)$ $Y_2^*(\omega)$, of the time domain dynamic spectra observed at v_1 and v_2 , the complex two-dimensional correlation intensity was defined as:

$$\Phi(v_1, v_2) + i \Psi(v_1, v_2) = \frac{1}{\pi T} \int_0^{\infty} Y_1(\omega) \cdot Y_2^*(\omega) d\omega \quad (2.3)$$

Since the correlation intensity is determined from dynamic spectral intensities observed at v_1 and v_2 , it became a function of two independent spectral variables.

The real and imaginary of the complex 2D correlation intensities, $\Phi(v_1, v_2)$ and $\Psi(v_1, v_2)$, are referred to as the synchronous and asynchronous correlation spectrum of the dynamic spectrum. Noda proved that the synchronous 2D

correlation spectrum can be computed without Fourier transforming dynamic spectral data, as shown in the following equation:⁴³

$$\Phi(\nu_1, \nu_2) = \frac{1}{T} \int_{-T/2}^{T/2} y(\nu_1, t) \cdot y(\nu_2, t) dt \quad (2.4)$$

which is equivalent to the time average of the product of dynamic spectral intensities measured at two wavenumbers. However, to compute the asynchronous 2D correlation spectrum, the Fourier transform of dynamic spectrum is required. Noda indicated that in order to go around the requirement of transforming spectral data into the Fourier domain, it is possible to compute a special type of asynchronous spectrum called the two-dimensional disrelation spectrum, $\Lambda(\nu_1, \nu_2)$. The magnitude of the disrelation spectrum is directly calculated from a set of synchronous correlation intensities as:

$$|\Lambda(\nu_1, \nu_2)| = \sqrt{(\Phi(\nu_1, \nu_1) \cdot \Phi(\nu_2, \nu_2) - \Phi^2(\nu_1, \nu_2))} \quad (2.5)$$

This disrelation spectrum, $\Lambda(\nu_1, \nu_2)$, is not the same as the asynchronous correlation spectrum, $\Psi(\nu_1, \nu_2)$, but is a good approximation.⁴¹

One of the main advantages of 2-D correlation is to simplify complex spectra consisting of many overlapped peaks. In addition, it enhances spectral resolution by spreading peaks over the second dimension. Also, 2-D correlation technique enables us to show the infrared bands that change together in time as either positive or negative band intensities in the synchronous 2-D correlation,

while the infrared bands that have much different decay characteristics give rise to band intensities in the asynchronous 2-D correlation spectrum.

2.1.c Properties of 2D correlation spectra

I : Synchronous Spectrum

The synchronous 2D correlation spectrum of dynamic spectral intensity variations represents the simultaneous changes of spectral intensities measured at wavenumbers, ν_1 and ν_2 . Figure 2.1 shows a typical example of a synchronous 2D correlation spectrum plotted as a contour map. A synchronous spectrum is a symmetric spectrum corresponding to spectral coordinates $\nu_1 = \nu_2$. Correlation peaks appear at both diagonal and off-diagonal positions. The diagonal peaks are referred to as autopeaks. These peaks correspond to the autocorrelation of a dynamic signal detected at a wavenumber ν_1 . The off-diagonal positions of a synchronous 2D spectrum represent the simultaneous changes of spectral signals at two different wavenumbers and are referred to as cross peaks. In the example spectrum, there are four autopeaks located at the spectral coordinates: **A**, **B**, **C** and **D**. They represent the overall extent of dynamic fluctuations of spectral intensity at the specific wavenumber during the period of time. In the example spectrum, bands **A** and **C** are synchronously correlated, as well as bands **B** and **D**. Therefore, two separate synchronous correlation squares could be drawn. The sign of cross

peaks can be either positive or negative. If the spectral intensities at corresponding wavenumbers are either increasing or decreasing together as functions of time during the observation period, the sign of synchronous cross peaks become positive. On the other hand, the negative sign of cross peaks indicates that one of the spectral intensities is increasing while the other is decreasing.

II : Disrelation Spectrum

A disrelation spectrum is an antisymmetric spectrum consisting of positive and negative cross peaks. Disrelation cross peaks represent independent variations of spectral intensities for all Fourier frequency components of the dynamic spectrum probed during the observation. Cross peaks develop only if the intensities of the individual spectral elements do not vary simultaneously. The major advantage of using a disrelation spectrum is that it is directly calculable from $\Phi(\nu_1, \nu_2)$ as shown in equation 2.5.

Noda proved that the sign of the cross peaks of the disrelation spectrum gives the order of the actual sequence.^{41, 53} This information can be used to study the mechanisms and kinetics of chemical interactions among functional groups. If there is a cross peak located at the upper left section of the contour plot ($\nu_1 > \nu_2$), and the peak is positive, then the species associated with the band at the higher wavenumber, ν_1 , takes place faster or before the species associated with the band

at lower frequency, ν_2 . In addition, if the positive cross peak is located at the lower right section of the spectrum ($\nu_1 < \nu_2$), then the species at lower wavenumber, ν_1 , takes place faster or before the component at ν_2 . On the other hand, for negative cross peaks, the temporal relationships described in the above arguments are reversed. Furthermore, if the disrelational correlation intensity at the coordinates disappears, i.e., $\Lambda(\nu_1, \nu_2) = 0$, then the two components probably occur simultaneously. The signs in Figure 2.2 indicates that the intensity changes at bands **A** and **C** occur after the changes at **B** and **D**.

Figure 2.1: This Figure shows a synchronous two-dimensional correlation spectrum which is constructed from a dynamic spectrum. A one-dimensional reference spectrum is also provided at the top and side of the 2D map.

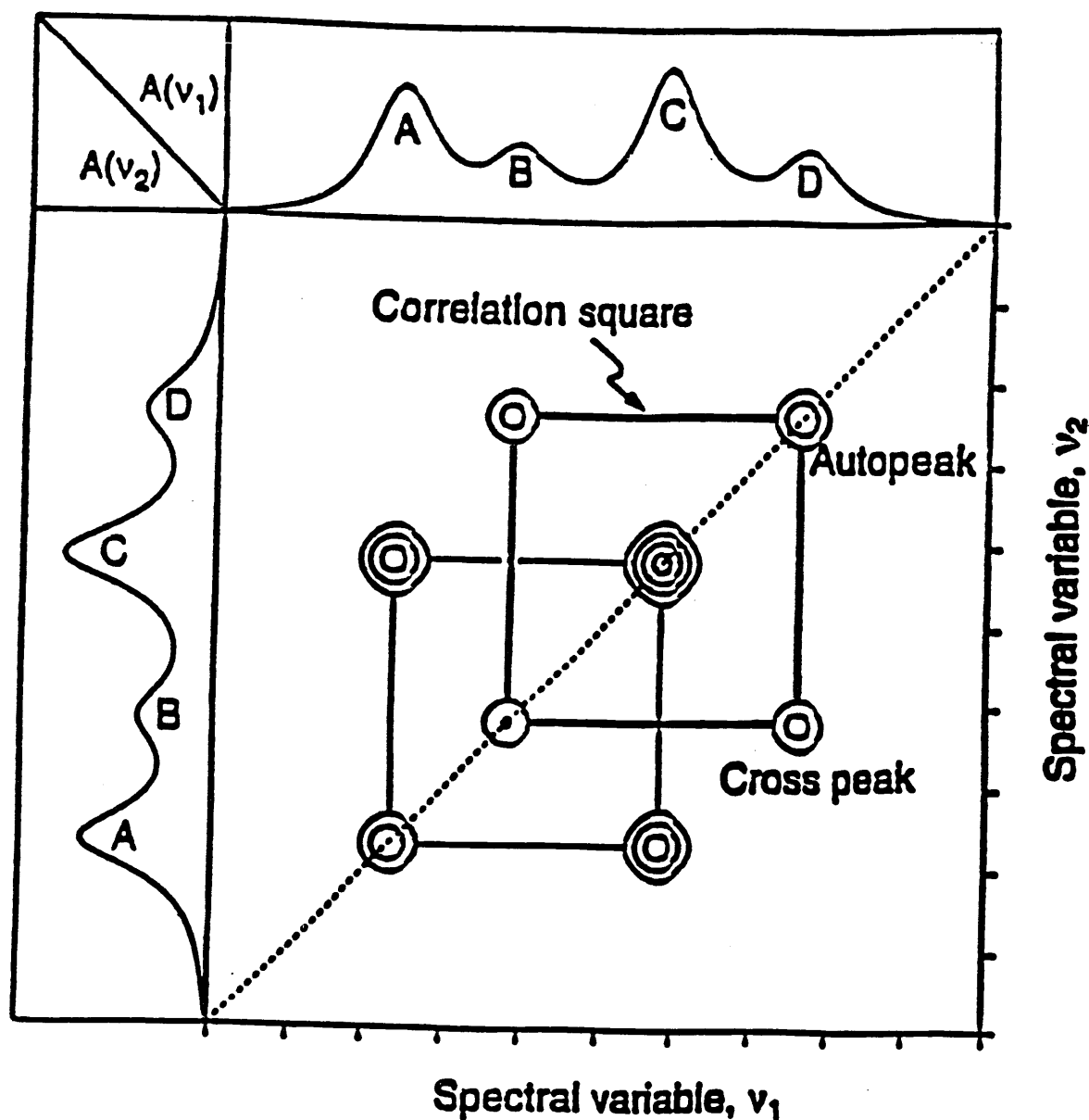
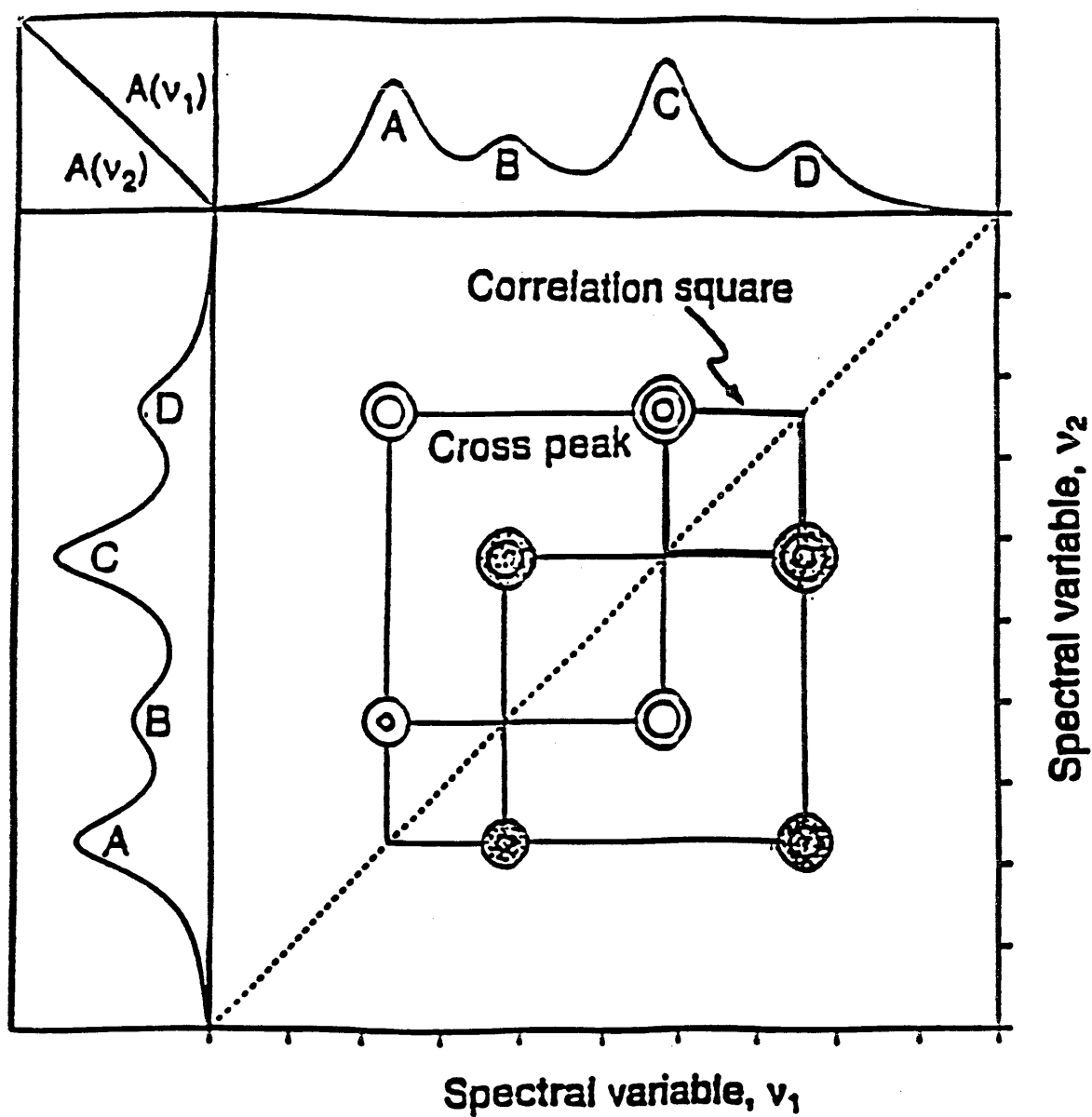


Figure 2.2: This Figure shows a disrelation two-dimensional correlation spectrum which is constructed from a dynamic spectrum. The shaded area indicates negative intensity.



2.2: Singular value decomposition (SVD):

2.2.a. Historical background:

There are many chemometric techniques developed for extracting the useful information from a large amount of data. Some of these procedures involve a mathematical method called eigenanalysis.⁵⁴ Such procedures produce eigenvalues and associated eigenvectors. The most commonly used methods using these procedures are the power method, the Jacobi method, singular value decomposition (SVD), and nonlinear iterative partial least squares (NIPALS). Among these methods, SVD is the preferred technique because it is most stable under the widest range of applications.⁵⁵⁻⁵⁷ The term, SVD, is sometimes used interchangeably with the terminologies principal component analysis, PCA, or principal factor analysis, PFA.⁵⁸ PCA forms the foundation for multivariate data analysis. In chemistry, PCA was introduced by Malinowski around 1960 under the name principal factor analysis.⁵⁵ Computer search on eigenanalysis shows that there are tremendous amount of chemical applications have been published in the literature using various algorithms. SVD was found to be more efficient than the other eigenanalysis methods.⁵⁹ It can distinguish between eigenvectors that differ minutely. On the other hand, NIPALS method is faster if just the the first few principal components are to be computed. In NIPALS, the process can be

terminated at any desirable point without requiring extraction of all eigenvectors. In certain applications, this can reduce the analysis time considerably.

In this work, SVD method was applied on the time-resolved data collected by the IRLA spectrometer. This will enable us to check all the principal components computed in terms of important and unimportant variation in the data matrix. Historically, SVD had been noticed by spectroscopists prior to 1970 but mainly to detect deviations from a standard in a set of spectra. Kankare was the first investigator to use SVD as a technique for studying chemical reactions.⁶⁰ His approach was purely mathematical rather than conceptual, which accounted for slow acceptance for its use. Nevertheless, Sylvestre and his group gave a clearer explanation and provided a method for estimating noise assuming uniform variance throughout the data.⁵⁵ In 1986, Shrager extracted useful information from equilibrium and kinetic studies using SVD.⁶⁰ He managed to determine the number of chemical transitions required to explain his data. His data consisted of optical absorbance at 100 wavelengths each measured at 80 titrant concentration, 8000 numbers in all, arranged in an m by n matrix. He managed to determine pK value using SVD method. More recently, Buydens and her group used the SVD method in the identification of plastics among nonplastics in mixed waste by remote sensing near infrared imaging spectroscopy.⁶¹⁻⁶² They managed to reduce

experimental artifacts and separate specular reflection from the important sample structures in the images using SVD. They concluded that SVD is a powerful tool for analyzing and improving multivariate images and optimizing the experimental setup with respect to undesired artifacts. There are several hundred other studies found in the literature based on SVD analysis. Details of these studies go beyond the scope of this dissertation.

2.2.b. Theory of SVD:

Basically, the SVD method provides the mean to determine the number of components involved in a data matrix. SVD of the time-resolved spectra yields orthogonal basis vectors that change with respect to time. Selecting the basis vectors with the largest variance determines the number of principal components. One of the main advantages of SVD analysis, is that it determines the spectrum of the pure components even though the original time-resolved spectra have overlapping bands. In addition, the time-resolved trace of the pure components can be detected and tested with kinetic models that accurately describe the time trace of the pure components. SVD is based on the following theorem of linear algebra: any $M \times N$ matrix A whose number of rows M is greater than or equal to its number of columns N , can be written as the product of an $M \times N$ column-

orthogonal matrix $\mathbf{U}$, an $N \times N$ diagonal matrix $\mathbf{W}$ with positive or zero elements, and the transpose of an $N \times N$ orthogonal matrix $\mathbf{V}$. Singular value decomposition technique produces the new basis set by finding the three matrices $\mathbf{U}$, $\mathbf{W}$, and $\mathbf{V}$, so that:

$$\mathbf{A} = \mathbf{U} \cdot \mathbf{W} \cdot \mathbf{V}^t \quad (2.6)$$

The column vectors in matrix $\mathbf{U}$ define the eigenvectors of the rows of $\mathbf{A}$. These are orthogonal and normalized. Matrix $\mathbf{U}$ shares the eigenvalues in $\mathbf{W}$ with matrix $\mathbf{V}$. In a time-resolved experiment, the column vectors in matrix $\mathbf{U}$ represent the temporal components.⁵⁶ The singular values on the diagonal in the diagonal matrix $\mathbf{W}$ represents the variance in the actual data. These are arranged in order of decreasing size, with the largest singular value at the top of the diagonal ($\mathbf{W}_{1,1}$), the second largest coming next ($\mathbf{W}_{2,2}$), and so on, down to the smallest singular value at ($\mathbf{W}_{N,N}$). The column vectors in matrix $\mathbf{V}$ are the eigenvectors of the columns of $\mathbf{A}$ and are orthogonal and normalized. In a time-resolved experiment, the column vectors in matrix $\mathbf{V}$ represent the spectral components. Complete procedure for obtaining $\mathbf{U}$, $\mathbf{W}$, and $\mathbf{V}$ matrices can be found in the literature.⁵⁴

The spectral and temporal components obtained by SVD do not necessarily represent real spectra and dynamics, because SVD is a purely mathematical operation.⁵⁶ Only appropriate linear combinations of the components are

meaningful. Therefore, Gaussian Elimination as matrix method in solving simultaneous linear equations need to be applied. This method leads to a systematic reduction to triangular form by repeatedly multiplying one row by an appropriate factor and adding to another row. If we consider as an example that there are n equations and n unknowns such that

$$a_{11}x_1 + a_{12}x_2 + \dots + a_{1n}x_n = c_1$$

$$a_{21}x_1 + a_{22}x_2 + \dots + a_{2n}x_n = c_2 \quad \Leftrightarrow \quad A x = c$$

$$a_{n1}x_1 + a_{n2}x_2 + \dots + a_{nn}x_n = c_n$$

Thus multiplying the $(n-1)^{\text{st}}$ equation by $(a_{n1} / a_{n-1,1})$ and subtracting from the n^{th} equation annihilates a_{n1} and converts the n^{th} equation to

$$0 + (a_{n2} - a_{n1}a_{n-1,1})x_2 + \dots + (a_{nn} - a_{n1}a_{n-1,n}/a_{n-1,1})x_n = c_n - a_{n1}c_{n-1}/a_{n-1,1}$$

Repeated application of this procedure converts the problem to the triangular form

$$a_{11}x_1 + a_{12}x_2 + \dots + a_{1n}x_n = c_1$$

$$a_{22}x_2 + \dots + a_{2n}x_n = c_2$$

$$a_{n-1,n-1}x_{n-1} + a_{n-1,n}x_n = c_{n-1}$$

$$a_{nn}x_n = c_n$$

Solving from the bottom up gives $x_n = c_n / a_{nn}$, $x_{n-1} = (c_{n-1} - a_{n-1,n}x_n) / a_{n-1,n-1}$, etc.

Unfortunately, the rotation factors are unknown to us in this research problem. We

will use the following guidelines for determining the pure components. For two components, we subtracted the intensity profile of one component from the other one by a certain factor and saved as a pure component. In the same fashion, we subtracted the second component from the first in such a way that none of the pure intensity profiles falls below zero. Using the same subtraction factors, we subtracted the spectrum of one component from the other to yield the pure spectral components. The procedure was iterated until we get reasonable results. The goodness of fit was evaluated so that the initial increase in component 2 could not be faster than the initial decay of component 1, both intensity profiles do not show negative values and finally, the pure intensity profiles are fitted to several kinetic models that reasonably describe the original data.

2.2.c. Determination of main components:

In SVD analysis, the first basis vector represents the most variation in the data, the second the next most, and so on. Having these vectors separated means that they can be examined consecutively for their contribution to the complete data set. If a temporal component shows random fluctuations around zero and its corresponding variance is below the noise level then that component and the following ones are ignored. This method was used by Hamaguchi.⁵⁶

Chapter 3

Experimental and Data Collection

3.1. The Infrared Linear Array Spectrometer

A diagram of the linear array spectrometer is shown in Figure 3.1. The infrared light source is a globar which is focused at the sample, collected and refocused onto the entrance slit of an $f/4$ monochromator. The slit width is typically 1-2 mm. A mechanical chopper is positioned in front of the monochromator. The chopper blade has a slit cut in it which transmits a light pulse to the monochromator and also generates a reference signal which acts as a trigger for timing of the spectrometer. This reference signal is the millisecond decay from an infrared sensor that has been blocked from a light emitting diode (LED) by the blade of the chopper. The monochromator has a grating with 75 grooves/mm, a linear dispersion of $0.500 \mu\text{m}/\text{cm}$, a blaze angle of 10.0° and a blaze wavelength of $4.65 \mu\text{m}$. The grating disperses the light and a 5 cm focal length cylindrical lens collects it. This lens compresses the image in the vertical direction but does not alter the image in the horizontal direction. It focuses the light onto a Cincinnati Electronics 32 element InSb linear array detector. The linear array detectors are placed horizontally in the focal plane of the monochromator exit slit. The size of the detector element is $0.2 \times 0.2 \text{ mm}$ with a

Figure 3.1. A block diagram of the infrared linear array spectrometer.

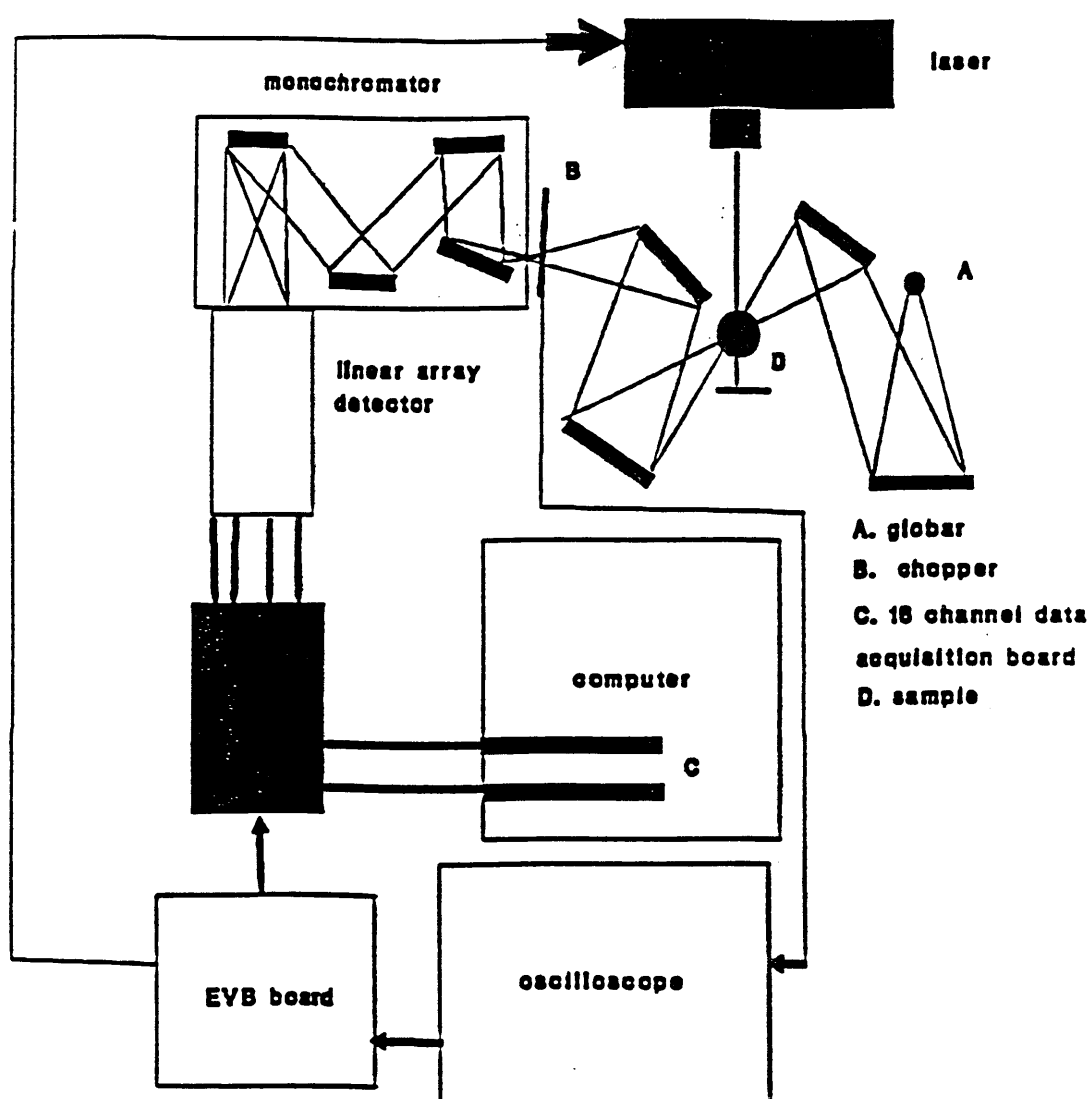
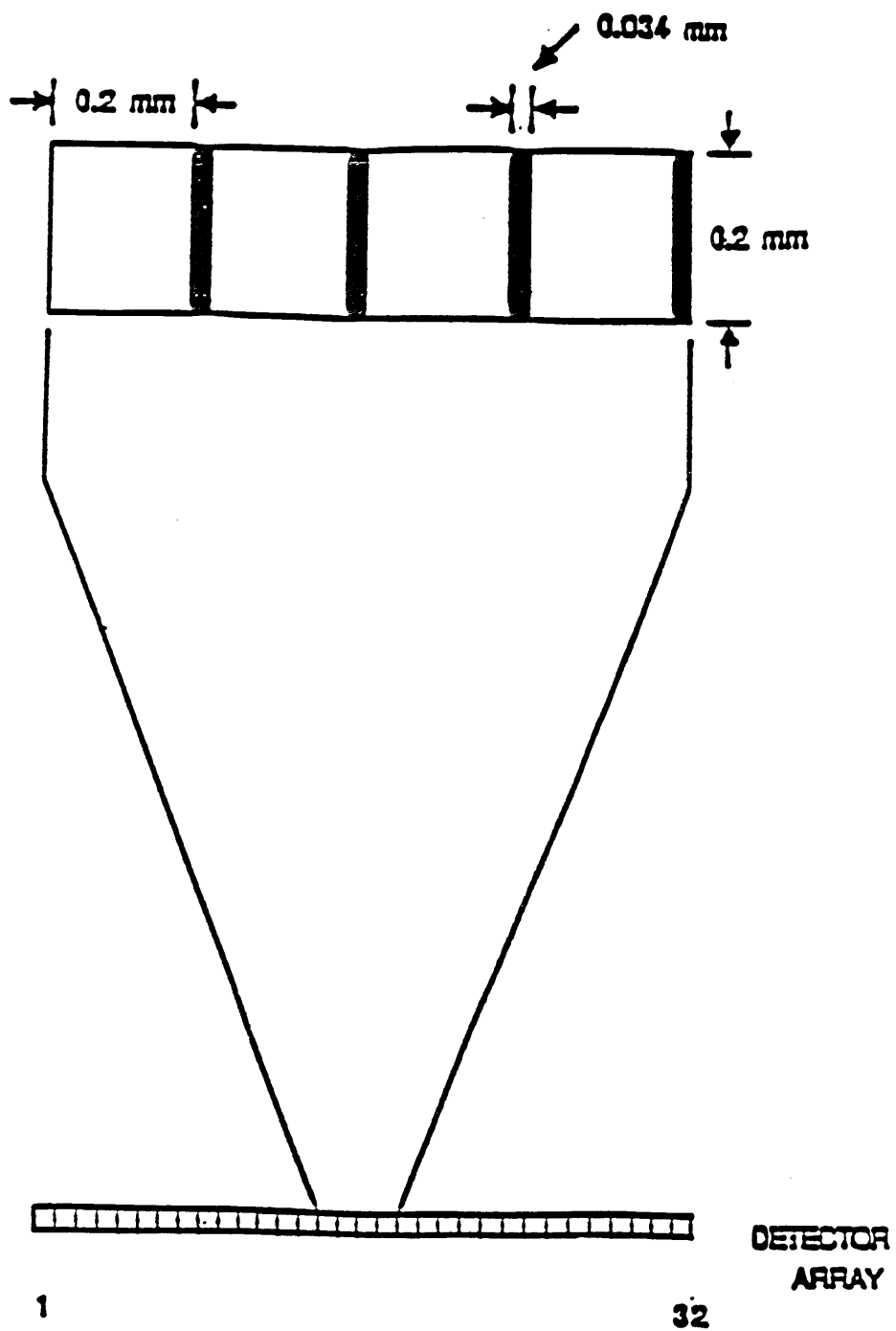


Figure 3.2. An enlargement of the linear array detector elements.

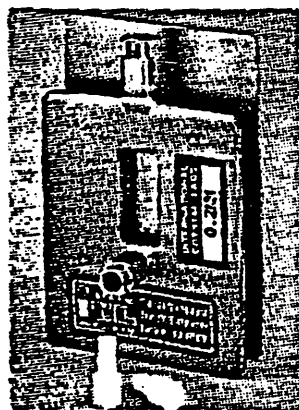


center to center distance between each element of 0.234 mm as shown in Figure 3.2. The detector elements have a quantum efficiency around 0.8. A cutoff filter, cooled to 77 K, is placed in front of the linear array detector. This filter only transmits light at frequencies less than 4000 cm^{-1} . The signal from each detector element is converted to a voltage by its corresponding preamplifier. The output signal from the preamplifier is a.c. coupled and amplified with a postamplifier gain of 10. The a.c. time constant is about 100 ms.

3.2. The Sample Cell

The sample cell is a flow cell, purchased from Perkin Elmer, as shown in Figure 3.3. CaF_2 windows with dimensions 5 x 10 mm are attached to each end. The pathlength is 0.1 mm. The samples were loaded into the cell in a glovebox under argon atmosphere to avoid sample exposure to air. All photolytical experiments were carried out at room temperature.

Figure 3.3 The reaction flow cell used for the photolysis of $\text{Mo}(\text{CO})_6$.



3.3. Sample Preparation

Mo(CO)_6 was purchased from Aldrich Chemical Company and purified by sublimation. Mo(CO)_6 was sublimed every time before preparing the sample for proteolysis. The solvent, cyclohexane, was purchased from VWR Scientific. The solvent is 99.99% pure, and further purified by distillation to minimize olefinic and aromatic impurities. The procedure was started by shaking the solvent with a mixture of equal volumes of concentrated sulfuric and nitric acids. This was repeated three times, then washed thoroughly with distilled water. The organic layer was separated and dried over calcium chloride. Finally, the solvent was distilled three times and saved in the glovebox under argon atmosphere. A sample of Mo(CO)_6 in cyclohexane with concentration of 1.0×10^{-3} M was prepared in the glovebox. The sample was moved to a sonic bath and sonicated for about 2 hours to get rid of most of the dissolved gases. Freeze and thaw was also applied to the sample at liquid nitrogen temperature to further degas any dissolved gases. The sample was pumped to about 10 mTorr, thawed and shook. This process was repeated 5 or 6 times for each sample. Saturation of the solution with CO was accomplished by bubbling CO gas (99.999% pure) that had passed through a liquid nitrogen trap into the solution. Benzene, and acetone were purchased from Fisher Scientific with purity of 99.95 % and 99.9 % respectively. They were used, with

no further purification, as ligands in some of the experiments. The sample was transferred into the reaction cell by a microsyringe to minimize air contact.

3.4. The Data Acquisition System:

A Motorola M68HC11EVB Evaluation Board (EVB) computer is used to trigger data acquisition. The timing involved in data collection is as follows: A BK precision 100-MHz oscilloscope Model 1590 A is triggered on the reference signal from the slow decay of the infrared sensor which has been blocked by the chopper. The oscilloscope generates a square wave pulse which is fed into an input port of the EVB. When the EVB detects the signal from the oscilloscope, an assembler program is executed. This program counts down the correct time delay between the reference signal and the time that the slit in the chopper blade and the entrance slit of the monochromator become aligned. The time delay is ~ 1 ms. The EVB then generates a trigger pulse to either trigger the Lumonics excimer laser and/or start data acquisition.

The data acquisition system is composed of two RC-Electronics ISC-16 data acquisition boards. Each board contains two A/D converters. Each board contains 16 inputs which can sequentially be digitized at $1\ \mu\text{s}$ per input. The signals from the first 16 detector elements are fed into the first data acquisition

board and the signals from detector elements 17-32 are fed into the second data acquisition board. With both boards running simultaneously, the signals from all 32 detector elements can be digitized in 16 μ s. Each data acquisition board has 64 K of buffer memory to store information. The data are stored as 2 byte words and it is possible to store 32768 data points; 2048 data points for each of the 16 detector elements. Data is collected until the buffer is filled, allowing about 32 ms of data collection in which the entire infrared spectrum is collected every 16 μ s.

The UV light source is the Lumonics excimer laser with a KrF gas fill. A 10 ns laser pulse with wavelength of 249 nm is pulsed approximately 1 ms after initiation of the data acquisition system. Data acquisition continued until the data buffer was filled. Before the next data acquisition sequence was initiated, a four second dead time was placed in between the laser pulses to allow the Mo(CO)_6 solution to return to the original composition.

In some cases, the sequential, as oppose to parallel, data acquisition leads to problems in the IR spectrum if the transients shorter than 16 μ s are observed. Under these conditions better time resolution was obtained by sampling only two inputs at a time and piecing the spectrum together afterwards. In this mode, the same input is sampled every 2 μ s. piecing the spectrum together, two inputs at a time, requires that after each laser pulse the solution must return to the original

composition. This is indeed the case and 20 laser pulses are averaged. The data acquisition in this mode was set so that every other input was sampled (8 inputs per acquisition board). Each sampling session collected 2 inputs per board. In this way, the entire spectrum was collected in four data acquisition sessions in which 20 laser pulses were averaged.

In the experiments that involved acetone as a ligand, a different data acquisition method was developed. This is because we found the decay time of the acetone complex with the unsaturated metal carbonyl was lengthened in the order of seconds. In these experiments, 32 sweeps of data are collected with time delay of 4 seconds between each sweep. A data file is collected before irradiation and saved as file 1. Another data file is collected on the same sample, but this time, a broad band Xe-lamp was used and started to irradiate the sample at the beginning of the data file. The lamp was blocked around the sixteenth sweep, and sweeps 17 through 32 probed the decay in the $\text{Mo(CO)}_5\text{L}$ concentration. This data file was stored as file 2. The difference data file (file 2 minus file 1) gives the change in the Mo(CO)_6 solution after irradiation with respect to time.

3.5. Data treatment before analysis

A Pascal program is used to signal average the number of scans taken for the sample before and after irradiation with the laser pulse respectively. The single

beam spectra of the UV irradiated solution were converted into absorbance spectra using the IR spectrum of pure cyclohexane solution as a reference.

All time-resolved data were subjected to baseline correction. The correction was carried out as follows: The time traces of the first three detector elements were averaged together and saved as A_1 , and the time traces of the last three detector elements were averaged and saved as A_3 . A_1 and A_3 were also averaged and saved as A_2 . Multiple point interpolation was performed on A_1 , A_2 , and A_3 to construct the time-resolved spectra of the baseline. The time-varying baseline was subtracted from the original data. These baseline corrected time-resolved data were converted into difference spectra by subtracting the static absorbance spectrum of Mo(CO)_6 solution. These difference spectra are the starting point of all of our spectral analysis.

3.6. Formatting the time-resolved data for 2D-IR correlation and SVD

techniques:

Grams/386 software (Galactic Industries Corporation, Salem, NH) is used to do the manipulation of data using gateway 2000 (486/33) PC. The data analysis is started by mean centering the time-resolved difference spectra, then rotating them 90 degrees. This results into a multiple file which consists of the intensities at specific wavenumbers as a function of time. This multiple file is split into

single vectors. These vectors are transferred into Microsoft excel (version 5.0c) for regrouping. Collecting all these vectors would result in a formation of new matrix with a dimension of $M \times N$, where M is the number of data points in the temporal region, and N is the number of data points in the spectral region. The synchronous and disrelation correlation spectra were generated using subroutines written in Matlab (The Math Works, Inc.), based on Noda's algorithm.^{44,53} The actual SVD analysis was carried out in Matlab as well, then the new matrices U , W , and V were transferred into Grams/386 for proper rotation.

Chapter 4

Solution photolysis of Mo(CO)_6 in cyclohexane saturated with CO

4.1. Introduction:

Mo(CO)_6 in cyclohexane solution was selected as our system to perform time-resolved study using the infrared linear array spectrometer. Solutions of Mo(CO)_6 in cyclohexane with concentrations of 1.0×10^{-3} M were prepared as described in chapter 3. We have performed the photolysis of Mo(CO)_6 in cyclohexane at different levels of data acquisition to explore the IR spectra between 2060 cm^{-1} and 1880 cm^{-1} .

4.2. Data Analysis for the photolysis of Mo(CO)_6 in cyclohexane with time resolution of $16 \mu\text{s}$ and low spectral resolution ($\Delta\lambda=0.078 \mu\text{m}$):

Time-resolved IR difference spectra of irradiated sample of 1.0×10^{-3} M of Mo(CO)_6 in cyclohexane solution ($\lambda_{\text{exc}}=249 \text{ nm}$) is shown in Figure 4.1. The difference spectra are obtained by subtracting the IR spectrum before laser excitation from the spectrum after irradiation. The excimer laser is pulsed approximately 4 milliseconds after the start of the IR spectral data initiation. In this figure, 2048 spectra are shown all $16 \mu\text{s}$ apart. These spectra are the average of 9 laser shots. The temporal region before the laser pulse is reasonably flat

around zero. This confirms that after each laser pulse the Mo(CO)_6 solution returns to the original composition. In the vicinity of the laser pulse, a transient is observed that decays with time. The transient has both positive and negative peaks.

Figure 4.2 shows the change in absorbance at 1979, 1972, 1966, and 1952 cm^{-1} as a function of time for the data in Figure 4.1. Three regions in the time trace are indicated by letters A, B, and C. Region A is the point in time immediately following the laser pulse and is characterized by a rapid decay in intensity. Region C is a point in time far removed from the laser pulse where very long decays are observed. Region B follows region A. A representative spectrum from each of the three regions shown in Figure 4.2 (A, B, and C) is shown in Figure 4.3, and gaussian bands were fitted to the IR spectrum. The actual data points in the IR spectrum are shown as crosses (+). One of the bands located at $\sim 1990 \text{ cm}^{-1}$ is a negative band due to loss of Mo(CO)_6 . The positive bands in Figure 4.3 A at $\sim 1970 \text{ cm}^{-1}$ and 1934 cm^{-1} shift instantly towards, slightly lower frequencies, $\sim 1950 \text{ cm}^{-1}$ and $\sim 1920 \text{ cm}^{-1}$ respectively. There is another positive peak at 2010 cm^{-1} . This peak is observed only in the first spectrum immediately after laser excitation and disappears at once afterwards when using $16 \mu\text{s}$ time resolution. The wavenumbers where the time traces were taken in Figure 4.2 are

highlighted in Figure 4.3 as circles around the actual data points. In spectrum B, and C of Figure 4.3, the change in absorbance at 1979 cm^{-1} is zero because the negative peak contribution from loss of Mo(CO)_6 is canceled out by the positive peak contribution of the 1950 cm^{-1} . The data matrix for this set of experiments was transformed to a 2D-IR correlation map that shows which wavenumbers are synchronously and asynchronously correlated. We used the generalized algorithm developed by Noda.⁵³ Figure 4.4 (A and B) shows the synchronous 2D correlation spectrum of the data in Figure 4.3 for a sampling period of $800\text{ }\mu\text{s}$ following the laser pulse in a contour representation and in a 3D plot. Two broad autopeaks centered at 1953 cm^{-1} and $\sim 1992\text{ cm}^{-1}$ are observed in the synchronous spectrum. There is a hint that a cross peak exists at 1953 cm^{-1} and 1920 cm^{-1} . Negative broad cross peaks are also observed between 1992 cm^{-1} and 1953 cm^{-1} . This indicates that the disappearance of the band at 1953 cm^{-1} occurs at the same rate as the reformation of the parent molecule, Mo(CO)_6 . The disrelation spectrum for this data is shown in Figure 4.5. In this Figure, a broad cross peak is observed at 1953 cm^{-1} and 1970 cm^{-1} . This cross peak implies that there are at least two distinct chemical components that are formed after the photolysis. One has an IR band

Figure 4.1. The difference spectra of Mo(CO)_6 in cyclohexane solution irradiated with 249 nm laser excitation. There are 2048 spectra shown each 16 μs apart.

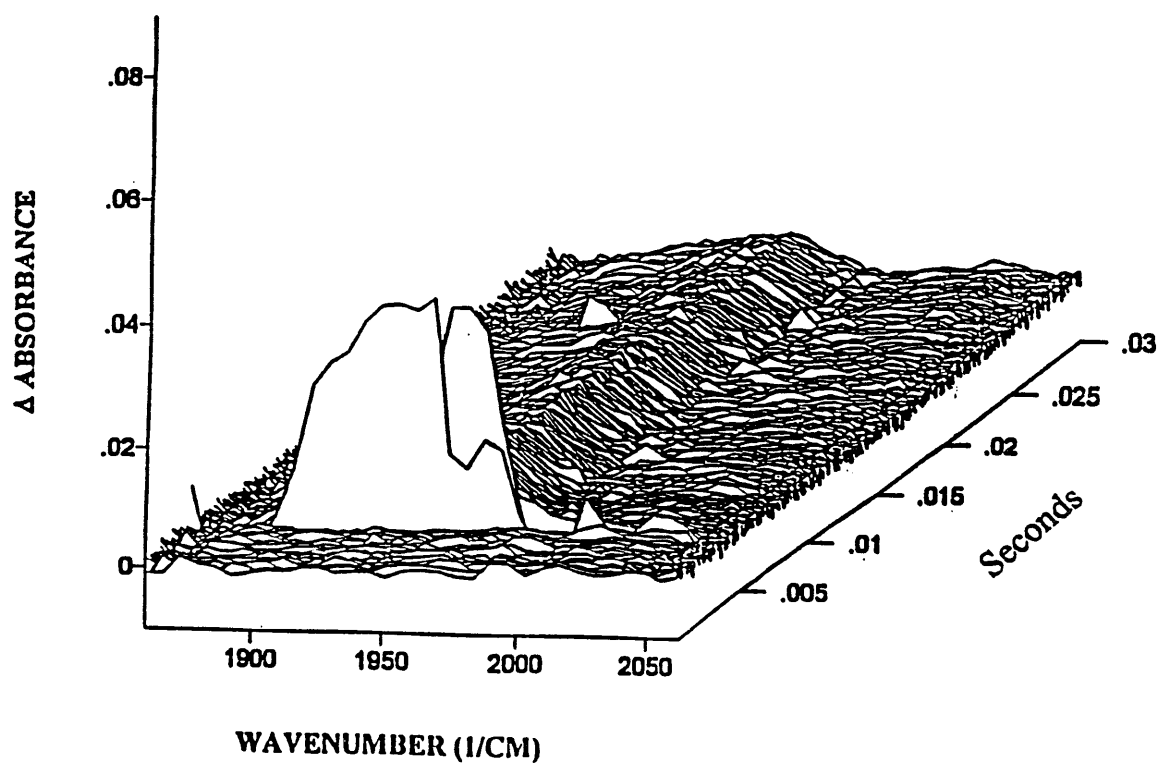
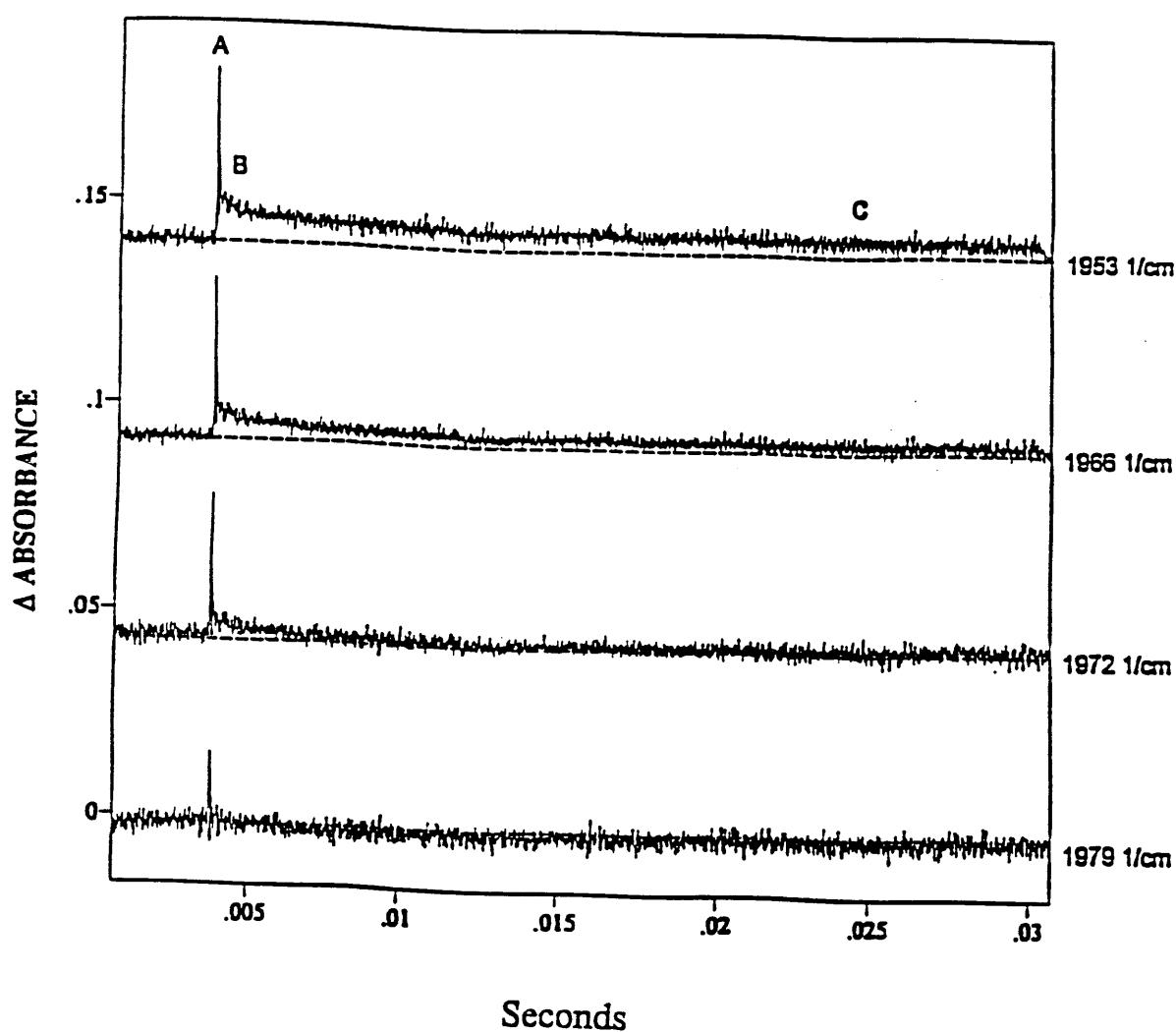


Figure 4.2. The change in absorbance at 1952, 1966, 1972, and 1979 cm^{-1} as a function of time for the data in Figure 4.10. Region A immediately follows the laser pulse. Region B follows region A, and region C is a point in time far removed from the laser pulse.



near 1970 cm^{-1} and the other has an IR band around 1953 cm^{-1} . The cross peak in the disrelation spectrum indicates that the band at around 1970 cm^{-1} occurs before the band at around 1950 cm^{-1} . On the other hand, it is not possible to determine the second lower wavenumber band in the 1970 and 1950 cm^{-1} peaks because the bands are smeared together into a large broad band. The data matrix is further analyzed to obtain principal components using singular value decomposition. Figure 4.6 is a plot of the singular values on the diagonal in the diagonal matrix S . This tells us the amount of variation (variance) in the data. Only the first component is significant. The rest of the components are within the noise level. The intensity profile and the vibrational spectrum of the first component are shown in Figure 4.7. The intensity profile shows a spike at time zero due to the laser shot. Then, a very slow decay with a rate constant of about 200 s^{-1} . It is not possible to get the fast decay component from SVD because the disappearance of this component, that has a peak at $\sim 1970\text{ cm}^{-1}$, occurs too fast. The original data shows only one spectrum, immediately after the laser pulse, with a band at $\sim 1970\text{ cm}^{-1}$. This band disappears in the following spectrum taken after $16\text{ }\mu\text{s}$. This suggests that this component decays with a half life in the order of microseconds. Therefore, better time resolution need to be obtained in order to characterize the

Figure 4.3. A representative spectrum from each of the three regions shown in Figure 4.2. Gaussian bands were fitted to the IR spectrum. The actual data points are shown as crosses (+).

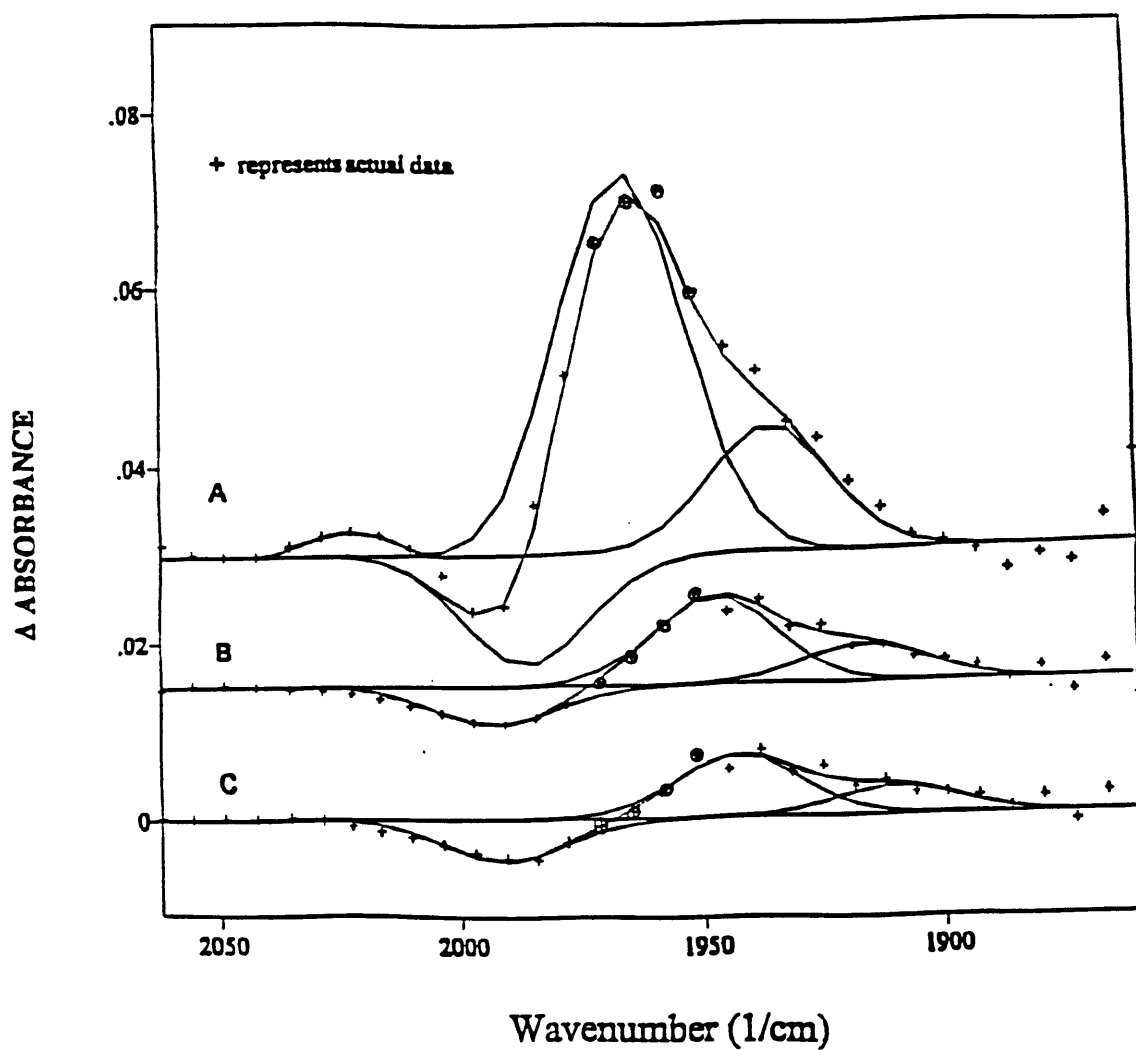


Figure 4.4. The synchronous 2D correlation spectrum for the data collected with 16 μs time resolution and low spectral resolution ($\Delta\lambda=0.078\text{ }\mu\text{m}$). A is a contour representation of the 3D plot in B.

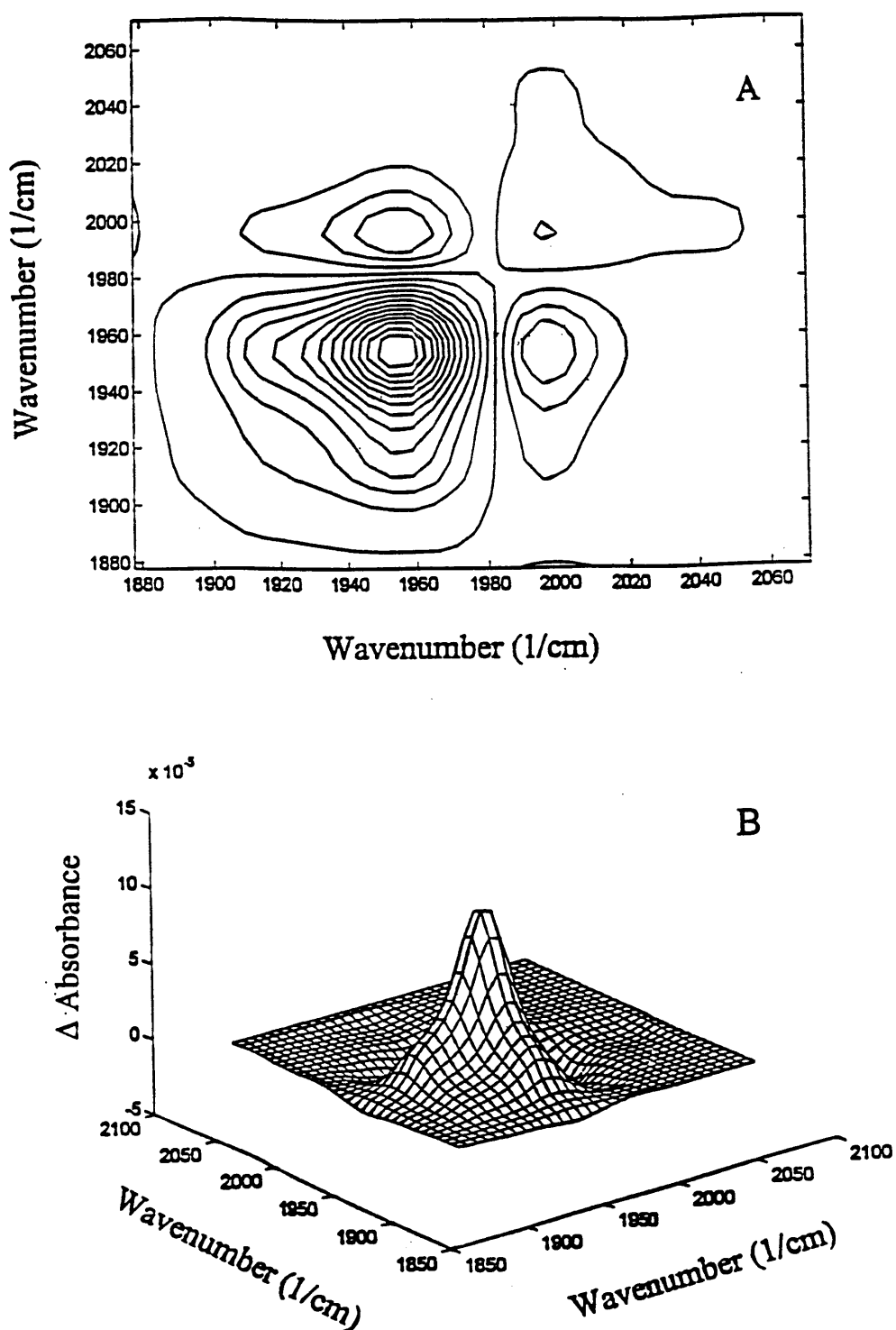


Figure 4.5. The disrelation 2D correlation spectrum for the data collected with 16 μs time resolution and low spectral resolution ($\Delta\lambda=0.078\text{ }\mu\text{m}$). A is a contour representation of the 3D plot in B.

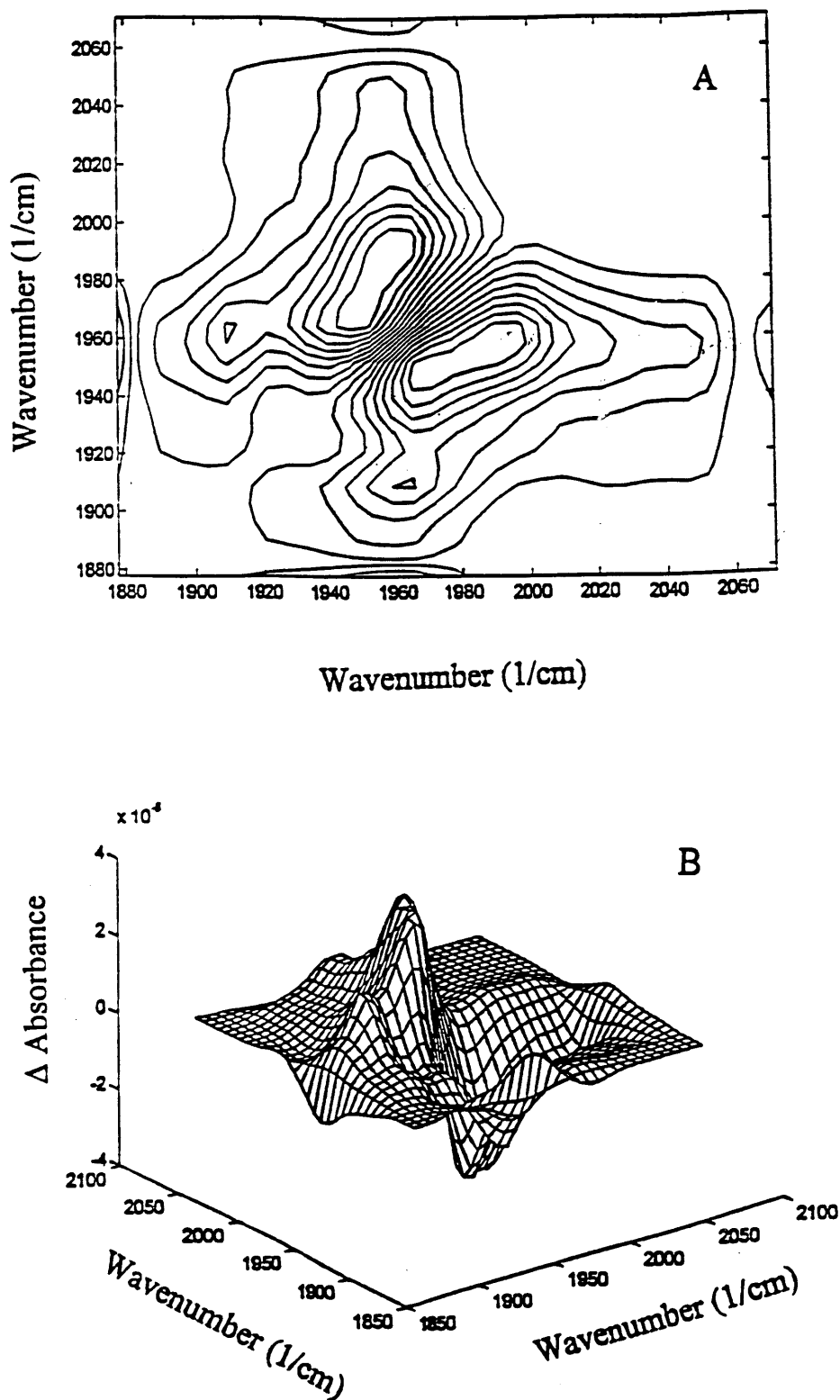


Figure 4.6. A plot of the singular values on the diagonal in the diagonal matrix W as a result of SVD analysis for the data described in Figure 4.3.

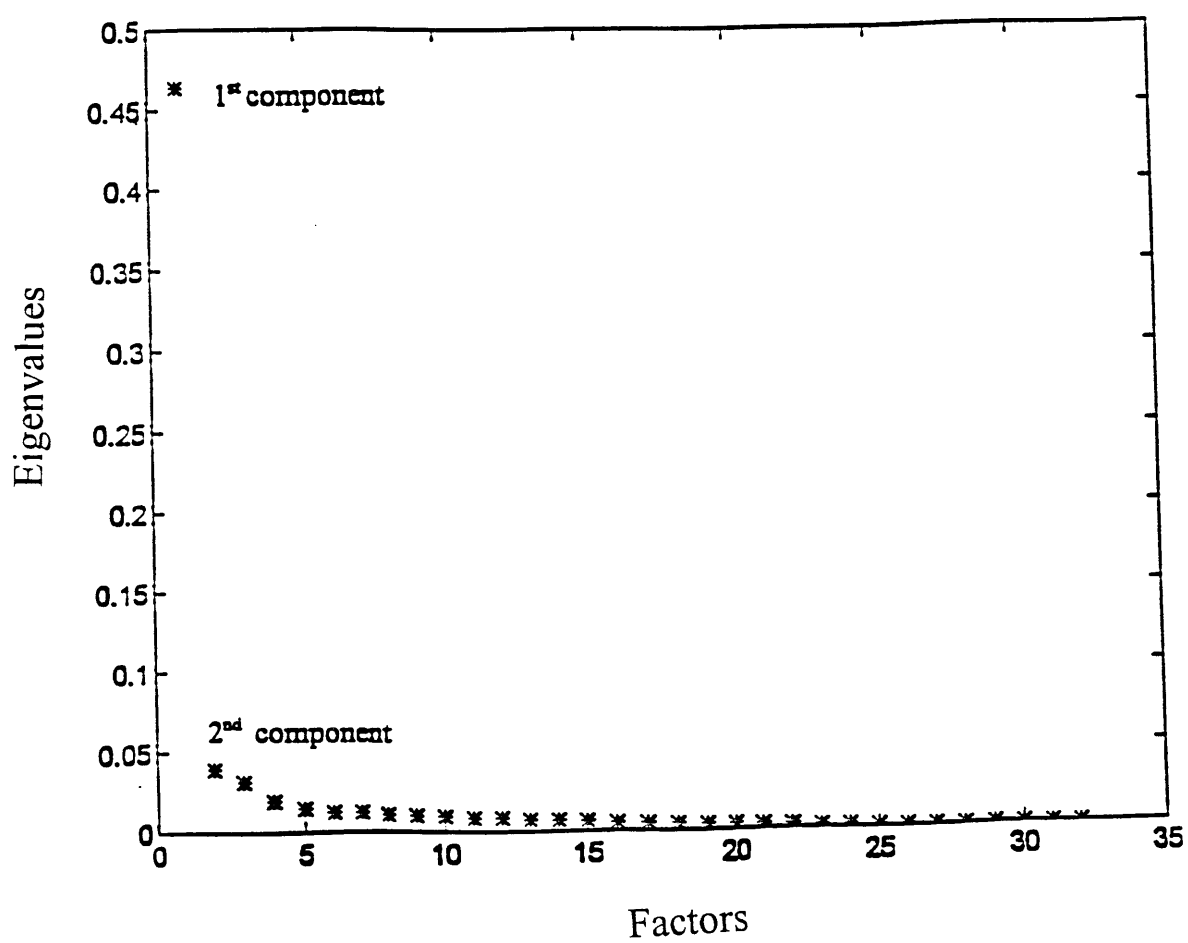
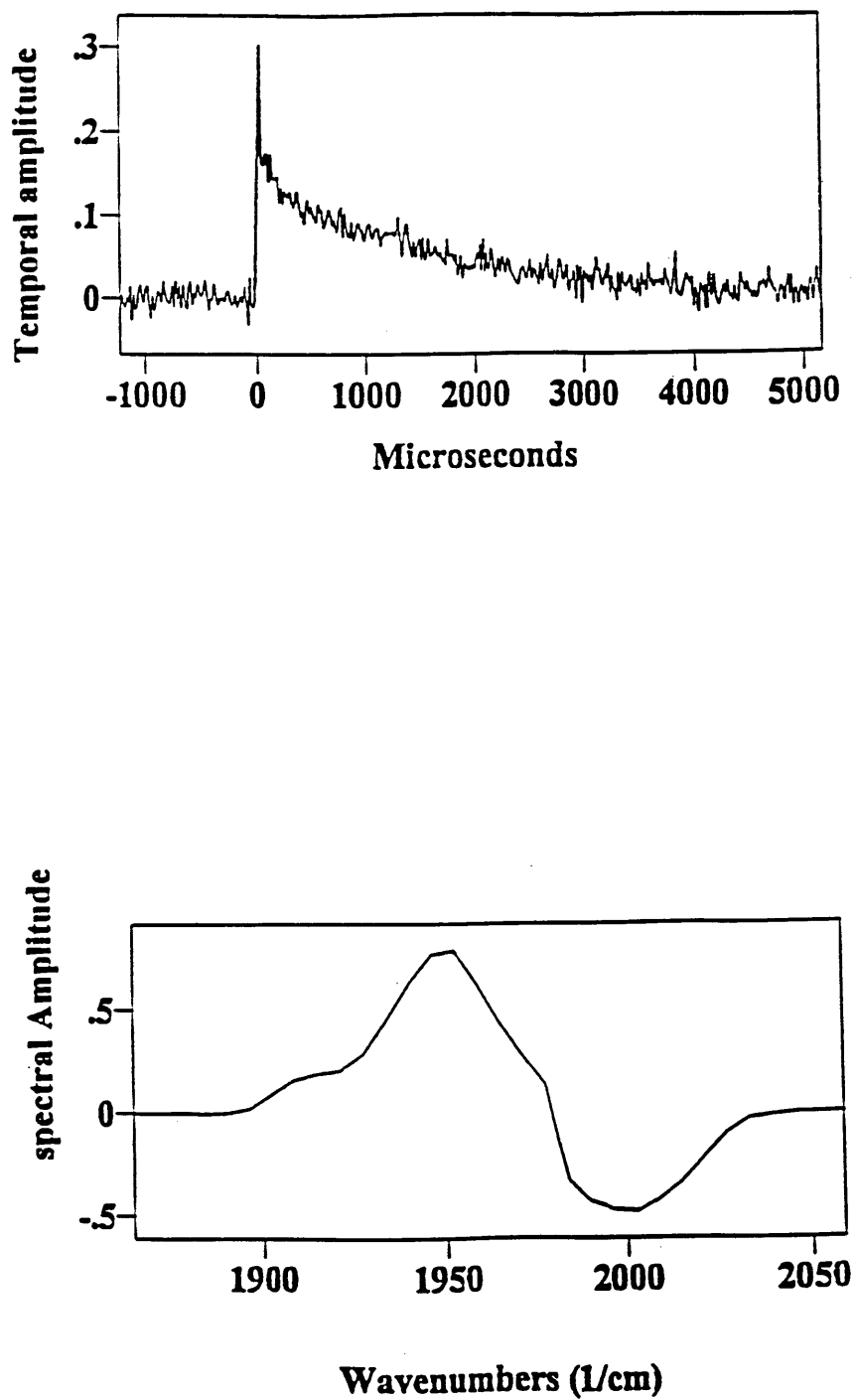


Figure 4.7. The first temporal and spectral component as a results of the SVD analysis. This corresponds to the largest singular value. The rest of the components represent random noise (not shown).



bands at 1970 and 2010 cm^{-1} . Section 4.4 will discuss the results and the analysis for the data obtained with 2 μs time resolution, but before that, a discussion on the data obtained as a result of the photolysis when the monochromator grating is shifted from the first order to the second order is presented in the next section.

4.3. Data Analysis for the photolysis of $\text{Mo}(\text{CO})_6$ in cyclohexane with time resolution of 16 μs and high spectral resolution ($\Delta\lambda=0.039 \mu\text{m}$):

This experiment was performed in a similar fashion as the one in the previous section, except that the grating was shifted to the second order. In second order, the spectral range is reduced to 0.25 μm , but the spectral resolution is increased to 0.039 μm (FWHM). The difference spectra is obtained similarly by subtracting the IR spectrum before laser excitation from the spectrum after irradiation. A single difference spectrum is shown in Figure 4.8 for clarity. The peaks at 1920, 1950, and 1990 cm^{-1} are now very well resolved.

Figure 4.9 shows the synchronous 2D correlation plot of spectra collected using the second order of the grating for a sampling period of 800 μs following the laser pulse. Autopeaks are shown at 1990, 1950, and 1920 cm^{-1} . All three peaks are correlated. A positive cross peak is observed between 1920 cm^{-1} peak and the

Figure 4.8. The difference spectrum as a result of the photolysis of Mo(CO)_6 in cyclohexane collected with time resolution of $16\ \mu\text{s}$ using the second order of the grating.

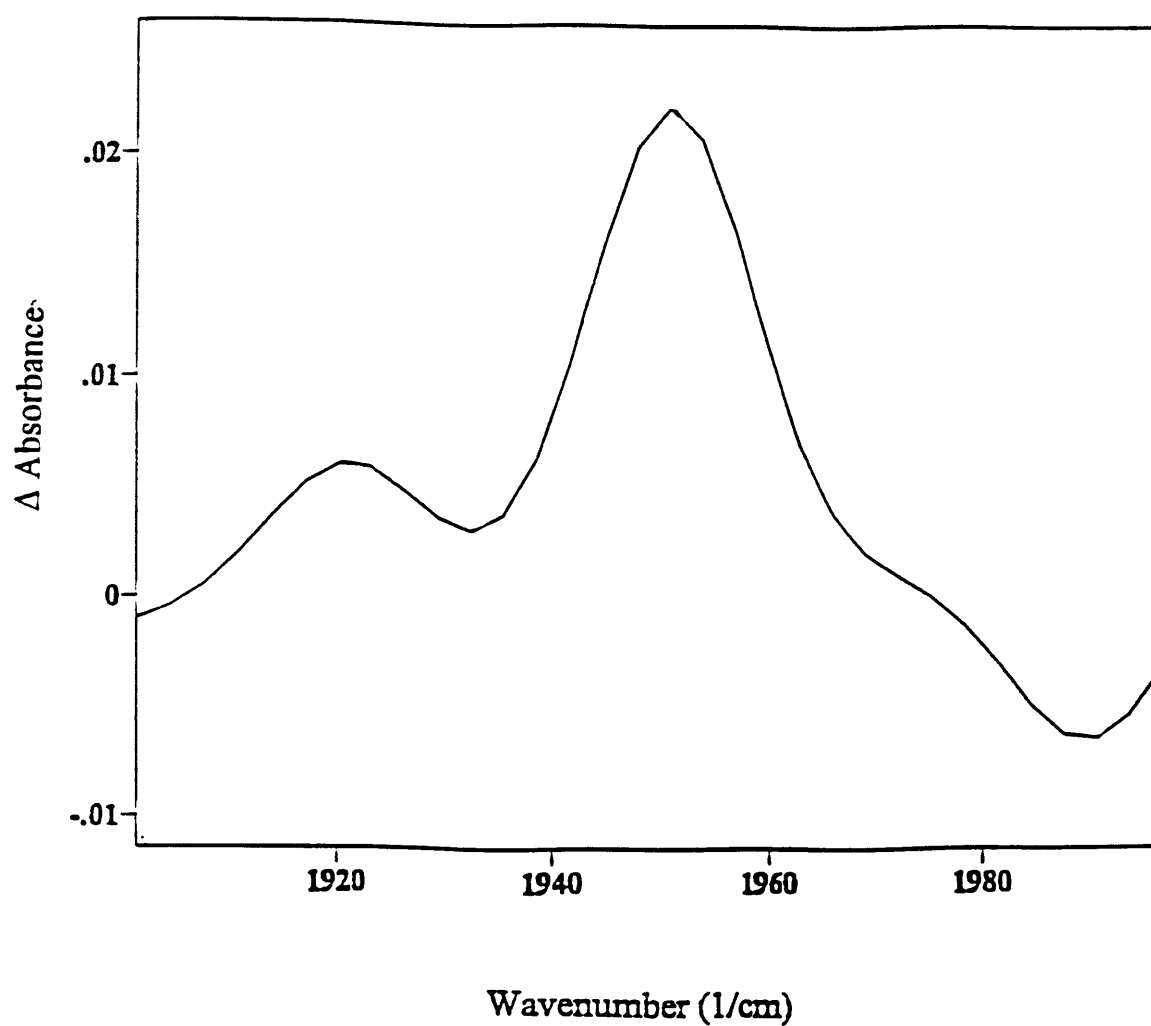
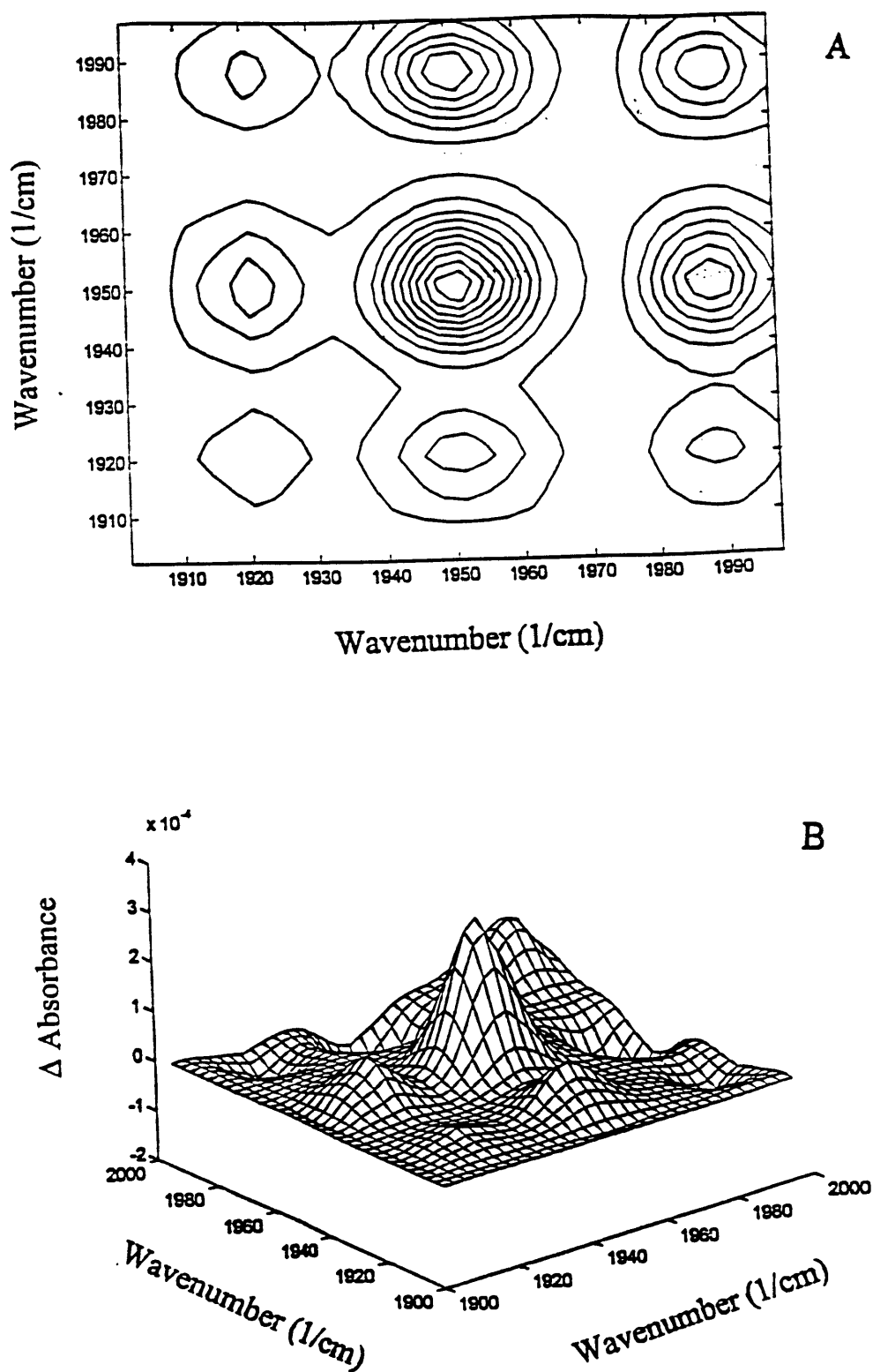
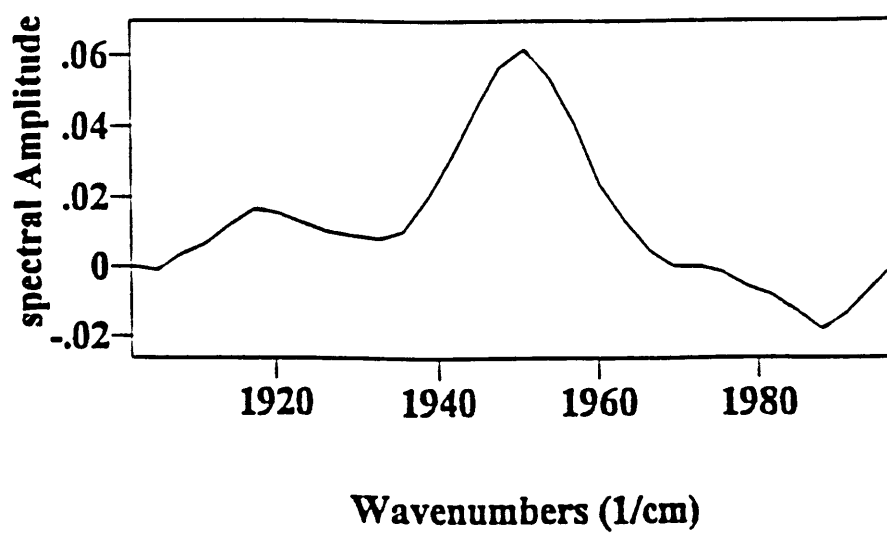
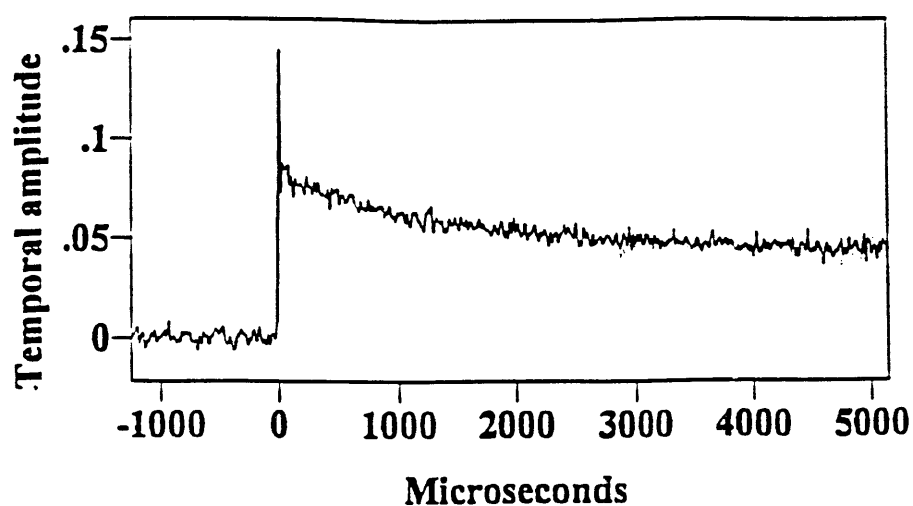


Figure 4.9. The synchronous 2D correlation spectrum for the data collected with $16\text{ }\mu\text{s}$ time resolution and high spectral resolution ($\Delta\lambda=0.039\text{ }\mu\text{m}$). A is a contour representation of the 3D plot in B.



1950 cm^{-1} peak. Negative cross peaks are observed between the 1990 cm^{-1} peak and the 1920 cm^{-1} and 1950 cm^{-1} peaks. This result proves that the peaks at 1920 and 1950 cm^{-1} belong to the same component, and concludes that the rate of disappearance of this complex is the same as the rate of formation of the parent molecule, $\text{Mo}(\text{CO})_6$, represented by the peak at 1990 cm^{-1} . The results here are identical to the ones shown in the last section except that the bands at 1950 cm^{-1} , and 1920 cm^{-1} are very well resolved. SVD analysis on this data set, to obtain principal components, gave identical results to the previous experiment. Only one component is significant in this data. The rest of the components are within the noise level. The intensity profile and the vibrational spectrum of the first component are shown in Figure 4.10. The intensity profile shows a spike at time zero due to the laser shot, then a very slow decay with a rate constant of about 200 s^{-1} . The previous work done on the photolysis of $\text{Mo}(\text{CO})_6$ in cyclohexane showed that following the photolytic loss of CO, $\text{Mo}(\text{CO})_5$ combines with the solvent to form $\text{Mo}(\text{CO})_5\text{S}$. This complex decays with a pseudo first order rate constant greater than 20,000 s^{-1} .³⁴ Therefore, the experiment described in sections 4.2 and 4.3 need to be performed with different data acquisition technique in order to be able to capture the fast decay component and measure its rate constant. In this manner, two inputs are sampled at a time and piecing the spectrum together

Figure 4.10. The first temporal and spectral component as a results of the SVD analysis. This corresponds to the largest singular value. The rest of the components represent random noise (not shown).



afterwards. This method is described in section 3.4. In this way, the time resolution was increased to 2 μ s.

4.4. Data Analysis for the photolysis of Mo(CO)₆ in cyclohexane with high time resolution (2 μ s):

In this experiment, time-resolved data are collected for the photolysis of Mo(CO)₆ in cyclohexane in four data acquisition sessions. Each sampling session collected two inputs per board. The difference spectra of irradiated solution ($\lambda_{\text{exc}}=249$ nm) of 1.0×10^{-3} M of Mo(CO)₆ in cyclohexane is shown in Figure 4.11. The difference spectrum is obtained similarly by subtracting the IR spectrum before laser excitation from the spectrum after irradiation. The excimer laser is pulsed approximately 4 milliseconds after the start of the IR spectral data initiation. In this figure, 2001 spectra shown are all 2 μ s apart. These spectra are the average of 20 laser shots. The temporal region before the laser pulse is again reasonably flat around zero, which proves that after each laser pulse the Mo(CO)₆ solution returns to the original composition. In the vicinity of the laser pulse, a transient is observed that decays with time. The transient has two major peaks at around 1970 and 1930 cm^{-1} and a smaller peak at around 2010 cm^{-1} . This transient decays very fast and slightly shifts to a lower wavenumber. The shift toward lower wavenumber can not be seen clearly in Figure 4.11, but can be observed

when fewer spectra are shown. Figure 4.12 shows a few representative IR spectra taken from Figure 4.11 at different times. Spectrum A is taken before laser excitation while spectra B, C, D, and E are afterwards. The spectrum labeled B in Figure 4.12 is taken immediately following laser excitation ($2\ \mu\text{s}$) and shows three broad positive IR absorbance bands at 2010 , ~ 1970 and $1930\ \text{cm}^{-1}$. The intensity of the band at $1970\ \text{cm}^{-1}$ appears to decay in time and the peak position shifts to lower wavenumber. After $26\ \mu\text{s}$ (spectrum C in Figure 4.12) a slight negative band at $2005\ \text{cm}^{-1}$ appears in the spectrum. The peak intensity at $1952\ \text{cm}^{-1}$ changing with respect to time is shown in Figure 4.13. The data taken before time zero is sampled before the laser pulse. This data is labeled A in Figure 4.13 and the corresponding vibrational spectrum is shown in Figure 4.12A. A large intensity increase is observed immediately following the laser pulse (labeled B in Figure 4.13 and corresponds to spectrum B in Figure 4.12) that decays quickly and then levels off into a much slower decay (labeled C, D, and E in Figure 4.13 and corresponds to spectra C, D, and E in Figure 4.12). The solid line curves labeled F and G in Figure 4.3 is an artistic representation of a possible kinetic fit that would explain the experimental data. The fast exponential decay (labeled F) is from a molecule that is generated by the laser pulse, has a vibrational band that absorbs at

Figure 4.11. The difference spectra of Mo(CO)_6 in cyclohexane solution irradiated with 249 nm laser excitation. There are 2001 spectra shown each 2 μs apart. These spectra are the average of 20 laser shots.

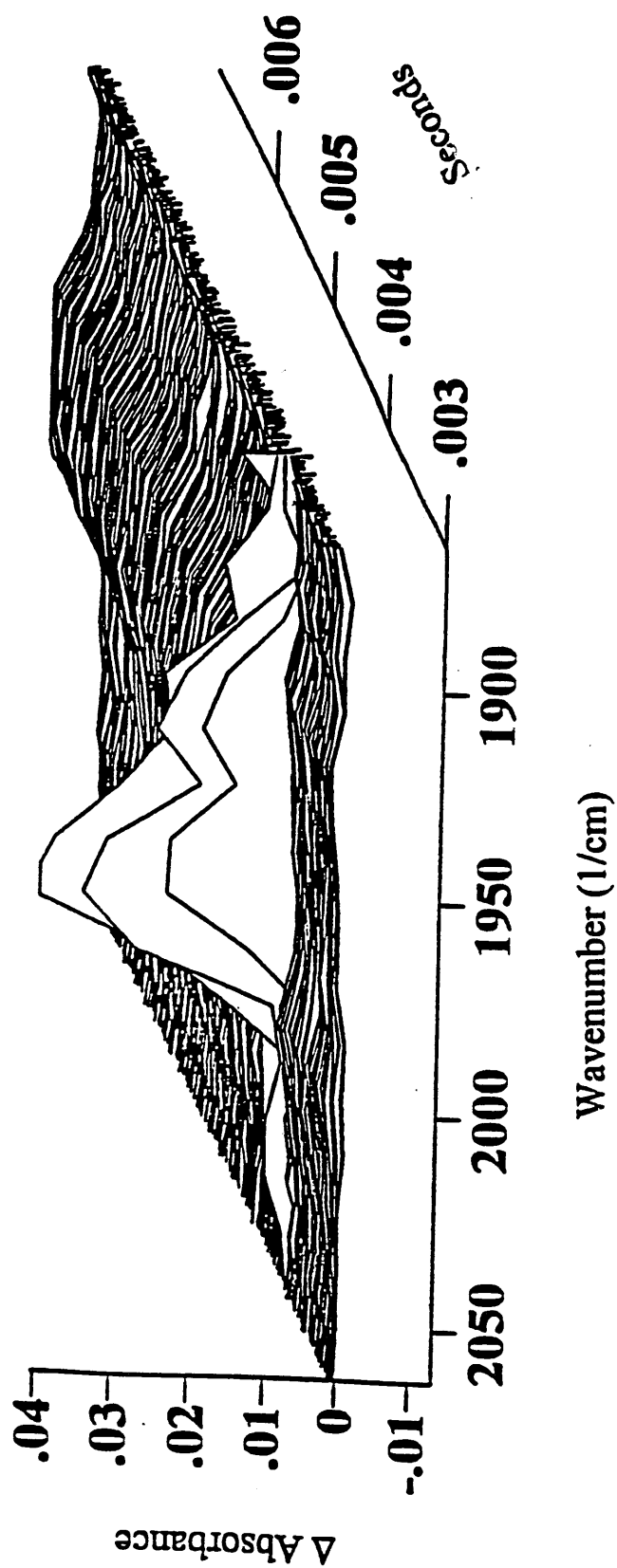


Figure 4.12. A few representative IR spectra taken from Figure 4.11 at the following times: Spectrum A is taken at 0 μs , while spectra B, C, D, and E are taken at 2, 26, 336, 1600 μs respectively after laser excitation.

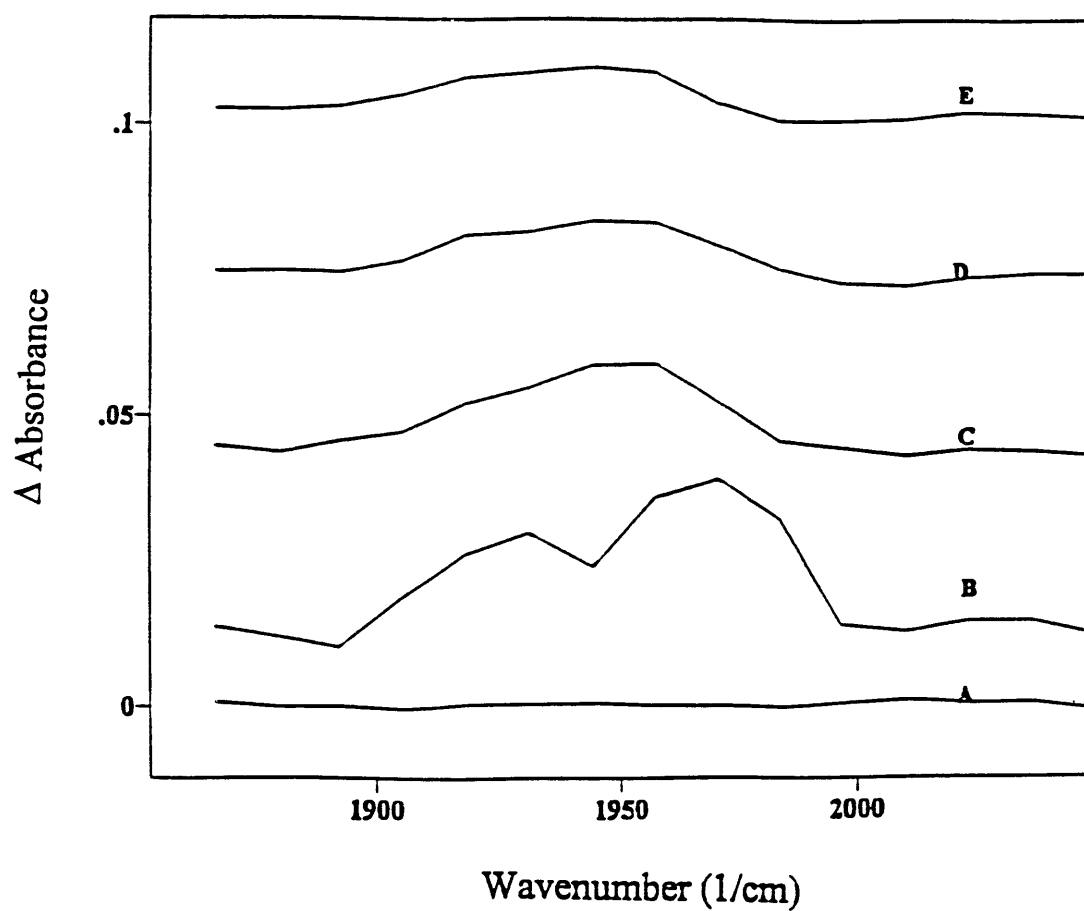
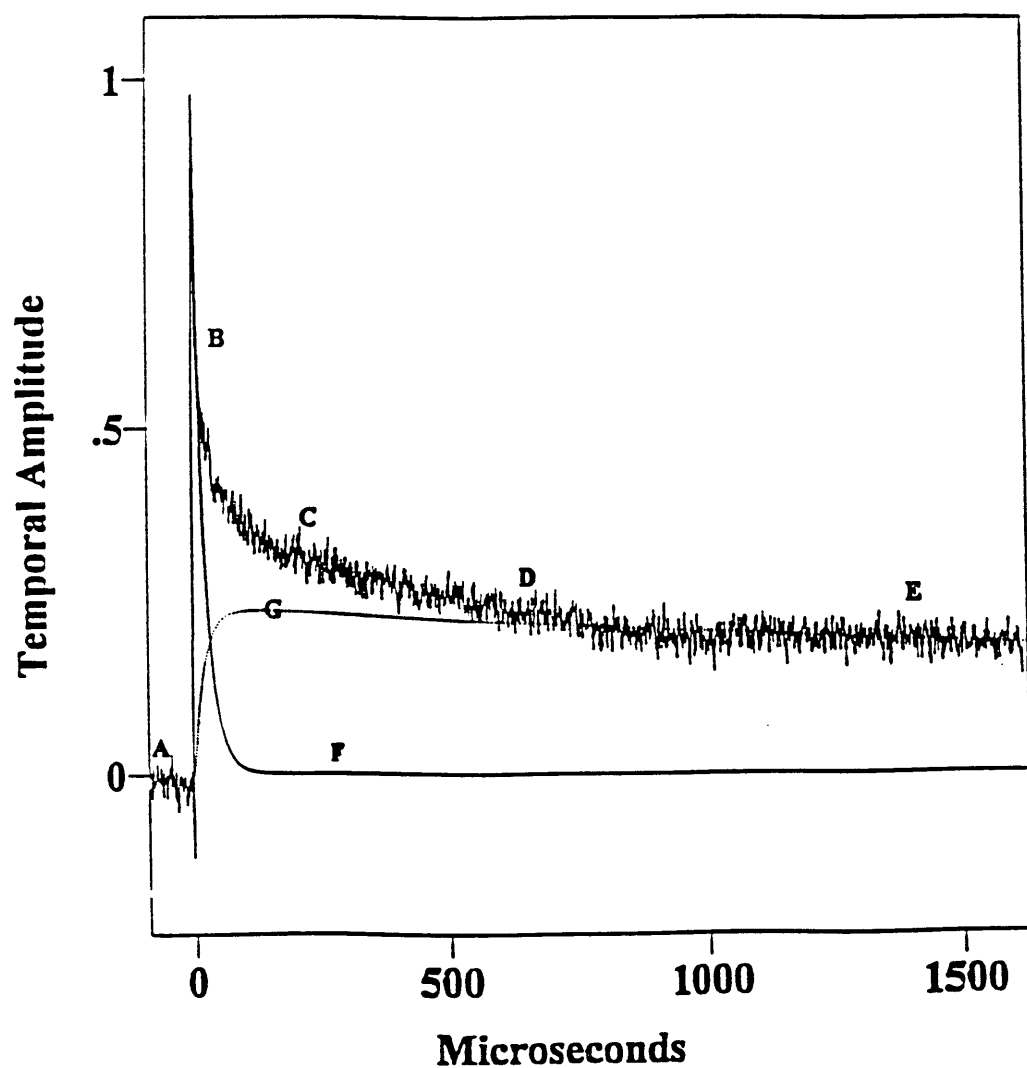


Figure 4.13. The time trace of the photolysis of $\text{Mo}(\text{CO})_6$ in cyclohexane solution at 1952 cm^{-1} . Region A is before excitation while B, C, D, and E are different regions after laser excitation. Traces F and G represent a possible fit to the time trace.



1952 cm^{-1} and is converted into other molecules that do not have vibrational band that absorb at 1952 cm^{-1} . The time trace labeled G, which is from an intermediate molecule that absorbs at 1952 cm^{-1} , has zero initial concentration and reaches a steady state concentration after 400 μs . The data analysis for this set of experiments was started by transforming the data matrix, consisting of intensities taken at specific wavenumbers as a function of time, to a 2D-IR correlation map that shows which wavenumbers are synchronously and asynchronously correlated. In this set of data, one dimensional interpolation was performed on the data matrix. Cubic spline interpolation to smooth the data was used. Figure 4.14 shows a contour representation of the disrelational correlation map. In the upper quadrant, there is a large positive cross peak between 2010 cm^{-1} and 1952 cm^{-1} and a large positive cross peak between 1970 cm^{-1} and 1945 cm^{-1} .

The disrelational correlation map shows that there are vibrational bands in the original data matrix that are changing with respect to time with different rate constants. Positive correlation intensities in the upper quadrant indicates that the vibrational band at the higher wavenumber changes in time before or is faster than the changes in the vibrational band at the lower wavenumber. This trend is reversed if the disrelational correlation intensities at that particular map point are negative but in this case the disrelational correlation map has positive correlation

intensities. The positive correlation intensity at the 2010 cm^{-1} and 1952 cm^{-1} map point indicates that the 2010 cm^{-1} band changes in time before the 1952 cm^{-1} and likewise the band at 1970 cm^{-1} changes in time before the 1945 cm^{-1} band. The disrelational correlation map sheds no light on the relationship between the 2010 cm^{-1} band and the 1970 cm^{-1} band as well as any relationship between the 1952 cm^{-1} band and the 1945 cm^{-1} band. The synchronous correlation map is shown in Figure 4.15. It has a large positive autopeak located at 1952 cm^{-1} that dominates the 2D spectrum. This autopeak shows that there is an overlap with another peak at slightly lower wavenumber which appears as a shoulder. There is little useful information in this correlation map.

The next level of the data analysis is to convert the data matrix into principal components using singular value decomposition. The procedure for performing SVD analysis is described in chapter 3. The intensity profiles and vibrational spectra of the first two components are shown in Figure 4.16. Only the first two components are shown because all of the remaining components showed random fluctuations around zero and were eliminated as being non-significant. The intensity profile from both components start above zero but one of the components decays below zero. This nonphysical condition suggests that the orthogonal components from the SVD analysis need to be rotated to yield the pure principal components. The degree of rotation is somewhat arbitrary.

One criterion that can be used to direct the amount of rotation is to require that none of the intensity profile falls below zero. This result is shown in Figure 4.17A along with the vibrational spectrum of the components in Figure 4.17B. These profiles appear to be more believable. One component has a fast exponential decay to zero while the other component starts at zero, increases to a maximum, and then has a slow decay. This degree of rotation forces the fast exponential decay to zero.

The vibrational spectrum of the rotated vectors yields some insight into whether the proper rotation has been performed to separate the two components into pure components. The large negative band at 2010 cm^{-1} for component 2 in Figure 4.7 overlapping with the large positive band for component 1 indicates that the vectors need to be further rotated to completely separate the pure components. Using the vibrational spectrum of the rotated vectors as a guide to separate the original vectors into pure components yields the result shown in Figure 4.18. The intensity profile is not forced to zero. Now, the vibrational spectra look quite satisfactorily but the intensity profiles have some anomalies. It should be pointed out that this rotation still has an overlapping positive band at $\sim 1930\text{ cm}^{-1}$. Another problem with this rotation is that the initial increase in component 2 occurs much faster than the initial decay of component 1. The steady state intensities and the

Figure 4.14. The disrelation (A and B) 2D correlation spectrum for a period 800 μs following the laser pulse and collected with 2 μs time resolution. A is the contour representation of the 3D plot in B.

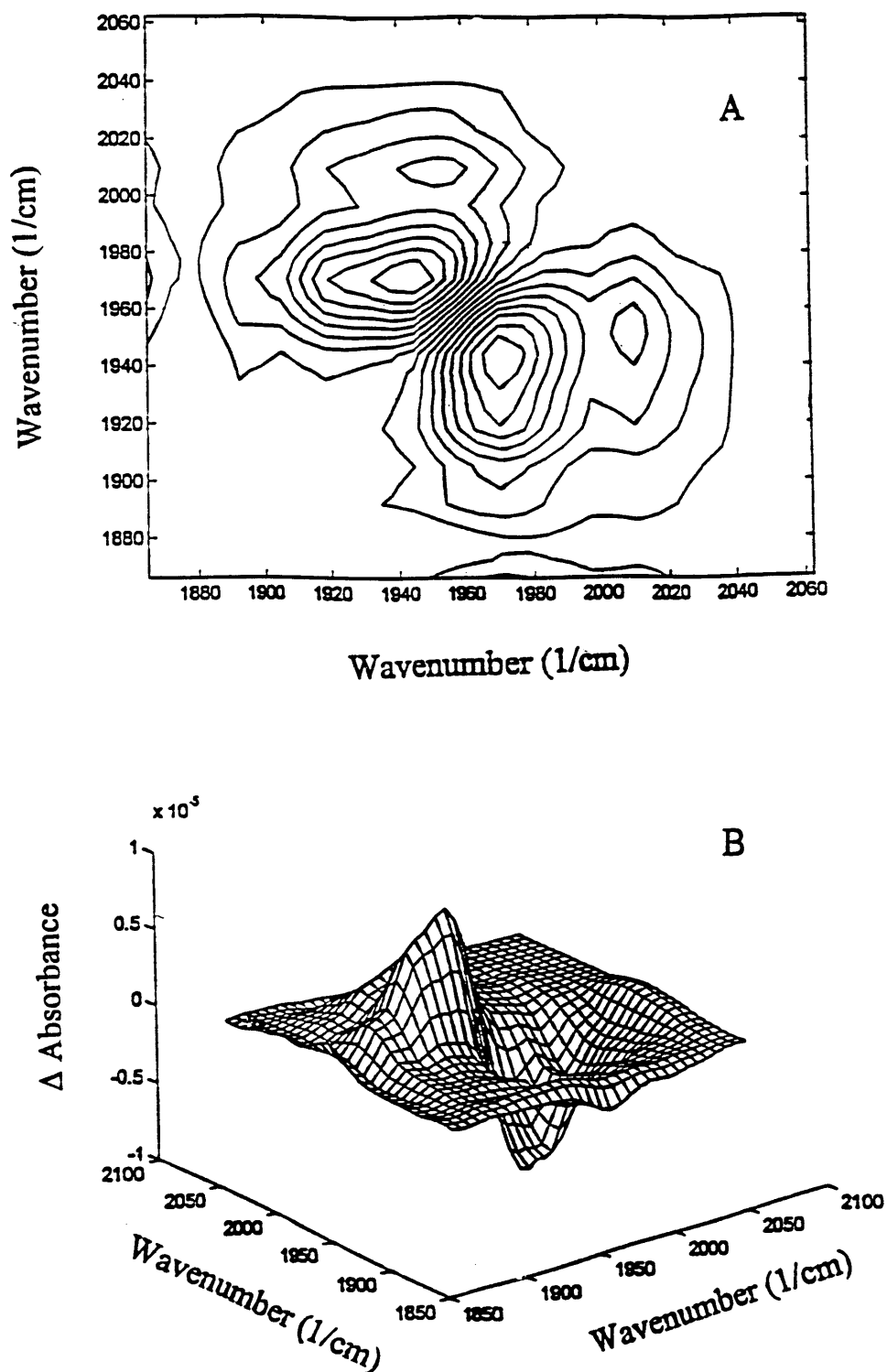


Figure 4.15. The synchronous (A and B) 2D correlation spectrum for a period 800 μs following the laser pulse and collected with 2 μs time resolution. A is the contour representation of the 3D plot in B.

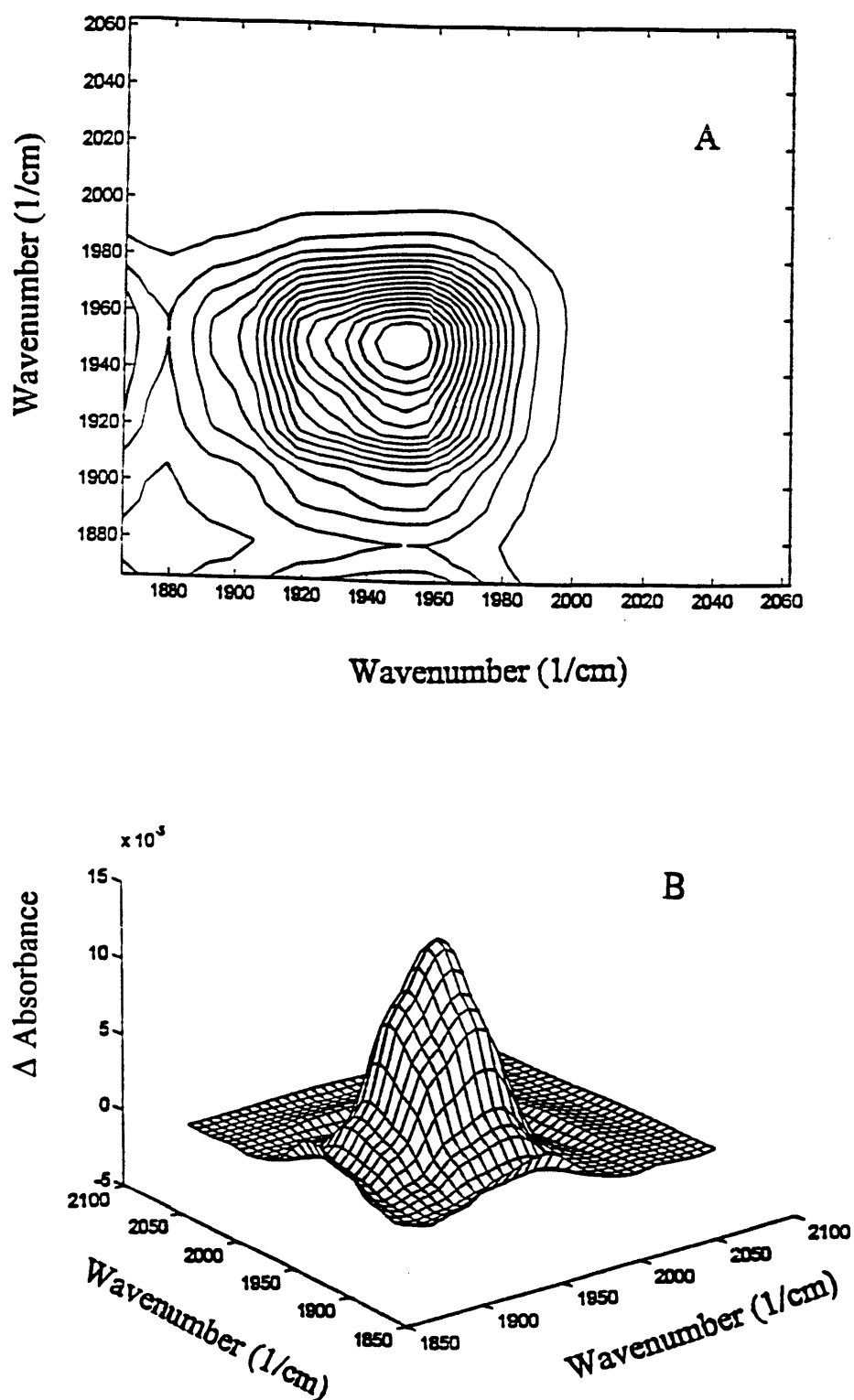


Figure 4.16. The first two temporal and spectral components as a results of the SVD analysis. These two sets of components correspond to the two largest singular values. The rest of the components represent random noise.

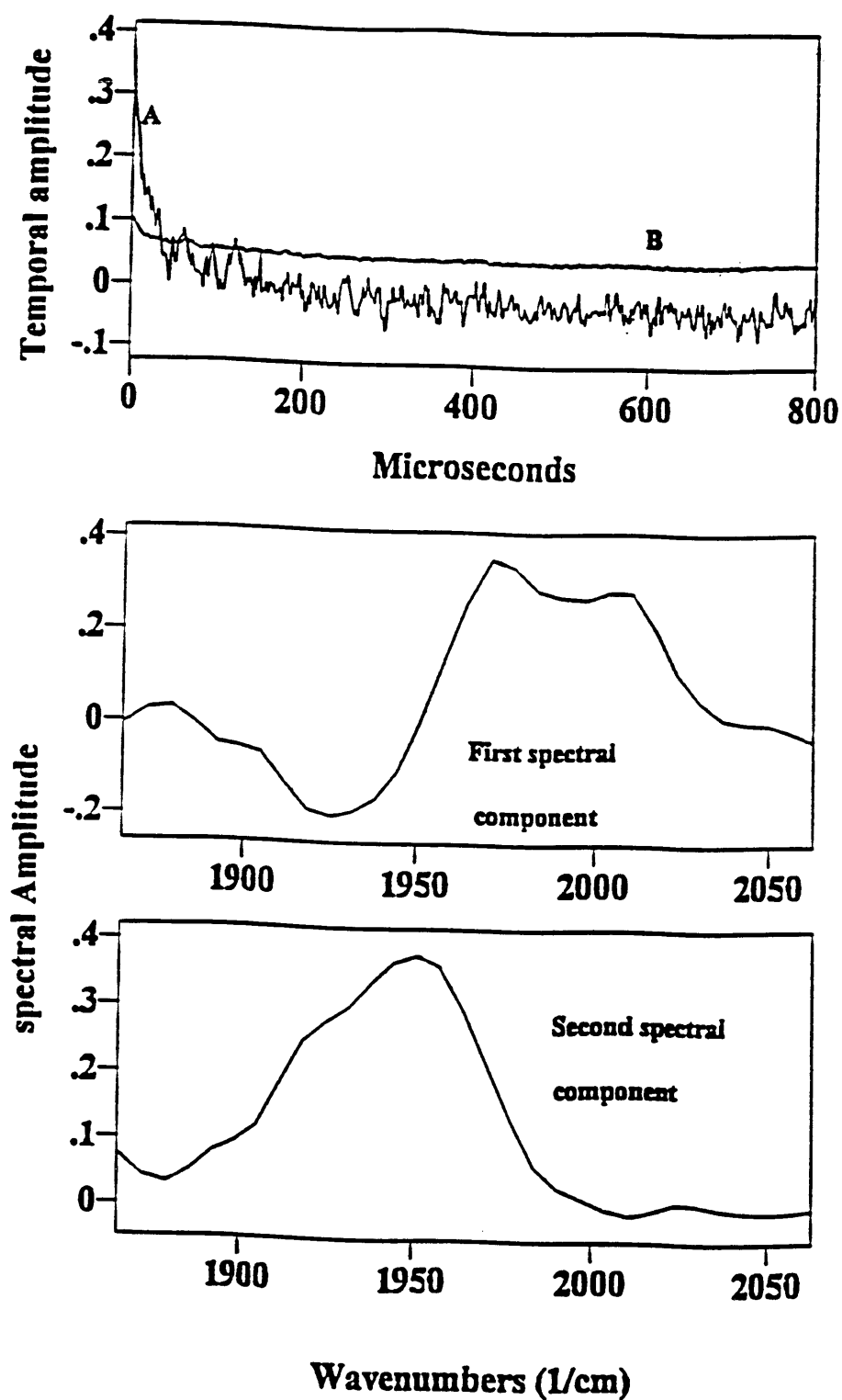
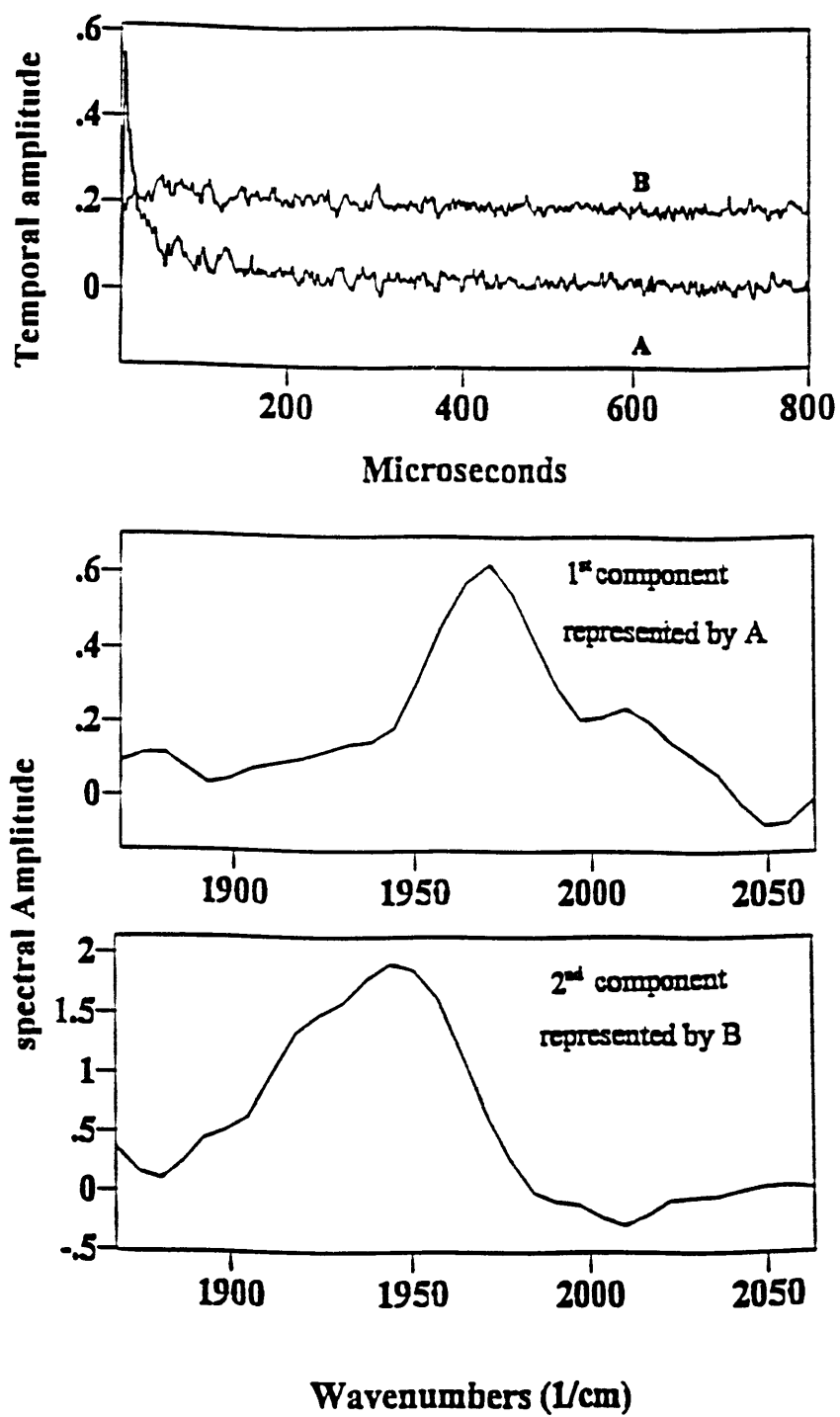


Figure 4.17. The first two temporal and spectral components after an initial rotation.



initial rate of increase in component 2 are very sensitive to the amount of rotation used to separate the principal components. Figure 4.19 reveals what we believe to be the best rotation. The pure spectrum and the intensity profile of the two components are shown here. The negative overlapping band at 2010 cm^{-1} and the positive overlapping band at 1920 cm^{-1} have been eliminated. The steady state values are consistent with the rate constants and the initial rate of increase of component 2 matches the initial decay of component 1. The pure spectrum of component 1 can be fitted with two Gaussian bands. One band has a peak wavenumber at 2010 cm^{-1} while the other band has a peak wavenumber at 1970 cm^{-1} . Both have a band width (FWHM) of 30 cm^{-1} . The pure spectrum of component 2 can be fitted with two positive bands and one negative band with a band width of 30 cm^{-1} . We are now at a point where our 2D-IR correlation analysis can be compared with the SVD analysis. The correlation analysis suggests that bands at 1970 cm^{-1} and 2010 cm^{-1} should change in time before the band at 1952 cm^{-1} . This is substantiated by the SVD analysis. One of the pure components has a fast decay and a vibrational spectrum with bands at 2010 cm^{-1} and 1970 cm^{-1} while the other component has a slower decay and a vibrational spectrum with bands at 1952 cm^{-1} and 1923 cm^{-1} . From our analysis so far, we can

Figure 4.18. The first two temporal and spectral components after a different degree of rotation than the ones in Figure 4.17.

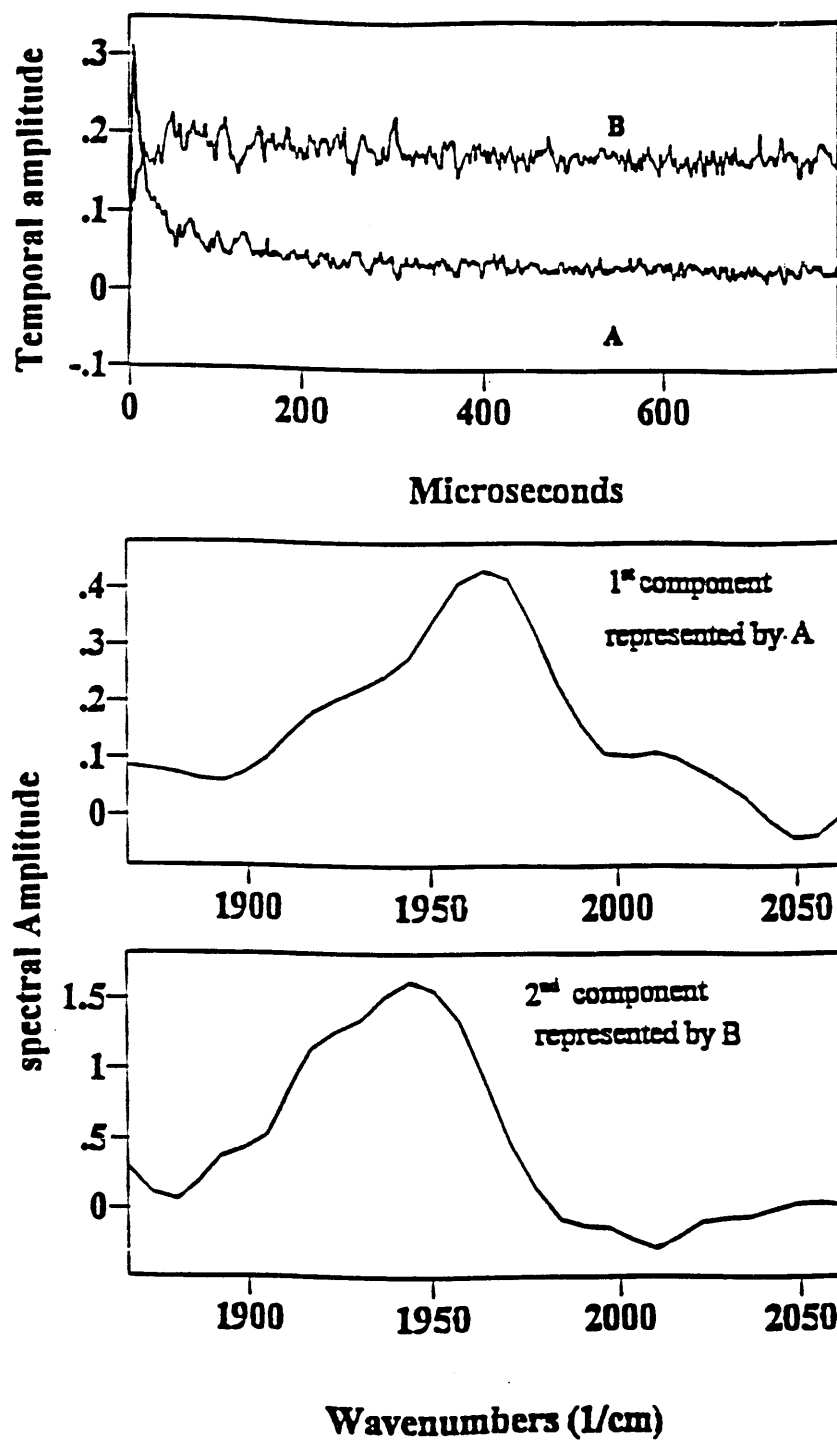
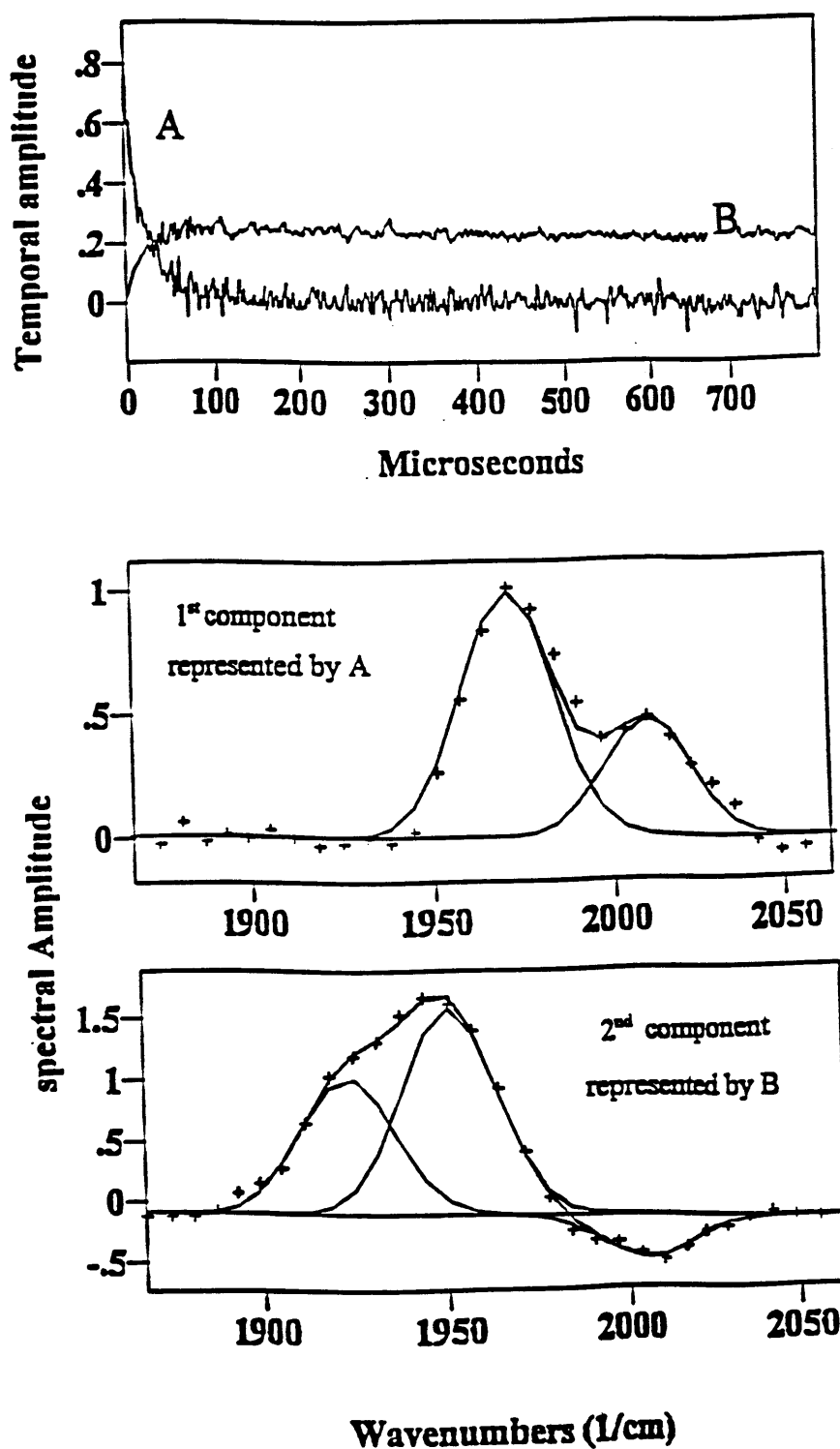
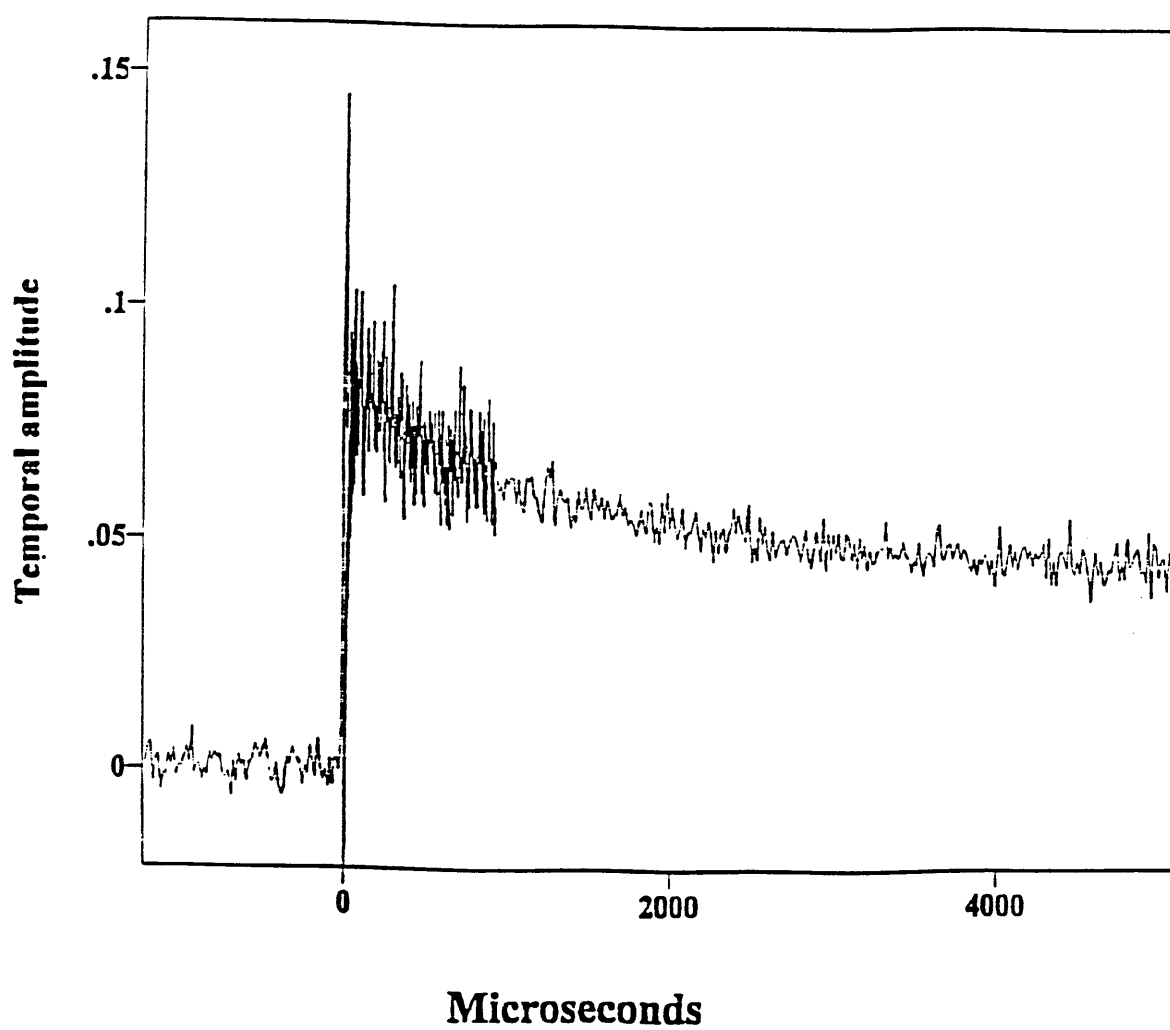


Figure 4.19. The first two pure temporal and spectral components as a result of the SVD analysis and proper rotations. The spectral components are fitted with Gaussian bands.



make some assignments of the pure components. The first component has a fast decay and is Mo(CO)_5 complex with cyclohexane, i.e., the solvent complex. However, the vibrational spectrum of this component is surprising. The observed band at 1970 cm^{-1} is expected and has been observed in low temperature matrices.^{29,30} On the other hand, we observed, for the first time, a band at 2010 cm^{-1} that shows an identical behavior to the band at 1970 cm^{-1} . This vibrational band has not been previously assigned in solution photolysis of this metal carbonyl. It has been repeatedly observed in all of our spectra immediately after the laser excitation and disappears in a similar fashion as the solvent complex. The second pure component can be assigned to a Mo(CO)_5 complex involving a stronger complexing agent than cyclohexane and referred to as a contaminant complex, $\text{Mo(CO)}_5\text{X}$. This complex has a vibrational spectrum with bands at 1952 cm^{-1} and 1930 cm^{-1} as expected.^{33-34,36} The bands of the contaminant complex were consistent and attainable in both $2\text{ }\mu\text{s}$ and $16\text{ }\mu\text{s}$ time resolution experiments. Figure 4.20 shows an overlay plot of the decay of the contaminant complex measured at $2\text{ }\mu\text{s}$ and $16\text{ }\mu\text{s}$ time resolution. The dotted trace represent the measurement at $16\text{ }\mu\text{s}$ time resolution. Finally, the negative band at 1990 cm^{-1} was assigned to the parent molecule as expected.

Figure 4.20. An overlay plot of the decay of the contaminant complex measured at $2\ \mu\text{s}$ and $16\ \mu\text{s}$ time resolution. The dotted trace represent the measurement at $16\ \mu\text{s}$ time resolution.



The band at 2010 cm^{-1} forces us to believe that there is another reaction taking place immediately after the photolysis. We believe that a dimer is formed during the photolysis as shown in the following reaction.



The reaction, shown in equation 4.1, has been recently observed and confirmed in the gas phase.³⁹⁻⁴⁰ It has been reported that this dimer, $\text{Mo}_2(\text{CO})_{11}$, had two bands at 1990 cm^{-1} and 2010 cm^{-1} . We are showing for the first time that this reaction could take place in solution. The results of this experiment also suggest that an equilibrium is established between the dimer and the solvent complex. In the following section, possible mechanisms will be presented and tested kinetically.

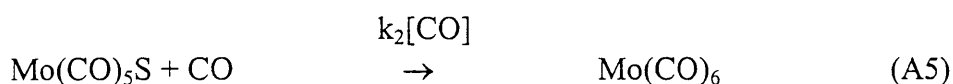
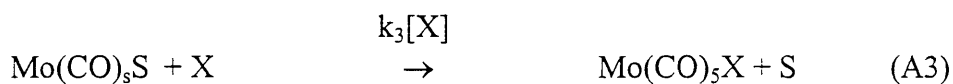
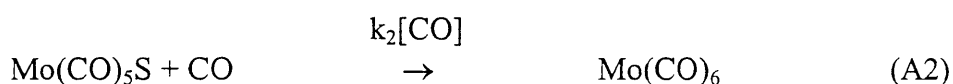
4.5. Kinetics and Mechanism of the photolysis of Mo(CO)_6 in cyclohexane:

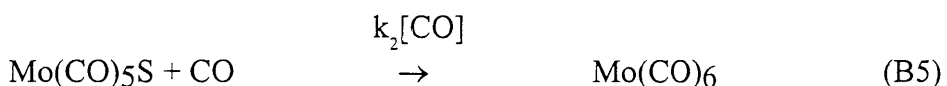
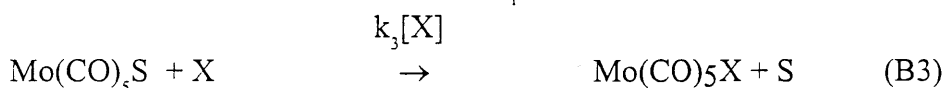
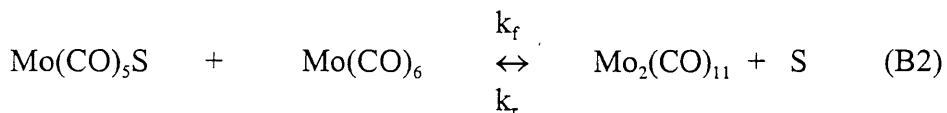
From the previous experiments, several results were obtained. Following the photolysis of Mo(CO)_6 in cyclohexane solution, an intermediate is rapidly formed. This species has two bands at 1970 and 2010 cm^{-1} . Our analysis indicates that these two bands change in a similar fashion. In addition, the disappearance of the contaminant complex takes place simultaneously with the reformation of the parent molecule, Mo(CO)_6 . SVD analysis suggests that the solvent complex and the contaminant complex reach a steady state approximately $150\text{ }\mu\text{s}$ after the laser

pulse. The contaminant complex decays very slowly with an approximate rate constant of 200 s^{-1} .

The following schemes are the proposed mechanisms for the photolysis of Mo(CO)_6 in cyclohexane based on the behavior of the original data and the results of the data analysis. These schemes start with the formation of the solvent complex. We can not measure the formation of the solvent complex, because it is too fast to be detected by our linear array spectrometer. Scheme 1 has been proposed earlier by Herman and his coworker.³⁴ The second scheme is our proposed mechanism for the photolysis of Mo(CO)_6 in cyclohexane solution.

Scheme 1:



Scheme 2:

$\text{Mo(CO)}_5\text{S}$ and $\text{Mo(CO)}_5\text{X}$ are the complexes involving Mo(CO)_5 and a solvent or contaminant molecule respectively. Step 2 in scheme 1 occurs with a pseudo first order rate constant of $k_2[\text{CO}]$. While in scheme 2, step 2 shows an equilibrium reaction with a forward rate constant of k_f and a backward rate constant of k_r . Step 3 in both schemes has a rate constant of $k_3[\text{X}]$, and step 4 has a rate constant of k_4 . Finally, the termination step is shown in equation 5 in both mechanisms.

Both of the above schemes were tested and fitted on the experimental time traces. Figure 4.21 shows the fit, based on scheme 1, on the experimental time traces. Although the reaction mechanism in scheme 1 offers a reasonably good fit,

it can not fully account for our actual data. The band at 2010 cm^{-1} , which is due to the formation of a dimer, is totally ignored in this mechanism. In addition, this mechanism suggests that the parent molecule is rapidly reformed immediately after the photolysis, but the original data indicates differently. The first few spectra immediately after the laser shot in our $2\text{ }\mu\text{s}$ time resolution data show no spectral band at around 1990 cm^{-1} . The absence of this band is due to the fact that the negative peak contribution from loss of $\text{Mo}(\text{CO})_6$ is canceled out by the positive peak contribution of the dimer, $\text{Mo}_2(\text{CO})_{11}$.

The mechanism shown in scheme 2 agrees with the results obtained from the data analysis and also gives a consistent fit to the experimental time traces. This is shown in Figure 4.22. The values for k_f , k_r , $k_2[\text{CO}]$, $k_3[\text{X}]$, and k_4 used to fit the experimental data are 100000, 120000, 31700 ± 4500 , 11480 ± 540 , and $200\pm25\text{ s}^{-1}$, respectively. No further effect is observed in the kinetic modeling even as we increase the values of the rate constants k_f and k_r to higher ones, indicating that the values mentioned above represent the upper limit. This verifies that the equilibrium may take place in an extremely fast rate that can not be detected by our IRLA spectrometer. Scheme 2 is the first reaction mechanism in the history of solution photolysis of $\text{Mo}(\text{CO})_6$ in which dimer is formed.

Experiments with faster time resolution should focus on this system and quantitatively measure these rate constants.

4.6. Conclusion:

In this chapter, the data for the photolysis of Mo(CO)_6 in cyclohexane were presented with different time and spectral resolutions. The data were very consistent and reproducible with different time resolutions using the IRLA spectrometer. Two-dimensional IR correlation and SVD analysis were very successful in analyzing the time-resolved data. The band at 2010 cm^{-1} proved the formation of the dimer, $\text{Mo}_2(\text{CO})_{11}$. This is the first study that a dimer is seen as a transient of a solution photolysis of Mo(CO)_6 . We believe that this dimer exist in an equilibrium with the solvent complex. These two species disappears in a very fast rate to form new products. One of the products is the contaminant complex, $\text{Mo(CO)}_5\text{X}$. This complex decays very slowly. The other product is the reformation of the parent molecule. SVD and 2D-IR correlation showed that the reformation of the parent molecule and the disappearance of the contaminant complex take place at the same rate. This is why SVD analysis could not separate the contaminant complex from the parent molecule. Finally, the experimental time traces were explained according to the mechanism shown in scheme 2.

Figure 4.21. The modeled intensity profiles as the solid lines fit the experimental time traces based on scheme 1.

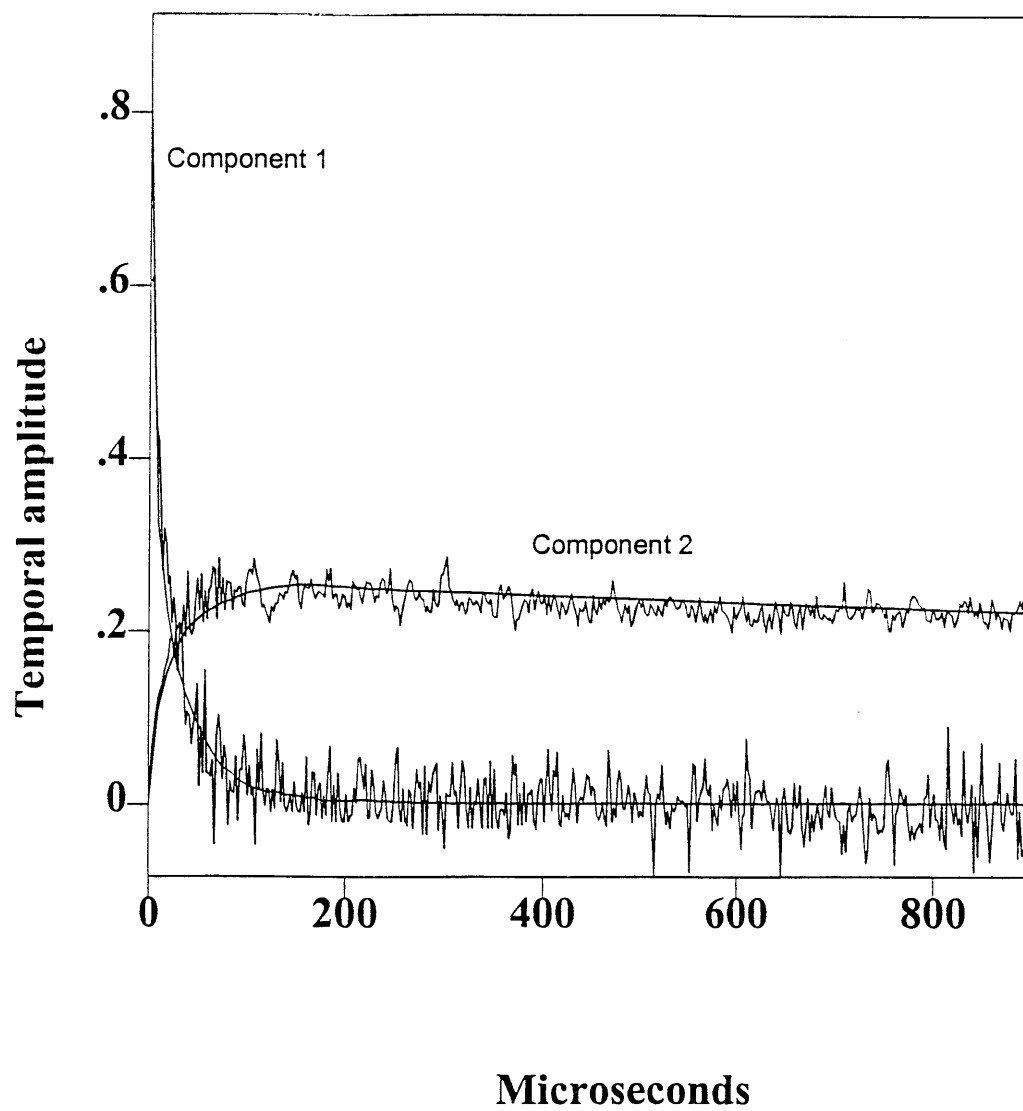
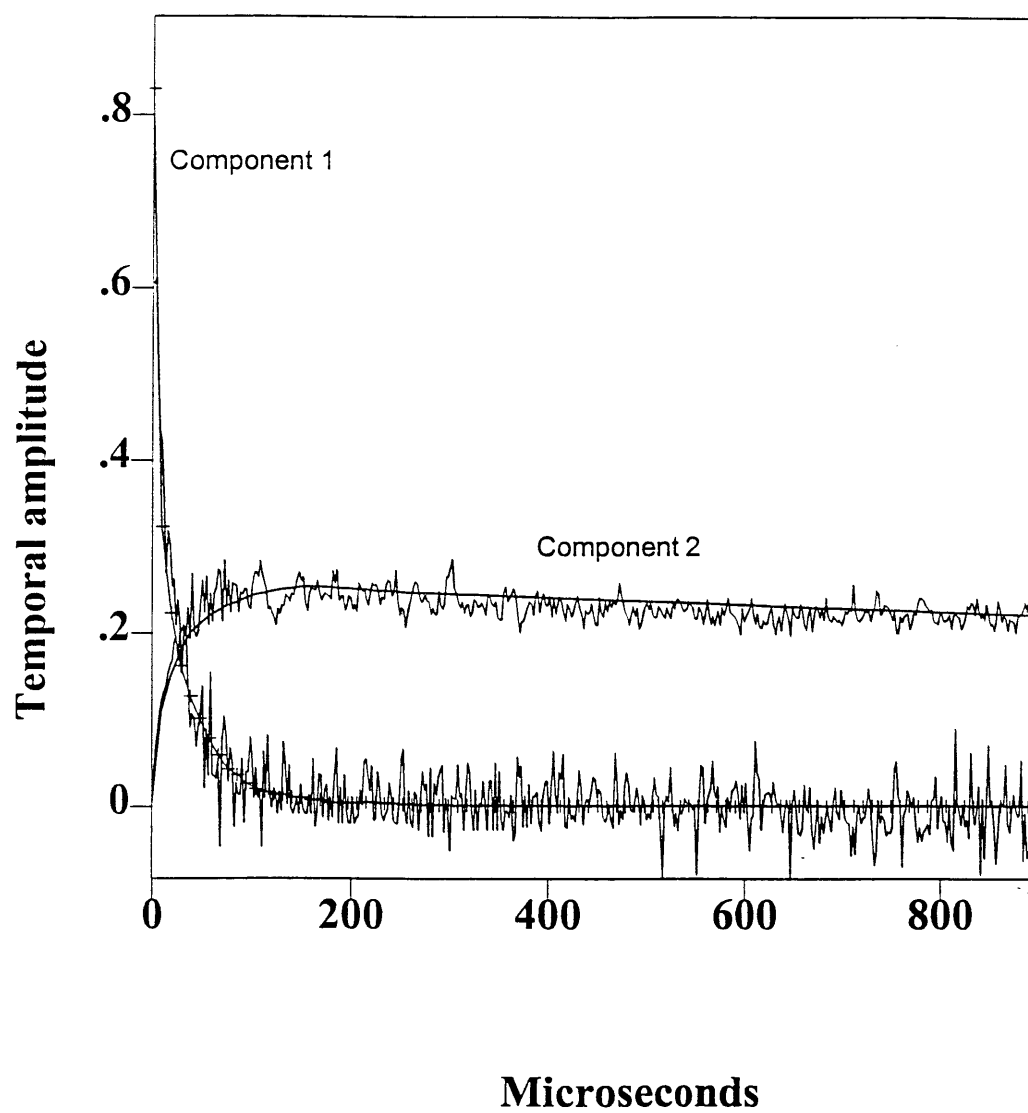


Figure 4.22. The modeled intensity profiles fit the experimental time traces based on scheme 2.



Chapter 5

Irradiation of Mo(CO)_6 in cyclohexane doped with benzene

5.1. Introduction

In chapter 4, we learned that the time resolved data collected by our IRLA spectrometer for the photolysis of Mo(CO)_6 in cyclohexane agree with the second scheme shown in section 4.5. In this scheme, we could not measure precisely the rate constants for the equilibrium reaction in step 2, because they are too fast to be detected by our spectrometer.

If the mechanism for the reaction is a combination of steps 3, 4, and 5, then, the rate of consumption of $\text{Mo(CO)}_5\text{S}$ is given in equation (5.1) where k_c is $(k_2[\text{CO}] + k_3[\text{X}])$

$$d[\text{Mo(CO)}_5\text{S}]/dt = -k_c [\text{Mo(CO)}_5\text{S}] + k_4 [\text{Mo(CO)}_5\text{X}] \quad (5.1)$$

After most of the $\text{Mo(CO)}_5\text{S}$ has been converted into either Mo(CO)_6 or $\text{Mo(CO)}_5\text{X}$, then the rate of disappearance of $\text{Mo(CO)}_5\text{X}$ is given by equation (5.2) where the steady state approximation has been applied to equation (5.1).

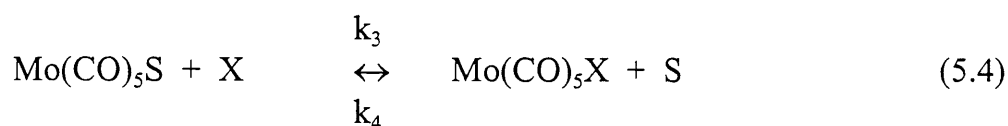
$$d[\text{Mo}(\text{CO})_5\text{X}]/dt = -\{k_2[\text{CO}]k_4/k_c\}[\text{Mo}(\text{CO})_5\text{X}] \quad (5.2)$$

The experimentally observed rate constant (k_{exp}) is given by the collection of rate constants ($k_2[\text{CO}]k_4/k_c$) which can be rearranged to produce equation 5.3.

$$\frac{1}{k_{\text{exp}}} = \frac{1}{k_4} + \frac{k_3[X]}{k_2k_4[\text{CO}]} \quad (5.3)$$

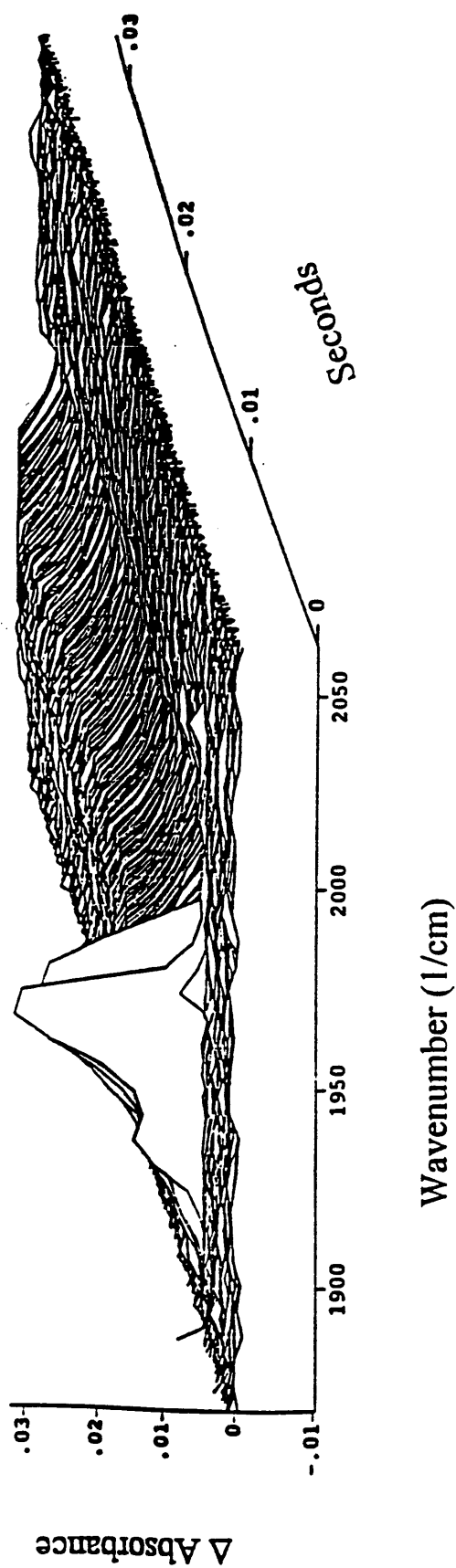
Equation 5.3, which was also derived by Herman and Kelly³³⁻³⁴, tells that the reciprocal of the experimentally observed rate constant (k_{exp}) is directly proportional to the ligand, $[X]$, concentration.

In this chapter and the next one, we will examine equation 5.3 by doping the system with different amounts of known ligand concentrations, and observe the experimental rate constant k_{exp} as a function of ligand concentration. In this way, we can determine k_3 and k_4 . The value for k_4 can be obtained by calculating the reciprocal of the intercept of equation 5.3. The rate constant k_3 can be obtained by plugging the known values of $k_2[\text{CO}]$ and k_4 into the slope of equation 5.3. Once k_3 and k_4 are evaluated, then the equilibrium constant for the process 5.4 may be calculated, giving a measure of the stability of $\text{Mo}(\text{CO})_5\text{X}$ complex.



The experiment in this part is started by preparing 1.0×10^{-3} M solution of Mo(CO)_6 in cyclohexane as described before in section 3.3. Different amounts of benzene were added to Mo(CO)_6 solution. The photolysis was performed with the Lumonics excimer laser with a KrF gas fill. Each set of data collected is pretreated in a similar fashion as in chapter 4 in terms of signal averaging and baseline correction. The infrared spectra for this set of experiments are collected with 16 μs time resolution. The difference spectra as a result of the photolysis are shown in Figure 5.1. The difference spectrum is obtained similarly by subtracting the IR spectrum before laser excitation from the spectrum after irradiation. The laser is pulsed approximately 4 milliseconds after the start of the IR spectral data initiation. In this figure, the 2048 spectra shown are all 16 μs apart. These spectra are the average of 10 laser shots. It can be seen from this figure that Mo(CO)_6 solution returns to the original composition after each laser pulse. After the laser pulse, a broad band transient is observed that decays with time. The transient has both positive and negative peaks. The transient has two major positive peaks at around 1955 and $\sim 1925 \text{ cm}^{-1}$ and a negative peak at $\sim 1990 \text{ cm}^{-1}$. This negative peak has been assigned to the parent molecule, Mo(CO)_6 , as described in chapter 4. We are expecting that the positive peak is due to the benzene complex, $\text{Mo(CO)}_5\text{B}$. But published literatures in matrix isolation and condensed phases

Figure 5.1. The difference spectra of Mo(CO)_6 in cyclohexane solution, doped with 2.5 μL of benzene, irradiated with 249 nm laser excitation. There are 2048 spectra shown each 16 μs apart. These spectra are the average of 10 laser shots.



suggest that the benzene complex absorbs at 1960 cm^{-1} with a weaker band at 1928 cm^{-1} .²⁹⁻³⁴ There is a possibility that the benzene complex is overlapping with the contaminant complex and appears as a broad band with a slightly lower frequency. Therefore, the data sets are formatted into matrices for 2D correlation and SVD analyses in order to determine the pure components, and investigate the effect of introducing different amounts of benzene to the Mo(CO)_6 in cyclohexane upon irradiation.

5.2. Results and Discussions:

5.2.A. Two-dimensional correlation analysis

The set of data in Figure 5.1 is formatted for 2D correlation and SVD analysis as described earlier in chapter 3. Figure 5.2 shows a contour representation of the 2D correlation map. In the upper quadrant, there is a large positive cross peak between 1960 cm^{-1} and 1948 cm^{-1} . The 2D correlation map shows that there are vibrational bands in the original data matrix that are changing with respect to time with different time constants. Positive correlation intensities in the upper quadrant indicates that the vibrational band at 1960 cm^{-1} changes in time before or is faster than the changes in the vibrational band at 1948 cm^{-1} . The peak at 1960 cm^{-1} is due to the benzene complex. This

assignment agrees with the results published earlier.^{29,33} This leads to the conclusion that the other band at $\sim 1948\text{ cm}^{-1}$ belongs to the contaminant complex. The synchronous correlation map is shown in Figure 5.3. It has a large positive autopeak located at $\sim 1948\text{ cm}^{-1}$ that dominates the 2D spectrum. This autopeak shows that there is an overlap with another peak at slightly lower wavenumber which appears as a shoulder. There is another autopeak at 1990 cm^{-1} . These autopeaks are correlated. Negative cross peaks are observed between the 1990 cm^{-1} peak and the 1948 cm^{-1} peak. This result indicates that the rate of disappearance of this complex is the same as the rate of formation of the parent molecule, $\text{Mo}(\text{CO})_6$, represented by the peak at 1990 cm^{-1} . This is basically all the qualitative information that can be obtained from 2-D correlation. We should be able to regenerate these results when SVD is performed on these sets of data, and be able to measure the rate at which these transients are changing with respect to time.

5.2.B. Singular value decomposition:

At this stage, the original data matrix for this experiment is converted into principal components by singular value decomposition method. The intensity profiles and vibrational spectra of the first two pure components are shown in Figure 5.4. Only the first two components are presented, because all of the

Figure 5.2 The disrelation (A and B) 2D correlation spectrum for the data in Figure 5.1. A is the contour representation of the 3D plot in B.

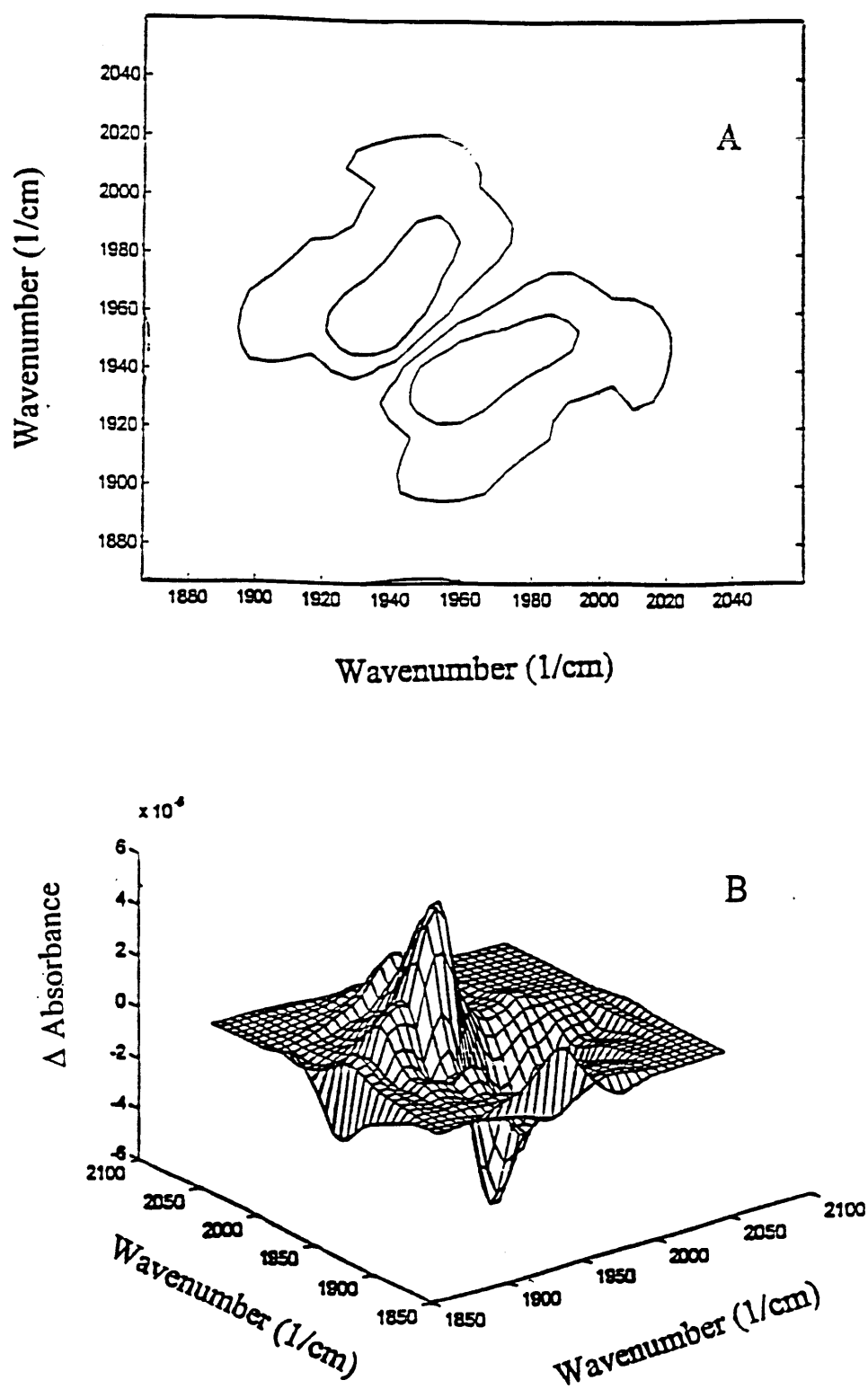
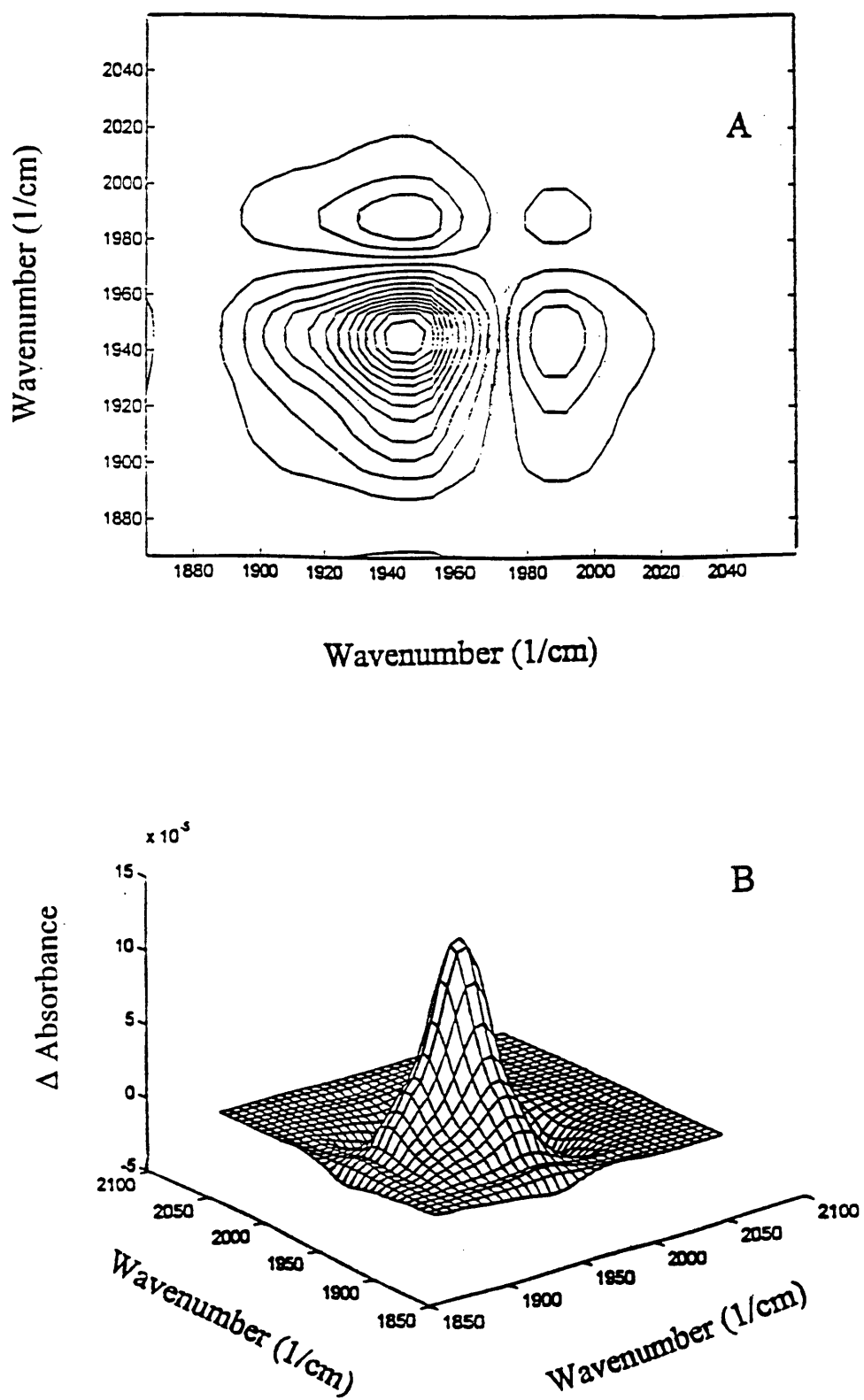


Figure 5.3. The synchronous (A and B) 2D correlation spectrum for the data in Figure 5.1. A is the contour representation of the 3D plot in B.



remaining components showed random fluctuations around zero and were eliminated as being non-significant. The top of Figure 5.4 represents the intensity profiles for the two pure components. Profile A has a spike at time zero due to the laser shot then decays in a faster rate than the second component labeled B. The component B has a rate constant identical to the rate constant of the contaminant complex presented in chapter 4. This leads us to believe that the second component is actually the contaminant complex, $\text{Mo(CO)}_5\text{X}$. The middle and bottom plots in Figure 5.4 refer to the first and second components, respectively. The first component shows a band at 1960 cm^{-1} with a weaker band at $\sim 1925\text{ cm}^{-1}$. We assigned this component to the benzene complex, $\text{Mo(CO)}_5\text{B}$. This assignment agrees well with published results.^{29,33-34} The second component shows two positive bands and a negative band. We have already assigned the positive peaks to the contaminant complex and the negative peak to loss in the parent molecule. SVD could not separate these two components because the rate of disappearance of the contaminant complex is the same as the rate of reformation of the parent molecule.

One of the main goals of this chapter and the next chapter is to examine equation 4.4, in which the reciprocal of k_{exp} is proportional to the ligand concentration. Therefore, we have doped the system, Mo(CO)_6 in cyclohexane

solution and CO gas, with different amounts of benzene. Each experiment with benzene concentration was photolysed as before, and the data was analyzed by 2D correlation and SVD analysis. Each set of these experiments was performed as a replica of 6. In these experiments, the reaction mechanism is extended when another component, benzene, is added. The extended mechanism is shown in scheme 3.

Scheme 3:

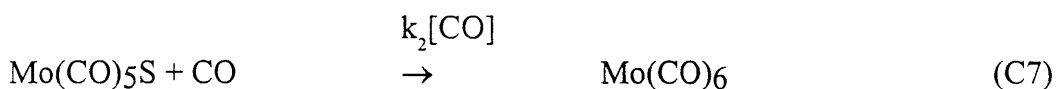
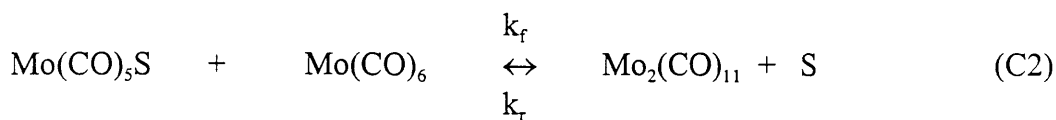
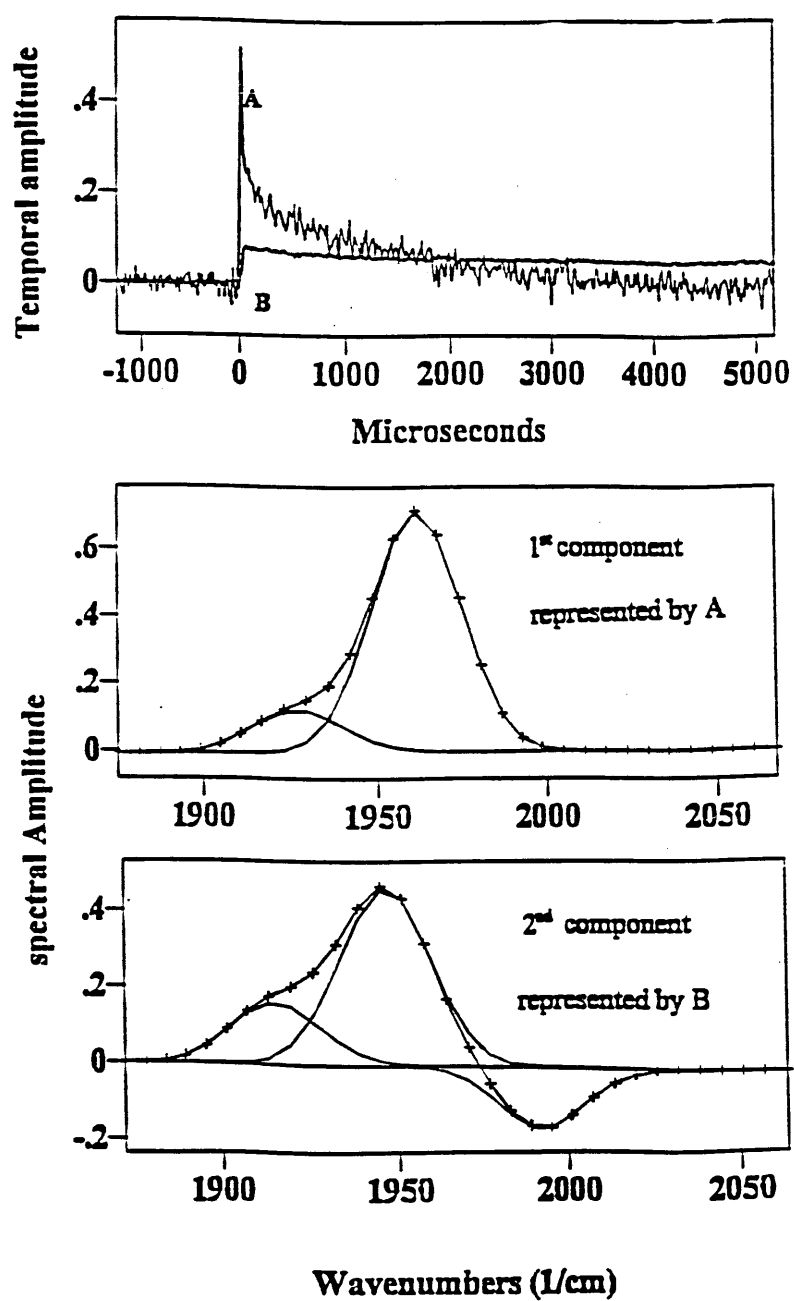


Figure 5.4. The first two pure temporal and spectral components as a result of the SVD analysis and proper rotations. The spectral components are fitted with gaussian bands.



2D correlation analysis was performed on all of these experiments. This analysis gave identical results to the plots shown in Figures 5.2 and 5.3. SVD analysis, on the other hand, produced interesting results. The life time and intensity of the transient bands at 1960 and 1925 cm^{-1} increased with increasing benzene concentrations, but the second component which absorbs mainly at 1950 cm^{-1} did not show any change in its life time with different amounts of benzene. This suggests that the amount of contaminant present in the system was constant.

In order to test equation 4.4, the time traces of the raw data at 1960 cm^{-1} need to be considered. This is the frequency at which benzene complex, $\text{Mo(CO)}_5\text{B}$, absorbs. Figure 5.5 shows few time traces at 1960 cm^{-1} of the raw data collected at different benzene concentrations. We attempted to fit these experimental time traces with first order rate constants. Figure 5.6A shows a first order fit on an experimentally observed time trace taken at 1960 cm^{-1} with 3.26×10^{-4} M benzene concentration. It can be seen very clearly that the time trace is not a first order decay. This experimental time trace at 1960 cm^{-1} shows initially a fast decay that does not go to zero due to an interference with the contaminant complex. The concentration of contaminant complex, which is obtained from SVD analysis, starts at zero, increases to a maximum, and then disappears very slowly with a rate constant of 200 s^{-1} . This is shown in Figure 5.6B. When the

contaminant complex is subtracted from the experimental time trace taken at 1960 cm^{-1} , it was possible to fit it with a first order decay as shown in Figure 5.6C. Consequently, we subtracted the intensity profiles of the contaminant complex as a result of SVD analysis from each corresponding experimental time trace at 1960 cm^{-1} in order to eliminate the contaminant complex effect. This enabled us to fit the treated experimental time traces with first order rate constants successfully. The following Table shows the k_{exp} values that fits the treated time traces of benzene complex at 1960 cm^{-1} at different concentrations.

Benzene Conc.(M)	$k_{\text{exp}}\text{ (s}^{-1}\text{)}$	μ^*
2.62E-04	1.95E+03	± 27
3.26E-04	1.75E+03	± 38
3.90E-04	1.65E+03	± 19
4.49E-04	1.05E+03	± 12
5.23E-04	7.80E+02	± 21
5.60E-04	3.70E+02	± 13
6.83E-04	3.10E+02	± 9.5
1.22E-03	2.90E+02	± 11.0
1.70E-03	2.00E+02	± 18
2.34E-03	1.48E+02	± 22
2.94E-03	1.50E+02	± 8.3

1

Table 5.1. The first order rate constants at various benzene concentrations.

¹ μ^* represents the 95% confidence interval of the mean

Figure 5.5. Few representative of the experimental time traces at 1960 cm^{-1} with various benzene concentrations. A, B, C and D represent 3.26 , 5.23 , 12.2 , and $23.5 \times 10^{-4}\text{ M}$ benzene concentrations respectively.

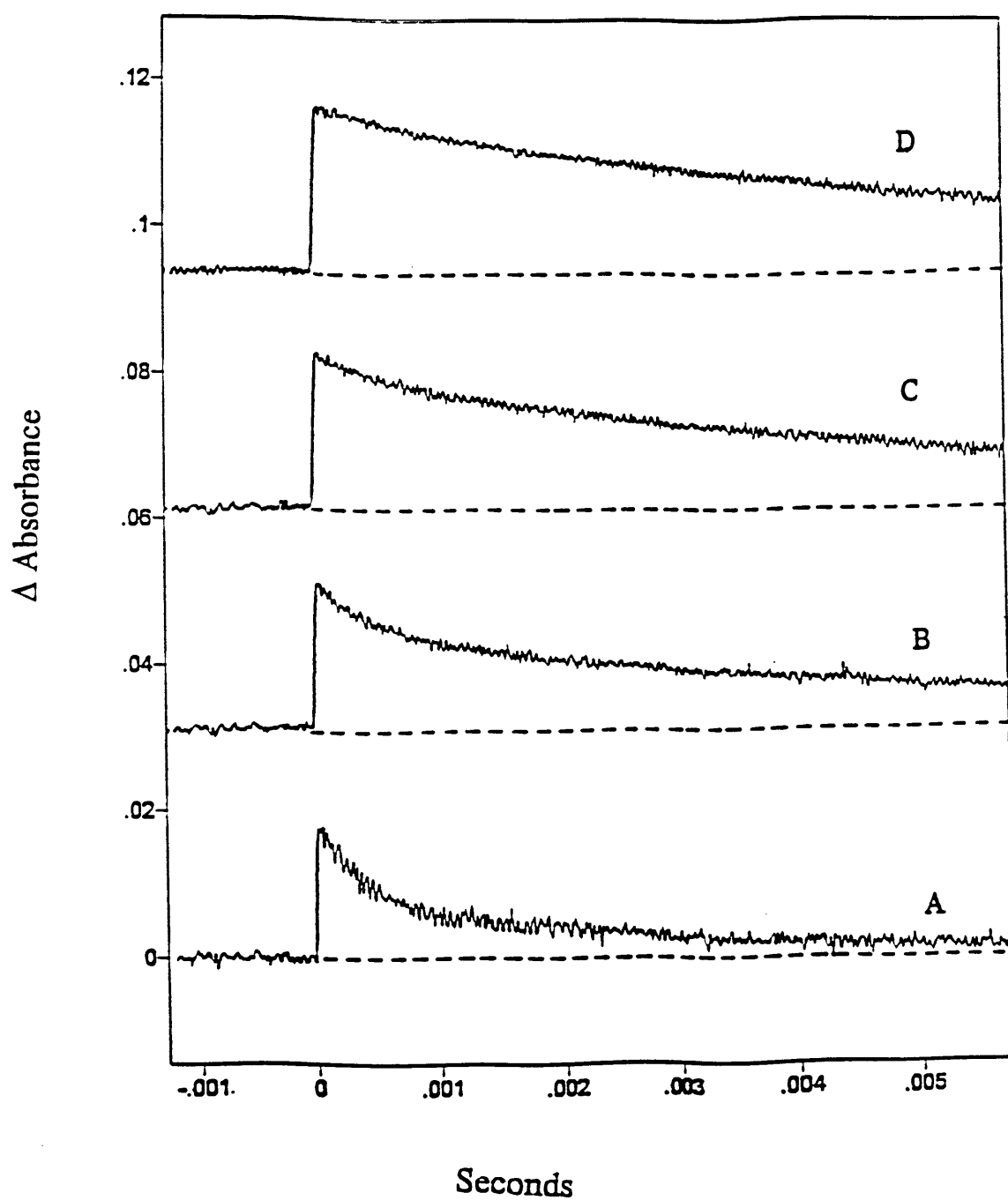
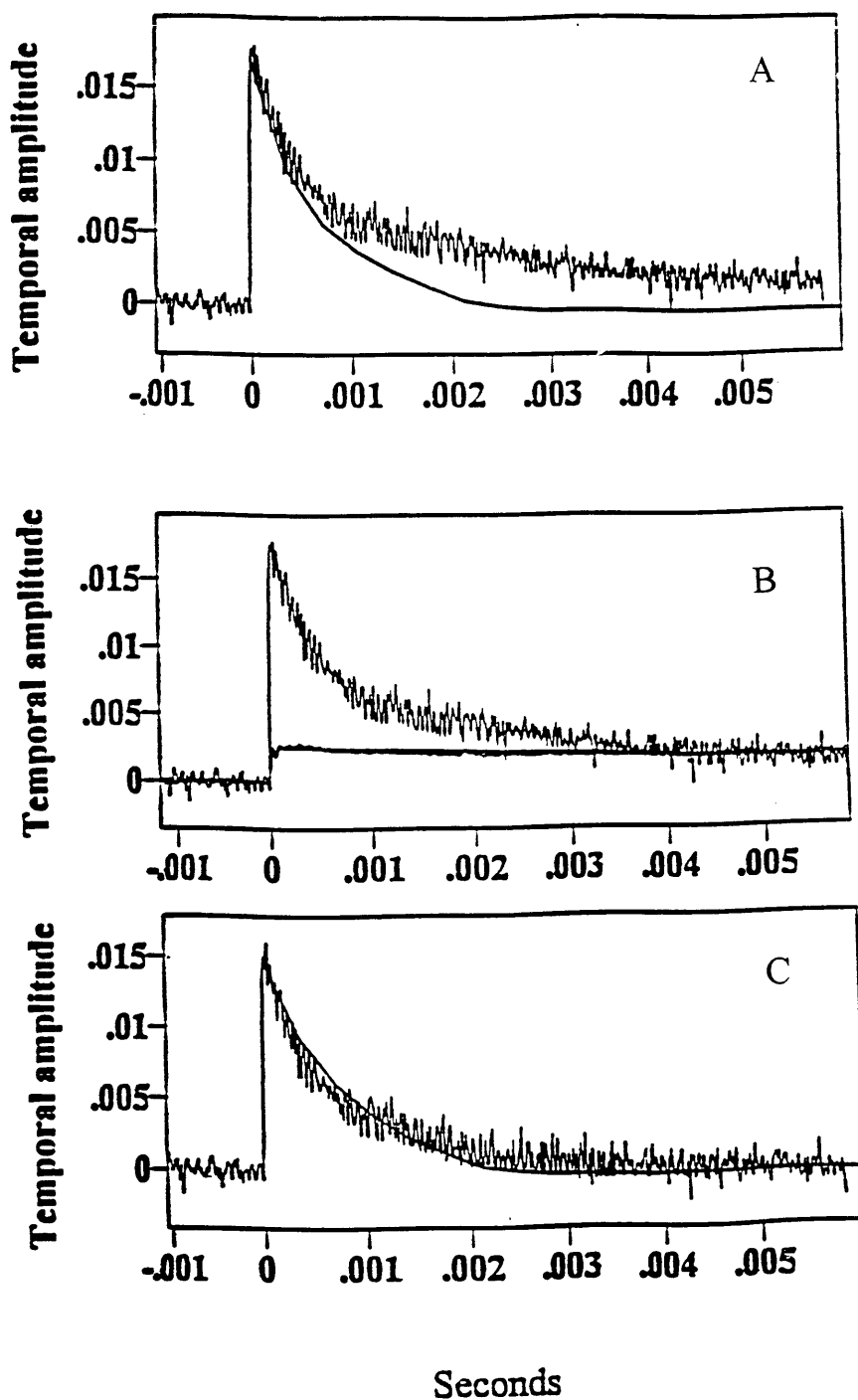


Figure 5.6. the experimental time trace at 1960 cm^{-1} of a sample with benzene concentration of $3.26 \times 10^{-4}\text{ M}$. In A, the time trace is compared with a first order decay. The effect of the contaminant complex is shown in B. The bottom trace, C, shows the time trace after subtracting the contaminant complex from it and fitted with a first order decay.



The data in Table 5.1 were plotted as $1/k_{\text{exp}}$ vs. benzene concentrations.

This is shown in Figure 5.7. The data points were fitted with linear regression.

The intercept, for the data in Table 5.1, was equal to 3.033×10^{-4} . This intercept is equal to the reciprocal of the rate constant, k_4 . Therefore k_4 equal to 3296 s^{-1} . The slope for the line of regression equals to 2.492. From equation 4.3 the slope of the

line equals to $\frac{k_3}{k_2 k_4 [\text{CO}]}$. From this relationship, substituting values of $k_2 [\text{CO}]$

and k_4 , as 3.0×10^4 , and 3296 s^{-1} respectively, the rate constant, k_3 can be obtained

as $2.46 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The rate constants obtained in this work agree reasonably

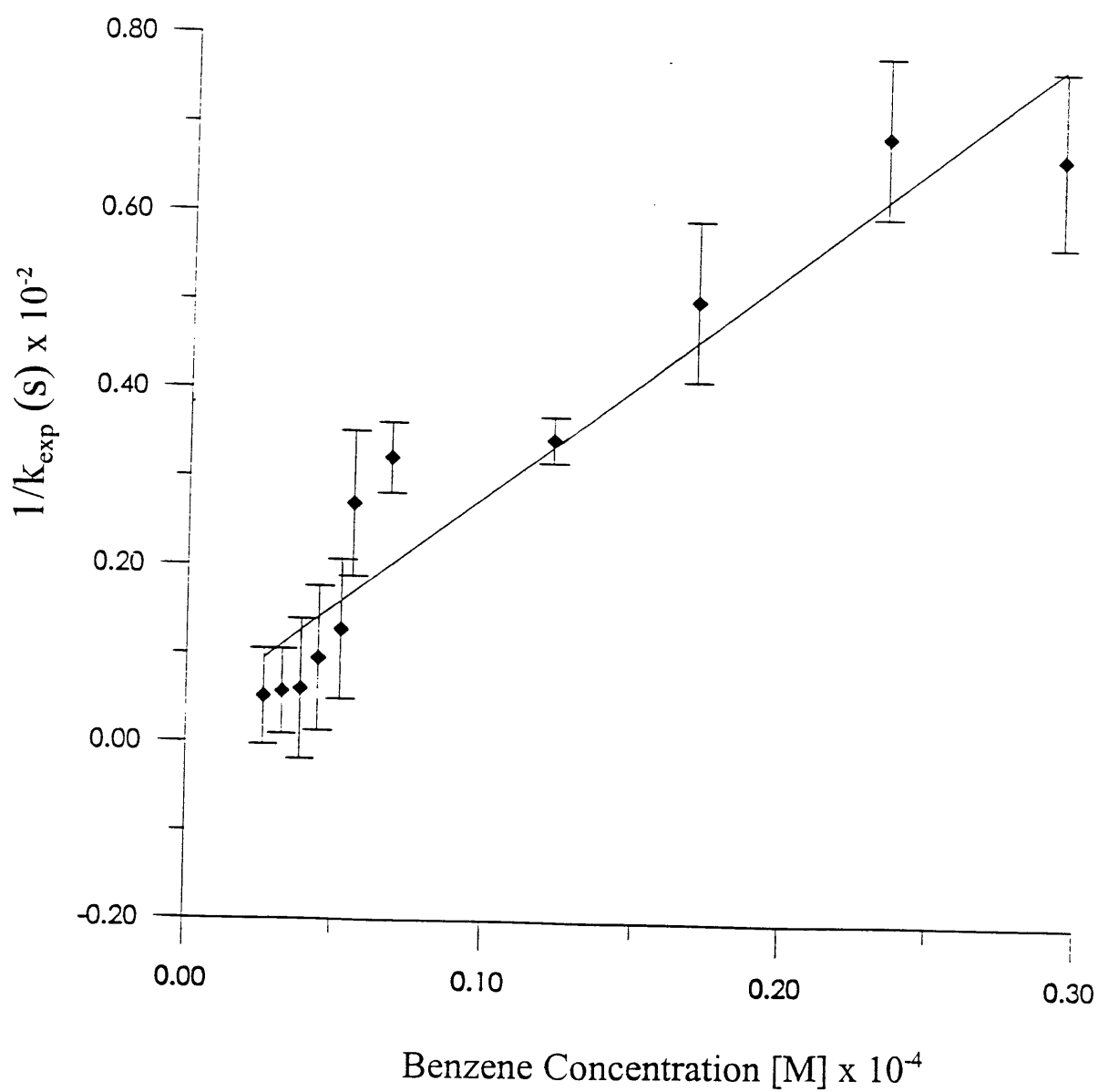
with the published values in references 33 and 34 as summarized in the following

Table.

Rate constant	In this work	Reference 34	Reference 33
$k_2[\text{CO}] (\text{s}^{-1})$	$3.0 \times 10^4 \pm 2.5 \times 10^2$	2.8×10^4	2.2×10^4
$k_3 (\text{M}^{-1} \text{s}^{-1})$	$2.5 \times 10^8 \pm 7.3 \times 10^6$	3.0×10^8	6.7×10^6
$k_4 (\text{s}^{-1})$	$3.3 \times 10^3 \pm 8.0 \times 10^1$	6.6×10^3	2.2×10^5

Table 5.2. A comparison between the rate constants determined in this work and the published values.

Figure 5.7. Dependence of life time ($1/k_{\text{exp}}$) of $\text{Mo}(\text{CO})_5\text{B}$ on the benzene concentration measured at 1960 cm^{-1} .



The rate constants shown in Table 5.1 indicate that our results are consistent with Hermann's results which were measured with infrared detection.³⁴ It is very interesting to note that Hermann's results differed significantly from Kelly's UV-VIS data³³ Hermann attributed this significant difference in the two studies to the kinetic influence of the trace contaminant X. We find in this study that the presence of a contaminant is not substantial, because we managed to separate the principal components and eliminate the effect of the contaminant on the rate constants. The rate constants measured in this study are in a good agreement with Hermann's but not consistent with Kelly's.

5.3. Conclusion:

Data sets on the solution photolysis of Mo(CO)_6 in cyclohexane saturated with CO gas and doped with different amounts of benzene were collected. Both 2-D correlation and SVD analysis suggest the existence of two components. One of them absorb at 1960 cm^{-1} with a weaker band at $\sim 1925\text{ cm}^{-1}$. This component is assigned to the benzene complex, $\text{Mo(CO)}_5\text{B}$. The other component showed a broad band at 1948 cm^{-1} . A negative band was also observed along with this component at 1990 cm^{-1} . The negative band is due to the loss in the parent molecule. The component with the band at 1948 cm^{-1} was assigned to the contaminant complex. Upon increasing the benzene concentration in the solution,

the life time and intensity of the transient bands at 1960 and 1925 cm^{-1} were increased, while the transient band at 1948 cm^{-1} did not change. First order rate constants were fitted to the experimental time traces at 1960 cm^{-1} after subtracting the contaminant complex time trace from the experimental time traces. The first order rate constants are shown in Table 5.1. The rate constants, k_3 , and k_4 obtained from the relationship in equation 4.3 were consistent with the published literature.

Chapter 6

Irradiation of Mo(CO)_6 in cyclohexane

doped with acetone using a broad band Xe-lamp

6.1. Introduction

In this chapter, the photolysis of Mo(CO)_6 in cyclohexane doped with acetone is investigated. Solutions of 1.0×10^{-3} M of Mo(CO)_6 in cyclohexane were prepared as described earlier in section 3.3. Different amounts of acetone were added to Mo(CO)_6 solutions. The photolysis was carried out using a broad band Xe-lamp. The data acquisition method for this part of the research is described in detail earlier in chapter 3, in which 32 sweeps of data are collected with time delay of 4 seconds between each sweeps. The lamp was blocked around the sixteenth sweep, and sweeps 17 through 32 probed the decay of transients. The transient has a very long relaxation time, i.e. in the order of seconds. The reaction mechanism for this system is identical to the one shown in scheme 3, except benzene is replaced by acetone. The change in absorbance for the solution photolysis of Mo(CO)_6 in cyclohexane in the presence of acetone is shown in Figure 6.1. The negative peak at $\sim 1990 \text{ cm}^{-1}$ corresponds to a loss in absorbance

of the irradiated sample and positive peaks to the formation of a new species at ~ 1950 and $\sim 1918 \text{ cm}^{-1}$. These two bands are assigned to a $\text{Mo}(\text{CO})_5$ complex involving acetone and referred to as a ligand complex, $\text{Mo}(\text{CO})_5\text{L}$. The disappearance of $\text{Mo}(\text{CO})_5\text{L}$ followed a first order rate law, i.e.

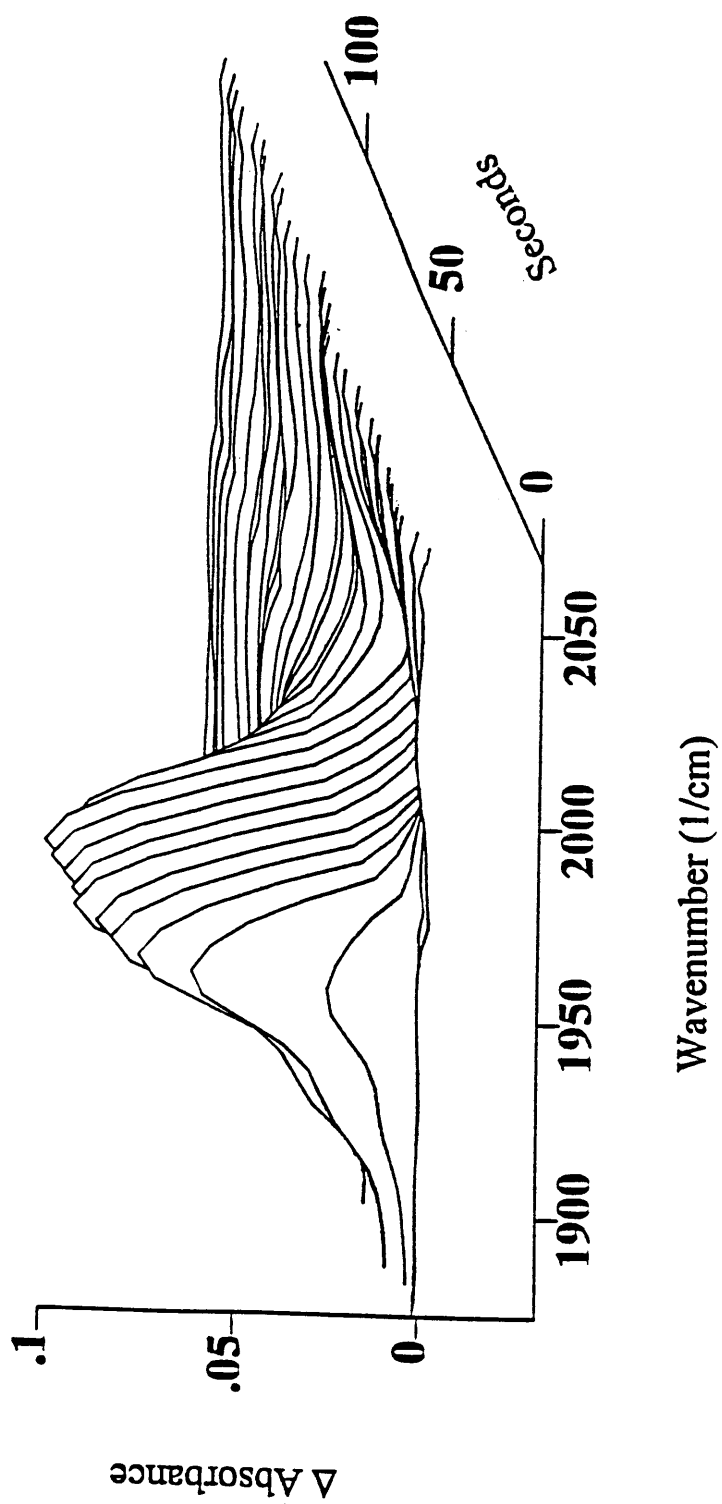
$$d[\text{Mo}(\text{CO})_5\text{L}]/dt = -k_{\text{exp}} [\text{Mo}(\text{CO})_5\text{L}] \quad (6.1)$$

where k_{exp} is the experimental first order rate constant for decay of the complex, $\text{Mo}(\text{CO})_5\text{L}$. In this experiment, the solvent complex, $\text{Mo}(\text{CO})_5\text{S}$, can not be detected at this time resolution. We have found, in chapter 4, that the solvent complex disappears within microseconds. Furthermore, the disappearance of the contaminant complex, $\text{Mo}(\text{CO})_5\text{X}$, takes place faster than the relaxation time of acetone ligand complex, indicating that acetone is a stronger complexing agent than the contaminant. This result also shows that the relaxation of the transient at 1950 cm^{-1} is mainly due to $\text{Mo}(\text{CO})_5$ complex with acetone. Therefore, equation 6.1 can be rewritten as shown in equation 6.2 where $k_c = (k_2[\text{CO}] + k_3[\text{L}])$.

$$d[\text{Mo}(\text{CO})_5\text{L}]/dt = -\{k_2[\text{CO}] + k_3[\text{L}]\} [\text{Mo}(\text{CO})_5\text{L}] \quad (6.2)$$

Rearranging the equality, $k_{\text{exp}} = k_2[\text{CO}] + k_3[\text{L}]$, then equation 6.3 will be obtained.

Figure 6.1. The difference data file (after Xe-lamp irradiation minus before irradiation) of 1.0×10^{-3} M of Mo(CO)_6 in cyclohexane solution, and 0.05 ml of acetone was added to the solution as a ligand.



$$\frac{1}{k_{\text{exp}}} = \frac{1}{k_4} + \frac{k_3[L]}{k_2 k_4 [\text{CO}]} \quad (6.3)$$

Equation 6.3 is the same one that we have come across in chapter 5, which we made the conclusion that the reciprocal of k_{exp} should increase linearly with the ligand concentration. We have examined this relationship experimentally in chapter 5 in which benzene was used as the ligand. In this chapter, acetone, which is a stronger complexing agent than benzene is introduced, and its effect on the photolysis of $\text{Mo}(\text{CO})_6$ in solution is studied.

6.2. Results and discussion

The sets of data collected in this experiment were first analyzed by 2-D correlation. Figure 6.2 shows the synchronous 2D correlation spectrum of the data shown in Figure 6.1. Two broad autopeaks at 1990, 1950 cm^{-1} are observed. There is a hint that a cross peak exists at 1950 cm^{-1} and 1920 cm^{-1} . Negative broad cross peaks are also observed between 1990 cm^{-1} and 1950 cm^{-1} . This indicates that the disappearance of the ligand complex and the reformation of the parent molecule, $\text{Mo}(\text{CO})_6$ are mutually dependent and occurs at the same rate. The disrelation spectrum for this data is shown in Figure 6.3. The disrelation 2D

correlation spectrum does not have any predominant peaks because all the peaks are correlated as seen from the synchronous spectrum in Figure 6.2.

SVD analysis on this data set showed only one principal component. The rest of the components are within the noise level. The intensity profile and the vibrational spectrum of the first component are shown in Figure 6.4. The intensity profile is truncated in order to show the region when the ligand complex starts to decay. The time at which this complex begin to disappear is set to zero. This is the time when the Xe-lamp was blocked and the decay of the transient was probed. The intensity profile in Figure 6.4 shows a first order rate constant as expected from the original data in Figure 6.1. The original data in Figure 6.4 are represented by crosses and fitted with a first order rate constant.

Irradiation of Mo(CO)_6 in cyclohexane doped with acetone using a broad band Xe-lamp was repeated but with different amounts of acetone added to the sample. The 2D correlation analysis on these experiments gave identical results to the original experiment shown earlier in this chapter. SVD analysis also showed one principal component but with different rate constant for different acetone concentrations, as expected from equation 6.3. The rate constants were obtained by fitting a single exponential decay to the experimental data. The rate constants obtained for different acetone concentrations are shown in Table 6.1. These results

Figure 6.2. The synchronous 2D correlation spectrum for the data shown in Figure 6.1. A is a contour representation of the 3D plot in B.

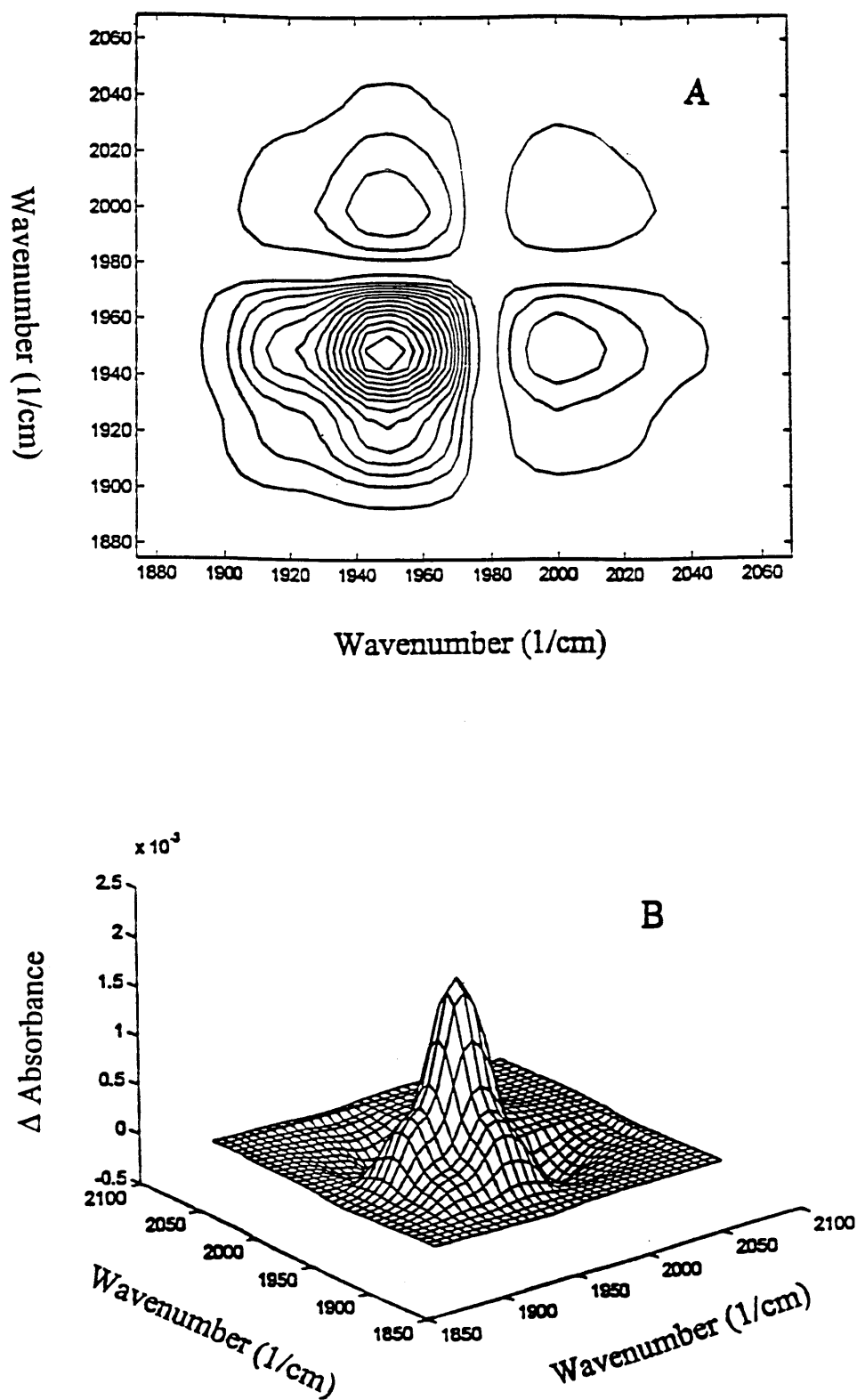


Figure 6.3. A contour plot of the disrelational 2D correlation spectrum for the data shown in Figure 6.1.

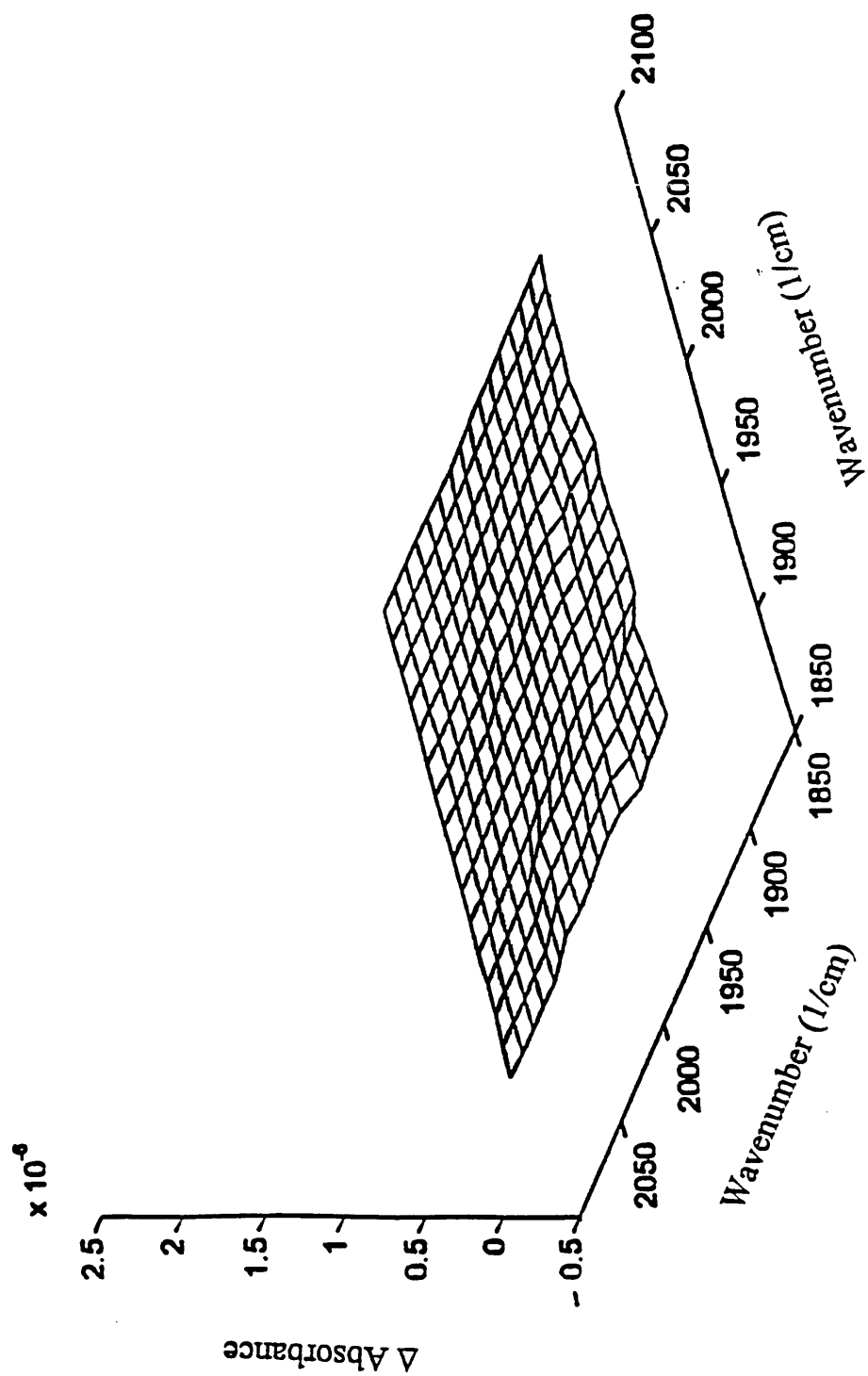
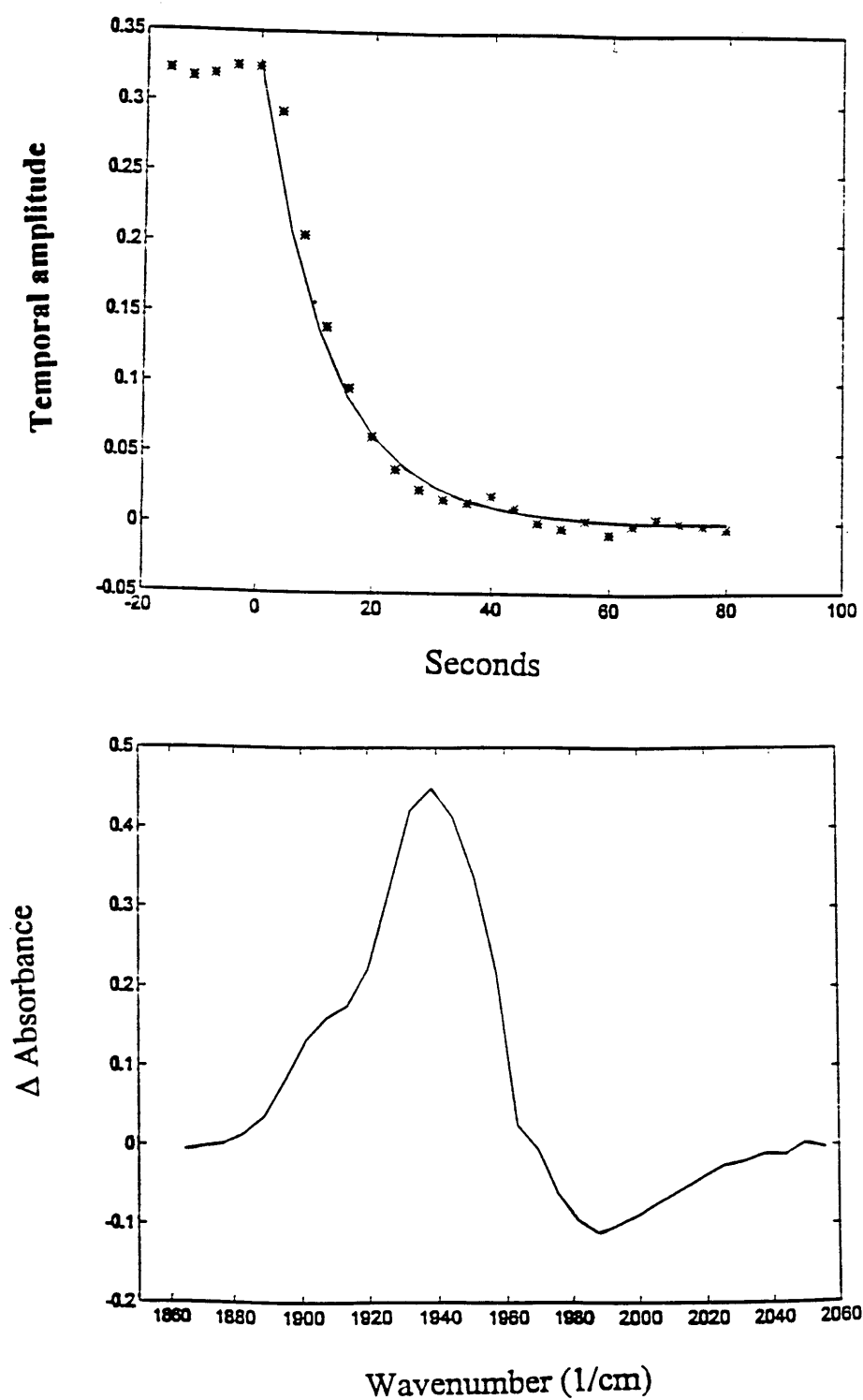


Figure 6.4. The first temporal and spectral component as a results of the SVD analysis for the data obtained by Irradiation of $\text{Mo}(\text{CO})_6$ in cyclohexane doped with acetone using a broad band Xe-lamp. The temporal component is represented by crosses and fitted with a first order rate constant.

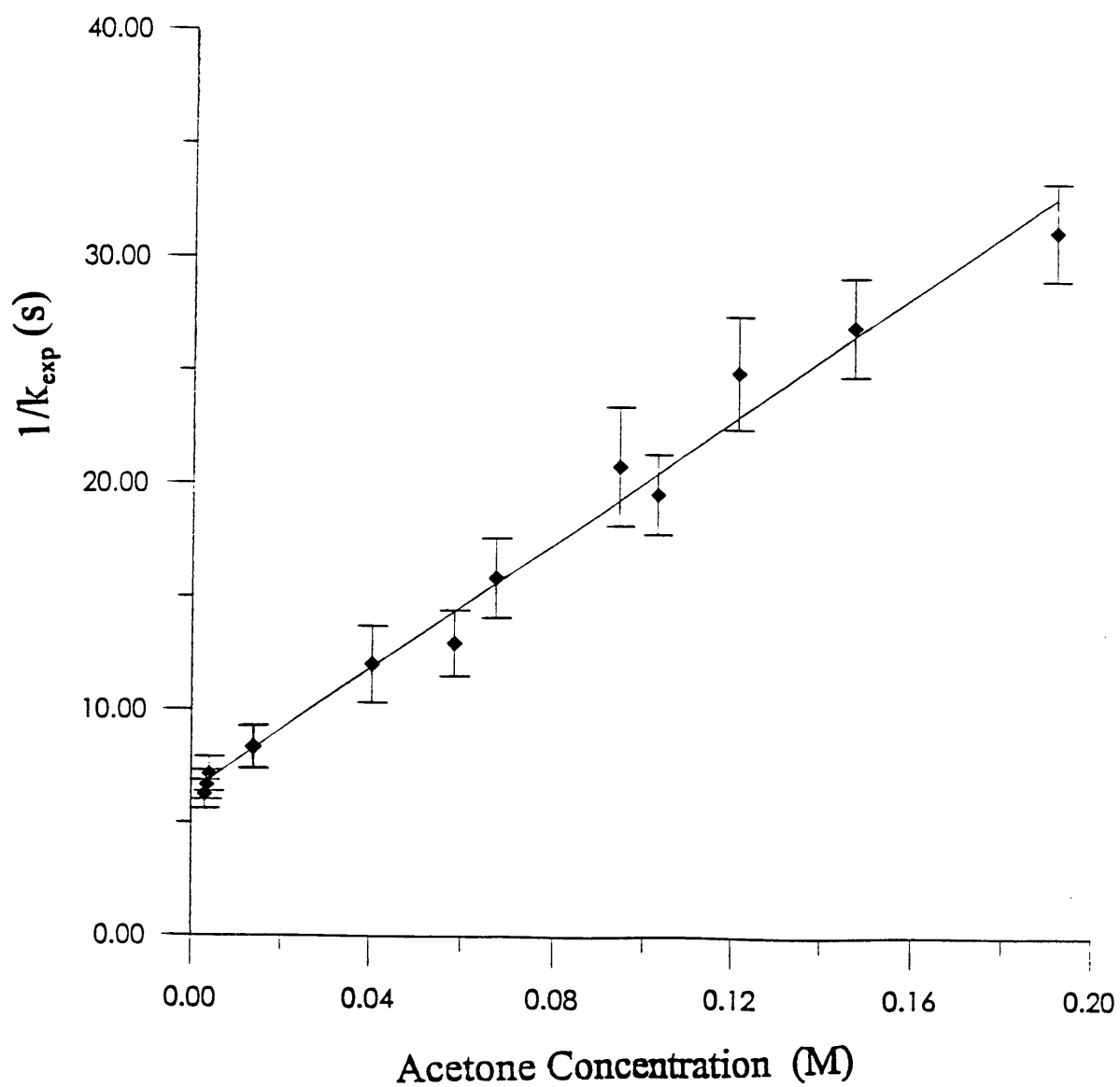


suggest that k_{exp}^{-1} is directly proportional to the ligand concentration. This effect is shown in Figure 6.5.

Table 6.1. A list of the experimental rate constants, k_{exp} , at various acetone ligand concentration in $\text{Mo}(\text{CO})_6$ in cyclohexane.

[Acetone] (M)	k_{exp} (s^{-1})
0.0030	0.16 $\pm$ 0.0080
0.0035	0.15 $\pm$ 0.0073
0.0040	0.14 $\pm$ 0.0074
0.0135	0.12 $\pm$ 0.0066
0.0139	0.12 $\pm$ 0.0069
0.0405	0.083 $\pm$ 0.0058
0.0585	0.077 $\pm$ 0.0043
0.0675	0.063 $\pm$ 0.0035
0.0945	0.048 $\pm$ 0.0030
0.1031	0.051 $\pm$ 0.0023
0.1215	0.040 $\pm$ 0.0020
0.1477	0.037 $\pm$ 0.0015
0.1923	0.032 $\pm$ 0.0011

Figure 6.5. Dependence of life time (k_{exp}^{-1}) of $\text{Mo(CO)}_5\text{L}$ on the ligand concentration of L (L = acetone).



The slope and intercept of the plot of $1/k_{\text{exp}}$ against acetone concentration were 131.67 ± 8.86 and 6.56 ± 0.79 respectively with 95 % confidence limit. From these results, it was possible to calculate the rate constants k_4 and k_3 using equation 6.3. The values for these rate constants are shown in Table 6.2.

Table 6.2. A comparison between the rate constants determined in this work and the published values for acetone as a doping ligand.

Rate constant	In this work	Reference 34	Reference 33
$k_2[\text{CO}] \text{ (s}^{-1}\text{)}$	$3.0 \times 10^4 \pm 2.5 \times 10^2$	2.8×10^4	2.2×10^4
$k_3 \text{ (M}^{-1}\text{s}^{-1}\text{)}$	$5.9 \times 10^8 \pm 9.2 \times 10^6$	3.0×10^8 ²	1.0×10^7
$k_4 \text{ (s}^{-1}\text{)}$	0.15 ± 0.03	0.23	15

Once again, our results for the photolysis of Mo(CO)_6 in cyclohexane doped with acetone are in good agreement with Hermann's data.³⁴ The rate constant k_4 in Kelly's report, is approximately ten orders of magnitude greater than the rate constant obtained in our study and Hermann's report. The value of k_3 in Kelly's

² * these reference values contain a possible experimental error of ± 20 % according to the author's claim.

report is also inconsistent with the other studies. This suggests that kinetic studies on such systems are more appropriate in IR than in UV-VIS spectroscopy.

6.3. Conclusion

The experiments performed on irradiation of Mo(CO)_6 in cyclohexane doped with acetone using a broad band Xe-lamp yield two main components, Mo(CO)_6 , and $\text{Mo(CO)}_5\text{L}$. These two components were found to be synchronously correlating based on 2-D correlation results. The reaction mechanism in scheme 2 in chapter 4 can be used to explain the reactions in these experiments. The reformation of the parent molecule is dependent on the rate determining step which involves the consumption of $\text{Mo(CO)}_5\text{L}$ disappears. 2D correlation analysis on this experimental data confirms that Mo(CO)_6 , and $\text{Mo(CO)}_5\text{L}$ are negatively correlating. In other words, as the ligand complex starts to disappear, the parent molecule will be formed at the same rate. This behavior is also shown in SVD analysis. Only one principal component was detected. This component follows first order kinetics. The observed rate constant decreases with increasing ligand concentration. The rate constants found in this experiment are consistent with Hermann's results.

Chapter 7

Summary and Future Work

The time-resolved study on the photolysis of Mo(CO)_6 in cyclohexane solution using IRLA spectrometer can be summarized as follows:

1. The infrared linear array spectrometer is capable of collecting time-resolved data with microsecond time resolution. Data were collected with 2 μs and 16 μs time resolution on the photolysis on Mo(CO)_6 in cyclohexane solution.
2. Transients with broad peaks were observed in the time resolved data. For the first time, a transient with a band at 2010 cm^{-1} was observed. This species was assigned to a dimer, i.e., $\text{Mo}_2(\text{CO})_{11}$.
3. A reaction mechanism was postulated and tested. The postulated mechanism is presented in scheme 2. SVD analysis showed that the dimer that has a band at 2010 cm^{-1} is correlating with the band at 1970 cm^{-1} . The band at 1970 cm^{-1} is due to the solvent complex.
4. The transient species, with monochromator grating in first order, appears with broad bands. One way to increase the spectral resolution was to collect data with monochromator grating in second order. This was shown in section 4.4. The spectral resolution was increased by a factor of 2 when the grating was shifted from first to second order.

5. In the photochemistry of Mo(CO)_6 in cyclohexane solution, it was possible to observe the loss of the parent, Mo(CO)_6 , upon flashing and its subsequent reappearance. The intermediate species were also observed and investigated kinetically.
6. When the system was doped with benzene or acetone, an interesting pattern was observed. The life time and intensity of the experimentally observed rate constant was increased with increasing ligand concentration.
7. Two well established techniques in chemometrics were used to analyze the time-resolved data. The first one, 2-D IR correlation, showed to be a useful method in qualitative analysis. It cannot be used for quantitative analysis. In this methodology, correlation among IR bands which belong to the same chemical group have been observed in the synchronous plots of the 2-D IR correlation. The bands that behave differently, on the other hand, were observed in the disrelation spectra. This method helped in determining the sequence in which these intermediates appear as a result of irradiation.
8. The second method, SVD, is a powerful method used in analyzing time-resolved IR data quantitatively. This is a useful technique in extracting dynamical information from a set of multi-component time-resolved spectra. Because principal components, determined by SVD, represent linear

combinations of the various components present in the system, they have to be properly rotated to obtain the pure components. SVD managed to separate the principal components and helped in eliminating the contaminant effect.

9. The rate constants for the solution photolysis of Mo(CO)_6 obtained in this work were very consistent with the published results based on IR detection.³⁴

Future Work:

Some work is being investigated in our lab to resolve the overlapping peaks observed in our data. One way to enhance the data is to take the second derivative on the original data matrix. This approach is being tested on the time-resolved data. Second derivative is frequently used in spectroscopy to resolve overlapping peaks. One of the main advantages of performing second derivative in the spectral direction of the data matrix is that the pure compounds' concentration profiles are kept unchanged and any overlapped peaks in the original spectrum is transformed into single peaks without any side lobes in the final spectrum.

The linear array spectrometer opens many new areas to be studied. Systems that are not so well characterized in the field of organometallic can be investigated. For example, the reaction mechanism of vanadium, osmium, and iron carbonyl complexes in solution are not very well understood.⁶³⁻⁶⁶ These have been noted as effective catalysts for the reactions of olefins and hydrogen.

One of the areas that is still being investigated in the field of atmospheric chemistry is the heterogeneous reactions on ice clusters. Photolysis of CFC and HFC compounds on clusters at very low temperatures has not been rationalized. Time-resolved infrared spectroscopy of these reactions is one method that may be studied on such reactions in explaining the observed depletion of ozone. It is known that heterogeneous reactions on the surfaces of polar stratospheric clouds (PSCs) have important role in converting inactive chlorine to active forms which subsequently deplete ozone through catalytic cycles.⁶⁷⁻⁷⁴ Therefore, focusing in this area may help find ways to solve this environmental problem.

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