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UNIVERSITY OF OKLAHOMA GRADUATE COLLEGE

Effects of non - adiabatic coupling in

photofragmentation of CO_2 using Resonance Enhanced

Multiphoton Ionization Techniques

A Dissertation

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

Doctor of Philosophy

By

Kushlani Dharmasena

Norman, Oklahoma

1997

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Effects of non - adiabatic coupling in photofragmentation of CO_2 using Resonance Enhanced Multiphoton Ionization Techniques

A Dissertation APPROVED FOR THE DEPARTMENT OF PHYSICS & ASTRONOMY

BY



Dedication to My Parents

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Abstract

We observed Resonance Enhanced Multiphoton Ionization (REMPI) spectra of $nf^2\Pi_{\Omega}$ Rydberg states of CO_2 for n = 4 to 8. In addition, we also did a laser power dependence study of these states for n = 5 to 7. We compared our results to two other studies by Johnson and coworkers and Dobber and coworkers.

In the present study we observed that dissociation rate increased with increasing frequency. Also, we observed a clear difference in rates of dissociation for the two spin-orbit components of each nf state. This difference was not consistent, in some states the $\Omega = 1/2$ component dissociated more while in the others $\Omega = 3/2$ dissociated more. When comparing with Dobber and coworkers REMPI-Photoelectron Spectra (REMPI-PES), a good correlation between the observed symmetric vibrational progressions and our dissociation rates was noticed. We also found that these rates stayed remarkably constant for different powers of the laser even though the production of CO^+ ions required more photons than CO_2^+ ions. From this observation we came to the conclusion that the two-photon transition was saturated. What was surprising was, the amount of CO_2^+ ions observed despite the fact that the two-photon transition X ${}^2\Pi_g \rightarrow \rightarrow$ $C^2\Sigma_g^+$ was saturated. The observed ratio of CO^+/CO_2^+ ratio never was lower than 6. These observations led us to believe that CO^+ ions were predominantly made by predissociation rather than direct dissociation. We propose that the two-photon transition is X ${}^{2}\Pi_{g} \rightarrow \rightarrow C^{2}\Sigma_{g}^{+}$ followed by predissociation of the

 $C^2 \Sigma_g^+$ state. In our model, predissociation must occur through a potential barrier in the C $^2\Sigma_g^+$ state which is on the order of an electron volt above the dissociation limit. We estimated the mean lifetime of this state to be about 600 psec by using the ratio of CO^+/CO_2^+ from our spectra.

This model explains two other phenomena observed in REMPI spectra. First is the observation of increased dissociation with increasing principal quantum number in the nf Rydberg states. The second is the lower dissociation rate observed in Dobber and coworkers' spectra for picosecond laser compared to the nanosecond laser.

Chapter 1

Effects of non-adiabatic coupling in photofragmentation

Photofragmentation of molecules occurs by two different processes: photodissociation, where the molecule breaks into two or more segments due to interactions with photons, or photoionization, where an electron is removed from the molecule due to the effects of photons. In a molecule there are many stateselectronic, vibrational and rotational- that lie close together in energy. Due to the close proximity of these states they can interact with one another, creating effects that make interpretation of results more complicated. These interactions are known as non-adiabatic couplings of states. The details about these couplings will be explained in the next paragraph.

1.1 Non-adiabatic coupling of states

When calculating the electronic states of a molecule one has to make some approximations in order for the Schrödinger equation to be solvable. The first approximation in calculating molecular states is the Born-Oppenheimer ap-

proximation. which is based on the vast difference in the mass of the electrons and the nuclei. This is also known as the adiabatic approximation. Since the mass of the electron is so small, when the nuclei change their geometry the electrons can be assumed to instantly adjust to their new positions. Hence, according to the Born-Oppenheimer approximation, one can freeze the nuclei and solve the Schrödinger equation for the moving electrons. Therefore, the nuclear dimensions (for instance internuclear distances) can be treated as parameters instead of co-ordinates. This makes the Schrödinger equation solvable. To get the electronic energy, U(R), as a function of different positions of the nuclei R $(R_1, R_2...)$, the parameters R can be adjusted and the Schrödinger equation can be solved for each set of nuclear coordinates. By doing this for many points, a curve showing the dependence of the electronic energy of each state of the molecule for different geometries of the nuclei can be constructed. Potential energy curves for several electronic states of a diatomic molecule are shown in figure 1.1. These are called the adiabatic molecular potential energy curves and each curve represents a different electronic states of the molecule. In the adiabatic approximation, some of these states cross each other (see figure 1.2(a)). For a diatomic molecule, this is not allowed for states which have the same projection of total orbital angular momentum on the nuclear axis. Λ , and the same overall symmetry. These crossings come about only because of the approximations made in calculating these curves. If no approximations are made the curves will take the form shown in figure 1.2(b). These crossings



Figure 1.1: Potential energy curves for a diatomic molecule with respect to the internuclear distance. R. The dots show the calculated electronic energies for different values of the parameter R.



Figure 1.2: (a) Potential energy curve crossings due to approximations made in calculations.(b) Real curves. calculated by taking the non-adiabatic approximations into consideration.

lead to states that are coupled together. The new. non-adiabatic states are a combination of the approximate adiabatic states. This phenomena is referred to as the non-adiabatic coupling of states. The initial adiabatic states, Φ_a and Φ_b , cannot be treated as two independent states. Since Φ_a and Φ_b are coupled together the new coupled states, Φ'_c and Φ'_d , will be two states which are a linear combination of the states Φ_a and Φ_b . Φ'_c and Φ'_d can be denoted by

$$\Phi_c'(R) = a_c(R)\Phi_a(R) + b_c(R)\Phi_b(R)$$
$$\Phi_d'(R) = a_d(R)\Phi_a(R) + b_d(R)\Phi_b(R)$$

. where the coefficients a_c , b_c and a_d , b_d depend on the non-adiabatic coupling involved.

1.2 Predissociation

These non-adiabatic couplings bring about two interesting phenomena: predissociation and autoionization. Figure 1.3 depicts the mechanism for predissociation. As shown, predissociation is due to coupling of a bound state with either a dissociative state or another bound state that leads to a lower dissociative continuum. Since these states are coupled together the new state is a linear combination of the bound state and the dissociative state. Therefore a molecule that reaches the quasi-bound predissociative state can ultimately dissociate. This action is named predissociation. Figure 1.3 shows coupling of a bound state with a dissociative state in 3(a) and with another bound state



A - B Bond Length

Figure 1.3: Predissociation due to coupling of a bound state with i) (a) and (c) a dissociative state or ii) (b) and (d) a lower electronic state

that leads to a lower dissociative limit in 3(b). If the molecule is in any of the vibrational levels in case (a) or above the vibrational level n = 4 in case (b), it is above the dissociative limits of the lower level. Therefore, if we consider the combined states in figures 1.3(c) and (d) we can expect the molecule to tunnel through the small potential barrier between the two states and dissociate. Since predissociation requires the molecule to tunnel through a potential barrier it is a slower process than direct dissociation. Hence, there are finite lifetimes for predissociative states. Due to this, predissociative states support vibrational and sometimes rotational motion in the molecule.

1.3 Autoionization

Autoionization is another process very similar to predissociation. In this case the autoionizing bound state is coupled to an ionic state of the molecule. This autoionizing state is most often a Rydberg state converging to the ground ionic state (rotationally or vibrationally excited) or to an excited ionic state which lies above the ionization potential. A Rydberg state is a state in which only one electron is very highly excited. This electron is bound to an ionic core which may be the ground state of the ion or some excited electronic state. The molecule can be thought of as nominally hydrogen-like. If the ion core is vibrationally, rotationally or electronically excited, the Rydberg state may have enough energy to ionize. If it does ionize, the process is known as autoionization. The question is: what type of energy has to be transferred into kinetic



A - B Bond Length

Figure 1.4: Autoionization due to (a) rotational excitation (b) vibrational excitation energy of the outgoing electron for the molecule to be ionized. As shown in figure 1.4. in case (a) or (b) the autoionizing state is a Rydberg state leading to the ground ionic state. In situation (a) the molecule has rotational energy which puts it above the ionization continuum. If this rotational energy can be transferred into the outgoing electron, the molecule can be ionized. Similarly, in situation (b) the molecule has vibrational energy which can be transferred into the outgoing electron.

In figure 1.5 the ground ionic state is coupled to a Rydberg state leading to an excited ionic state, where the core is electronically excited. In a situation like this, the Rydberg electron can gain enough energy from the excited electron in the core to ionize and leave the ion in its ground states. This can leave



Figure 1.5: Electronic autoionization leading to many vibrational states in the ionic state

the molecule in any of the rotational or vibrational states below this energy. As can be expected, autoionization takes more time than direct ionization and therefore autoionizing states have finite lifetimes.

1.4 Resonance Enhanced Multiphoton Ionization

In our study we used Resonance Enhanced Multiphoton Ionization (REMPI) techniques to investigate the above mentioned processes and therefore the nonadiabatic coupling effects of photofragmentation processes in CO_2 . Resonance Enhanced Multiphoton Ionization. (REMPI), as the name suggests, is ionization due to absorption of more than one photon simultaneously. As can be expected this process calls for very high intense lasers. In addition to ionization in these experiments molecules can go through other processes such as dissociation, predissociation, and autoionization. In the present study we observed (3+1) REMPI spectroscopy of CO_2 where the molecule absorbed 3 photons simultaneously to reach a resonant intermediate state and then 1 more photon to get ionized. In REMPI it is the ions coming out of these reactions that is finally detected. A more complete discussion about REMPI will be given in Chapter 2 and the reader is referred to it for more details.

In our experiment we used CO_2 as our molecule of study for two major reasons. Firstly, CO_2 is a linear triatomic molecule made up of first row elements in the periodic chart which makes it important in the fundamental sense to compare with theory. The second reason is that it is a very important constituent in the atmosphere. It plays an important role in the life cycle, greenhouse effect, and combustion processes. CO_2 has been studied extensively in the past by numerous scientists and most of the lower states has been assigned but not without controversy. A review of these studies will be given in chapter 3.

In Chapter 4. a detailed description of the experiment and the set up will be discussed. In Chapter 5. the REMPI spectra of the nf Rydberg series in our study and how it compares to the results of previous experiments by other scientists will be discussed. Also a brief description of a new technique of obtaining lifetimes of highly excited ionic states utilizing saturated transitions will be given in this chapter. Chapter 6 will conclude this dissertation.

Chapter 2

Resonance Enhanced Multiphoton Ionization (REMPI) Spectroscopy

2.1 **REMPI** Experiment

Resonance Enhanced Multiphoton Ionization (REMPI) as the name suggests is absorption of more than one photon simultaneously by molecules or atoms and subsequent ionization. As can be expected this process requires a highly intense, monochromatic light source. In a very intense visible or UV light field, instead of just one photon, a molecule can absorb multiple photons to reach high lying excited electronic states. The molecule can then absorb additional photons to leave this resonant state and be ionized or dissociated. In the case of dissociation, the fragments may also subsequently be ionized. In REMPI experiments, it is these ions that are finally detected. The wavelength dependence of the ion signal holds a wealth of information about the electronic states and ionization and dissociation dynamics of the molecule. Absorption of multiple photons by atoms or molecules was predicted as early as in 1929 by the future Nobel prize winner Maria Gopert-Mayer [1]. Such an experiment could only be imagined at that time because of the lack of a proper intense monochromatic light source. In the 1960's, when the powerful Q-switched Ruby laser was discovered, Kaiser and Garrett carried out their famous experiment where Eu^{2+} doped into CaF_2 crystals produced ultraviolet fluorescence by absorption of red photons. [2]. The subsequent development of the tunable dye laser, particularly by Hänsch in the 1970s [3], served as the driving force behind much of the activity that has taken place in visible-UV multiphoton electronic spectroscopy over the last two decades. The multiphoton ionization technique, in particular, was developed independently by Dalby [4] and Johnson [5, 6] in 1975, and has made great contributions, particularly to the spectroscopy of molecular Rydberg states.

A schematic of a typical REMPI experiment is shown in figure 2.1. As can be seen it has a few major components: a powerful pulsed laser, a tunable dye laser pumped by the pulsed laser. a vacuum system which holds the molecules under study, an ion mass spectrometer, and an ion detector and the electronics to analyze the ion signal. The molecules are generally fed into a vacuum chamber by a direct line or a nozzle and the light from the dye laser is sent through a horizontal axis of this chamber. Usually a focusing lens is kept on the path of the laser to focus it to an intense spot at the reaction area. This increases the photon density at the point where the reaction occurs. Since the dye laser can



Figure 2.1: Schematic diagram of the REMPI experiment

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be tuned in wavelength the laser can be scanned across a certain energy region. While scanning, if a resonance state is present at the m-photon energy, the molecule can absorb m photons simultaneously to reach this resonant state. If the laser is still present it may absorb further photons to be ionized. For instance if the number of photons absorbed after excitation to the resonant state is n. then the above process is said to be an (m+n) REMPI process. Once the molecule is ionized it can absorb additional photons and be dissociated into fragment ions. In addition, instead of ionization after reaching the resonant state, it is possible that the molecule will dissociate and, if the laser is still present. these fragments may subsequently be ionized due to the absorption of more photons. Therefore, in addition to molecular ions there may also be ion fragments in the reaction area. In REMPI it is these ions that are detected. If the power density of the laser is P and the intensity of the ion signal is I then in the absence of saturation or dissociation the intensity of the ion signal will vary like $I \propto P^n$ where n is the number of photons absorbed in a given step. To find out the number of photons absorbed in the multiphoton transition a log plot of P and I can be made where the slope will give the number n. In general. it often deviates from this equation due to saturation effects and dissociation occurring in molecules. Nevertheless, a lower limit to the number of photons can be gained from this analysis.

In the experiment the detection of these ions can be done by applying a voltage across the reaction area. This voltage will make the ions accelerate
to the detector. Depending on the charge and the mass of the ions, they will gain different velocities due to the voltage and hence will reach the detector at different times. Therefore it is possible to detect the molecular and fragment ions separately. This is the principle behind the time-of-flight ion mass spectrometer. For more details on our particular experiment the reader is referred to Chapter 4 where a detailed account of the experiment performed at The University of Oklahoma is given.

2.2 Other Spectroscopic Experiments

In the past, two of the major techniques used to characterize electronic states were single-photon absorption and emission spectra. In absorption experiments the amount of light absorbed by the molecules is monitored with respect to the wavelength. Once the energy of the photons matches a resonant state of the molecule, there will be a lot of absorption leaving a dip in the spectra. Hence when scanning the laser one can get the energy levels of the molecule.

For some states the cross section for absorption of photons is very small. This makes the sensitivity of the above experiment low. The reason is that the intensity of the incoming and the outgoing light are large quantities but the difference will be small. One way to increase the sensitivity is by using path lengths which are very long, but this is not suitable for radicals which are made in small quantities or for molecules which cannot be obtained in large quantities. To overcome this problem, instead of measuring the outgoing light. the fluorescence from the excited states may be measured. The intensity of the fluorescence will give a direct measurement of the amount of energy that was absorbed by the molecules. Therefore, by observing the fluorescence one can map out the initial absorption to the excited state. This method is known as the fluorescence excitation spectroscopy or if excitation is made by a laser, it is known as laser induced fluorescence (LIF) spectroscopy.

In the above case the fluorescence is usually due to transitions to different lower states and will consist of different wavelengths. To separate these wavelengths the fluorescence can be made to go through a monochromator. Knowing these wavelengths the energy levels of the lower states can be found. This technique is known as emission spectroscopy. As can be seen different spectroscopic methods give different information about the molecules. In the following discussion I will summarize some of the advantages of REMPI spectroscopy.

2.3 Advantages of REMPI Spectroscopy

REMPI is a very sensitive technique as almost 100% of the ions from a REMPI process can be detected as all the ions can be directed towards a detector using a voltage. Due to this sensitivity, it can work at very low pressure. One major aspect of REMPI is that it can reach higher states due to absorption of multiphotons with high resolution. Therefore REMPI spectroscopy becomes very useful when studying colorless molecules.

Colorless molecules do not absorb visible light as single photons. The excited states of these molecules cannot be reached by single visible photon absorption since these states are at higher energies than that can be accessed by single visible photons. In the past these states were observed by either excitation due to synchrotron radiation which lies in the vacuum ultraviolet range or vacuum UV lamp and monochromator combination. The bandwidth of these light sources is not as narrow as the bandwidth of laser radiation. Therefore the resolution of these spectra are low compared to laser spectroscopy. Since most of the lasers are in visible or near UV range, REMPI spectroscopy becomes very handy in observing these state. In REMPI spectroscopy multiple photons are absorbed coherently to reach these high lying electronics states.

In most molecules, the first few electronic states lies far apart in energy from each other. Generally, after these states the energy difference between the other states become lesser and lesser. In other words density of states rises with energy. Therefore, in REMPI after the initial multiphoton step the subsequent steps are either single photon resonant transitions or nearly resonant transitions. Considering the laser intensities used in these experiment the subsequent steps are usually saturated. Hence, a REMPI spectrum follows the structure of the initial resonant state. Due to this, in an (m+n) REMPI process even though (m+n) photons are absorbed, the intensity varies with an exponent of m instead of (m+n).

In atomic and molecular transitions there are selection rules involved which

make some of the states more easily accessible than the others. An important difference about multiphoton absorption compared to single photon absorption is that they may have different selection rules. Therefore, some of the states that are forbidden in single photon spectra are allowed in multiphoton spectra. Even though these transitions are forbidden due to selection rules, in reality there still may be weak transitions if the intensity of the light source is powerful enough and if there is coupling between states. However, REMPI allows us to observe strong transitions to these electronic states which are not or barely observable in single-photon spectra. For example, if we consider a symmetric molecule with inversion symmetry, the wave functions are either even or odd functions known as gerade and ungerade and denoted q and u. In single photon spectra of a symmetric molecule. $g \Leftrightarrow g$ transitions are forbidden and $g \Leftrightarrow u$ transitions are allowed, but in two-photon spectra the $g \Leftrightarrow g$ transitions are allowed and $g \Leftrightarrow u$ transitions are forbidden. Therefore, in 2-photon spectra the excited gerade states can be observed. For example in one of Johnson et al.'s earlier experiments on butadiene [6], he observed strong two photon transitions in the wavelengths below 400 nm above the three photon ionization potential (see figure 2.2). These states are 2-photon allowed and single-photon forbidden transitions and they were barely visible in the single photon spectra. The only reason they were visible is because of the breaking of symmetry due to vibronic interactions.

Even though single-photon transitions have different selection rules than



Figure 2.2: Schematic diagram of (3+1) REMPI process of CO_2



Figure 2.3: (3+1) REMPI spectra of butadiene [6]

2-photon transitions, 3-photon transitions mimic them to a certain extent. Selection rules for 1. 2, and 3 photon transitions are tabulated in Table 2.1. In REMPI once the molecule reaches the resonant state it has to wait in that state for another photon to come along to be ionized. Since it is these ions that are detected the molecules that dissociate or fluoresce from this resonant state before the ionizing photon is absorbed will not appear in the REMPI spectra. Therefore, non-dissociating states are much stronger in REMPI spectra than states which dissociate prior to ionization. An example of this can be found in the same experiment by Johnson et al. on butadiene recalled above. In Johnson's REMPI spectra of butadiene in figure 2.3, some of the peaks seen above 420 nm in wavelength were not present in single photon spectroscopy. The peaks between 470 and 420 nm are all due to transitions to Rydberg states of butadiene. A Rydberg state is a state in which a single electron of the

	one photon	two photon	three photon	
$\Delta J: \text{ for } \Sigma \not \to \Sigma$	-1,0,1	-2,-1,0,1,2	-3,-2,-1,0,1,2,3	
for $\Sigma \rightarrow \Sigma$	-1,1	-2,-1,1,2	-3,-2,-1,1,2,3	
Δν	No	No	No	
۵۸	-1,0,1	-2,-1,0,1,2	-3,-2,-1,0,1,2,3	
g or u sym.	g <=> u	g <=> g,	g <=> u	
		u <=> u		
+ or - sym.	+ <=> +	+,• <=> +,•	+,- <=> +,-	
Allowed	p, f	s, d	p, f	
Rydberg series				
ΔS	0	0	0	

Table 2.1: Selection rules for one, two, and three photon transitions.

. .



Figure 2.4: Typical structure of a Rydberg state.

molecule has been excited to a very high energy level while the other electrons stay in their ground state. This puts the excited electron (Rydberg electron) far away from the rest of the molecule which can be treated as a core, see figure 2.4. This leads to a molecule that in some ways resembles a hydrogen atom in which the nucleus (a proton for hydrogen atom) has been substituted by the core. However, the molecular Rydberg states will be more complex than those of the hydrogen atom. For instance the core will have at least two nuclei and will rotate and vibrate. In addition there will be the core electrons to deal with. Nevertheless, these Rydberg states are more likely to be ionized by ejecting the highly excited electron than to be dissociated. By contrast, a valence state is a state in which more than one electron is excited. If one of these excited



Figure 2.5: (3+1) REMPI spectra of Benzene [5]

electrons is antibonding, these states are more like two atomic or molecular fragments bound together. Therefore, these states are more likely to dissociate than to ionize. Therefore, in REMPI spectroscopy you are more likely to observe Rydberg states than valence states. In an experiment on Benzene by Johnson et al. [5] (see figure 2.5), they were able to observe (2+1) REMPI spectra of the ${}^{1}\Sigma_{g}$ Rydberg state which was totally covered in single photon spectra by a huge valence state in the vicinity [6].

In addition, if a state is present in spectra of single photon absorption and is not present in REMPI spectra, information about the state's lifetime can be obtained. For instance, this state will either have a very short lifetime: it may be coupled to a dissociative state and therefore is a predissociative state which causes the molecule to dissociate before it gets ionized. For example some of the states seen in Cossart-Magos et al.'s single photon absorption spectra of CO_2 [7] were absent in Johnson et al.'s [8] (3+1) REMPI spectra. One of the states that was missing in the REMPI spectra was a $2p\pi_u^{-1}\Sigma_u^+$ which was actually coupled to a valence dissociative state. Hence, the dissociation rate of this state is presumed to be much higher than the ionization rate.

In the early days, REMPI spectroscopy was used mainly to discover and identify new electronic states. Now it is also used in studying the mechanics of photofragmentation and the effects of non-adiabatic coupling. In the presence of a high intense laser field, in addition to photoionization, the molecules undergo intense photodissociation. This was first experimentally observed by Zandee and Bernstein in 1979 [9]. When experimenting with Benzene (C_6H_6) in addition to observing Benzene ions, they observed C^+ ions. This is only possible if the Benzene is strongly dissociated. Even though the production of C^+ ions needed at least absorption of nine photons kinetically, they observed only an exponent of 3.5 in the power dependence. The reason was that after the initial multiphoton step, the subsequent steps were fully or partially saturated.

As seen above a wealth of information about excited electronic states can be gained by REMPI spectroscopy. In the present study we have used REMPI spectroscopy to study Rydberg states of CO_2 . As you go through the chapters you will be able to appreciate the amount of new information that can be gained through this technique on this molecule and its ionization and dissociation dynamics.

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Chapter 3

Experiments on CO_2

Carbon dioxide is an important constituent in our planet's atmosphere; also it plays a role in combustion processes and the greenhouse effect. In addition CO_2 is the principle atmospheric component on Mars and Venus and a thorough understanding of the molecule is crucial to studying these atmospheres.

In this chapter, I will give an overview of the experiments done on CO_2 up to this date. This will be divided into two sections. In the first section the early experiments on CO_2 will be discussed and in the second section more recent studies on the molecule will be dealt with.

3.1 Early Experiments

 CO_2 has been studied extensively by numerous experimentalists and theoreticians at least for the last 60 years. Despite this fact there are many controversies in the assignments of its spectra and disagreements about its dissociation and ionization mechanisms.



Figure 3.1: Vibration modes of CO_2 .

The ground state of CO_2^+ has linear geometry and it belongs to the $D_{\infty h}$ symmetry group. Its ground state electronic configuration is given by

 $\dots (3\sigma_g)^2 (2\sigma_u)^2 (4\sigma_g)^2 (3\sigma_u)^2 (1\pi_u)^4 (1\pi_g)^{4-1} \Sigma_g^+$

The ground ionic state of CO_2 is a ${}^{2}\Pi_{g}$ state. Therefore it has a net spin of 1/2 and a projection of the electronic orbital angular momenta on the internuclear axis. λ , of 1. Depending on how the spin and the orbital angular momentum add up will lead to two spin-orbit limits with total angular momentum on the internuclear axis. $\Omega = 3/2$ and 1/2, with different energies. The energy splitting for these states is about 160 cm⁻¹ and of the two limits. $\Omega = 3/2$ has lower energy.

Since CO_2 has 3 atoms it has 3 vibrational modes, as shown in Figure 3.1. These are the symmetric stretch mode, ν_1 , the bending mode, ν_2 , and the asymmetric stretch. ν_3 , with frequencies of 1244.27, 511.35 and 1423.08 cm^{-1} respectively [1, 2].

3.1.1 Spectra of CO_2 (first bands of CO_2)

 CO_2 is transparent in the visible and near UV regions. The first few absorption bands are reviewed by Rabalais et al. in his paper in 1971 [3]. The first absorption peak observed is around 1900 Å. This first structureless peak in the spectrum is barely visible and is assigned by Rabalais to a forbidden transition ${}^{1}\Sigma_{u}^{-} \leftarrow {}^{1}\Sigma_{g}^{+}$. The second band, observed around 1475 Å is weak and has a complex vibrational structure. Gardner and Kasha assigned it to the transition. ${}^{1}\Delta_{u} \leftarrow {}^{1}\Sigma_{g}^{+}$, which is weakly allowed by the first order vibronic coupling. This explains the weakness and the complexity of the band [4]. A third band around 1332 Å with seemingly simple vibrational structure was observed by Price and Simpson [5] in 1932. They assigned the upper level of this band to a Π_g state. Even though the vibrational structure seemed simple, the intervals between the vibrational peaks were irregular, which made the assignment of them non-trivial. According to Price and Simpson these bands consist of two progressions in the symmetric normal mode, ν_1 , but Rabalais et al disagreed with this assignment. They suggested that the upper state ${}^{1}\Pi_{g}$ is slightly bent and that the vibration in question belongs to the bending mode ν_2 . The irregularity of the vibration was suggested to be due to the interaction of vibrational and rotational angular momenta due to the slight bending of the state. The

next absorption band seen is around 1120 Å and was assigned to the transition ${}^{1}\Sigma_{u}^{+} \leftarrow {}^{1}\Sigma_{g}^{+}$ by Inn et al. [6] in 1953. Embedded in this band were some sharp peaks that were assigned to Rydberg states ${}^{1}\Pi_{g}$. From the progression of these Rydberg states Inn et. al determined the first ionization potential to be at 13.8 eV. This value was later revised and will be discussed in the next section.

3.1.2 Photolysis of CO_2

In addition to spectra, photolysis of CO_2 has also been studied intensively by numerous scientists. In the early stages the major concern in these studies was the quantum yields of the photolysis products, oxygen and carbon monoxide. For photolysis wavelengths longer than 1082 Å the allowed dissociation product channels are

$$CO_2 \xrightarrow{h\nu} CO({}^{1}\Sigma^{+}) + O({}^{3}P) \quad \lambda < 2275 \mathring{A}$$
(3.1)

$$CO_2 \xrightarrow{h\nu} CO({}^{1}\Sigma^{+}) + O({}^{1}D) \ \lambda < 1671 \mathring{A}$$
(3.2)

$$CO_2 \xrightarrow{h\nu} CO({}^{1}\Sigma^{+}) + O({}^{1}S) \ \lambda < 1286 \mathring{A}$$
(3.3)

Table 3.1, taken from Ashfold et al. [7], gives a listing of the energies needed to access other channels. For wavelengths longer than 1082 Å, excited states of CO are not energetically accessible and photolysis of CO_2 can be divided into three different regions depending on the accessible dissociation continua. According to equation (3.1) the first dissociation limit of CO_2 lies at 2275 Å which leaves both the O and CO in their ground states, ${}^{3}P$ and ${}^{1}\Sigma^{+}$ respectively. The second continua begins at 1672 Å which leads to O in its first excited state

CO ↓		$O \rightarrow {}^{3}P_{2}$ (0.00)	¹ D ₂ (1.97) ^b	'So (4.19) ⁸	
x'z*	(0.00)	(5.4\$3) ^c 227.5	(7.42) 167.1	(9.64) 128.6	<u></u>
a ³ 11	(6.01) ^a	(11.46) 108.2	(13.43) 92.3	(15.65) 79.2	
¢,3∑+	(6.86)^a	(12.31) 100.7	(14.28) 86.8	(16.50) 75.1	
ď۵	(7. 52) ª	(1 2.97) 9 5.6	(14.94) 80.9	(17.16) 70.7	
4 <u>7</u> 2-	(7.90) ^a	(1 3.48) 92.0	(1 5.45) 80.3	(17.67) 70.2	
A ¹ Π	(8.03) ⁸	(13.59) 91.2	(1 5.56) 7 9. 7	(17.78) 69-8	

Table 3.1: Threshold energies for primary product channels in the photodissociation of CO_2 (upper values, in brackets, are in electron volts, lowere values are in nanometers) [7]

¹D and CO in its ground state (Equation (3.2)). Therefore the first region in photolysis studies is assigned to the region between these two limits of the continua. In this region the only accessible path leaves O and CO in their ground electronic states.

The third dissociation continuum begins at 1286 Å in which the O atom is left in the ¹S state and CO in the ground state. This basically defines the second region in the photolysis studies 1672 Å - 1286 Å where both ³P and ¹D states for the O atom is energetically possible. The third region is for wavelengths below 1286 Å and in this region all three states ³P. ¹D and ¹S are allowed.

Above 1672 Å

In region one the photolysis reaction can be written as $CO_2 \xrightarrow{h\nu} CO + O({}^3P)$. In this region, from their photoabsorption studies Demore and Mosesman [8], in 1971, determined a quantum yield of 1 for the above process by monitoring the $O({}^3P)$ yield. However, when CO and O_2 (O_2 from the reaction $O({}^3P) + O({}^3P) + X \rightarrow O_2 + X$), were monitored, quantum yields of less than the limiting values 1 and 0.5, respectively, were measured. They obtained O_2/CO ratio of 0 to 0.4, depending on the wall conditions, which is less than 0.5 expected. Later, in 1970, Slanger et al. [9] established that the reason for this is due to heterogeneous processes occurring on the cell wall subsequent to the production of $O({}^3P)$. Inn and Heimerl [10] and Krezenski [11] and co-workers measured a quantum yield of 1 for CO at 1750 to 2100 Å and 1849 Å respectively.

1200 to 1672 Å Region

In the second region between 1286-1672 Å both ${}^{3}P$ and ${}^{1}D$ states for O are energetically accessible. The reaction expected is [12]

$$CO_2 \xrightarrow{h\nu} CO + O({}^1D) \lambda = 1200 - 1620 \mathring{A}$$
(3.4)

$$O(^{1}D) + CO_{2} \xrightarrow{h\nu} O(^{3}P) + CO_{2}$$

$$(3.5)$$

$$O(^{3}P) + O(^{3}P) + X \xrightarrow{h\nu} O_{2} + X$$
(3.6)

In this region, even though $O({}^{1}D)$ is the initial product it is not possible to observe it directly using resonance fluorescence spectroscopy, which is the method used in these experiments. There are two reasons: one is that $O({}^{1}D)$ has a very long radiative lifetime, and the second is that it undergoes very rapid quenching from CO_2 by means of reaction (3.5). Collisions with CO_2 molecules cause $O({}^1D)$ atoms decay to $O({}^3P)$ before they can radiate to the ground state [13]. In 1968. Slanger et al. determined that this process is 100% efficient [14]. Thus in most experiments the $O({}^3P)$ state was detected, instead of the $O({}^1D)$ state. Unfortunately, this method cannot distinguish between $O({}^3P)$ formed by reactions (3.1) and (3.5). Similar to region 1, up to 1966, the ratio O_2/CO was found to be far less than 0.5 expected [15, 16], indicating a lack of O_2 . In 1966, Slanger in their absorption studies reported that this lack of O_2 was again due to $O({}^3P)$ reacting with the surface of the vessel that causes the deficiency in O_2 , and that proper treatment of the vessel walls resulted in the expected O_2/CO ratio of 0.5 [17]. In 1971, in another paper Slanger et. al also showed that the quantum yield for reactions (3.4) and (3.5) are both unity indicating the wall reactions occurred after the formation of $O({}^3P)$ [13].

The next problem in this region came up when Sach [18], Inn [19] and Slanger [20] determined an absolute quantum yield for CO (absolute CO production) of less than 1, which indicated that the quantum yield for reaction (3.5) is not unity which is inconsistent with $O({}^{3}P)$ yield of 1. Subsequently, in 1977. Slanger et al. [12] measured the $O({}^{3}P)$ yield which again turned out to be 1. He then compared the O/CO ratio which turned out to be the same for two different wavelengths which indicated that the quantum yield of CO too is one. These results indicate unit quantum efficiency for photodissociation of CO_2 at all wavelengths above 1286 Å.

Below 1200 Å

In the photolysis reaction of CO_2 in region 3 between 1060 - 1200 Å there is enough energy for the O atom to reach the ${}^{1}S$ state in addition to ${}^{1}D$ and ^{3}P states. In 1972, Lawrence stated that the quantum yield for the reaction $CO_2 \longrightarrow CO + O(^1S)$ was unity throughout the region 1060 - 1150 Å [21]. whereas. in 1975. Koyano et. al [22] observed an abrupt dip in the quantum yield that starts at 1095 Å. This dip was also observed by Slanger et al. [23] in 1977, when monitoring the emission from the transition $O({}^{1}S) \rightarrow O({}^{1}D)$ and was found to center around 1089 Å. Within this dip the preferred channel was found to be $CO(^{1}S) + O(^{1}D)$ with a maximum quantum yield of 0.65. They explained that it is due to a Rydberg state, ${}^{1}\Pi_{u}$, that lies exactly in the same wavelength region [23]. The reason for this is shown by the correlation diagram in Figure 3.2, taken from Ashfold et al [7]. At 1089 Å wavelength there is enough energy for the molecule to reach the ${}^{1}\Pi_{u}$ Rydberg state, but this state only correlates to two channels that leads to O atom in ${}^{3}P$ or ${}^{1}D$ states. Therefore when this Rydberg state is accessed the $O(^{1}S)$ channel is not preferred. This causes the dip in the emission spectrum. The reason why $O(^{1}D)$ channel is preferred to $O(^{3}P) + CO(a^{3}\Pi)$ is because at 1089 Å the latter reaction is endothermic. This causes a higher population of $O({}^{1}D)$.

Going down to wavelengths below 1286 Å Gilpin and Welge [24]. in 1971.



Figure 3.2: Adiabatic singlet electronic state correlation diagram for CO_2 dissocciation [7].

observed a time-of-flight spectrum of $O({}^{1}S)$ for wavelengths 1050 - 1160 Å. They observed it to be broad, which indicates vibrational and rotational states of the $CO({}^{1}\Sigma^{+})$ electronic state. Slanger et al., in 1977, established that $O({}^{1}S)$ atoms were produced solely by dissociation of CO_{2} in ${}^{1}\Sigma_{u}^{+}$ state (see figure 3.2).

Lawrence [21], in 1972. did a study on photolysis using wavelengths between 850 - 1090 Å. In this region there is enough energy to access the first excited state of CO. $(a^{3}\Pi)$. In his study he observed the emission from $CO(a^{3}\Pi) \rightarrow$ $CO(^{1}\Sigma^{+})$. known as the Cameron band. The fluorescence from $CO(a^{3}\Pi)$ was zero at threshold but was found to increase monotonically to a maximum of 0.5 at the first ionization potential at 901 Å. In another study by Slanger. in 1978. a quantum yield of unity for CO, and a quantum yield of 0.60 ± 0.06 for $O(^{1}S)$ at 1067 Å was determined [25]. From Lawrence's experiments quantum yield for $CO(a^{3}\Pi) \sim 0.05$ [21], therefore indicating a quantum yield of 0.35 for $O(^{1}D)$.

Going even further down in wavelength to 764 - 923 ÅJudge and Lee [26] observed visible emission from other triplet states of CO. $a'^{3}\Sigma^{+}$. $d^{3}\Delta$ and $e^{3}\Sigma^{-}$. They also determined a higher yield of triplet CO than Lawrence. By analyzing the emission from the excited CO states $a^{3}\Pi$. $a'^{3}\Sigma^{+}$. $d^{3}\Delta$ [27] and $A^{1}\Pi$ [28] the accessed vibrational states were determined. Later in 1978. in a theoretical study using Franck-Condon and half collision considerations by Band and Freed [29, 30], these vibrational distributions were reproduced except for the ones belonging to the $a^{3}\Pi$ state. This was attributed to contributions from predissociative states at the relevant energies. At even shorter wavelengths (down to 700 Å) $CO(A^{1}\Pi)$ too was detected by three different groups [31, 32, 33] and it was observed that the production of $CO(A^{1}\Pi)$ increased with shorter wavelengths and that photodissociation competes with photoionization, since these wavelengths reach the ionization continuum.

Above the ionization potential, it is well established that the lowest ionic states are $X^{2}\Pi_{g}$, $A^{2}\Pi_{u}$, $B^{2}\Sigma_{u}^{+}$ and $C^{2}\Sigma_{g}^{+}$ due to removal of electrons from $1\pi_{g}$, $1\pi_{u}$, $3\sigma_{u}$ and $4\sigma_{g}$ respectively from the ground state of CO_{2} .

 $\dots (3\sigma_g)^2 (2\sigma_u)^2 (4\sigma_g)^2 (3\sigma_u)^2 (1\pi_u)^4 (1\pi_g)^{4-1} \Sigma_g^+.$

Figure 3.3 shows the threshold energies of these states. The ground ionic state, $X^2\Pi_g$ is split into two components due to spin-orbit interactions. The energy difference between these components, $X^{-2}\Pi_{3/2}$ and $X^{-2}\Pi_{1/2}$, is ~ 160 cm^{-1} . Out of these two states the $X^{-2}\Pi_{3/2}$ has lesser energy according to Hünd,s rules. The above mentioned excited ionic states have been studied extensively by fluorescence spectroscopy [34, 35] and photoelectron spectroscopy [36, 37, 38, 39]. The $A^{-2}\Pi_u$ state was found to have a considerably larger bond length, C - O, (1.2274 Å) than the $X^{-2}\Pi_g$ state (1.1769 Å). Due to this strong symmetric vibrational activity was found in the $A^{-2}\Pi_u \rightarrow X^{-2}\Pi_g$ fluorescence spectroscopy [35]. It was also found that this state couples to the $X^{-2}\Pi_g$ state via the asymmetric vibrational mode [40]. However, the $B^{-2}\Sigma_u^+$ and the $C^{-2}\Sigma_g^+$ ionic states have bond lengths that are closer to the bond length of the ground ionic state. Therefore, the fluorescence spectra via $B^{-2}\Sigma_u^+ \rightarrow X^{-2}\Pi_g$ show a



Figure 3.3: Energy level diagram of $X^{2}\Pi_{g}$. $A^{2}\Pi_{u}$. $B^{2}\Sigma_{u}^{+}$ and $C^{2}\Sigma_{g}^{+}$ states [74].

strong 0 - 0 vibrational transition. From the vibrationless ground state of CO_2 transitions to odd levels of ν_2 and ν_3 vibrations of the X ² Π_g state are strictly forbidden in the Born-Oppenheimer approximation [41]. However, these levels have been observed in various experiments [21, 36, 37, 38, 42, 43, 44, 45, 46, 47]. The reason for these observations was said to be due to coupling of the X ² Π_g ionic state to the B ² Σ_u^+ state via the ν_2 bending vibration [38, 42, 46, 47] or due to coupling with bent superexcited valence states [44, 46, 47, 48]. Fluorescence from the C ² Σ_g^+ ionic state has not been observed and it was deduced that this state is completely predissociated.

The Rydberg states leading to these ionic states have been observed in the past. The Rydberg states leading to the ground ionic state, $X^{2}\Pi_{g}$, were the last to be observed and will be discussed in section 3.2 of this Chapter and in Chapter 5. The Rydberg states leading to the $A^{2}\Pi_{u}$ ionic state was observed by Tanaka and Ogawa [49] and is named Tanaka-Ogawa series. This series was tentatively assigned to a transition of the $1\pi_{u}$ electron to $ns \sigma_{g}$ orbital [50, 51]. Two Rydberg series have been assigned as Rydberg series leading to the $B^{2}\Sigma_{u}^{+}$ ionic state due to electronic transitions of the $3\sigma_{u}$ electron to $nd\pi_{g}$ and $ns \sigma_{g}$ orbitals. These were observed by Henning [49, 52] and assigned by Fridth et al.[51]. These series are known as Henning sharp and Henning diffuse series. respectively. However, the assignment of the sharp series was questioned by two studies afterwards [53, 48]. Three Rydberg series leading to the $C^{2}\Sigma_{g}^{+}$ ionic level have been reported. These three, known as Tanaka-Jursa-LeBlanc

absorption, weak absorption and emission series, are due to the excitation of the $4\sigma_g$ electron. Single-photon absorption studies of these Rydberg series have shown that these states undergo extensive competing processes between electronic autoionization and dissociation [44, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66].

3.2 Recent studies on CO_2

3.2.1 Single Photon Absorption Studies

Cossart-Margos et al.. in 1982, did gas phase absorption spectra of CO_2 between 880 - 2000 Å with a resolution of 0.008 Å[67, 68]. In this region the only state that was rotationally resolved was at 1106 Å and was assigned to $...3p\pi_u {}^{3}\Sigma_{u}^{1}$ Rydberg state. Prior to this work, the only other state that has been rotationally analyzed was by Dixon [69] in the emission band corresponding to a transition from the lowest bent state.

Cossart-Margos et al. later analyzed and assigned the rest of the bands in the spectra in the region between 898 - 1145 Å[68]. They carried out Hartree-Fock calculations in the Frozen-Core-approximation to assign the lower Rydberg states of the s, p, d and f series converging to the ground ionic state of CO_2 . $X^2\Pi_g$.

In single photon absorption processes s and d Rydberg states are forbidden by one and three photon transitions, but a few diffuse states were observed

for principal quantum number, $n \leq 4$. In the p series, except for the above mentioned sharp state, the others were diffuse. This was explained as due to the interaction of these states with dissociative valence states. This would lead to predissociation and make the lifetime of the state short. If the lifetime of the state is shorter than the rotational period, the spectrum will show no rotational structure. In other words, if the lifetime is short the uncertainty in energy is large according to Heisenberg's uncertainty principle $\Delta E \cdot \Delta t \geq \hbar/2$. Therefore, the rotational states will be diffuse in the spectrum. The np Rydberg series splits into two series: $np\sigma$ and $np\pi$, depending on the projection of the p orbital angular momentum on the internuclear axis. Interactions with the molecular core then results in an energy difference between these series. Prior to these experiments there was a long standing controversy as to which of these series lie higher in energy: whether its the $np\sigma$ series or the $np\pi$ series. Lindholm [70]. in 1968, based on his experience with diatomic molecules, placed the $np\pi$ series at a higher energy than the $np\sigma$ series. Later Foo et al. [71], in 1971, working on energy-loss spectra adopted the same placing. Betts et al. [72], in 1983. calculated the above order for the two series. On the other hand McDiarmid et al. [73], in 1984, in a study of electron energy loss spectra and a comparison with the analysis done on their previous studies on the molecule CS_2 (which is analogous to the CO_2 molecule), concluded that the ordering of the states should be reversed. [73] Cossart-Margos and co-workers, according to their single-photon spectra and *ab initio* calculations, agreed with McDiarmid et al.

and placed the $np\sigma$ series at a higher level than $np\pi$.

Nevertheless Cossart-Margos and her group [68] disagreed with McDiarmid et al.'s [73] assignment of the nd series and assigned them to the $nf^2\Pi_g$ series. Unlike McDiarmid's short of series (n = 3..7). Cossart-Magos observed the of series for n = 4 to 28 and 32 respectively for the two spin orbit limits, $\Omega_c = 3/2$ and 1/2 respectively. In view of the fact that in single-photon absorption the nd Rydberg series is not allowed in the dipole approximation and the nf series is, it is reasonable to assume that the above mentioned series is the nf Rydberg series. In addition to this, they also observed the spin-orbit splitting to be about $160 \, cm^{-1}$ which is also the energy difference between the two spin-orbit limits of the ground state of the CO_2 ion $X^2\Pi_g$, which has the same configuration as the core of the nf Rydberg states. However, from this nf series. Cossart-Magos. deduced a new revised value for the first ionization potential, $111201 \pm 2 \ cm^{-1}$. In Cosart-Magos' spectra, the nf series had sharp features in their rotational contours. unlike the np series, indicating longer lifetimes. This meant that these states were relatively free from interference by the other states and therefore free of processes such as predissociation.

3.2.2 REMPI and REMPI-PES Studies

Johnson et al.'s studies

Between 1989 - 1992 Johnson and his coworkers performed a number of studies on CO_2 [[[77-81]. Their technique was (3+1) Resonance Enhanced Multiphoton Ionization (REMPI) spectroscopy. In a (3+1) REMPI process, 3 photons are absorbed coherently to the resonant state first, then one more photon is absorbed to reach the ionization continuum. It is the ion that is finally detected in REMPI spectroscopy. In their study of CO_2 the range of the photon wavelengths were from 2750 Å to 3380 Å. These energies correspond to 916 - 1127 Å range in single-photon absorption spectra. In REMPI the molecule has to be in the resonant state long enough to absorb more photons to get ionized, therefore, only the stable states are visible in this spectroscopy. Another highlight of REMPI is that it can detect the photodissociated products of the molecule under study if they undergo ionization while been photodissociated or if the dissociated products absorb photons and then get ionized. In Johnson's group's study in addition to CO_2 they observed its photodissociated products CO^+ and O^+ .

Johnson and coworkers agree with Cossart-Magos et al.[68] in the assignment of the spectra. However, some of the peaks visible in the Cossart-Magos spectra were not seen in their spectra and other additional peaks were [74]. In the pRydberg series, the $3p\pi_u^{-1}\Sigma_u^+$ state seen in Cossart-Magos, spectra were not observed in REMPI spectra but additional peaks were observed at 3330.3 Å and 3337 Å (single photon 1110.2 Å and 1113.5 Å) and were assigned to the two spin-orbit components of $3p\pi_u^{-1}\Delta_u$. Johnson et al. suggested that the reason for not seeing the $3p\pi_u^{-1}\Sigma_u^+$ state is because it is interacting with a dissociating valence state and that the dissociation rate is much higher than the ionization rate. Whereas the additional state $3p\pi_u \, {}^1\Delta_u$ seen in REMPI is explained by a 3-photon transition and not by a single photon transition.

In addition to the p states mentioned above. Johnson and his coworkers observed both the components $\Omega = 1/2$ and 3/2 of the nf series for n = 4 and 5 separated by ~160 cm^{-1} , agreeing very well with Cossart-Magos' spectra. Johnson et al. were able to monitor this spectra by observing the CO_2^+ ions as well as their fragmented products CO^+ ions for both n = 4 and 5. In addition they did a laser power dependence study on the 4f and 5f states to find out the number of photons absorbed to be ionized. In principal with no saturation or intermediate resonances affecting the intensity, the power dependence curves should follow the equation $I \propto P^n$ where I is the intensity of the ion signal, Pis the laser power and n is the number of photons absorbed. If dissociation and predissociation processes are important, then this power dependence will not hold and only an effective exponent can be derived from the above equation by plotting log of I and log of P.

According to their power dependence study. Johnson et al. [74] observed a consistently higher effective n for CO^+ than for CO_2^+ . From this data, they deduced that CO^+ ions are predominantly produced by dissociation of CO_2^+ ions after these are formed and not by the other two methods, namely dissociation occurring simultaneously while ionization or ionization subsequent to dissociation. As you will see later the above conclusions about dissociation were continually evolving.

In addition to the nf states, Johnson and coworkers also observed seven very sharp peaks to the high energy side of 4f and 5f states. In their second paper, they attributed these to autoionization from the 4-photon resonant states belonging to Rydberg series converging to the A and B ionic states [75]. The unusual strength of these lines were suggested to be due to a coincidence of the $B \leftarrow X$ transition with the photon energy. This attribution, however, was later disputed by another group, and will be discussed later.

Johnson and his coworkers also did a theoretical analysis of the 4f spectrum and fitted their data to a rotational contour [75]. In this analysis they ignored the singlet-triplet splitting, which is a good approximation for a completely decoupled Rydberg electron, and came out with a rotational contour that fitted the data very well. From this they concluded that in the nf series, the Rydberg electron was very detached from the rest of the molecule.

In 1991 Johnson et al. did a REMPI-Photoelectron Spectroscopy (REMPI-PES) via 3p. 4f and 5f Rydberg states of CO_2 [76]. In REMPI-PES experiments the wavelength of the incoming light is fixed at a resonance peak (in this case 3p, 4f or 5f) and the electrons coming out from the ionization process are monitored. By measuring the kinetic energy of the electrons the ionic states that are reached can be determined by the equation:

 $E = nh\nu - K.E.$

Here, E is the energy of the final ionic state, n is the number of photons absorbed, $h\nu$ and K.E. are the photon energy and the electronic kinetic energy respectively. This process is shown in Figure 3.4.

Figure 3.5 shows the kinetics occurring in REMPI-PES in Johnson et al.'s study. According to the figure when the experiment is done via the 4*f* Rydberg state there is enough energy to reach the ground ionic state with 4-photons but not to any other excited states of the ion. Nevertheless in the REMPI-PES spectra Johnson et al. observed two bands they assigned to the X and C electronic states of the ion. This was revised later by another group and will be dealt with later in the next section. However, going along Johnson et al.'s arguments, to reach the C ionic state it requires an absorption of at least five photons, which requires absorption of photons above threshold. Since Johnson and coworkers used low laser powers they eliminated the possibility of this occurring due to conventional ATA processes or due to Ponderomotive force. These two processes will be explained in the next two paragraphs respectively.

ATA Process: In a strong laser field sometimes molecules absorb additional photons above the ionization threshold in a coherent manner. In this process photoelectrons are produced with discrete kinetic energy with an energy difference of the input photon energy in the spectra. This process is known as Above Threshold Ionization or Absorption (ATI or ATA). This process is shown in Figure 3.6.

Ponderomotive Force: A strong laser field can be considered an oscillating electromagnetic field. Due to this field an electron in the ionization continuum



Figure 3.4: Schematic diagram of REMPI - PES process of CO_2 : the kinetic energy of the photoelectron depends on the final state.



Figure 3.5: Energy levels of CO_2 and CO^+ reached in (3+1) REMPI spectra [74].



Figure 3.6: ATA process. The potential energy curves are not actual curves of CO_2

can be considered a particle moving under a conservative force with a potential energy function which is called the Ponderomotive potential. This potential delays the removal of the electron from the molecule and allows more time for absorption of additional photons. Nevertheless this force is negligible for weak fields.

Johnson et al. explained that above-threshold absorption is due to the molecule undergoing resonance with autoionizing states. Since these states are relatively long-lived the molecule can absorb more photons to reach the ionic excited states. To distinguish this process from the other two processes mentioned above, they called it the Resonance Enhanced Above Threshold Absorption (REATA) process [76].

In a paper in 1991, Johnson et al. stated another surprising feature they observed in their REMPI-PES spectra [77]: long vibrational progressions belonging to X. B and C ionic states, which are very surprising considering the Franck-Condoon principle. The Franck-Condon principle states that the absorption of a photon occurs very rapidly, so there is not enough time for the nuclei to rearrange during the transition period. Therefore the transition rate is proportional to the overlap of the initial, $\langle \Psi_v^i \rangle$, and the final, $| \Psi_v^f \rangle$, vibrational wavefunctions, $\langle \Psi_v^i | \Psi_v^f \rangle$. The ground ionic state of CO_2^+ , $X^2\Pi_g$, and the $nf^2\Pi_g$ Rydberg states leading to it have very similar potential energy curves and therefore, the vibrational states will look very similar in these states. Since, in a given electronic state different vibrational states are orthogonal to each other, if the potential curves are very similar, the Franck-Condon overlap between the nf state and the ground ionic state, $\langle \Psi_v^i | \Psi_v^f \rangle$, will nearly be orthogonal. Due to this, one would expect the transition starting from the ground vibrational level of the Rydberg state to be predominantly to the ground vibrational level of the ground ionic state of CO_2^+ . Similarly the first vibrationally excited state of the resonance state to lead to the first vibrationally excited state of the ionic state, and so on. In view of this, long vibrational progressions observed in the PES spectra were unexpected.

When observing REMPI-PES spectra via 3p states. Johnson and his coworkers observed symmetric and asymmetric vibrational progressions belonging to the ground ionic states, X, and in the PES via the 4f state they again saw asymmetric vibrational progressions which they attributed to the ground ionic state. X, and symmetric vibrational progressions which they attributed to the C ionic state. They also observed that the PES peaks corresponding to the C states are enhanced when tuned to the sharp peaks which were assigned to autoionizing states to the high energy side of the 4f states. This agrees well with their argument about the REATA processes, since REATA processes are additional absorption of photons from autoionizing states. However, Johnson et al.'s assignments of the vibrational levels of the C state were later disputed by Dobber et al.[79] and will be discussed in the following section.

When resonant with the 5f Rydberg state. the 4-photon transition to the X state and the 5-photon transition to the B state give out electrons with similar
kinetic energies [77]. Due to this and the low resolution of their experiment Johnson et al. did not assign the PES spectra via the 5f Rydberg states. Nevertheless they mentioned the possibility of a new CO_2^+ state based on analysis of the PES spectra via the 5f states. They also observed that this new state is enhanced when PES spectra are observed via the sharp autoionizing peaks to the high energy side of the 5f states.

Photofragmentation studies by Johnson et al.

Photofragmentation of CO_2 is an interesting subject in itself. In their paper that came out in 1991 April, Johnson et al. [77], considering the unexpected vibrational progressions in their REMPI-PES spectra, suggested that the dissociation and ionization of CO_2 occurs simultaneously. They explained that the 3-photon resonance state is mixed with a dissociative valence state, therefore altered the Franck-Condon factors between the 3-photon intermediate state and the final ionic state. This contradicted their initial conclusion about CO^+ ions been produced by dissociation of CO_2^+ , which came from the power dependence study of CO^+ and CO_2^+ ions in their first paper in this series [74].

Later, in October 1992, Johnson's group, in a quest to find out the level (3photon or 4-photon level) at which the dissociation occur, collected REMPI-PES spectra for different laser intensities [78]. They argued, assuming the dissociation occur at the 3-photon level, that for high laser power the molecule will not stay too long in the 3-photon level before another photon comes along and gets absorbed. Therefore it will not evolve too far in this predissociative state and hence will not affect the Franck-Condon factors very much. Whereas for low laser power the molecule will have to wait longer for the next photon to be ionized. Therefore for the lower laser powers a longer vibrational progression is expected compared to higher laser powers. Nevertheless in their experiment they observed similar vibrational profiles for all the different laser powers used. From this observation they concluded that the dissociation occur at the 4 or 5-photon level instead of at the 3-photon level. This disproved their earlier model where they said a dissociative state coupled to the intermediate state causes the long vibrational progressions.

As a result, Johnson and coworkers suggested that for 3p, 4f and 5f states, autoionization was the cause of the vibrational progressions and also that autoionization dominates direct ionization. This conclusion was made considering the long vibrational progressions observed in their PES spectra [78] as in direct ionization one expects only one vibrational level, corresponding to the selection rule $\Delta \nu = 0$. However, for autoionization to dominate direct ionization, strong oscillator strengths for transitions to autoionizing states are required. Strong oscillator strengths are expected because of accidental resonances with A $\leftarrow X$ transitions when the intermediate state is 3p and with B $\leftarrow X$ when 4f and 5fare the resonant intermediate states. From this it can be inferred that there will be strong oscillator strengths for transition from Rydberg states leading to X with Rydberg states leading to A and B ionic states. They also concluded that there was relatively strong coupling of these Rydberg autoionizing states with neutral dissociative states from the long asymmetric stretching progressions observed in the photoelectron spectra.

The studies of Dobber et al.

More recently. in 1994. another group, Dobber et al. [79] used the same technique. REMPI-PES to study CO_2 with higher resolution than Johnson and coworkers. In their REMPI spectra they observed the $({}^{2}\Pi_{\frac{3}{2},\frac{1}{2}})nf$ Rydberg series for n = 4 - 13 while REMPI-PES spectra was observed for n = 4 - 7. Their spectra agree very well with Cossart-Margos assignments. When comparing REMPI spectra with Johnson et al.'s spectra there were some discrepancies. Johnson et al. stated that they did not observe CO_{2}^{+} ions in the nf series for n larger than 5 whereas in Dobber et al.'s study they observed CO_{2}^{+} . CO^{+} and O^{+} for all the n's up to 13. Nevertheless, Dobber's group observed the CO_{2}^{+}/CO^{+} ratio to decrease with increasing n but the CO^{+}/O^{+} ratio to stay nearly constant for all nf states. They also observed C^{+} ion spectra which looked like the structure of the nf resonances only to a very limited extent.

Dobber and his coworker's also studied the nf series with nano and picosecond lasers. They found the spectra to look the same for both the situations. The only difference they observed was the ratio of CO_2^+ : CO^+ : O^+ which yielded typical values of 0.13 : 0.73 : 0.14 for the nanosecond laser and 0.50 : 0.35 : 0.15 for the picosecond laser. This indicates that there is much less fragmentation for the picosecond laser.

There was another major disagreement between the studies of Johnson et al. and Dobber's group in assigning the sharp features to the high energy side of 4fand 5f Rydberg states. Johnson and coworkers assigned them to autoionizing states of CO_2 but Dobber assigned them to Carbon ions, for the reasons given below. Dobber and coworkers also concluded that at least 90% of these C^+ ions were produced by dissociation of organic molecules, such as are found in pump oil, and only about 10% was due to dissociation and ionization of CO_2 . The reasons for assigning these peaks to C^+ ions are:

- 1. They fall exactly on the transition $2s^2 2p^2 {}^3P^e_{0,1,2} \rightarrow 2s^2 2p 3p^3 D^e_{1,2,3}$ and $2s^2 2p^2 {}^3P^e_{0,1,2} \rightarrow 2s^2 2p^3 {}^3P^e_{0,1,2}$ of atomic C.
- The time-of-flight spectrometer gives a m/e ratio of 12 for the ions responsible.
- 3. PES taken at sharp features show only one peak which correspond to the $2s^2 2p^2 {}^3P_{f}^{e} \rightarrow 2s^2 2p 3p ({}^3D_{f'}^{e}, {}^3P_{f'}^{e}) \rightarrow {}^2P_{\frac{1}{2}, \frac{3}{2}}^{0}$ (2+1) ionization process of carbon.
- 4. Several other (2+1) REMPI transitions out of $2s^2 O({}^3P) 2p^2 {}^3P_{0,1,2}^e$ and $2s^2 2p 3p^3 D_{1,2,3}^e$ have been observed in the study.

In their REMPI-PES Spectra via nf (n = 4 - 7) Rydberg states Dobber's group did agree with Johnson and co-workers in observing long vibrational progressions in their photoelectron spectra. However, they disagreed with Johnson et al.'s assignments of PES Spectra on the basis that their spectra had a higher resolution compared to Johnson and coworkers'. Dobber et al. assigned most of the vibrational progressions to the symmetric stretch mode in the ground. X. state whereas Johnson et al.'s assignments were predominantly to the asymmetric stretch mode. The long symmetric stretch progression in the C state seen in Johnson et al.'s study was missing in Dobber's. Johnson's group also stated that these peaks were enhanced when PES was taken via the sharp structures to the high energy side of the 5f peaks. Taking this into consideration and their belief that the sharp structures belong to the C^+ ions. Dobber et al. concluded that they belong to the photoelectrons due to the ionization of Carbon atoms. Dobber also didn't observe any electrons due to REATA process observed in Johnson's study. Even though, Dobber and co-worker's assignments of the of PES spectra were predominantly to the symmetric stretch vibrations, they nevertheless, observed a few asymmetric stretch and bending vibrations in their spectra.

In their attempt to find out which level (3-photon or the 4-photon level) is causing the non-Franck-Condon like behavior Dobber et al. did two experiments. In the first experiment they used nano and picosecond lasers. As with Johnson's group low and high intense laser study, nano and picosecond lasers should give long and short vibrational progressions respectively, if the cause for the vibrational progressions is in the 3-photon level. When nanosecond lasers are used there is more time for the molecule to evolve in the intermediate level before it gets ionized compared to the time available with the higher power density present in the picosecond laser. Nevertheless, in their experiment the vibrational profiles were similar for nano and picosecond lasers in their spectra, indicating that the vibrational progressions are due to some effect in the 4 or 5-photon level.

The second experiment used two colors. When observing the $4f^2\Pi_{\Omega}$ states they observed a lot of vibrational activity in the $\Omega = 1/2$ state compared to $\Omega = 3/2$. Manipulating the two colors first, they fixed the intermediate level (3-photon) at the $4f^2\Pi_{3/2}$ state and scanned the 4-photon energy. This 4photon energy in the two color experiment fell on the 4-photon energy when scanning the $4f^2\Pi_{1/2}$ in the one color experiments. They called this the Constant Excited State (CES) mode, see figure 3.7. In this figure the shaded peak on the right was assigned to the vibrationless state of the ground ionic state of CO_2^+ and the two shaded peaks on the left were assigned to the ${}^2\Pi_g(0, 0, 2)$ and ${}^2\Pi_g(0, 1, 2)$ levels. In this mode they observed dramatic changes in the REMPI-PES spectra, which indicated that the 4 or 5-photon level is involved in the vibrational progressions.

In the second part of this experiment they fixed the 4-photon energy when using two colors at the 4-photon energy when scanning the $4f^2\Pi_{1/2}$ component in single color experiments and scanned the $4f^2\Pi_{3/2}$ state at the 3-photon level. They called this mode the Constant Ionic State (CIS) mode. In this mode they claimed that they observed "more or less the same" structures in the PES Spectra, (see figure 3.8) again indicating the 4 or 5 level is the cause for the non Frack-Condon like vibrational progressions. In figure 3.8, the spectra on the left-hand-side shows the CIS spectra and the right-hand-side spectra shows single color spectra where the excited resonant state tallies with the CES spectra at the same level. If we consider the two shaded peaks in the left and right side of the CIS spectra the peak on the left always stay smaller than the peak on the right. However the ratio changes and therefore it is not obvious that CIS mode has no change at all.

Production of CO_2^+ and CO^+ ions: Dobber's theory

According to the above experiments. Dobber et al. were convinced that the long vibrational progressions were due to some phenomena going on at the 4-photon energy. They agreed with Johnson et al. that these were due to autoionizing states at this level.

When considering the production of CO_2^+ and CO^+ ions. Dobber et al. considered their occurrence at the 4 photon energy due coupling of dissociating valence states to the autoionizing states. They rejected this idea since if dissociation occurred at this level, they would have observed more of the asymmetric stretch in their PES spectra. Dobber also ruled out the possibility of photons being absorbed directly at the autoionizing level to produce CO^+ and O^+ ions since they did not observe any photoelectrons due to this process. Almost all the photoelectrons they observed were assigned to numerous vibrational levels



Figure 3.7: Two - color photoelectron spectra forming a CES series. The three photon level is fixed at the $4f^2\Pi_{3/2}$ state and the four photon level is scanned 10 cm^{-1} at a time. The shaded peak on the right was assigned to the vibrationless state of the ground ionic state of CO_2^+ and the two shaded peaks on the left were assigned to the ${}^2\Pi_g(0,0.2)$ and ${}^2\Pi_g(0,1.2)$ levels. The peak with the asteric is to be ignored as it is assigned to a different process [79].



Figure 3.8: Two - color photoelectron spectra forming a CIS series are shown on the left hand side. The four photon level is fixed at the four photon level of the single color experiments when scanning the $4f^2\Pi_{1/2}$ state. The three photon level is scanned over the $4f^2\Pi_{3/2}$ state 10 cm⁻¹ at a time. On the right-hand-side, the series of spectra shows single color spectra where the excited resonant state (at three photon energy) tallies with the CIS spectra at the same level. The peak with the asteric is to be ignored as it is assigned to a different process [79].

of the CO_2^+ ground ionic state. Therefore, they deduced that the CO^+ and O^+ ions were produced primarily by dissociation of CO_2^+ ions by absorption of at least two additional photons. More details about this transition will be given in chapter 5.

As you can see, understanding of dissociation and ionization dynamics of CO_2 is very complex and is continually evolving. In Chapter 5, I will present and discuss our contribution to this puzzle.

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Chapter 4

Experiment

In this chapter I will first give an overview of the experiment and then will discuss the equipment used and its role in detail. A schematic diagram of our experiment is shown in figure 4.1. The main components of this experiment are: a laser system. a vacuum system and electronics to manipulate the ion signal from the REMPI process. The laser system consists of three components: a Nd:YAG pulsed laser (section 4.1), a tunable dye laser which was pumped by the Nd:YAG laser (section 4.2), and a doubling crystal which doubled the frequency of the visible dye output (section 4.3). It is the ultraviolet, frequency doubled light which was used in our experiment to excite and subsequently ionize the CO_2 molecules. The light was focused to a tiny spot by a lens. The REMPI processes then occurred at the focal spot, where the energy density was sufficiently high.

The vacuum system consisted of two chambers: the interaction chamber and the detection chamber. The REMPI processes took place in the interaction



Figure 4.1: Schematic diagram of a REMPI experiment. (a) Laser system. (b) Vacuum system. (c) Electronics.

chamber. The resulting signal was measured in the detection chamber. More details about the vacuum system will be given in section 4.4. The REMPI signal was amplified, integrated and then sent to a computer to be stored. Further details about the electronics will be given in section 4.5. This stored wavelength *versus* signal intensity constitute the REMPI spectrum. This will be discussed in detail in section 4.6.

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4.1 Nd:YAG pump laser

The pump laser that we used in our experiment is a Quantel (now Continuum) 581-C YAG pulse laser. For this experiment on CO_2 we used the 2nd harmonic. which gives a wavelength of 532 nm. The laser was operated at a pulse rate of 10 Hz, giving about 500 mJ of energy per pulse of 532 nm green light. The pulse length of the laser was about 8 nsec and the diameter of the pump beam was about 1 cm.

4.2 Tunable dye laser

The advantage of a dye laser is that it can be tuned across a range of wavelengths depending on the dyes used. In the present experiment we used the dyes: Rhodamine 590 and 575. They were pumped by the 2nd harmonic, 532 nm. light of the Nd:YAG laser. From about 500 mJ per pulse of 532 nm YAG laser energy we were able to achieve about 100 mJ/pulse of dye laser energy. More details about dye concentrations used and laser energies achieved are given in Table 1.1 and Table 1.2.

A dye laser consists of an oscillator and amplifiers, as shown in figure 4.2. The oscillator allows one to pick out a certain wavelength and the amplifiers increase the intensity of the output from the oscillator. In our laser, the oscillator was commercially made and it is of Littman design [1, 2]. A schematic diagram is shown in figure 4.3.

Dye	Oscillator	lst	2nd	3rd	4th
		Amp.	Amp.	Amp.	Amp.
Rhodamine 590				· .	
Dye Concentration (g/l)	0.2	0.10	0.05	0.025	0.013
Laser pulse energy (mJ)		4	25	60	100
Rhodamine 575					
Dye Concentration (g/l)	0.115	0.0575	0.55	0.027	0.014
Laser pulse energy (mJ)		1	6.5	50	100

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Table 4.1: Dye concentrations and laser pulse energy.

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Dye	Freq. doubled	Doubling	Notes
	energy (mJ)	crystal	
Rhodamine 590	10	KDP A	Long lasting dye;
		- -	Dissolves fast in MeOH
		· · · · · · · · · · · ·	
Rhodamine 575	9	KDP B	Long lasting dye;
			Dissolves fast in MeOH

Table 4.2: Frequency doubled laser pulse energy and doubling crystals used.

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Figure 4.2: Schematic diagram of the dye laser.



Pump Laser

Figure 4.3: Schematic diagram of the dye laser oscillator.

About 8% of the YAG laser is used to pump the oscillator. As shown, the pump beam is focused onto the dye cell by a 10 cm focal length cylindrical lens. Photons from this beam are absorbed by the dye molecules and reach an excited state. Due to the collisions the excited molecules undergo radiationless transitions to lower vibronic states. from which then fluoresce. A typical energy level diagram is shown in figure 4.4 (a), and the absorption and fluorescence spectra of Rhodamine 590 dye are shown in figure 4.4 (b). As shown in figure 4.3, the fluorescence from the dye cell is reflected back by the end mirror back through the dye cell and reaches the grazing incidence grating. From this grating, light is directed to the Littrow grating. Since the angle of the reflection from the grating depends on wavelength, there will be only one wavelength for



Figure 4.4: (a) Schematic energy level scheme and pumping cycle in dye molecules. and (b) absorption and fluorescence spectrum of Rhodamine 590 dissolved in ethanol [1]

which the Littrow grating will reflect the light back on its original path. and therefore back into the dye cell. By using two gratings the fluorescence is dispersed twice. increasing the dye laser resolution. By turning the angle of the Littrow grating, this wavelength can be changed. In our dye oscillator this grating is installed on a stepping motor, which is controlled by the computer and therefore the wavelength can be controlled by the computer. In our dye laser the output is the zeroth-order reflection from the grazing incidence grating.

Following the oscillator there are four home-made amplifiers. These are longitudinally pumped: the pump beam and the dye beam combine lengthwise in the dye cell. This allows us to produce a circular, homogeneous beam from our dye laser. More than one amplifier is used in order to achieve a narrow bandwidth laser. A narrow bandwidth cannot be achieved with a single amplifier. since this would mean pumping this amplifier with 95% of the pump beam. This would lead to saturation and therefore broadening of the linewidth of the dye beam. Thus, four amplifiers were used in our experiment. In our power dependence study the laser pulse energy was changed by changing the voltage supplied to the flash lamps in the Nd: YAG laser. In order to maintain the quality of the pump laser beam at lower laser energy the 4th amplifier was blocked, in addition to changing the voltage. A discussion of the laser power density is given in Appendix B.

4.3 Doubling crystal

A doubling crystal was used to double the frequency of the dye laser. This was a commercially made Autotracker II crystal system by INRAD company. The crystals used for the experiment were KDP "A" and "B" which worked for input wavelength 259 to 295 nm. When scanning the dye laser the doubling angle was corrected automatically by a feedback system to achieve maximum energy output of the doubled laser. Of about 100 mJ/pulse of dye laser energy we were able to achieve about 10 mJ/pulse of doubled energy.

4.4 Vacuum system

The vacuum system consists of two differentially pumped vacuum chambers (see figure 4.5). This means that the two chambers are at different pressures. This



Figure 4.5: Vacuum system and time-of-flight mass spectrometer.

is possible if the aperture between them is minimal. In our case the aperture connecting the two chambers is 3 mm in diameter. Of the two chambers the first one is the interaction chamber. This chamber is pumped by a diffusion pump made by Norton (NRC brand products- model number 0183) which has the capability of taking the pressure down to 10^{-6} Torr. CO_2 is fed into this chamber by a 1/4" tube or by a nozzle with 0.001 mm diameter. Both the 1/4" tube and the nozzle was regulated by a needle valve installed further up in the line, closer to the CO_2 cylinder. For the majority of the data in the present experiment we used the nozzle to introduce CO_2 into the chamber. The nozzle was built in our shop and will be described in section 4.4.2. Between the interaction chamber and the diffusion pump a manual gate valve was installed to regulate the CO_2 pressure in the chamber. The CO_2 pressure was maintained at a constant value around 10^{-4} Torr by controlling the pump rate from this chamber.

The laser was sent through the interaction chamber. This laser was focused to a tiny spot at the center of the chamber. It was at this spot that the ionization takes place, as the density of photons at this spot was sufficiently high for REMPI processes to occur. The ions that were produced by the REMPI processes were then accelerated towards the detector chamber, through the time-of-flight ion mass spectrometer. The time-of-flight ion mass spectrometer will be discussed in section 4.4.1.

The detector used in this experiment is a multichannel plate made by Gallileo.

When this plate is set at a high voltage each ion striking the detector creates a large number of electrons. which can then be extracted as a current pulse. When detector is operating, the detection chamber has to be kept under low pressure (below 10^{-5} Torr). Therefore, the detector chamber is kept at a pressure at 10^{-6} Torr region with a Turbomolecular pump. The Turbomolecular pump was made by Pfeiffer Balzers (model number TPU 510). With no CO_2 flowing into the chamber, it has the capability of pumping the detection chamber down to the 10^{-8} Torr range.

4.4.1 Time-of-flight ion mass spectrometer

A time-of-flight ion mass spectrometer was used to separate the ions of different mass created by the REMPI processes. This was done by applying a voltage across the interaction region with three metal wire meshes. these meshes are located on either side of the interaction region, as shown in figure 4.2. The first mesh was biased at -1100 V, the second at -1000 V, and the third at 0 V. The laser was focused between the first and the second meshes so that the REMPI processes could occur at a relatively low voltage. This avoided any effects due to high voltages. However, the 100 V difference was sufficient to cause the ions to accelerate towards the second mesh. These ions were then further accelerated by the 1000 V potential between the second and the third mesh towards the detection chamber.

Depending on the charge-to-mass ratio of the ions the time the ions take

to arrive at the detector changes. Thus the CO_2^+ ions and the fragmented ions can be separated. If the charges on these ions are the same they acquire the same kinetic energy due to the voltage applied. This kinetic energy is qV. where q is the charge and V is the applied voltage. Hence, the molecules with the same charge-to-mass ratio will gain the same velocity while those with different charge-to-mass ratios will gain different velocities. Time-of-flight mass spectrometer is simply a tube through which the ions travel. By traveling along this 50 cm tune at different velocities, the various ions reach the detector at different times. If any two ion masses are known we can calibrate the time-offlight by using the equation.

$$qV = \frac{1}{2}mv^2 = \frac{1}{2}m(l/t)^2,$$

where *m* is the mass of the ion, *v* is the velocity, *l* is the length of the timeof-flight mass spectrometer tube, and *t* is the arrival time at the detector. A typical signal measured by the oscilloscope is shown in figure 4.6. The different peaks here are due to ions with different charge-to-mass ratios. The time-offlight was calibrated by filling the chamber with air instead of CO_2 . This gave us signals from a range of masses starting from $H^+C^+O^+$, CO^+ and CO_2^+ . due to air and pump oil.

4.4.2 Nozzle

The nozzle was built in our instrument shop. We were able to adjust its position in three directions: x. y and z. This allowed us to orient the tip of the nozzle



Figure 4.6: Typical REMPI signal seen by the oscilloscope. The different peaks are for different masses.

directly above the focus of the laser and therefore maximize the signal. A schematic diagram of the nozzle is shown in figure 4.7. The two knobs on the top let us adjust the x and the y positions, and the knob above the long cylinder lets us adjust the z position. These adjustments can be made under vacuum and the experiment is underway. Because there was a voltage applied across the reaction area, the tip of the nozzle needed to be electrically floating to avoid changing the potentials in the ion extraction region. Thus the tip of the nozzle was made out of acrylic, with a diameter of 0.001 mm. We measured spectra at various nozzle backing pressures (from 800 mm Hg to 260 mm Hg). For higher backing pressure, we observed some supersonic cooling by the nozzle. Information about pressure in the interaction and detection chamber for different nozzle backing pressure are given in Table 1.3.



Figure 4.7: Schematic diagram of the nozzle.

Backing	Needle valve	Source	Detector	Signal height
pressure	reading	pressure	pressure	(mV)
> 800mm Hg	23	3 x 10 ⁻⁴	3 x 10 ⁻⁶	70
790mm Hg	15	1 x 10-4	1.1 x 10*	35
460mm Hg	13.5	6 x 10 ^{-s}	5.6 x 10 ⁻⁷	20
260mm Hg	12.5	2.8 x 10 ⁻⁵	2.8 x 10 ⁻⁷	10

Table 4.3: Supersonic cooling effect due to the nozzle: backing pressures.

4.5 Electronics

The current from the multichannel plate detector was extracted by a homebuilt filter. This separated the direct voltage supplied to the multichannel plate from the transient current which was actual REMPI signal. The REMPI signal was then amplified by a timing filter amplifier made by ORTEC (model number 474), and sent into a gated boxcar averager (Stanford Research Systems - model number SR250). The gated boxcar averager allowed us to integrate a signal during a given time range, or gate. For instance, if the gate is set at the time when the CO_2^+ ions arrive, the signal due only to CO_2^+ ions can be integrated as a function of laser wavelength. This integrated signal was then sent to a microcomputer, where it is converted into a digital signal by an analog-to-digital converter card and finally stored in a data file. In the case where more than one mass of ions was monitored simultaneously, for example CO_2^+ and CO^+ , two boxcar averagers, and therefore two gates, were used.

4.6 Computer software

A Pascal program was used to interface with the experiment. This program was used to scan the laser, to convert the signal from analog to digital format. then to store it in a file. The block diagram of the program is given in figure 4.8.

The computer program controlled the stepping motor which scanned the dye laser. The laser was scanned by rotating the angle of the Littrow grating. This grating was attached to a stepping motor (Aerotech- model number ART-50). From our program we were able to control the number of steps. and therefore the change of wavelength, and to control the amount of time spent in that particular wavelength. The stepping motor had a stepsize of 25,000 steps per revolution, which corresponds to a wavelength resolution of about 1.3 x 10^{-3} Å/step. The time spent at each step could be determined by the clock in the computer or by the number of laser shots. In this experiment we used the laser-shot mode, which was more reliable than the clock-mode in getting the same signal strength at each data point.

The computer program was also used to collect and record the data. The analog REMPI signal as a function of wavelength was converted to a digital



Figure 4.8: Block diagram of the computer program.

signal and stored in a file. Typically we would sum the signal for 20 laser shots and then store the sum at each data point. One scan usually covered about 10 Å. Each scan took about 45 minutes, and multiple scans were recorded for each wavelength range observed. We had to be careful that the doubling crystal did not get out of synchronization and that the pressure in the chambers was steady. While scanning, the spectra could be observed on a graph on the computer. This was very convenient as any error in the scan could be instantly detected.
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Chapter 5

Results and Discussion

5.1 Introduction

In our study we observed the $nf \, {}^{2}\Pi_{\Omega}$ Rydberg states of CO_{2} via (3+1) Resonance Enhanced Multi-Photon Ionization (REMPI) spectroscopy for the principle quantum number n = 4 to 8 (see figure 5.1 through 5.3). A Rydberg state is a state in which a single electron of the molecule has been excited to a very high energy level while the other electrons stay in their ground state, as was discussed in detail in section 2.3. In the $nf \, {}^{2}\Pi_{\Omega}$ state the nf is the Rydberg electron which has a principle quantum number of n and an orbital angular momentum of 3, since it is an f state. ${}^{2}\Pi_{\Omega}$ is the molecular state of the core. The value of multiplicity, 2, indicates that it has a spin of 1/2 and since it is a Π state. its projection of the orbital angular momentum on the internuclear axis is 1. Depending on how the spin and the orbital angular momentum combine the total angular momentum, Ω_{c} , can take the values 1/2 or 3/2 (see figure

5.4). Hence, for each nf state there exists two spin-orbit components $nf^{2}\Pi_{1/2}$ and $nf^{2}\Pi_{3/2}$. Of the two, $\Omega_{c} = 3/2$ has less energy according to the Hünd's rules.

As discussed in Chapter 2. Resonance Enhanced Multiphoton Ionization REMPI spectroscopy is done using a high-powered dye laser. This laser has to be strong enough to make the molecule absorb several photons simultaneously and ultimately be ionized. It is the ions coming out from the interaction region that are finally detected. Ions are extracted by applying a voltage across the interaction region. Our experimental setup is discussed in Chapter 4.

In a (3+1) REMPI process the molecule absorbs 3 photons simultaneously to get to a resonant state and from there, one more to reach the ionization continuum, as shown in figure 5.5. In our study the resonant states reached are the $nf^{2}\Pi_{\Omega}$ Rydberg series of CO_{2} for n = 4 to 8 which are shown in figures 5.1, 5.2 and 5.3. One major advantage of REMPI spectroscopy is that we can observe CO_{2}^{+} ions as well as their dissociated products CO^{+} or O^{+} ions. This is done using a time-of-flight apparatus, which makes it possible to distinguish between different masses, and therefore between CO_{2}^{+} and CO^{+} ions. By observing CO_{2}^{+} and CO^{+} ions simultaneously we can get more information about ionization and the dissociation dynamics of CO_{2} . As can be seen in the figures the structure of the nf Rydberg states is visible in the CO_{2}^{+} ion spectra as well as the CO^{+} ion spectra. This indicates that the dissociation of CO_{2} occur sometime after the intermediate resonance state. A lengthy discussion of the



Figure 5.1: (3+1) REMPI spectra of via 4f ${}^{2}\Pi_{\Omega}$ state when monitoring (a) CO_{2}^{+} ion (b) CO_{2}^{+} ion signal. The peaks in each curve show the two spin-orbit components of $\Omega = 3/2$ and 1/2.



Figure 5.2: (3+1) REMPI spectra of via 5f ${}^{2}\Pi_{\Omega}$ state when monitoring (a) CO_{2}^{+} ion (b) CO_{2}^{+} ion signal. The peaks in each curve show the two spin - orbit components of $\Omega = 3/2$ and 1/2.



Figure 5.3: (3+1) REMPI spectra of via 6f. 7f. and 8f ${}^{2}\Pi_{\Omega}$ states when monitoring (a) CO_{2}^{+} ion (b) CO^{+} ion signal. The peaks in each curve show the two spin - orbit components of $\Omega \approx 3/2$ and 1/2.



I state, so Projection of Orbital Angular momentum on the internuclear axis $\Rightarrow \Lambda = 1$

Since multiplicity =2, Spin, S = 1/2Projection of the spin on the internuclear axis $rac{1}{2} = \pm 1/2$

$$\frac{\Lambda}{\Sigma} \qquad \Omega = 3/2$$

$$\frac{\Sigma}{\Lambda} \qquad \Omega = 1/2$$

Figure 5.4: Spin - orbit coupling of the core of the Rydberg molecule.

most recent work in ionization and dissociation dynamics of CO_2 was given in section 3.2.2 in Chapter 3.

5.2 Spectra of CO_2

In the recent past CO_2 was investigated in the energy region 880 - 2000 Å by three different groups using photoabsorption. REMPI and REMPI-PES methods: Cossart-Margos et al. [1] using single photon absorption spectroscopy, and two other groups, Johnson and coworkers [2, 3, 4, 5, 6] and Dobber et al. [7] both using REMPI and REMPI-PES spectroscopy methods. In section 3.2 in Chapter 3. I have summarized most of these results, nevertheless these will be discussed briefly again to compare with our experimental results.

Cossart-Magos et al. in their single photon absorption studies observed the



Figure 5.5: Schematic diagram of the (3+1) REMPI process of the $nf^{2}\Pi_{\Omega}$ resonance state of CO_{2} molecule.

nf Rydberg series of CO_2 for n = 4 to 28 for the $\Omega_c = 3/2$ spin-orbit component and n = 4 to 32 for the $\Omega_c = 1/2$ component. They carried out Hartree-Fock calculations in the Frozen-Core-approximation to assign these Rydberg states. which converge to the ground ionic state of CO_2 , $X^2\Pi_q$ [1]. In addition to this, they observed the spin-orbit splitting to be about 160 cm^{-1} , which is also the energy difference between the two spin-orbit limits of the ground state of the CO_2 ion $X^2 \Pi_q$, which has the same configuration as the core of the nf Rydberg states. In the present study we observed the energy levels of the $nf^{2}\Pi_{g}$ series via (3+1) REMPI spectroscopy for n = 4 to 8. As in singlephoton spectroscopy, the nf series is an allowed transition in (3+1) REMPI spectroscopy. Our spectra agree very well with Cossart-Magos group's spectra. As do Cossart-Magos', our spectra showed that each nf state was split into two spin-orbit components separated by about 160 cm^{-1} , as in the ground ionic state. In Cosart-Magos' spectra, the nf series had sharp features in the rotational contours, indicating long lifetimes. This meant that these states were relatively free from interference by the other states and therefore free of processes such as predissociation. In our REMPI spectra, we observed some sharp features in the rotational contours of the nf series. These were more prominent for 4f, 5f and 7f than 6f and 8f.

In Johnson et al.'s study they observed the $nf^{-2}\Pi_{\Omega}$ states for n = 4 to 6 using REMPI techniques. They monitored both CO_2^+ and CO^+ ion signals using a time-of-flight apparatus. In their spectra CO_2^+ ion signal was present only in the 4f and 5f Rydberg states, but a CO^+ ion signal was observed for all the states including 6f. They observed an O^+ signal which was very small. In our study CO^+ and CO_2^+ ion signals were present for all states of the nfRydberg series observed up to n = 8 and an O^+ signal almost to the order of the CO^+ ion signal was observed for 6f state. These O^+ spectra are shown in figure 5.6, at the same scale as the CO^+ signal for comparison. Johnson et al. mentioned additional sharp features to the high energy side of the 4f and the 5f states. These peaks were missing in our spectra and will be discussed in section 5.3. Except for these discrepancies, the rotational contours and positions of our spectra agreed well with those of Johnson and his co-workers.

In their study Johnson and his co-workers [2] also did a power dependence study on CO_2^+ and CO^+ ion spectra. If there are no saturation effects or dissociation or predissociation occurring, the intensity of the ion signal should follow the equation

 $I \propto P^n$.

Here P is the laser pulse power density and n is the number of photons absorbed. A plot of log(I) verses log(P) should give a slope of n.

According to their study they got an exponent of 2.06 for the CO_2^+ ion signal and 4.05 for the CO^+ ion signal for the 4f state. In our power dependence study we deduced exponents in the range 2 to 3 for CO_2^+ ion signal and 2.5 to 3.5 for the CO^+ ion signal for 5f. 6f and 7f spectra. The exponent for the CO^+ ion signal was always higher than the exponent for the CO_2^+ ion signal (see figure



Figure 5.6: Schematic diagram of (3+1) REMPI of CO_2^+ when monitoring (a) O^+ (b) CO^+ signals. The figures are drawn to scale to show the ratio of O^+/CO^+ .

5.7). Since we are considering a (3+1) photon absorption process an exponent of at least 3 is expected for CO_2^+ ion signal. Since this is not the case it is likely that the 3-photon absorption is at least partially saturated.

In their second paper Johnson and his coworkers also did a theoretical analysis of the 4f spectrum and fitted their data to a rotational contour. In this analysis they ignored the singlet-triplet splitting, which is valid for a completely decoupled Rydberg electron, and came out with a rotational contour that fitted the data very well. From this they concluded that in the nf series, the Rydberg electron was very detached from the rest of the molecule.

The third group. Dobber et al., observed the nf series from n = 4 up to 13. using the same technique, REMPI, as Johnson's group and us. Our spectra agree remarkably well with their spectra. Unlike Johnson et al., Dobber et al. were able to monitor the nf series with both CO_2^+ and CO^+ ions for all n. Nevertheless, Dobber's group observed the CO^+/CO_2^+ to increase with increasing n. They also observed the O^+ and C^+ signals in their spectra. Unlike Johnson's group, they found the O^+ signal to be large and to follow the nfresonances very well; as mentioned earlier this was observed in our study too. In Dobber et al.'s study, the ratio CO^+/O^+ was found to stay nearly constant for all nf states. Also, unlike the O^+ signal, the C^+ signal followed the nfstates only to a limited extent. The sharp features to the high energy side of the 4f and 5f states observed in Johnson et al.'s spectra were assigned to C^+ ions by Dobber's group for reasons discussed in section 3.2. All the above



Figure 5.7: log I vs log (laser power) curves to estimate the number of photons n. in the transition.

observations in Dobber's group study were observed in our study.

Dobber and his coworkers also studied the nf series with nano and picosecond lasers. They found the spectra to look the same for both the situations. The only difference they observed was the ratio of CO_2^+ : CO^+ : O^+ which yielded typical values of 0.13: 0.73: 0.14 for the nanosecond laser and 0.50: 0.35: 0.15 for the picosecond laser. This indicates that there is much less fragmentation for the picosecond laser.

In addition to REMPI. both Johnson et al. and Dobber et al. did REMPI-PES studies via the nf Rydberg series. In REMPI-PES studies the wavelength of the laser is fixed at the energy of a resonance state and the electrons coming out of the ionization process are monitored. The kinetic energy of the electrons ejected subtracted from the absorbed photon energy gives the energy of the final ionic state of CO_2 (see figure 5.8).

Both of the above groups observed long vibrational progressions in their PES spectra, which is very surprising considering the Franck-Condon principle. The Franck-Condon principle states that the absorption of a photon occurs very rapidly that there is not enough time for the nuclei to rearrange during the transition period. Since the ground ionic state of CO_2 , X ${}^2\Pi_g$, and the nf Rydberg states leading to it have very similar potential energy curves, they expect the transition starting from the ground vibrational level of the Rydberg state to be predominantly to the ground vibrational level of the ground ionic state of CO_2^+ . And similarly the first vibrationally excited state of the resonance



Figure 5.8: REMPI - PES process. The curve shown are not actual curves for the CO_2 molecule.

state should lead to the first vibrationally excited state of the ionic state, and so on. A lengthy explanation of this is given in section 3.2.2. In view of this, the long vibrational progressions observed in the PES spectra were unexpected. The details of what might cause these long vibrational progressions will be discussed in section 5.3.

In Johnson et al.'s study these vibrational progressions were assigned to vibrational levels in the ground ionic state, $X^2 \Pi_g$, the $C^2 \Sigma_g^+$ state, and a brand new state never before mentioned in previous studies. Also, their vibrational states were assigned predominantly to the antisymmetric stretch mode. Dobber et al.'s PES spectra were collected with much higher resolution than those of Johnson et al.. Their assignment of some features in the vibrational spectra differ from Johnson et al.'s. Dobber et al. assigned them to the vibrational levels of the ground ionic states and mostly to the symmetric stretch instead of the asymmetric stretch assignments for three reasons:

- 1. Their experiments were done with higher resolution.
- 2. They believe that the sharp structures to the high energy side of the 4f and 5f states belong to the C^+ ions and gave detailed reasons for their conclusions.
- 3. In our study we have not seen these structures in CO_2^+ or CO^+ spectra.

5.3 Dissociation and Ionization Mechanisms of CO_2

In addition to its spectra, the dynamics of dissociation and ionization of CO_2 is also a very interesting subject. One major advantage of REMPI and REMPI-PES spectroscopy is that it gives an insight into the dynamics of these mechanisms. This will be demonstrated by the following discussion.

In this section, I will be discussing Johnson et al.'s and Dobber et al.'s REMPI and REMPI-PES studies related to this area, and our REMPI studies that give insight into dissociation and ionization mechanisms in chronological order.

In the first publication [2] in Johnson et al.'s series of publications in this area [2-6] they discussed laser power dependence on the CO_2^+ and CO^+ ion spectra. As mentioned earlier in section 5.2, in their study Johnson and his co-workers calculated the effective number of photons, n, for CO_2^+ and for CO^+ ion spectra to be 2.06 and 4.05 respectively. Considering that CO_2^+ ions are produced in (3+1) REMPI process, these numbers indicate that either saturation effects or dissociation. Nevertheless, since the CO^+ spectra gives a higher value for n than the CO_2^+ spectra they suggested that production of CO^+ occurs subsequent to the production of CO_2^+ ions, and therefore that CO^+ is generated predominantly by dissociation of CO_2^+ ions [2].

However, in their next publication, they discussed the surprising observation of long vibrational progressions in their REMPI-PES spectra. As mentioned earlier in section 5.2, the long progressions of vibrational states were unexpected. A more elaborate discussion of why they are unexpected was given in section 3.2.2.

There are two questions pertaining to this unexpected phenomenon. The first is which level contributes to these progressions: whether it is at a 3photon energy or a 4-photon energy. The second is what kind of a dynamic process causes these vibrational progressions at this level. In 1991. Johnson et al. attributed the cause for this non Franck-Condon like behavior to the 3photon resonance level [3]. They suggested that a dissociative state is coupled to the resonant Rydberg state and therefore that the state is predissociative. Nevertheless, if the laser is powerful enough there still will be time for the molecule to absorb another photon and be ionized. In other words the molecule will ionize while being dissociated. As a result of predissociation the Franck-Condon factors between the 3-photon resonant and 4-photon ionic states are altered (see figure 5.9). This alteration will give rise to the observed vibrational levels.

At this point in our study we had observed the 4f and the 5f Rydberg states via REMPI spectroscopy, see figures 5.1 and 5.2. Looking at these spectra we noticed a definite difference in the dissociation rate of the two spin-orbit components $\Omega_c = 1/2$ and $\Omega_c = 3/2$. We were able to get an idea of the amount dissociated in the limit $\Omega_c = 3/2$ by taking the ratio of the integrated area under peaks of CO^+ to CO_2^+ of $\Omega_c = 3/2$, and similarly for the component $\Omega_c = 1/2$. From this it was clear that the $\Omega_c = 1/2$ component dissociated



Figure 5.9: Coupling of singlet dissociative state with the nf Rydberg state. The curve shown are not actual curves for the CO_2 molecule.

more than the $\Omega_c = 3/2$ component. To see how this changes with laser power, we did a laser power dependence study on the 5f Rydberg state, as the dye curve in this region was sufficiently flat. Figure 5.10 shows how the 5f Rydberg state changes with laser power. The ratio $\Omega_c = 1/2 / \Omega_c = 3/2$ changed slightly but the dissociation rate $CO^+ / (CO^+ + CO_2^+)$ calculated was always higher for the $\Omega = 1/2$ compared to $\Omega = 3/2$.

In order to find out why the two spin-orbit components differ in their dissociation rates we considered angular momentum coupling schemes for CO_2 in the nf Rydberg series. Figure 5.11 shows a correlation diagram between the two limiting coupling schemes for a $\pi^3\delta$ configuration when the nf Rydberg electron is coupled to a ${}^{2}\Pi_{\Omega}$ ion core. On the left-hand side of the diagram is $\Lambda - \Sigma$ coupling scheme suitable when the Rydberg electron is closely coupled to the nuclear framework. On the right hand side is (Ω_c, ω_R) coupling scheme appropriate for the Rydberg electron that is further away from the molecule. The solid lines show the correlation of the two coupling schemes between states that are closest in energy. The dashed lines show the states that are correlated but are further away in energy. From this figure it is clear that the $\Omega_c=1/2$ state has more singlet characteristics and the $\Omega_c=3/2$ has more triplet charateristics. Therefore, we suggested a model in which there is a dissociative state coupled to the Rydberg intermediate state and this state is a singlet state, thus explaining why the $\Omega = 1/2$ component dissociated more. If this is all true. the vibrational progressions seen in Johnson et al.'s study should be due to the



Figure 5.10: Laser power dependence of the 5f Rydberg states.



Figure 5.11: Correlation diagram between $\Lambda - \Sigma$ coupling and (Ω_c, ω_R) coupling for a $\pi^3 \delta$ configuration of a triatomic linear molecule. Correlation to the nearest state are shown in solid lines and states further away in energy are shown in dashed lines.

coupling of a singlet dissociative state to the 3-photon resonance state.

In their second paper Johnson and his coworkers also did a theoretical analysis of the 4f spectrum and fitted their data to a rotational contour. In this analysis they ignored the singlet-triplet splitting, which is valid for a completely decoupled Rydberg electron, and came out with a rotational contour that fitted the data very well. From this they concluded that in the nf series, the Rydberg electron was very detached from the rest of the molecule. This means that the singlet-triplet characteristics are minimal for the nf Rydberg series and the best angular momentum coupling scheme is the one on the right hand side of figure 5.10. In view of these facts, there should not exist such a contrast in dissociating ratios to the spin-orbit limits in this series as what we have observed in our data. Therefore, it was not a surprise to find out later that the mystery of the dissociating ratios lies on another reason. Why dissociating ratios are different for different spin-orbit components will be discussed later.

Later, in 1992, Johnson et al. did another study to verify that the vibrational progressions were due to a coupling of a dissociative state at the 3-photon Rydberg state [6]. They did a laser power dependence REMPI-PES experiment via 4f and 5f. In this experiment they fixed the laser wavelength at either the 4f or the 5f level and observed the photoelectrons. They repeated this procedure for different powers of the laser. Their argument was that if the laser power is high, the molecule will ionize very fast and will not have much time to evolve into the dissociative state. This will lead to a short vibrational progression.



Figure 5.12: REMPI-PES through the $4f^2\Pi_{\Omega}$ for $\Omega = 3/2$ intermediate Rydberg states at a number of laser intensities [6]

Whereas if the power is low the molecule will have to wait for a longer time in the 3-photon resonant state for another photon to come along to be ionized. This will give the molecule enough time to evolve to the dissociative state and hence alter the Franck-Condon factors dramatically to produce long vibrational progressions. However, in their PES spectra they did not see a difference in the vibrational profiles for different powers of the laser (see figure 5.12). This experiment indicated that the reason for the vibrational levels does not lie in a dissociative state coupled the 3-photon level. This leads to only one other possibility, that is, reason for the vibrational levels lies in the 4 or 5-photon energy level.

Later, in 1994, Dobber and his coworkers, performed two other experiments

to determine the level, the resonance (3-photon) or the ionic (4-photon) level, which is responsible for the non Franck-Condon like vibrational progressions. The first experiment involved two different lasers: nanosecond and picosecond. If the reason for the vibrational progressions lies in the coupling of a dissociative state to the 3-photon resonance state, they should see a long vibrational progression for the nanosecond laser, because the nanosecond laser has a lower energy density and allows more time for the molecule to evolve to the dissociative state and therefore alter the Franck-Condon factors dramatically. Since the shorter picosecond pulse laser has a higher power density in a short pulse, and gives less time for the molecule to evolve to the dissociative level and they expected to observe a shorter, sharper vibrational progression. Nevertheless in their experiment they did not observe any difference between the two PES spectra. This too indicated that some physical phenomena that goes on at 4 photon energy is responsible for the non Franck-Condon like behavior.

In their second experiment, Dobber et al. used two colors. This was done in two modes: 1. CES, constant excited state mode and 2. CIS, constant ionic state mode. In the CES mode they manipulated the two colors to set the excited (resonance) state at the same level and scanned the ionic level. In this mode they saw a dramatic change in their PES spectra which indicates that the ionic state is responsible for the vibrational progressions. In the CIS mode the ionic state was constant but the resonant state was changed. They claimed this mode produced "more or less similar PES spectra". Therefore this experiment too indicate the 4-photon level to be the one which causes the vibrational progressions. This experiment was explained in detail in section 3.2.2.

However, in their analysis. Johnson and Dobber and their co-workers agreed that long vibrational progressions are not due to any activity at the 3-photon energy. They attributed these to autoionization at the 4-photon energy. They agreed that after the 3-photon transition one more photon is absorbed to excite the autoionizing states (Rydberg states leading to A and B ionic states). From these states, they concluded that the CO_2 molecule will autoionize into the various vibrational levels of the ground ionic level (see figure 5.15) causing the long vibrational progressions in the PES spectra.

If this is the case, our attribution of a singlet dissociative state coupled to the resonant state as the reason for the different branching ratios for the two spin-orbit limits is not correct. Considering the above experiments, the reason why $\Omega = 1/2$ spin-orbit component dissociates more than the $\Omega = 3/2$ component for 4f and 5f Rydberg states is expected to be due to some process occuring at the four-photon energy or beyond that energy.

Even though REMPI-PES spectroscopy provides details of the excitation. ionization and autoionization up to the point the electron is ejected, it does not give insights into the dynamics beyond that point. In our experiments we performed a laser power dependence study in the hopes of obtaining information about what goes on after the ejection of the electron. To do this we changed



Figure 5.13: Autoionization that leads to vibrational progressions. The curves shown are not actual curves for CO_2 molecule.

the laser pulse energy from about 2 mJ to 8 mJ and recorded the CO_2^+ and the CO^+ ion signals simultaneously for each different laser energy. This was done for the 5f. 6f and 7f resonance states as the dye laser curve was sufficiently flat over each pair of the spin-orbit components of these nf states.

Observing our REMPI spectra, it was clear that the two spin-orbit components of each state had different ionization and dissociation rates. The rates also varied with the intermediate resonant state. See figures 5.1, 5.14, 5.15 and 5.16 for the 4f, 5f, 6f and 7f states respectively.

Considering the spectra of 4f, figure 5.1, the $\Omega = 1/2$ peak in CO_2^+ ion spectra is much smaller compared to the peak belonging to $\Omega = 3/2$; in the CO^+ ion spectra, this is reversed. From this we deduced that $\Omega = 1/2$ component produces more CO^+ ions, and therefore undergoes more dissociation than the $\Omega = 3/2$ component in the 4f state.

Figure 5.14 shows the REMPI spectra of 5f and its dependence on laser pulse power. In the CO_2^+ ion spectra at 7 mJ laser pulse power the $\Omega = 1/2$ peak is smaller than the $\Omega = 3/2$ peak. In the CO_2^+ ion spectra this is reversed. However when the laser power is lowered the ratio of $\Omega = 1/2$ to $\Omega = 3/2$ tends to decrease in CO_2^+ spectra, but this ratio seems to stay constant in the CO^+ ion spectra. Considering these observations it is clear that for the 5f state the $\Omega = 1/2$ spin orbit component dissociates more.

The 6f states are shown in figure 5.15. Unlike in the 5f state, in the 6f state the $\Omega = 3/2$ component seems to dissociate more. In the laser pulse power



Figure 5.14: Laser power dependence of the 5f state.



Figure 5.15: Laser power dependence of the 6f state.



Figure 5.16: Laser power dependence of the 7f state.

range in our experiment the CO^+ ion spectra for 6f gives a very similar curve, with $\Omega = 1/2$ been far smaller than the $\Omega = 3/2$ component. However, the ratio of the spin-orbit components in the CO_2^+ spectra varied with laser pulse power. At 6.5 mJ per pulse, the $\Omega = 1/2$ peak is larger than the $\Omega = 3/2$ peak. but for lesser laser powers it seems reversed. Nevertheless, considering both the CO_2^+ and CO^+ ion spectra we can safely say that dissociation is greater for the $\Omega = 3/2$ state regardless of the laser pulse power.

In the 7f spectra, figure 5.16, both CO_2^+ and CO^+ seems to give similar patterns. Just by observing the spectra it is hard to decide which component dissociates more. In the CO_2^+ ion spectra the $\Omega = 1/2$ component is smaller than the $\Omega = 3/2$ indicating that $\Omega = 1/2$ component dissociates more. But in the CO^+ ion spectra, the $\Omega = 1/2$ state is smaller than the $\Omega = 3/2$ indicating that $\Omega = 3/2$ component dissociates more. Therefore a more quantitative study was required to find out the dissociation rates. This will be discussed below.

To investigate the dissociation rates in more detail we integrated the areas under these curves. The areas under each spin-orbit component in each nfstate for all the laser pulse powers were calculated for both CO_2^+ and CO^+ ion spectra in a manner explained below. These are given in tables 5.1, 5.2 and 5.3 for 5f, 6f and 7f respectively.

In calculating the areas, first we took the data points in the spectra which had two columns: 1. the wavelength and 2. the intensity of the signal for each wavelength. The wavelength was increased by a constant step size in each

Lsr Eng(mJ) Area(CO:	1/2] Area(CO:	3/2, Area(CO2:1/2)	Area(CO2:3/2)	1/2: CO/CO2 3/	2: CO/COZ
2.25	200	130.5	37.5	31.15	5.3	42
3.5	424.5	261	91	83	4.7	31
4	692.5	365	128.5	101.5	5.4	36
4	580	406	72.9	73.5	8.0	5 5
4 75	1091	552.5	140	130	78	43
5	947	840	92.615	120	10.2	70
5.5	1511.5	771	158.5	160	9.5	4 8
6	1912	1288	120	200	15.9	54
7	3901	3436	265	389	14.7	8.8
8	4300	3640	325	600	13.2	6.1

Table 5.1: Ratio of CO^+/CO_2^+ for the two spin-orbit limits of the 5f state for different powers of the laser.

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Lar Eng(mJ) Area(CO:	1/2] Area(CO:	3/2; Ares(CO2:1/2)	Area(CO2:3/2	2) 1/2: CO/CO2	3/2: CO/CO2
3	389	1260	83.5	105	4.7	12.0
4	1130	3368	163	194	6.9	17.4
5.5	1906	5268	319	313	6.0	16.8
6.5	5084	12372	835	650	8.1	19.0
5	708	1464	220	192	3.2	7.7
6.75	19146	3648	536	377	35.7	9.7
7.25	2436	3342	620	383	3.9	8.7
2.25	124	384	18	28	6.9	13.7
3	192	612	40	54	4.8	11 3
4	628	1648	101	96	6.2	17 2
5.25	1312	3072	212	177	6.2	17.4
0.75	2280	5016	414	296	5.5	16.8

Table 5.2: Ratio of CO^+/CO_2^+ for the two spin-orbit limits of the 6*f* state for different powers of the laser.

Lsr Eng	(mJ) Area(CO	:1/2) Area(CO:	3/2" Area(CO2:1/2)	Area(CO2:3/2	1/2: CO/CO2	3/2 CO/CO2
2.75	160	412	30.3	47	53	
[4	565	940	71	102	80	
5	1040	1708	181.4	228	57	75
5	1992	2960	215	262	93	111
6.25	3304	7228	387	474	85	152
8	2900	7294	290	459	10.0	15 9

Table 5.3: Ratio of CO^+/CO_2^+ for the two spin-orbit limits of the 7f state for different powers of the laser.

spectra. The area was calculated by the equation given below.

$$Area = \sum_{\lambda = 1}^{\lambda_{Max}} (Intensity - Baseline) \times Stepsize$$

The Baseline in the equation was decided by looking at a long enough scan to find a flat region of the spectra close to the wings on either side of the peaks. λ_{Min} and λ_{Max} are the wavelengths at which the peak begins and ends respectively. Uncertainties involved in this calculations are discussed in Appendix.

In order to investigate the ionization and subsequent dissociation of CO_2 through different resonant states, we can compare the ratios of CO^+/CO_2^+ ions for the spin-orbit components of each state. This ratio should give us an idea as to which states lead to more dissociation. Figures 5.17 a), b) and c) give the two spin-orbit components of the CO^+/CO_2^+ ratios verses the laser pulse power for the 5f, 6f and 7f states respectively.

The most striking fact in these graphs is the lack of or very little dependence of laser power in CO^+/CO_2^+ ratios. In particular in the $\Omega = 1/2$ of the 6f



Figure 5.17: Ratio of CO^+/CO_2^+ Vs Laser Energy for 5f. 6f. and 7f states.

Rydberg state the CO^+/CO_2^+ ratio is almost constant throughout the laser power range. What is remarkable is that in this state when the laser power is increased by a factor of 3, the signals for both CO_2^+ and CO^+ increased by a factor of 20. In spite of this the ratio of CO^+/CO_2^+ remained almost constant throughout the laser power range. Compared to the $\Omega = 1/2$ component of the 6f states, the ratio of CO^+/CO_2^+ for the other states showed a bit more dependence on the laser pulse power, but nevertheless it still was very little. However, the ratio varied quite a lot with the laser frequency. In the following discussion I will first discuss how the ratio of CO^+/CO_2^+ changes with respect to frequency and then will discuss the laser power dependence of it.

5.3.1 Frequency dependency of the ratio CO^+/CO_2^+

As discussed earlier, by observing the spectra, there definitely was a difference in the dissociating ratios of the two spin-orbit components in the nf Rydberg series. Our earlier theory about a singlet dissociative state being coupled to these states as the reason for it does not agree with Johnson and Dobber and their coworkers' more recent experiments. Also, if this theory were true, we would expect the $\Omega = 1/2$ state to dissociate more for all the nf states. Comparing the ratios of CO^+/CO_2^+ , we found that this definitely was not the case. According to our calculations of areas under each peak, as discussed earlier, the 4f and 5f Rydberg states produced higher CO^+/CO_2^+ ratios for the $\Omega =$ 1/2 component than for the $\Omega = 3/2$. This is reversed for the 6f and the 7f
states (See table 5.1, 5.2 and 5.3).

When we compared Dobber et al.'s [7] PES spectra via 5f. 6f and 7f resonance levels we found a remarkable correlation between our CO^+/CO_2^+ ratios and the states which produced a higher degree of symmetrical vibrational levels in the PES spectra. The states which produced more symmetrical vibrational levels had a higher ratio of CO^+/CO_2^+ , which indicate a higher dissociation rate. In Dobber et al.'s study PES spectra via the 5f state produced symmetric vibrational levels up to v=9 for the $\Omega = 1/2$ state and only up to v=3 for the $\Omega = 3/2$ state. Similarly in our spectra we got a higher ratio of CO^+/CO_2^+ for the $\Omega = 1/2$ state than for the $\Omega = 3/2$ state. The highest and the lowest amount of symmetric vibrational stretch was observed via the $\Omega = 3/2$ and the $\Omega = 1/2$ components of the 6f state respectively. Vibrational levels up to v=16 were observed for the $\Omega = 3/2$ component and similarly the most dissociation was observed for this level, whereas the PES spectra via $\Omega = 1/2$ component only produced v=0 and 1 of the symmetric stretch mode. This state had the lowest value of CO^+/CO_2^+ ratio in our study. For the 7f Rydberg state we found the $\Omega = 3/2$ component to dissociate more than the $\Omega = 1/2$ component. Likewise in the PES spectra, $\Omega = 3/2$ produced symmetric vibrational levels up to 9 and $\Omega = 1/2$ only up to 4. Dobber concluded that the symmetric vibrational levels seen were due autoionization from the Rydberg state leading to the A ${}^{2}\Pi_{u}$ ionic state. Since this state has a considerably large C-O bond length (1.2274 Å) than the ground ionic state (1.1769 Å). [8] this seems very

conceivable. Whatever the case, from the above discussion it is clear that the symmetric vibrational excitation in the CO_2^+ ion increases the fraction of dissociation.

In addition to these symmetric vibrational levels Dobber et al. also observed bending and asymmetric vibrations for all the states to a varying degree. For the 5f state for both the spin orbit components, the bending vibration, ν_2 , was observed up to 2 but for $\Omega = 3/2$, $\nu_2 = 1$ was missing. Asymmetric vibration, ν_3 , was observed from 1 to 3 for both the components of these states. PES spectra via the 6f state showed only $\nu_2 = 1$ for the $\Omega = 3/2$ component and $\nu_2 = 1$ and 2 for the $\Omega = 1/2$ component. This was reversed for the ν_3 vibration, where for $\Omega = 3/2$, $\nu_3 = 1$ and 2 were observed and $\nu_3 = 1$ was observed for $\Omega = 1/2$. In the 7f spectra the bending and asymmetric vibrations were observed up to 2 for both the components except for $\Omega = 3/2$ where the bending vibration was observed up to 5.

Dobber's group explained that the odd levels of the bending and asymmetric vibrational levels are forbidden for even photon transitions. The bending mode was due to coupling between the X ${}^{2}\Pi_{g}$ ground ionic state and the B ${}^{2}\Sigma_{u}^{+}$ ionic state and the Rydberg states leading to it via the ν_{2} bending vibration [9, 10, 11, 12]. Dobber's explanation for the asymmetric vibrational levels seen is the coupling between the X ${}^{2}\Pi_{g}$ ground ionic state and the A ${}^{2}\Pi_{u}$ and its Rydberg series via the asymmetric vibration.

5.3.2 Laser Power Dependency of the ratio CO^+/CO_2^+

The laser pulse power dependence of REMPI is another aspect which will give more insight into the mechanisms of ionization and dissociation. From the previous experiments by Johnson and co-workers and Dobber et al. it was established that autoionization dominates direct ionization for CO_2 via the nfseries and also that the CO^+ ions are produced by dissociation of CO_2^+ ions [6, 7]. In this case, once the resonance intermediate level is reached by a 3photon transition one more photon is absorbed to excite the autoionizing level (see figure 5.13). At this point CO_2 molecule will autoionize into the various vibrational levels of the ground ionic level. Even though the energy of 5-photons is sufficient to reach the CO^+ ($A^2\Pi$) + O (³P) dissociation continuum directly from the ground state of CO_2 , once it goes through autoionization and the photoelectron carries away kinetic energy, it requires 2 photons to reach this state even from the highest observed vibrational level of the ionic ground state. X, of CO_2 , (see figure 5.18).

Considering that production of CO_2^+ ions requires 4 photons opposed to 6 photons needed for the production of CO^+ ions. we were surprised to see such little laser power dependence in the CO^+/CO_2^+ ratio in our study. For the $\Omega = 1/2$ component of the 6f state this ratio is almost constant throughout the laser pulse power range in our experiment. Considering this lack of laser power dependence in the ratio CO^+/CO_2^+ we concluded that the 2-photon transition from ground ionic state, $X(^2\Pi_g)$ to the $CO^+(A^2\Pi)+O(^3P)$ continuum



Figure 5.18: Adiabatic correlation diagram of CO_2^+ with its dissociative products [5]

is saturated for the laser pulse energy range in our experiment. This is not surprising; as discussed in section 5.2, we found that the 3-photon resonance transition too is partially saturated.

When saturation is considered there is an important difference between a "closed" two level system and an "open" two level system. A "closed" two level system refers to a system in which the total population of both states is constant, whereas in an "open" two level system these states can be populated or depopulated due to decay and excitation to and from other states. At very high laser power one can neglect spontaneous emission and consider only stimulated emission and absorption. Consider the two level "closed" system in figure 5.19(a). If N_1 and N_2 are the population densities of the lower (1) and the upper (2) levels respectively, the rate equations for the non degenerate levels 1 and 2 can be given by:

$$\frac{dN_1}{dt} = -N_1\rho B_{12} + N_2\rho B_{21} + N_2A_{21}$$
(5.1)
and

$$\frac{dN_2}{dt} = -N_2\rho B_{21} + N_1\rho B_{12} - N_2 A_{21}$$
(5.2)

Here ρ is the laser power density. A_{21} is the Einstein's coefficient for spontaneous emission and B_{12} and B_{21} are the Einstein's coefficients for stimulated emission from level 1 to 2 and 2 to 1 respectively, since

$$B_{12} = |<1|D|2>|^2$$
(5.3)

and



•

Figure 5.19: (a) "Closed" two level system. where $N = N_1 + N_2$ is fixed. (b) "Open" two level system where level 2 gets dissociated.

$$B_{21} = |\langle 2|D|1\rangle^*|^2 \tag{5.4}$$

$$B_{12} = B_{21} \tag{5.5}$$

For very high laser power A_{21} term can be neglected. Therefore, for complete saturation the equations 5.1 and 5.2 become

$$\frac{dN_1}{dt} = (N_2 - N_1)\rho B_{12}$$
(5.6)
and
$$\frac{dN_2}{dt} = (N_1 - N_2)\rho B_{12}$$
(5.7)

Under stationary conditions $dN_i/dt = 0$ (i=1 or 2). Hence, from equations (5.6) and (5.7) $N_1 = N_2 = N/2$ where $N = N_1 + N_2$. Therefore, under complete saturation the system will leave each level with 50% of the population.

In an open system where the molecules may decay due to other mechanisms. like dissociation, the system will not have a constant population. Consider a two "open" level system as shown in figure 5.19 where the upper level decays. This system is analogous to our system for CO_2 after it reaches the ground ionic state. For example level 1 in this system could be our ground ionic state of CO_2 and level 2, the state which is reached after the two photon transition from the ground ionic state from which the ions dissociate. In a system like this the population will be constantly decreasing. Therefore at absolute saturation, the lower level will have a population between 0 to 50%, depending on how fast the upper level decays. If depopulation of the upper level immediatly follows the transition to the upper state, there will be no stimulated or spontaneous emission to the lower level.

If there is no saturation, increasing laser power would increase dissociation and therefore increase the ratio of CO^+/CO_2^+ . For an example from our experiment, if at 2.3 mJ pulse energy 85% of CO_2^+ ions are dissociated, then at 7.3 mJ there should be only one in $10^4 CO_2^+$ ions remaining. As in our experiment. for the ratio CO^+/CO_2^+ to remain constant throughout this range the transition should be completely saturated. What is surprising is that even under saturation conditions we see a significant amount of CO_2^+ ions. This indicates that either the dissociative state has a finite lifetime or a fraction of the molecules in the ground ionic state is transparent to the laser light. The later reason is unlikely since we see a ratio close to 6 to 1 for all the states with little symmetric vibrational excitation but varying degrees of bending and antisymmetric vibrational excitation. For example, if the asymmetric vibration is transparent to the laser, the states which show a lot of asymmetric vibrational activity should dissociate less, giving a CO^+/CO_2^+ ratio of less than 6. Since, this was not the case in our experiment, it is unlikely that the laser is transparent to some of the molecules. Therefore, this is not a reasonable argument for observing such a large fraction of undissociated CO_2^+ ions.

From the above discussion it seems likely that the dissociation of the upper level is not immediate and that it is sufficiently long lived to allow stimulated emission to the ground ionic level. Since a significant fraction. 18%. of molecules remain undissociated, the lifetime of the excited state should be comparable to the pulse length. A rough estimate of the lifetime of the excited state can be calculated by using the CO^+/CO_2^+ ratio after the laser pulse.

For our open two level system the equations can be written as

$$\frac{dN_1}{dt} = (N_2 - N_1)\rho B_{12}$$
(5.8)

$$\frac{dN_2}{dt} = (N_1 - N_2)\rho B_{12} - \alpha N_2 \text{ and}$$
 (5.9)

$$\frac{dN_3}{dt} = \alpha N_2 \tag{5.10}$$

where N_3 is the dissociation rate and α is a decay parameter, which is $\frac{1}{\tau}$ where τ is the lifetime of the state.

From equations (5.8) and (5.9)

$$\frac{d(N_1 + N_2)}{dt} = -\alpha N_2$$
 (5.11)

at saturation

$$N_1 = N_2 \equiv \frac{N}{2}.$$

Therefore, equation (5.11) becomes:

$$\frac{dN}{dt} = -\frac{N}{2}\alpha$$

$$\Rightarrow \int \frac{dN}{N} = \int -\frac{\alpha}{2} dt$$

$$\Rightarrow \ln N = -\frac{\alpha}{2}t + const.$$

$$\Rightarrow N = Ae^{\frac{\alpha t}{2}}$$
(5.12)

where A is an arbitrary constant.

At t = 0, $N = N_0$ total number of molecules $\Rightarrow A = N_0$

Equation 5.12 \Rightarrow

$$N = N_0 \exp(-\alpha t/2)$$
 and $f = \exp(-\alpha t/2)$

where $f = \frac{N}{N_0}$, the fraction of molecules remaining after a laser pulse of length t. Therefore, the fraction dissociated at the end of the pulse is

$$f_{dis} = 1 - \exp^{-(\frac{1}{2\tau})}$$
(5.13)

as $\alpha = \frac{1}{\tau}$, where τ is the lifetime of the upper state.

If, after the laser pulse, half of the remaining molecules are left in the upper state and if we assume that they all dissociate before they fluoresce to the lower state, than the total fraction of the molecules that dissociate, f_{dis} , is

$$f_{dis} = (1 - \exp^{-(\frac{t_l}{2\tau})}) + \frac{1}{2} \exp^{-(\frac{t_l}{2\tau})}$$
(5.14)
$$f_{dis} = 1 - \frac{1}{2} \exp^{-(\frac{t_l}{2\tau})}$$
(5.15)

If we define $CO^+/CO_2^+ \equiv \Gamma$

$$f_{dis} = \frac{CO^+}{CO_2^+ + CO^+} = \frac{\Gamma}{1 + \Gamma}$$
(5.16)

From equation (1.14) and $(1.15) \Rightarrow$

$$\tau \sim \frac{t_l}{2\ln(1+\Gamma)/2} \tag{5.17}$$

For a three-photon transition, the duration of saturation can be estimated as 8 nsec/ $\sqrt{6} \sim 3$ nsec for a 8 nsec pulse. If we assume the two photon transition occurs during half of this time, t_l can be estimated to be 1.5 nsec. For vibrationally cold molecules CO^+/CO_2^+ ratio, $\Gamma \simeq 6$ and the lifetime works out to be ~ 600 psec. For vibrationally excited molecules $\Gamma \simeq 20$ which yields a lifetime of 300 psec. However, this is a very crude estimate of the lifetime.

Starting from vibrationless level of the ground ionic state of CO_2 , a two photon transition can just about reach the $CO^+(A^2\Pi) + O(^3P)$ dissociative level [14]. Out of the A, B and C excited ionic states the C ionic state correlates adiabatically with this dissociation limit. The C ionic state is an allowed two photon transition from the ground ionic states. Therefore, it is very likely that the CO_2^+ ions absorb two photons to reach this state and get predissociated. In the wavelength range we have used in our experiment the two photon transition puts the molecule 0.4 to 0.7 eV above this dissociation limit. This makes us believe that there is a potential barrier that is higher than 0.7 eV above the dissociation limit (see figure 5.22) which causes predissociation. This is not unusual as according to Herzberg [14] it is very common to have a potential barrier separating the bound state and the dissociating limit.

In our experiment, due to autoionization higher vibrational levels in the ground ionic state are reached at the 4 photon energy. Due to this, molecules left in these levels will be able to reach above the potential barrier in the C state via the two photon transition. This will make these levels dissociate fast compared to the ones below the potential barrier. The ones that do not reach the potential barrier will have to overcome this barrier to dissociate. Therefore, these ions have enough time to undergo stimulated emission and deexcite into



Figure 5.20: Suggested curve of the predissociated $C^2\Sigma_a^+$ state. Not to scale.

the ground ionic state. We believe that this is why we see more dissociation for the states that undergo autoionization at the 4 photon energy. Two other facts support this model. First, is that dissociation increases with the principle quantum number in the nf series, which means that dissociation increases with energy. This makes sense as higher energies put the molecules in higher vibrational states and therefore, above the potential barrier or closer to the top of the barrier where they may tunnel through faster. The second is that Dobber et al.'s CO^+/CO_2^+ ratio for picosecond and nanosecond lasers work out to be 0.7 and 5.6. Our estimate for the lifetime of the state, 600 psec, is very long compared to their 3 psec laser width. For a pulse this short the system can be treated as a "closed" two level system. For complete saturation a CO^+/CO_2^+ ratio of 1 is ideal. Therefore a ratio of 0.7 observed agree very well with this model. The ratio of 5.6 observed with the nanosecond laser agrees remarkably well with our ratio of 6. This further agrees with our model that a finite lifetime is the reason for the significant amount of undissociated CO_2^+ .

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Chapter 6

Conclusion

The molecule CO_2 has been studied extensively by numerous scientist for at least the past sixty years. However, the assignment of its spectra and the dissociation and ionization dynamics of this molecule are still under a lot of controversy. Nevertheless, we believe that the spectra of $nf^2\Pi_{\Omega}$ Rydberg series has been well established by single-photon absorption studies by Cossart-Magos [1] and (3+1) REMPI studies by Johnson's and Dobber's groups [2, 3, 4, 5, 6, 7] and the present study. Two components due to spin-orbit splitting of ~ 160 cm^{-1} were observed for all the nf states in all the above studies. Sharp rotational features were also observed in the nf rotational contour in these studies. This lead to the belief that compared to the other allowed Rydberg series in single and three photon spectra, np, the nf series is much less perturbed by other dissociative states. Johnson and his coworkers did a theoretical study based on the assumption that the singlet-triplet splitting is zero, which is valid for a molecule whose Rydberg electron is very detached from the rest of the molecule. They were able to produce a very close rotational fit under this assumption, which led them to believe that the Rydberg electron is independent of the rest of the molecule. Another interesting observation in REMPI spectra was that the CO^+/CO_2^+ ratio increased with increasing *n*, principal quantum number, which meant that dissociation increases with increasing *n*. The explanation for this stems from the dissociation and ionization mechanisms of the CO_2 which will be summarized below.

Unlike the spectra of the nf series, a lot more work is needed to establish the dissociation and ionization mechanisms of CO_2 via these states. At first, Johnson et al. suggested that dissociation occurs while the molecules being ionized by a dissociative state coupled to the nf states. In our early studies, we associated this state to a singlet states by comparing dissociation rates of the two spin-orbit components of the 4f and 5f series. This model was further used to explain another interesting phenomena observed by Johnson and his co-workers: vibrational progressions in the ground ionic state, X ${}^{2}\Pi_{g}$. These progressions were highly unlikely according to the Franck-Condon principle. Nevertheless, in the above model, Franck-Condon factors are changed, and therefore these progressions can be explained. However this explanation of a dissociative state coupled to the nf states was proven unlikely by another study by Johnson's group and two more studies by Dobber 's group. Our further studies of the 6f and the 7f series also disproved this model.

Johnson and Dobber's groups did REMPI-PES studies and established that

the dissociation and the observed vibrational progressions are not due to any physical dynamics at the three photon nf Rydberg level but are due to some phenomenon at higher energy. They explained that the reason for the vibrational progressions is autoionization of the Rydberg states leading to excited ionic states at the four photon energy. However, because of the lack of asymmetric stretching mode in their PES spectra. Dobber et al. suggested that this is not the reason for dissociation. They speculated that dissociation takes place after ionization after another two-photon transition from the numerous vibrational levels of the ground ionic state. What was puzzling about their explanation is that their observation of a lower dissociation rate for a picosecond laser than for a nanosecond laser.

In the present study we observed a dramatic change of the dissociation rate with frequency. It was clear that the dissociation rate increased with increasing frequency, in other words with increasing principle quantum number n in the nf series. Also, we observed a clear difference in rates for the two spin-orbit components of each nf state. This difference did not depend simply on the identity of the intermediate state, in some states the $\Omega = 1/2$ component dissociated more while in the others $\Omega = 3/2$ dissociated more. We found that these rates stayed remarkably constant for different powers of the laser even though the production of CO^+ ions required more photons than CO_2^+ ions. From this observation we came to a conclusion that the two photon transition which we think is. X ${}^2\Pi_g \longrightarrow C^2\Sigma_g^+$, leading to dissociation of the ion was

saturated. When comparing with Dobber et al.'s PES spectra, a nice correlation between their observed vibrational progressions and our dissociation rates were noticed. The states and the components that showed a lot of symmetric vibrational levels in PES spectra, showed more dissociation in our spectra. If the two photon transition, X ${}^{2}\Pi_{g} \rightarrow \rightarrow C^{2}\Sigma_{g}^{+}$, which led to dissociation of CO_{2}^{+} ions was saturated we expected all the CO_2^+ ions to be dissociated. Therefore, it was a surprise to see a significant amount of undissociated CO_2^+ ions present in our spectra. These two observations led us to believe that a large fraction of the CO^+ ions are made by predissociation rather than direct dissociation. We believe that after reaching the various vibrational levels of the ground ionic state. CO_2^+ ions undergo a two-photon dipole allowed transition to the C $^2\Sigma_q^+$ excited ionic state which in turn gets predissociated. We also believe that the $C^{2}\Sigma_{g}^{+}$ state has a potential barrier to the order of an electron volt above the dissociation limit. This excites the molecules that are left in the higher vibrational levels (due to autoionization) above this potential barrier where they undergo prompt dissociation. Whereas, the ions left in the lower vibrational levels (mainly due to direct excitation from the nf states) reach below this potential barrier and tunnel through to become dissociated. Since the tunneling process takes time, this will lead to a certain lifetime of this state. We estimated the mean lifetime of this state to be about 600 psec by using the ratio of CO^+/CO_2^+ from our spectra.

This model explains two other phenomena observed in REMPI spectra. First

is the observation of increased dissociation with increasing principle quantum number in the nf Rydberg states. This makes sense, since increasing the frequency leads to higher excited vibrational levels which ultimately put the ions above the potential barrier in the C excited ionic state, leading to prompt dissociation. The second is the lower dissociation rate observed in Dobber and co-workers spectra for the picosecond laser compared to the nanosecond laser. For a 3 psec laser, the estimated lifetime of 600 psec for this state is long; therefore, the ion will not have much time to dissociate. But, a nano second pulsed laser will have enough time to dissociate a molecule which has a lifetime of 600 psec and will lead to higher dissociating rate.

This method of saturation spectroscopy can be used in future experiments to find lifetimes of exited states. In the past, lifetime studies have always required picosecond lasers or femtosecond lasers which are more expensive than nanosecond lasers. So this technique of measuring lifetimes will be an important addition to these studies.

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Appendix A

Calculation of uncertainites in signal area

In our calculations of CO^+/CO_2^+ ratios, we used three computer programs: Gnuplot to plot data. Microsoft EXCEL to calculate the areas, and cumulative uncertainties and Graphical Analysis for Windows for error estimates. Each spectrum consisted of about 2000 data points. We first plotted this data using Gnuplot. To calculate the areas of signal in each peak, we first had to determine a baseline. This was done using Microsoft EXCEL to calculate the average intensity in a flat region on either side of the peaks in our spectra. The sum of signal in these regions was obtained for several such areas in each spectrum. if possible, and the average baseline per channel was calculated. The area of actual signal under each peak was then calculated in Microsoft EXCEL, using the equation

$$Area = \sum_{\lambda_{Mun}}^{\lambda_{Mun}} (Intensity - Baseline) \times Stepsize$$

where λ_{Min} and λ_{Max} are the wavelengths at which a given peak begins and ends.

To estimate uncertainties in baseline and signal, we first used *Graphical Analysis for Windows*. From this program, we found the typical standard deviation for the baseline signal by taking small regions of the flat areas of the spectrum and fitting a line to these region. In the areas where there were peaks, we chose a small region of the spectrum and fitted a straight, sloped line to obtain the standard deviation of the shot-to-shot signal variation. This was done for several regions of each spectra. These errors were typically about 6% of the peak height (before baseline substraction was taken into account).

For low signal strengths, however, signal areas were very sensitive to the assignment of the baseline. To estimate the uncertainty due to baseline subtraction, we used *EXCEL* to vary the baseline and determine the resulting uncertainty in signal area. Having found the typical uncertainty in signal and the typical uncertainty in baseline, we can propagate these percentage errors to find the total uncertainty according to the formula:

$$\frac{\delta(CO^+/CO_2^+)}{(CO^+/CO_2^+)} = \left[\left(\frac{\delta(CO^+)}{(CO^+)} \right)^2 + \left(\frac{\delta(CO_2^+)}{(CO_2^+)} \right) \right]^{1/2}$$

The final uncertainties used in the graphs in figure 5.17 are given in Table 1.

5f	laser Energy (mJ)	co/co2: 1/2E	ror. 1/2	co/co2: 3/2error	: 3/2
	2.25	5.3	2.9	4.2	2.8
	3.5	4.7	1.1	3.1	0.8
	4	5.4	1.1	3.6	0.8
	4	8.0	2.3	5.5	1.6
	4.75	7.8	1.4	4.3	0.8
	5	10.2	2.4	7.0	1.4
	5.5	9.5	1.7	4.8	0.8
	6	15.9	3.7	6.4	1.2
	7	14.7	2.7	8.8	1.4
	8	13.2	2.4	6.1	1.0
6f	laser Energy (mJ)	co/co2: 1/2 en	ror: 1/2	co/co2: 3/2error:	3/2
	2.25	1.2	0.3	4.0	0.9
	3	4.7	1.2.	12.0	2.8
	3	4.8	2.5	11.3	4.5
	4	6.9	1.2	17.4	3.1
	4	6.2	1.5	17.2:	4.0
	5	6.4	1.2	15.5	2.9
	5.25	6.2	1.1	17.4	3.2
	5.5	6.0	1.0	16.8	2.7
	6.5	6.1	0.9	19.0,	2.4
	6.75	7.1	1.2	19.4	3.6
	6.75	5.5	0.9	16.8	3.3
	7.25	7.9	1.3	17.5	2.9
7f	laser Energy (mJ)	co/co2: 1/2 en	ror: 1/2	co/co2: 3/2error;	3/2
	2.25	1.2,	0.3	4.0	0.9
	3	4.7	1.2	12.0:	2.8
	3	4.8	2.5	11.3;	4.5
	4,	6.9	1.2	17.4;	3.1
	4	6.2,	1.5	17.2	4.0
	5	6.4	1.2	15.5	2.9
	5.25	6.2	1.1	17.4	3.2
	5.5	6.0	1.0	16.8	2.7
	6.5	6.1	0.9	19.0	2.4
	6.75	7.1	1.2:	19.4	3.6
	6.75	5.5	0.9;	16.8	3.3
	7.25	7.9	1.3	17.5	2.9

Table A.1: Errors in CO^+/CO_2^+ ratio for $\Omega = 1/2$ and 3/2 limits of 5f, 6f and 7f.

Appendix B

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Dependence of signal on laser power density

In REMPI experiments the signal intensity depends on the power density at the spot where the REMPI processes occur. In our study we used a power meter (Scientech, model number 361) to measure the laser power in Watts. This meter measured the average power over several laser shots. The laser operated at 10Hz and we calculated the average energy per pulse by dividing the power meter reading by 10.

To estimate the power density after focusing the laser we assumed the laser's radial intensity distribution has a Gaussian profile. Under this assumption the laser power density at the focal point will be proportional to the laser pulse energy, as measured by the power meter. For a Gaussian beam focused by a lens with focal length f and the waist size at the lens, w_s , the spot size in the beam waist, w_o , is, given, in the approximation $f \gg w_s$, by:

$$w_o = \frac{f\lambda}{\pi w_s}$$

Here, λ is the wavelength of the laser. Our laser spot size at the lens was

about $1 mm^2$, and the resulting waist size at the focus would be about 1.8×10^{-3} cm. The resulting power density would be about $1.3 \times 10^{11} W/cm^2$. By contrast, the work of Johnson and coworkers was performed at a power density of $1.3 \times 10^{11} W/cm^2$ and the work of Dobber et al. with a power density of $1.3 \times 10^{12} W/cm^2$.

We believe our laser beam is reasonably Gaussian because of the reasons given below.

- 1. The dye laser was longitudinally pumped, therefore the dye beam and the pump beam combined lengthwise almost parallel to each other in the amplifiers (see figure 4.2). The resulting dye beam was spatially homogeneous and circular. In contrast, a transversely pumped amplifier, where the two beams cross perpendicular to each other, the dye beam was pumped harder on one side. This led to a laser that was spatially inhomogeneous.
- In our study, each log(laser power) vs. log(ion intensity) curve fit a straight line very well as shown in figure 5.7. The calculated values for the slopes. n, were between 2 to 3 for CO₂⁺ ions and between 2.5 to 3.5 for CO⁺ ions. These values were similar to n = 2 for CO₂⁺ ions and n = 4 for CO⁺ ions in Johnson and coworkers' studies.
- 3. Even though our calculated power density at the focal spot was the lowest out of the three studies compared, our REMPI signal levels were very good. High signal levels require high laser power densities. This indicates that our laser was focused to a very small spot. Since Gaussian beam

focuses to the tightest waist size which leads to the highest power density. this indicates that our laser is reasonably Gaussian.

Our spectra were very reproducible as in our power dependence study the calculated CO^+/CO_2^+ ratios for the same laser energy were within the error bars (see figure 5.17). For an example, some spectra of the 5*f* state were taken four months apart. During this period, many adjustments were made to the dye laser components. This leads us to believe that the beam quality of our laser remained unchanged in our study.

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