Molecules, Light, and Chemical Reactions

Current Frontiers in the Chemical Physics of Astrobiology

Félix Fernández-Alonso

Department of Chemistry, Stanford University
Stanford CA 94305-5080 USA

October 20, 1999

1 Introduction and Scope

The field of Astrobiology is relatively novel. As such, it attempts to take full advantage of all the tools available for scientific inquiry that will enable a successful search for life forms elsewhere in the universe. The main purpose of this write-up is to show the relevance of various elementary physical and chemical processes to the field of Astrobiology. This motivation stems from a very simple realization, namely, that a more complete understanding of the chemistry and physics of galactic bodies will be crucial at assessing the potential for life to exist in other places.

1.1 Primary objectives

Morrison and Schmidt [1] have recently reviewed the main goals of the field of Astrobiology. The first thing that struck me as I read this monograph was the broad range of questions posed as relevant to this scientific discipline. Here, I summarize the areas that are directly related to the topics presented here.

1. To understand how life arose on Earth, it is necessary to understand the environmental conditions present at the time life emerged. Whereas this is ultimately the task of the atmospheric modeler, much remains to be known about the photophysics and photochemistry of the atmosphere, specially in those parts of the atmosphere where dense radiation fields prevail. Furthermore, since we know that the terrestrial Biosphere has co-evolved with the Earth for over 3.5 billion years, we have to understand how each affects the other and at the same time develop reliable markers that will be indicative of the coupling between the animate and the inanimate.

2. To investigate the limits for life on our planet and other planets, we require not only the study on Earth of life forms in extreme environments (i.e., high temperature, high UV flux, etc), but also an understanding of the physical conditions prevailing in other planets. Knowing the chemical composition of a planet's atmosphere and understanding its global atmospheric chemistry can be very valuable at making educated guesses about what possible life forms may or might have existed.

3. To determine how common are habitable worlds in the universe, it is necesary to expand our current observational data base to include measurements with improved spatial and spectral resolution. This will necessarily require further studies of the spectroscopy of molecules abundant in the universe and an understanding of the conditions that lead to observed spectral signatures. By pushing our limits of detection it will be possible to characterize protoplanetary disks and extra-solar planetary systems.

4. To recognize the signature of life on other worlds, we need to learn to identify the chemical signatures of life on distant worlds through remote sensing of its atmosphere and surface. It is also necessary we attempt to generalize the process of coevolution of planet and life (see item 1). Chemical analysis (composition, isotope fractionation) of meteoritic samples of known origin and of samples returned from space missions contain a vast amount of information. It is crucial we correctly interpret this data in the context of its place of origin, that is, we need to understand where to search and how to identify evidence for life.

1.2   The Need to Understand

In addressing the goals posed in the previous section it is essential we have at our disposal reliable models that can connect our observations with the processes that caused them. We could cite the following main areas where our understanding is still weak and calls for further study.

1. Learn to differentiate sources of organic material either remotely or in-situ. Organic molecules similar to those that are thought to have preceded life can be formed in a large variety of enviroments including cold (< 50 K) and low-density interstellar clouds. Synthesis of these species in the interstellar medium is still a matter of debate, specially in regard to the role of interstellar grains, radiation-induced processes, and gas phase neutral-neutral reactions. The development of predictive models relies on an accurate assessment of all processes that lead to significant and measurable signatures.

2. Determine the environmental conditions in those places where we suspect life exists or existed. To this end need to link measurements of composition, temperature and density with reliable kinetic models that

can account as accurately as possible for the observed trends. This can only be done if we understand the underlying network of chemical and physical processes. Of all these processes, relatively little is known about the response of many molecules to ultraviolet (UV) and vacuum-ultraviolet (VUV) radiation. The role of chemical reactions initiated by the photodissociation of atmospheric molecules is also known to play an important role in our planet, but their effect is largely unknown in other planetary bodies. Along the same vein, and once environmental conditions are known, it is possible to evaluate their effect on various known life forms and determine which one(s), if any, are more suitable for any given environment.

3. The detection of habitable planets outside the Solar System hinges upon our ability to carry out spectroscopic observations of key molecular species. For example, some of the factors that affect the stability of liquid water (thought to be essential for life to evolve) are the mass composition and dynamics of a planet's atmosphere. Ideally, we would like like to gather this information remotely and reliably.

4. Define a database of astronomically detectable spectroscopic features that may be indicative of habitable conditions. Accordingly, it is essential we develop a large spectroscopic database for interpreting these features. In some cases, that is, when in-situ exploration is possible it is also required we develop spectroscopic tools that will actively search for the key ingredients of life, i.e., water, organics, etc. This effort includes the development of spectroscopic sensors.

5. Identify aspects of the Earth's atmosphere that are strongly dependent on ecological processes and use these model systems to assess the likelihood of life in other parts of the universe.

1.3   The Tools

The field of molecular and chemical physics has benefited greatly from the use of laser techniques during the last forty years The word "laser" is an acronym for "Light Amplification by the Stimulated Emission of Radiation." They afford a means of generating copious amounts of monochromatic, coherent, polarized, and highly directional radiation suitable for the study of the interaction of matter with electromagnetic radiation.

We will illustrate the use of this technology in three different areas of Astronominal interest. The first one will be in Section 2, where we will be concerned with the identification and study of spectroscopic features of the hydrogen and carbon monoxide molecules. Both species are key ingredients of the interstellar medium. Of particular interest is the current assessment of the role of interstellar grains in the chemistry of the interstellar medium. Owing to its abundance, the detection of spectroscopic features from H_2 which are indicative of grain processes is a topic of much interest. Carbon monoxide, though less abundant than the hydrogen molecule, renders itself to an easier detection in the IR and ultraviolet regions and, therefore, deserves careful study. We close this section by discussing the prospects of Cavity Ring-down Spectroscopy (CRDS) as a compact, reliable, and sensitive tool for the detection of trace atmospheric constituents in planetary missions.

A laser beam can also be used to study the breaking of chemical bonds in a very well controlled fashion. We call this process photodissociation. Detection of the products of the photodissociation process by the use of spectroscopic techniques yields a large amount of information about the details of the bond-breaking process. Current bottlenecks in the study of molecules of atmospheric interest revolve around the difficulties associated with the production of laser radiation in the frequency regions prevalent in planetary stratospheres and in the so-called "active regions" of the interstellar medium (50-200 nm). To date, only a handful of detailed photodissociation studies have been performed in this frequency range. Moreover, the competition between photodissociation and ionization, dissociative ionization, etc at these wavelengths needs to be answered.

Finally, chemical reactions involving free radicals can be initiated by the photodissociation process previously described in Section 3. It is not surpising to find that Nature also uses photodissociation at high altitudes to drive the bulk chemistry of the atmosphere. The intricate interplay between the abundance of a given radical species and its reactivity is very difficult to unravel unless we carry out extensive laboratory measurements. A prime example is given by the photochemical destruction of ozone in our stratosphere and the subsequent delicate balance between ozone and oxygen atom concentrations in the stratosphere and total UV flux in the troposphere. In Section ?? we propose the study of several photoinitiated chemical reactions that are known to be key players in the neutral-neutral chemistry of the interstellar medium and planetary atmospheres. Their study will hopefully help establishing the role of neutral chemistry in these enviroments as well

as determining to what extent nonequilibrium conditions are prevalent.

2 Spectroscopy of Astrophysically Relevant Molecules

2.1 Preliminaries

Spectroscopy is concerned with the study of the response of atoms and molecules to radiation. It is then no surprise to find that progress in this field has been a necessary requirement for the emergence of astrophysics, astrochemistry, and more recently, astrobiology. To put it in simple language, "we know what we see." In most cases, astronomical distances only allow for the analysis of the radiation reaching us after travelling very long distances. A classic example is the discovery and study of the rotational spectrum of the CN molecule in the interstellar medium. It provided the first evidence for the 3 K cosmic background radiation, although this fact was overlooked for over twenty-five years [2]. Advances in spacecraft technology in the past thirty years has allowed in-situ investigation of planetary bodies in the solar system. However, it still remains quite unlikely these missions will, in the near future, become commonplace for extrasolar exploration. Therefore, direct observation of the universe still remains largely in the hands of those willing to analyze the very few photons coming from distant (light-year) objects.

At present, over a hundred molecules have been identified in the interstellar medium. These include H_2, CO, OH, H_2O, NH_3 as well as a large variety of organics [3]. Techniques for their detection range from the millimeter/radio frequency range up to the visible and ultraviolet regions of the electromagnetic spectrum. Spectral lines from a given molecular species can be used to gain information about the chemical composition, density and temperature of the medium. This information has been indispensable in order to establish and improve our current and highly hierarchical view of the universe. According to this view, the universe is composed of large organizations called galaxies. Galaxies are composed of stars (stellar materials) and interstellar material. Interstellar material is further subdivided into large structures (1-100 pc) named interstellar clouds. Depending on their density, interstellar clouds are classified as diffuse, translucent, and dense. Over time, galactic matter cycles between stellar and interstellar material in a complicated network of chemical, photochemical, and nuclear processes.

2.2 Goals

2.2.1 H_2 from Interstellar Grains

The spectroscopy of the hydrogen molecule has been investigated thoroughly during the last century. As a homonuclear diatomic molecule, the lack of a dipole moment makes conventional infrared spectroscopy very difficult for the study of the the ground state rovibrational energy levels. In the case of the HD isotopomer, the dipole moment is so small ($\sim 10^{-4}$ Debye) that only absorption experiments using long path length and multipass spectrometers have been possible [4]. Given these physical limitations, the only way to carry out sensitive spectroscopic studies of the hydrogen molecule has been by the use of electronic, Raman and quadrupole radiative transitions.

Figure 1 shows some of the electronic states of the hydrogen molecule. Parity rules show that the two lowest electronic states, labeled B $^1\Sigma_u^+$ and C $^1\Pi_u$, can only be accessed by an odd number of photons. The transition frequencies for electronic transitions in the hydrogen molecule all lie in the vacuum ultraviolet region (VUV) of the electromagnetic spectrum. Light sources in this frequency regime are not easy to construct and control. In the past few years, laser sources have been designed to reach these wavelengths via non-linear frequency mixing in rare gases [5–12]. This has fostered numerous studies of the excited states of hydrogen, particularly by the use of double resonance techniques. In typical double resonance experiments, the VUV photon is tuned to a particular B $^1\Sigma_u^+ \leftarrow$ X $^1\Sigma_g^+$ or C $^1\Pi_u \leftarrow$ X $^1\Sigma_g^+$ transition. A second, less-energetic photon is used to probe higher excited states. These techniques have provided a wealth of spectroscopic information. Ubachs and co-workers have recently perfomed systematic spectroscopic studies of several high-lying excited states of this molecule including the B $^1\Sigma_u^+$, C $^1\Pi_u$, and EF $^1\Sigma_g^+$ states of the HD molecule [13], the H$\bar{\text{H}}$ $^1\Sigma_g^+$ state in H_2 and D_2, the B″B $^1\Sigma_u^+$ state in HD [14], and the I′ $^1\Pi_g$ outer well state in H_2 and D_2 [15]. In the particular case of the HD molecule, investigation of the H $^1\Sigma_g^+$ and B $^1\Sigma_u^+$ electronic states [16] has assessed the presence of strong adiabatic interactions between energy levels, implying complete gerade-ungerade symmetry breaking over a wide range of molecular quantum states. Some of these spectroscopic transitions have been considered as potential carriers of some of the observed diffuse interstellar bands (DIBS) [17–19]. Tsukiyama and co-workers have also studied high-lying vibrational levels of the EF $^1\Sigma_g^+$ state in H_2 [20], and measured fluorescence lifetimes from the EF $^1\Sigma_g^+$, GK $^1\Sigma_g^+$,
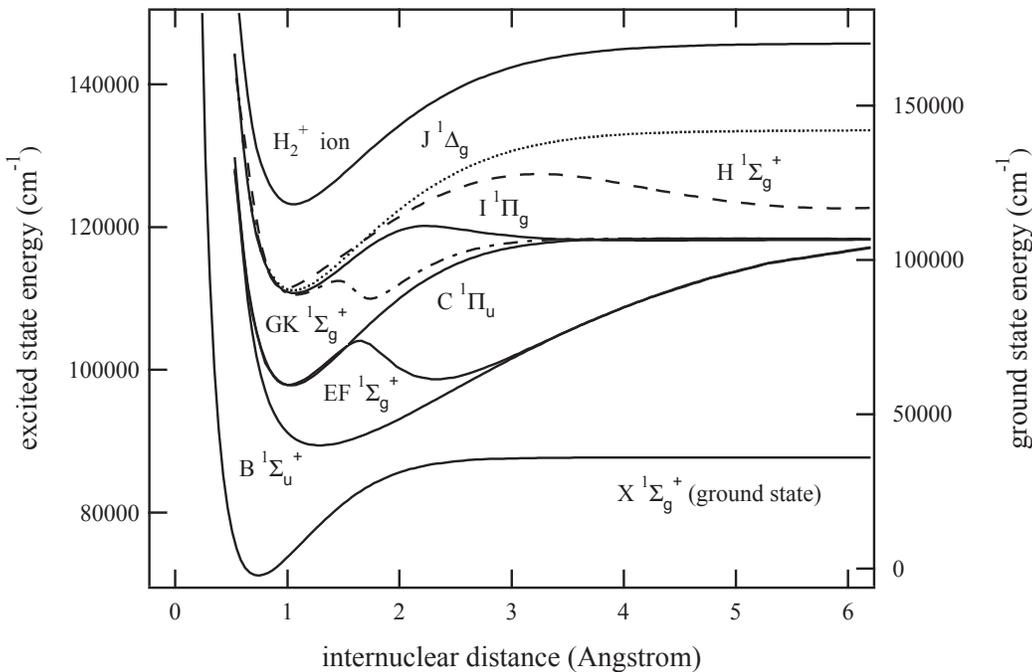
Figure 1: Potential energy curves for the ground and several excited electronic states of the H_2 molecule.

H $^1\Sigma_g^+$, I $^1\Pi_g$ and J $^1\Delta_g$ states in H_2 [21], as well as from the H $^1\Sigma_g^+$ and EF $^1\Sigma_g^+$ states in D_2 [22].

A different approach to the detection of the hydrogen molecule involves the use of multiphoton processes [23–25]. Owing to the gerade symmetry of the ground state, only states with the the same inversion symmetry are accessible via a two-photon transition. Of all these possible transitions, the only one which has been studied in detail involves the EF $^1\Sigma_g^+$ double-well state [26–28]. The frequencies required for this two-photon transition lie above 200 nm, wavelengths easily accessible with conventional dye lasers and non-linear optical doubling and mixing in BBO crystals. With typical laser output powers at these wavelenghts, mild focusing of the laser beam can yield sensitivities close to those attained via one-photon transitions.

The hydrogen molecule occupies a central role in the composition of the universe. The most abundant element is hydrogen (92 %) followed by helium (6 %), and the so-called "metals" with O (0.07 %), C (0.04 %), and N

11

(0.009 %) leading the list. One would expect that association of two hydrogen molecules would lead to the formation of this molecule in large amounts. Whereas this is what we observe, that is, the hydrogen molecule being the most abundant molecule in the universe, the formation mechanism is unclear. The association of two hydrogen atoms according to the process

$$H + H \rightarrow H_2 \tag{1}$$

cannot happen in the gas phase in the absence of a third body to dissipate the energy released as the H-H bond is formed. This sole fact calls for the inclusion in current chemical models of the interstellar medium of gas-grain processes. The exploration of the chemical role of grain processes in space is the subject of recent Faraday Discussion [29] To date, most working kinetic models have vastly neglected the heterogeous processes that take place at the interface of these grains, which are thought to account for ca 1 % of the interstellar mass. These interstellar grains are made up of carbon or silicate cores surrounded by amorphous ice mantles. It is thought that recombination of hydrogen atoms and subsequent desorption of H_2 molecules from the surface leads to a large degree of vibrational excitation of the molecule. Laboratory characterization of these surfaces clearly requires a knowledge of the spectroscopy of this molecule, either via the use of one-photon VUV or two-photon UV spectroscopy. This need, by itself, justifies further efforts at characterizing spectroscopically this molecule in the laboratory in an attempt to develop better ways of detecting this species.

Vibrational excitation following recombination of hydrogen atoms on surfaces is not a phenomenon restricted to interstellar grains [30–33]. During the course of my doctoral work, I have investigated and utilized this phenomenon to study several excited electronic states of the hydrogen molecule and isotopomers. Hydrogen atoms can be generated in a hot filament held at temperatures between 2000 and 3000 K. Recombination on the chamber walls of an ultrahigh-vacuum chamber leads to significant vibrational excitation of the diatomic product. The primary use of this "hot" H_2 has been in the search and calibration of the hydrogen two-photon spectrum via the EF $^1\Sigma_g^+$ state [34]. In the course of our investigations we have detected absorption features to higher excited states including I $^1\Pi_g$, J $^1\Delta_g$, and GK $^1\Sigma_g^+$ [35]. Figure 2 shows the two-photon spectrum of $H_2(v' = 3)$ via the I $^1\Pi_g \leftarrow$ X $^1\Sigma_g^+$ electronic transition, which has not been previously observed in the laboratory. Experimental knowledge of the energy level structure is necessary since
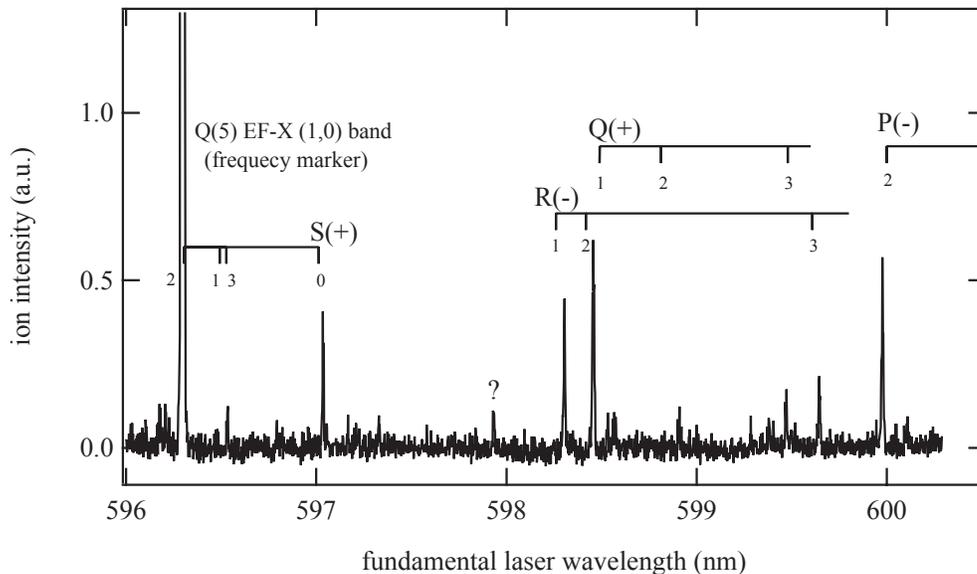
Figure 2: H$_2$ (2+1) REMPI spectrum ca. 198-200 nm.

ab initio calculations of comparable accuracy are generally not available owing to the large non-adiabatic couplings between different electronic states.

Ultimately, these spectroscopic studies in the VUV and UV regions will enable the laboratory characterization of the hydrogen recombination process in solid-gas interfaces resembling those found in the interstellar medium. Moreover, remote detection of vibrationally excited hydrogen molecules has to be necessarily preceded by a detailed spectroscopic study of these species in the laboratory. Measurement of the steady-state concentrations of these species in space could become a useful diagnostic to map the distribution and density of grains in space.

2.2.2 Carbon Monoxide

The presence of carbon monoxide in the universe is quite irregular. It is a very common species in the interstellar medium and protoplanetary nebulae with number densities approaching 10^{-4} of the hydrogen molecule concentration. In comets, it represents up to 10 % of volatile species, with only H$_2$O being more a more abundant gas-phase molecule. In Solar planets, however, it is very rare with concentrations not exceeding a few parts per million

(ppm). Despite CO is observed in most planets, its sources and sinks are not well understood [36]. It is currently thought that the planetary source of CO in most planets is not primordial. In terrestrial planets, for example, the major source of this molecule is thought to be the photodissociation of carbon dioxide in the upper layers of the atmosphere. Most of these conclusions are based on a limited set of data and largely remain tentative. The major problem resides in the lack of spectral resolution of current infrared spectrometers and the inability of mass spectrometers to discriminate CO from other species with the same mass as, for example, N_2 and C_2H_4.

Spectroscopically, however, carbon monoxide can be more readily detected than its more abundant partner H_2, whose higher number density is severely offset by the weakness of the quadrupole-allowed transitions in the infrared [37]. Infrared spectroscopy has been used to record the rovibrational spectrum of this molecule from a variety of cosmic sources. In addition, strong electronic emission in the Cameron (a $^3\Pi \leftarrow X\ ^1\Sigma$) bands have been observed in recent measurements of the Red Rectangle by the Hubble Space Telescope [38]. This emission has also been observed in the Mariner 9 space mission to Mars [39] and is thought to be the product of carbon dioxide photodissociation in the Martian atmosphere with an onset at 110 nm [40]. It seems that whenever this ubiquituous molecule has been detected, questions have been raised about its origin and distribution, many of which remain unsolved.

In summary, VUV spectroscopy of carbon monoxide still remains an active area of study in the laboratory. Double-resonance spectroscopic studies of the excited electronic states of this molecule deserve more attention so as to provide a good data base for comparison with emission measurements from space.

2.2.3 Measurements Beyond the Laboratory

Thus far we have been mainly concerned with the build-up of a reliable spectroscopic data base and an increase of our knowledge about the energy level structure of the hydrogen and carbon monoxide molecules.

Another use of laser spectroscopy involves the porting of measuring devices in planetary and space missions. Until now, most optical instrumentation relied on the measurement of emission spectra. There has been an enormous amount of information coming from these measurements, as for example, the extreme ultraviolet spectra measured by Voyager 1 [41, 42] and

R=99.99%   R=99.99%

time

Laser pulse
in

Cavity with
absorbing
species

Ring-down
signal out
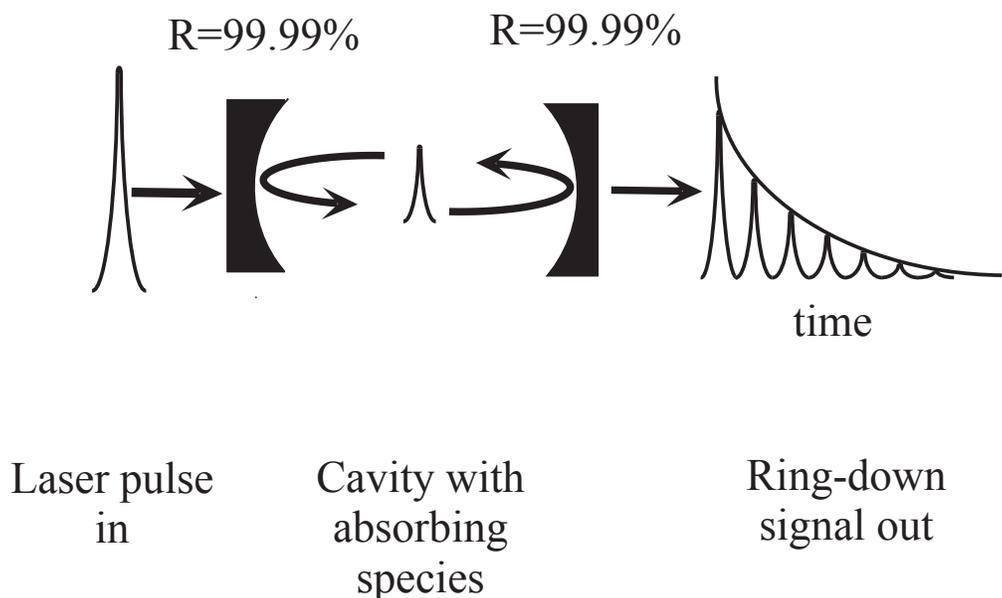
Figure 3: Schematic diagram of a typical cavity ring-down experiment.

Voyager 2 [43] in their encounter with Jupiter. Bright emission lines of sulphur III, sulphur IV, oxygen III and hydrogen (atomic and molecular) revealed previously undetected physical processes of significant proportions: electron temperatures of 10^{+5} K and a hot thermosphere (> 1000 K) with a large atomic hydrogen abundance.

Most molecules do not emit radiation in the visible or ultraviolet regions of the spectrum unless they are previously excited. They do, however, absorb radiation. Conventional absorption spectroscopy relies on the measurement of a signal extinction against a fluctuating total intensity background (the total signal) As a result, sensitivities are generally not as high as other optical detection processes such as laser-induced fluorescence or multiphoton ionization. Nevertheless, absorption spectroscopy has the advantage of being more a more quantitative method since a knowledge of the extinction through the sample medium and the absorption coefficient yields absolute number densities of the absorbing species.

In recent years, several groups throughout the world have implemented a technique by the name of Cavity Ring-Down Spectroscopy (CRDS) [44] with clear promises in regard to miniaturization and portability in planetary and space missions. A typical CRDS setup is schematized in Fig. 3. It consists of an optical cavity with two highly-reflecting mirrors of known reflectivity R. Laser radiation at the wavelength of interest is injected in the cavity. The amount of laser radiation leaking out of the cavity is measured as a function of time. If there are no absorbing species in the sampling medium, a laser pulse injected into the cavity will decay exponentially with a characteristic time constant τ_o. If we now add to the cavity a species that absorbs the laser radiation, the light will still decay exponentially but more rapidly with a characteristic time constant τ_{abs}. The relationship between these decay constants and the frequency-dependent absorption coefficient α is simply given by

$$\alpha = \left(\frac{1-R}{L} \right) \cdot \left(\frac{\tau_o - \tau_{abs}}{\tau_{abs}} \right) \tag{2}$$

where R is the mirror reflectivity and L is the cavity length. A complete absorption spectrum may be obtained by scanning the laser over frequency and recording τ. This measurement is therefore equivalent to a conventional absorption measurements but devoid of the noise introduced by fluctuations in the light source. The advent of diode laser technology in the infrared and visible regions has made this technique relatively simple to implement as well as very compact and portable. Very modest laser powers are required and the sensitivity can be pushed down to shot-limited levels (parts per trillion for a strong absorber). CRDS has been succesfully used for the detection of H_2O in the near infrared and infrared [], O_2 in the red cite, the CH radical at 430 nm [], the CH_3 radical in the far UV [], etc. One of major conclusions of the Astrobiology Advanced Measurement Workshop [45] in 1998 has been the need to bring current instrumentation to a point it is ready for flight. The requirements are quite stringent and include: space limitations, low power consumption, operability and survivability in extreme environments, etc. By taking advantage of a multidisciplinary team of people devoted to each and every aspect of the process, the dream of having a sensitive absorption spectrometer aboard a spacecraft may not be too far away in the future.

3 Photodissociation

3.1 Principles

Electromagnetic radiation can be very effective at breaking chemical bonds and produce free radical species. In a typical absorption experiment, the onset of photodissociation is generally manifested by the appearance of absorption continua corresponding to an excited state with no bound energy levels. This broad and typical absorption continuum usually contains very little information about the details of the upper electronic curves that eventually lead to the breaking of the chemical bond. In order to learn more about the character of the dissociating electronic state it is necessary we also observe all photodissociation channels energetically accessible.

We consider a generic photodissociation of a species AB isotropically distributed in space

$$AB + h\nu \rightarrow A + B \tag{3}$$

and let's assume that the photolysis radiation is linearly polarized along a given axis z. The interaction of the electric field $\vec{E}_z$ with the molecule is of the form

$$\vec{\mu} \cdot \vec{E}_z \propto \cos\theta \tag{4}$$

where $\vec{\mu}$ is the electronic transition dipole moment of molecule AB. θ is defined as the angle between z (polarization axis) and the transition dipole moment μ. For the case of a diatomic molecule, two possible types of electronic transition are possible, namely, parallel ($\mu \parallel$ bond axis) and perpendicular ($\mu \perp$ bond axis). Since the initial sample of AB molecules is originally isotropic, its interaction with a linearly polarized electric field $\vec{E}_z$ will lead to a $\cos^2\theta$ and a $\sin^2\theta$ spatial distribution of photofragment velocities respectively since the absorption probability is given by the square of Eq. (4). This is only strictly valid in the case of an instantaneous photodissociation, i.e., the AB molecule does not have enough time to rotate and wash out the original spatial anisotropy. Since the character of the ground state of the molecule is generally known, measurement of the photofragment spatial distribution of speeds can be used to determine the symmetry properties, and therefore the character, of the excited state. Conventional absorption spectroscopy is unable to provide this information.

Furthermore, depending on the energy of the photon, several channels may be possible. For example, if the A fragment is an atom, it could be in different electronic or hyperfine states. Similarly, if A is a diatomic fragment it can show varying degrees of rotational and vibrational excitation. The photodissociation spatial anisotropy and branching ratios are usually quite dependent on wavelength, reflecting the fact that as the photon energy is changed, new electronic states can participate in the process.

3.2 Photochemistry in Action

3.2.1 The Interstellar Medium

In Section 2 we already hinted at the complexity of the chemistry of the interstellar medium. Before we discuss the details of particular systems amenable to study in the context of photodissociation dynamics, it is necessary we first provide a more complete description of our current level of understanding in regard to this subject.

According to recent kinetic models [46, 47], the synthesis of molecules in the interstellar medium involves a sequence of exoergic, bimolecular ion-molecule reactions. The initiation of these processes is believed to proceed in the interior of these clouds via the direct ionization of H_2 and He by 100 MeV cosmic rays. The low densities and temperatures seem to allow only chemical sequences between ions and neutrals, which are known to proceed via Langevin (temperature-independent) reaction mechanisms. The availability of a large database for ion-molecule kinetic data has enabled a semi-quantitative assessment of this model under realistic conditions. Important reactions involving H_2^+ include

$$H_2^+ + H_2^+ \rightarrow H_3^+ + H \tag{5}$$

$$H_3^+ + CO \rightarrow HCO^+ + H \tag{6}$$

$$H_3^+ + N_2 \rightarrow HN_2^+ + H_2 \tag{7}$$

$$H_3^+ + CO_2 \rightarrow HOCO^+ + H_2 \tag{8}$$
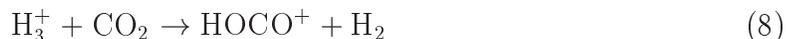
whereas for the He^+ ion the primary reaction sequences are initiated by the following processes

$$He^+ + CO \rightarrow He + C^+ + O \tag{9}$$

$$\text{C}^+ + \text{CH}_4 \rightarrow \text{various products} \tag{10}$$

$$\text{C}^+ + \text{C}_2\text{H}_2 \rightarrow \text{various products} \tag{11}$$

The last two reactions involving the C^+ ion are quite avid and initiate a chain of chemical reactions ultimately leading to the formation of a rich variety of interstellar organic molecules. Our extensive knowledge of ion-molecule chemistry allows for other possibilities to be excluded from the model. Such is the case of

$$\text{He} + \text{H}_2^+ \rightarrow \text{HeH}^+ + \text{H}, \tag{12}$$

which possesses an activation barrier of 0.8 eV and

$$\text{He}^+ + \text{H}_2 \rightarrow \text{HeH}^+ + \text{H}, \tag{13}$$
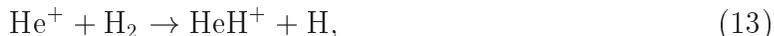
which is adiabatically forbidden, that is, the HeH^+ product state is born in a repulsive or dissociative state. This model demonstrates that the profusion of organic molecules is caused by the intimate details of electron transfer between helium and hydrogen, the two species that initiate a network of thousands of reactions. The detection of a large concentration of the X- ogen (HCO^+) ion [48] is in agreement with the expectations of this kinetic scheme.

Serious loopholes still remain despite all this progress. The role of heterogeneous chemistry in dusts and grains remains largely unanswered to date (see Section 2.2). Global models of all three types of interstellar clouds (diffuse, translucent, and dense) are still modeled using only ion-neutral gas-phase chemistry. These models also assume a large extinction of radiation by dust and molecules so that the photodestruction via external photons is unimportant. Photodestruction by internally generated photons produced by radiative decay of excited molecules is included, but large uncertainties remain due to lack of reliable experimental data [49, 50]. An even more serious assumption pertains that of temperature and density homogeneity. One should expect stark temperature and radiation gradients as well as appreciable photon penetration [51]. Recent observations of C, C^+, and highly excited CO [52] corroborate this suspicion. The so-called "active" regions of the interstellar region also fall into this special category of sites where other processes besides ion-molecule chemistry dominate and the physical conditions are subject to short timescale variations. These active regions can be of three types:

- Shocked portions of clouds. These astronomical objects were the first to be studied and have been invoked to account for the presence of CH^+ in diffuse interstellar clouds [53]. Shock fronts raise the temperature of these regions dramatically allowing dissociation and high-temperature chemistry to occur for prolongued periods of time.

- Photon-dominated regions (PDR's), usually located near bright stars (i.e., protosolar systems). Inside these regions, the large UV and VUV fluxes trigger molecular photodissociation. Models for PDR's usually attempt at predicting the right C^+, C, and CO balance balance [51, 54, 55]

- Star formation regions or "hot cores", which exist at temperatures ten times higher than the central part of interstellar clouds (ca 200-300 K) and possess high number densities ($10^{+5} - 10^{+6}$ cm^{-3}). Large chemical differences have been found between different hot cores owing to unknown factors, perhaps gas-grain heterogenous processes.

In both the shocked portions of clouds and in photon dominated regions, photodissociation processes of their main constituents, H_2 and CO, have not been addressed. Photodissociation experiments of these molecules can only occur in the VUV range. The detection of photofragments also requires the use of VUV for one-photon, and UV for two-photon spectroscopies. These experiments will greatly complement the proposed study of the higher electronic states of the hydrogen and carbon dioxide molecules proposed in Section 2. Spectroscopic identification of absorption continua will help at locating those wavelength ranges where repulsive and/or predissociative states exist. To date, only one study of the UV photoabsorption and photodissociation cross sections of CO between 88.5 and 115 nm has been carried out by Letzelter et al. [56]. Additionally, Forch and Merrow [57] have investigated the two-photon dissociation of CO at 193 nm which shows non-statistical spin-orbit populations of the oxygen atom. The line of work proposed here will allow the characterization of the photofragments and a better identification of the electronic states responsible for photodissociation in the VUV with the possibility of also increasing the range of photodissociation energies above and below those studied by Letzelter et al. [56]. Measurement of the branching ratios into different electronic states of the O and C atoms will also help assessing the potential reactivity of these photolysis products in the interstellar medium.

20

3.2.2 Planetary Atmospheres

Sheldon [58] has outlined a few of the basic requirements that makes a planet habitable. These include: (1) the presence of biota elements (H, C, O, N, P, ...); (2) an aqueous environment, and, (3) a mechanism to protect biota from harmful radiation. The main corollaries from these requirements generally imply that life is likely to emerge in planetary systems around second-generation stars that supply the heavier elements, and that there must be an atmosphere that greatly attenuates the amount of harmful radiation. On Earth, the key player is atmospheric ozone, created by the $O + O_2$ reaction in the presence of UV radiation (< 220 nm). Another important role of gas-phase species on Earth is to raise the surface temperature via infrared absorption of solar radiation (greenhouse effect). An Earth without greenhouse gases would be around 35 K cooler causing, for example, water to freeze (provided the atmospheric pressure remains close to the present value) and greatly impairing the development of most known life forms. Certain organisms such as the stromatolites [59] are well-known for their superb adaptation and resistance to UV radiation [59], but in our planet they are more of an exception than a rule. This extreme degree of adaptation in stromatolites appears to be a major impediment to their evolution into more complicated organisms. Thus, one might argue that while life may adapt to large influxes of UV radiation, it seriously impairs the further evolutionary development into more complicated organisms.

What other gases are known to act like ozone in other planetary systems? In both Venus and Mars, stratospheric photodissociation of CO_2 below 200 nm into CO and O not only attenuates greatly the flux of UV radiation but also triggers the chemistry of the atmosphere by production of O ^3P, O ^1D, and O ^1S [60]. The absorption spectra of CO_2 has been measured by Ogawa [61] in the Schumann and far-UV regions (171.8-216.0 nm), and down to 34.5 nm by Shaw et al [62]. Studies of the photodissociation dynamics of this molecule have been rather sparse. Zhu and Gordon [63] have measured the production of O ^3P at 157 nm, using a conventional F_2 excimer laser as a photolysis source. At this collision energy, both O ^3P and O ^1D are energetically possible. Their results indicate that O ^1D is preferentially formed, with a yield of 94%. Further experiments by Matsumi et al [64] have determined the multiplet branching ratio of the O $^3P_{0,1,2}$ levels also at 157 nm. Since the photodissociation process yields a large degree of internal excitation of the CO diatomic adduct, the spatial anisotropy of the oxygen atom was dif-

2p ^3P_J	Our work	Buijsee et al. Ref. [69]	Tonokura et al. Ref. [70]
0	1.00 ± 0.15	1.00 ± 0.26	1.00 ± 0.11
1	3.14 ± 0.37	3.33 ± 0.43	3.84
2	9.07 ± 0.92	9.00 ± 0.70	9.61 ± 1.15

Table 1: Multiplet branching ratios for the photodissociation of the oxygen molecule at 226 nm. Error bars indicate one standard deviation.

ficult to interpret. It was found that the oxygen atom Doppler profiles were consistent with a maximal alignment of the photofragments along the laser polarization axis (parallel transition) and a large degree of internal energy excitation of the CO product. In addition, Koshi et al. [65] have performed O ^3P concentration measurements from the photodissociation of thermally excited carbon monoxide at 193 nm. Their measurements did not include the measurement of either the branching fraction or the photofragment spatial anisotropy, crucial observables to assess the photolysis mechanism.

Given the lack of experimental data, it would be highly instructive as well as useful to perform the photodissociation of carbon dioxide near and below 200 nm. This measurement will allow the determination of photolysis branching ratios as well as the photolysis anisotropy of each individual channel. Initially, this could be achieved by observing the O ^3P_J atom using two-photon absorption plus ionization at 226 nm [66], but ultimately one would like to detect the CO(v',J') product and measure the spatial anisotropy as a function of rotation and vibration of the product. Fortunately, there are sensitive two-photon detection schemes for CO centered at 230 nm [67] and at 214 nm [68].

The photodissociation of CO_2 resembles in many respects the photodissociation of O_2 at wavelengths around 225-200 nm. The measured cross sections in this frequency range are very similar, approaching values in the order of 10^{-24} cm^{-2}. Despite the weakness of this process (typical cross sections at the peak of absorption continua are in the order of 10^{-19} cm^{-2}), we have been able to measure the photofragment branching ratio and spatial anisotropy for the
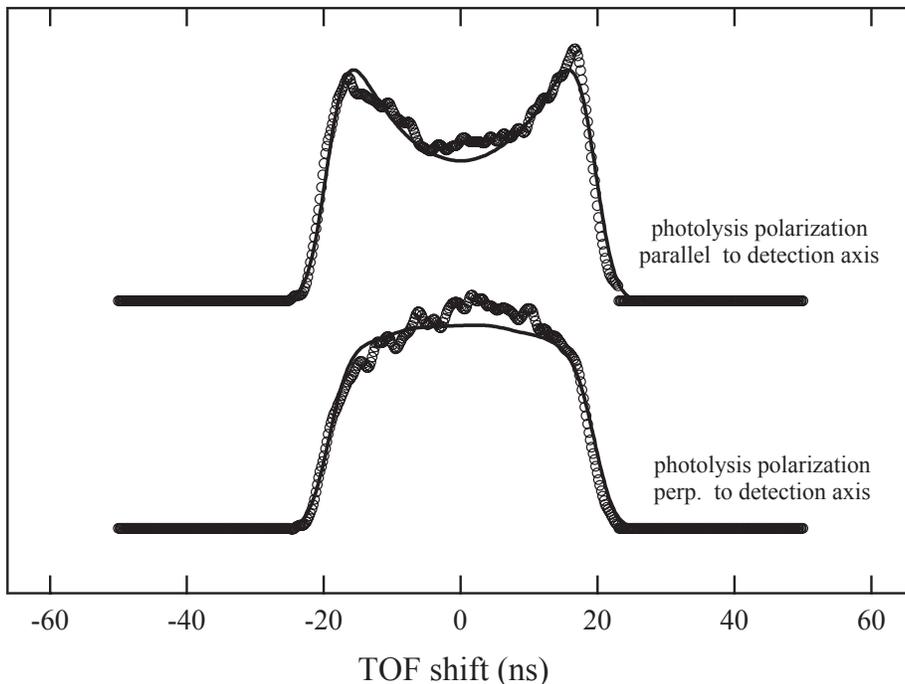
Figure 4: Time of flight profiles at two different photolysis laser geometries for the O $^3P_2$ fragment arising from the photodissociation of the O_2 molecule at 226 nm..

oxygen fragment arising from O_2 photodissociation [71]. In Table 1 we show the multiplet branching ratios as well as a comparison to the results of other experiments. Information about the spatial anisotropy is obtained by measurement of the nascent photofragment distribution of velocities in a velocity-sensitive time-of-flight spectrometer designed and constructed to carry out photodissociation and photoinitiated reaction studies [71]. A typical velocity or time-of-flight profile is shown in Fig. 4 for O $^3P_2$. By changing the angle between the polarization of the photolysis laser and the detection axis, it is possible to measure the photolysis spatial anisotropy, characterized by the anisotropy parameter β_{phot}. In this particular case, $\beta_{\mathrm{phot}} = 0.55 \pm 0.15$. This figure is indicative of several excited states, mostly with Σ symmetry, taking part in the process. Currently, we are assessing the experimental feasibility of experiments with CO_2 at similar wavelengths using oxygen-atom detection. This preliminary work will establish the experimental tractability of future

measurements.

Following the carbon dioxide measurements, the obvious direction to take is to move the photolysis frequency into the VUV and fully characterize the photodissociation dynamics of this molecule beyond the O ^{1}D and O ^{1}S thresholds. The availability of a VUV radiation source capable of achieving this goal will also enable the study of a large host of simple yet very relevant atmospheric species including O_2, H_2O, NH_3, etc. Whereas these molecules have been studied to some level of detail, much ground remains for extaustive studies of their photodissociation dynamics.

Another line of work in regard to CO_2 and other polyatomics pertains the study of the temperature dependence of the absorption and photofragmentation. The CO_2 molecule is by itself a very interesting case. Absorption of light around 200 nm is weak and largely forbidden, but it is found that it is greatly enhanced upon thermal excitation. The mechanism for this enhancement is related to the change in geometry of this molecule when the symmetric bending mode is excited at 10.5 μm, approaching the linear geometry of the excited state. Enhanced absorption of carbon dioxide into the near-UV (300 nm) has been observed in thermally excited samples heated up to 2000 K [72]. Other means of exciting the bending modes of this molecule involve the use of laser radiation (using, alas, a CO_2 laser!). Investigation of the photodissociation dynamics at these short wavelengths is technically and experimentally an easier task than the VUV photodissociation experiments and, despite the intrinsic interest in this greenhouse molecule, has not been explored at all.

4   Photoinitiated Chemical Reactions

4.1   The Photoloc Technique

We come to the subject which is closest to my heart, since the study of photoinitiated chemical reactions has been the central theme of my doctoral work at Stanford University [71]. To illustrate the main ingredients of the technique, I have chosen to use specific examples pertinent to the hydrogen exchange reaction. However, the major results of this section are applicable to any atom-diatom reaction and may be also generalized to more complicated systems such as diatom-diatom, atom-polyatom, etc.

Photoloc is an acronym for "*photo*initiated reaction analyzed via the *law of cosines.*" This name stems from the two major elements of the technique: first, laser photolysis initiates the chemical reaction in a mixture of a photolytic precursor and reagent; and second, the law of cosines relates the product laboratory velocity distribution to the center-of-mass angular distribution, i.e., the product differential cross section. In addition, rotational and vibrational integral cross sections can be easily obtained by integrating the differential cross section over all angles and detecting all possible rovibrational reaction products.

We have chosen to study the H + D_2 system because the reaction product, HD, can be easily differentiated from those arising from elastic and inelastic scattering. In the first step, a linearly polarized laser beam between 200 and 300 nm photolyzes the HBr molecule producing a monoenergetic population of H atoms according to the process

$$HBr \xrightarrow{h\nu} H + Br \tag{14}$$

The H-atom photofragments are produced with a well-defined laboratory speed and spatial anisotropy which subsequently collide with the D_2 molecule to generate HD and D products according to the reactive exchange process

$$H + D_2 \longrightarrow HD(v', J') + D \tag{15}$$

Finally, a second laser beam probes the HD(v', J') or C products. In the limit of zero relative speed between HBr and D_2, which is achievable by coexpanding them into a vacuum, the center-of-mass speed is solely dictated

by the photolysis wavelength and the nature of the photolytic precursor HBr. The translational energy of photofragment H is given by

$$E_H = \left(\frac{m_H}{m_{HBr}}\right) \cdot (h\nu - \Delta E_H) \tag{16}$$

where the m's are the masses of H and HBr, $h\nu$ is the photon energy and ΔE_H is the endoergicity of the photolysis process. From Eq. (16), and the fact that HBr and D_2 are stationary with respect to each other, the center-of-mass speed is fixed at a value

$$u_{CM} = \left(\frac{m_H}{M}\right) \cdot \sqrt{\left(\frac{2E_H}{m_H}\right)} \tag{17}$$

where $M = m_H + m_{D_2}$, and E_H has been calculated from Eq. (16). For a specific HD(v', J') product state of known endoergicity ΔE, conservation of energy and linear momentum in the center-of-mass frame yield the following expression for the magnitude of the center-of-mass speed of the HD(v', J') product

$$u_{HD} = \left(\frac{m_D}{M}\right) \cdot \sqrt{2\left[\frac{\left(\frac{\mu}{m_H}\right) E_A - \Delta E}{\mu'}\right]} \tag{18}$$

where μ and μ' are the reduced masses of the reagent and product collision partners respectively. Consequently, the product velocity $\vec{v}_{HD}$ is the vector sum of $\vec{u}_{CM}$ and $\vec{u}_{HD}$, whose moduli have been given by Eqs. (17) and (18) respectively, namely

$$v_{HD}^2 = u_{CM}^2 + u_{HD}^2 + 2u_{CM}u_{HD}\cos\theta_r \tag{19}$$

where θ_r is the center-of-mass scattering angle. An excellent way to picture the above quantites given by Eqs. (14)-(19) is to use a "collapsed" Newton diagram as shown in Fig. 5 The straightforward trigonometric relationship between $\vec{v}_{HD}$, $\vec{u}_{CM}$, and $\vec{u}_{HD}$ is very clear and it immediately implies that a measurement of the product laboratory distribution can be related to the center-of-mass scattering angular distribution, i.e., the product differential cross section.
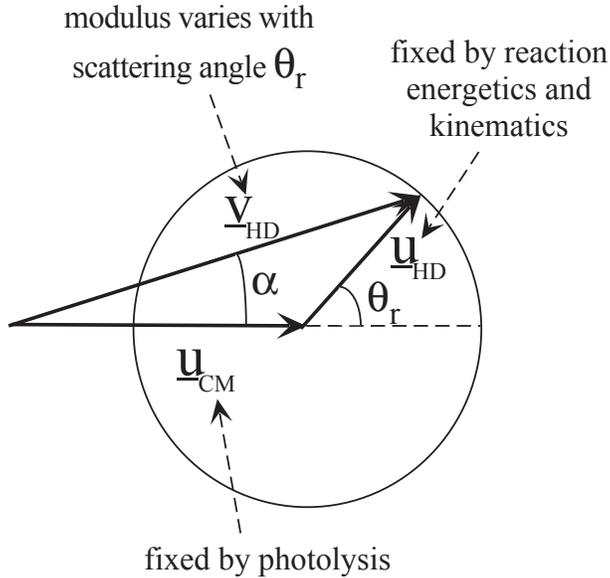
Figure 5: Collapsed Newton diagram pertinent to the photoloc technique. For detection of a particular $HD(v', J')$ state, the only vector in this figure with a variable modulus is the laboratory product speed. This change in modulus can be mapped directly into a change in center-of-mass scattering angle.

For the case of a single photolysis channel with anisotropy β_{phot}, photodissociation with linearly polarized light yields a spatial distribution of photogragment H laboratory speeds of the form

$$f\left(\vec{\underline{u}}_H\right) = \frac{1 + \beta_{phot} \cdot P_2\left(\vec{\underline{u}}_H \cdot \vec{\underline{\epsilon}}_{phot}\right)}{4\pi} \tag{20}$$

where $\vec{\underline{u}}_H$ and $\vec{\underline{\epsilon}}_{phot}$ are unit vectors corresponding to the photofragment velocity and photolysis laser polarization vectors, and $P_2(x) = \frac{1}{2}\left(3x^2 - 1\right)$ is the second Legendre polynomial. The argument in $P_2(x)$ is simply the cosine of the angle between the velocity vector of the photofragment and the direction of the laser polarization. This expression leads to the familiar perpendic-

ular and parallel angular distributions typically found in photodissociation processes under the fast-recoil approximation [73, 74].

From the above considerations, it is not surprising to find that if Eq. (20) governs the photodissociation step, then the laboratory distribution of HD(v′, J′) product velocities is given by an analogous expression, namely,

$$
f\left(\vec{\underline{v}}_{HD}\right) = \left(\frac{1}{2v_{HD}u_{HD}u_{CM}}\right)\left(\frac{1}{\sigma}\frac{\partial\sigma}{\partial\Omega_r}\right)\left\{1 + \beta_{rxn}P_2\left(\vec{\underline{v}}_{HD}\cdot\vec{\underline{\epsilon}}_{phot}\right)\right\} \tag{21}
$$

where $\frac{1}{\sigma}\frac{\partial\sigma}{\partial\Omega_r}$ is the normalized differential cross section into a particular solid angle Ω_r and β_{rxn} is a velocity-dependent anisotropy parameter. This expression has been defined so that it is normalized to unity. The similarites between Eqs. (20) and (21) are striking in the sense that for a single laboratory product speed, the spatial distribution has the same functional form as that of a photodissociation experiment with an anisotropy given by $\beta_{rxn}(v_{HD})$. It follows that the total distributions of laboratory speeds is a weighted sum of photolysis-like spatial distributions, the weights being proportional to the differential cross section for reaction at a particular scattering angle. Referring to Fig. 5, we find that the product anisotropy is related to the photolysis anisotropy by

$$
\beta_{rxn}\left(\vec{\underline{v}}_{HD}\right) = \beta_{phot}P_2\left(\vec{\underline{v}}_{HD}\cdot\vec{\underline{u}}_{CM}\right) \tag{22}
$$

where $\vec{\underline{v}}_{HD}\cdot\vec{\underline{u}}_{CM} = \cos\alpha$, and α is the angle between the center-of-mass velocity and the laboratory product velocity. This angle is fixed for a particular laboratory product speed by the expression

$$
\vec{\underline{v}}_{HD}\cdot\vec{\underline{u}}_{CM} = \cos\alpha = \frac{v_{HD}^2 + u_{CM}^2 - u_{HD}^2}{2v_{HD}u_{CM}} \tag{23}
$$

From Fig. 5, we can see that $\vec{\underline{v}}_{HD}$ has a maximum and minimum value corresponding to the vector addition of the center-of-mass vectors $\vec{\underline{u}}_{HD}$ and $\vec{\underline{u}}_{CM}$ in a parallel and antiparallel fashion, i.e., forward and backward center-of-mass scattering. The range of laboratory speeds possible for a particular HD(v′, J′) state depends on the particular details of the kinematics and energetics of the reaction of interest.

Fig 6 shows the measured rotational distributions of the HD product at collision energies ca 1.6 eV. The accompanying solid lines are the result of quasiclassical trajectory calculations by Blais and Truhlar [75, 76]. The
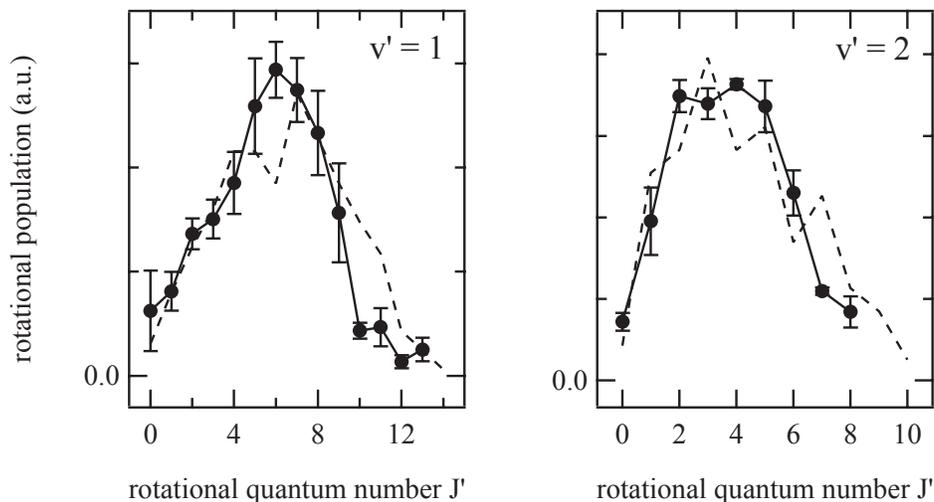
Figure 6: HD(v′ = 1, J′) and HD(v′ = 2, J′) rotational distributions at 1.6 eV. The dashed lines correspond to the quasiclassical trajectory calculations of Blais and Truhlar [75, 76]. Error bars represent one standard deviation.

amount of reactive product in each rovibrational product state has been obtained by scanning the probe laser over the whole rotational manifold for a particular vibrational level.

In addition to product rotational distributions, we have gone at great lengths to explain how the photoloc technique can be used to measure rovibrationally state-resolved angular distribution. An illustration of this capability is shown in Figs. 7 and 8. Fig. 7 shows the laboratory velocity distributions for three selected product states. These profiles are similar to those one would obtain by the use of conventional Doppler spectroscopy, with the added twist that each product laboratory velocity is constrained to appear at a unique arrival time at the detector. In practice, this constraint makes the inversion of the laboratory raw data into the corresponding center-of-mass differential cross section easier. Fig. 8 shows the corresponding angular distributions. The solid lines are the result of an "exact" quantum mechanical calculation by Kuppermann and co-workers [77] using the EQMC PES, the most accurate potential energy surface for this reaction system [78]. The agreement between theory and experiment is quite remarkable, specially in regard to the match of features changing over small angular ranges (note,
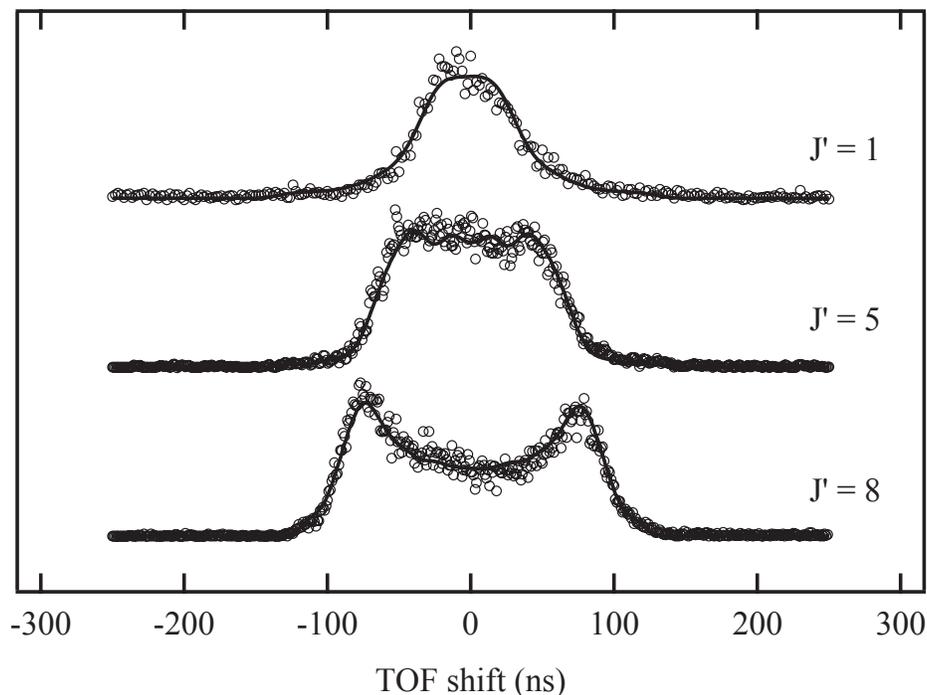
Figure 7: $HD(v' = 1, J')$ time-of-flight profiles from the $H + D2$ reaction at 1.6 eV. The solid lines are the result of a linear fit using Monte-Carlo generated basis functions.

for example, the local minimum exhibited by the $HD(v' = 1, J' = 5)$ angular distribution in the back-scattered region). Currently, we are extending this work in order to experimentally measure the degree of rotational polarization (i.e., the spatial distribution of rotational angular momenta) of the diatomic product, which is thought to be more sensitive to the specific details of the reactive event and the underlying potential energy surface.

In principle, these measurements are not restricted to the atom-diatom case. For the case, for example, of an atom-polyatom reactive collision, measurement of the spatial anisotropy of the reaction product can be valuable at estimating the internal energy deposition of the unobserved polyatomic product, and reliable differential cross sections can therefore be measured. Such is the case of recent studies by Zare et al. on the $Cl + CH_4$ [79], and C_2H_6 [80] reactions.
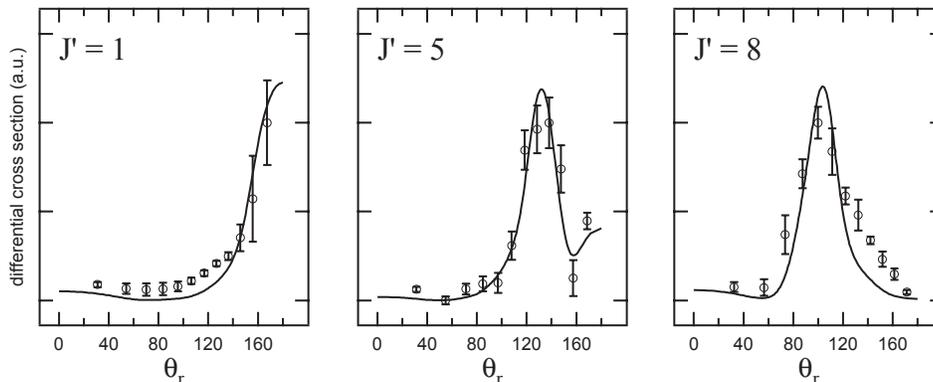
Figure 8: $HD(v' = 1, J')$ angular distributions obtained from the time-of-flight profiles of Fig. 7. The solid lines are the result of the quantum mechanical calculations of Wu and Kuppermann [77].

4.2 Some Challenges

4.2.1 Neutral-Neutral Chemistry

Section 3.2 gave a brief review of our present understanding of the synthesis of interstellar material. We also pointed out some of the pitfalls of a model that is only based on ion-molecule reactions and examined possible situations for its breakdown. The role of neutral-neutral reactions in the interstellar medium is still highly uncertain, as a result of our poor understanding of the underlying reaction dynamics [3]. Recent experimental data on radical-radical reactions at low temperatures [81] show very large reaction rates for even radical-stable processes, with Arrhenius preexponential factors displaying $\frac{1}{T^n}$ ($n > 0$) dependences. Reaction rates for radical species at low temperatures have been measured by the CRESU technique (Cinétique de Réactions en Ecoulement Supersonique Uniforme, or Reaction Kinetics in Uniform Supersonic Flow) pioneered by Rowe and co-workers [82, 83]. Total reagent depletion rates are measured via laser-induced fluorescence down to approximately 10 K. Whereas, such kinetic data is useful, the technique is severely hampered by the inability to detect and study the various reactive channels that may be operative at different temperatures. The photoloc technique, as explained above, affords a means of studying radical-stable and radical-radical reactions with a much finer control over initial and final

31

conditions (single collision conditions, well-defined collision energies). In addition to the inherent interest in understanding the basic reaction dynamics of these important reactions, photoloc studies may also serve the purpose of checking and validating the most controversial results obtained to date with the CRESU technique.

We have already discussed that CO is formed via a variety of processes. If we begin to consider neutral-neutral processes in the context of interstellar chemistry, the *unstudied* atom-radical reaction shown below becomes a favourite candidate.

$$CH + O \rightarrow CO + H \tag{24}$$
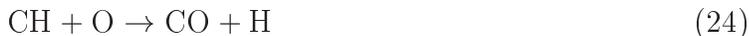
Whereas it is relatively hard to generate in a controlled fashion two free radicals in the laboratory, the reverse reaction easily lends itself to study by the photoloc technique. The experimental data then may be used to refine the potential energy surface for this reaction system which allows for a calculation of rate coefficients.

Likewise, the most likely candidates for the removal of CO is

$$OH + CO \rightarrow CO_2 + H \tag{25}$$

This reaction proceeds via initial formation of an energized adduct which then decays into products. The reverse reaction, namely, $H + CO_2$ has been investigated by Brouard and co-workers [84] who measured the OH product in particular rovibrational levels and inferred the first few moments of the differential cross section from the Doppler profiles. The forward OH+CO reaction is amenable to study by the photoloc technique. Copious amounts of OH radicals can be readily generated by photolysis of H_2O_2 in the ultraviolet [85–88]. Product detection can be accomplished by measurement of the H atom for total cross section measurements or by looking at the triatomic product using well-established detection schemes [].

Similarly, the ion-molecule synthesis of hydrocarbons and other organic species is very much affected by neutral-neutral reactions. Carbon insertion reactions may play an important role if they proceed via carbon insertion, and may solve the long-standing problem of ion-molecule reaction sequences not being capable of synthesizing some of the long-chain organics observed in the interstellar medium []. Some examples of these carbon insertion reactions are

$$C + C_2H_2 \rightarrow C_3H + H \tag{26}$$

$$C + C_3H \rightarrow C_4 + H \tag{27}$$

These experiments, however, are not likely to be performed in the near future. Photolytically, it is hard to make carbon atoms, yet one can envision the VUV photodissociation of CO as a likely candidate.

Further concerns about the validity of our current models of interstellar chemistry will undoubtedly foster an increased amount of research in this area and a search for alternative ways of studying free radical reactions.

4.2.2 Nonequilibrium Processes

In my own view, the role of nonequilibrium processes enters into the subject matter in two different ways. The first one stems from the well-established decoupling of radiation and particles that, according to the standard Big Bang Nucleosynthesis Model, occurred in the early stages of formation of the universe. The consequences of this phenomenon include some of the processes we already described throughout this report and include photodissociation and photoionization of atomic and molecular species. The second one is a bit more subtle and has to do with the differences in behavior (i.e., reactivity) between the same species in different internal or translational energy states as a consequence of some (unspecified) pumping process leading to nonequilibrium atomic and molecular distributions.

In fact, the role of nonequilibrium processes has silently accompanied most of our discussions in previous sections. Quoting W. Klemperer [46] from his review article on interstellar chemistry: *"the synthesis of large specific species by inanimate, uncatalyzed processes is important because it illustrates that chemistry can, in the absence of biological direction, achieve complexity and specificity"*. A dramatic example of the absence of thermodynamic equilibrium is the concentration of CO in the universe. Next to H_2, this molecule is the most abundant interstellar molecule, although typically down by a factor of at least 10^{-4}. Thermodynamic calculations predict that under typical dark cloud conditions (20 K, $H_2 \approx \sim 10^{+5}$ cm^{-3}) at chemical equilibrium, there would be fewer than one CO molecule in the volume of the observable universe! Nonequilibrium is the first requirement to be readily satisfied by any serious kinetic scheme attempting to explain the chemistry of the interstellar medium. It comes then as no big surprise that the central idea of this report revolves around the laboratory study of some of the processes that lead to such nonequilibrium conditions.

The recent text by Marov et al. [89] discusses in detail a whole range of scenarios in the planetary and cometary atmospheres where the presence of "hot" radical species becomes prominent. The major conclusion from this monograph is the realization of the great importance of various processes including photolysis, energetic electron impact, and *accompanying numerous chemical reactions* in the description of the structure, energy balance, and dynamics of the thermosphere.

Some of the reactions relevant to planetary atmospheres which fall into the category of nonequilibrium processes and which are amenable to study by means of the photoloc technique are discussed in the following paragraphs.

In the Venusian atmosphere, CO_2 photodissociation below 210 nm triggers a large proportion of the atmospheric gas-phase chemistry by production of O ^{3}P and O ^{1}D. Removal of the carbon monoxide adduct of carbon dioxide photodissiation is thought to proceed via the already familiar reaction with OH

$$OH + CO \rightarrow CO_2 + H \tag{28}$$

Thus far, neither gas chromatographic nor mass spectrometric methods from recent in-situ measurements provide evidence to resolve what other reactions may contribute as sinks of the CO molecule [].

Cl_2 and SO_2 are also known to be photolyzed under 320 nm in Venus. The reaction of chlorine atoms with H_2

$$Cl + H_2 \rightarrow H + HCl \tag{29}$$

becomes in this case the chemical analogue of the terrestrial reaction responsible for the disappearance of methane (already studied by the photoloc technique by Zare et al. [79]) as shown below

$$Cl + CH_4 \rightarrow CH_3 + HCl \tag{30}$$

Moreover, HCl is probably removed via photolysis in the VUV, which makes it amenable to study using the approach outlined in Sec 3.

The Martian atmosphere is also dominated by the photolytic breakup of carbon dioxide. However, the presence of other chemical species in significant quantities makes the subsequent chemistry quite different from that of Venus. UV absorption features show the presence of hydrogen atoms (121.6 nm), O atoms (130.4 nm), and molecular band systems of CO ($\sim$ 130 nm). H atoms

34

are most likely produced by the photodissociation of water vapor in the VUV and lead to a rich chemistry initiated by the reaction

$$H + O_2 \rightarrow OH + H \tag{31}$$

and

$$H + O_3 \rightarrow O_2 + OH \tag{32}$$
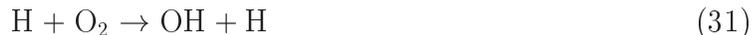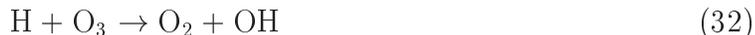
The O ^{1}D product of carbon dioxide photodissociation leads, owing to its greater reactivity than O ^{3}P, to reactions such as

$$O(^1D) + H_2O \rightarrow OH + OH \tag{33}$$

and the reverse of the H + O$_2$ reaction, namely,

$$O(^1D) + OH \rightarrow O_2 + H \tag{34}$$

Finally, for the external planets Jupiter and Saturn, less is known about the photochemistry and subsequent chemistry, mostly owing to the lack of knowledge of the vertical temperature structure of the atmosphere. Since hydrogen is the dominant constituent of these atmospheres, photodissociation below 100 nm and ionization below ~ 80 nm leads to the formation of neutral as well as charged H atoms. At lower altitudes, methane and ammonia undergo photolysis. The chemistry these free radicals undergo is largely unknown, but the more recent discovery of CO on Jupiter shows that photochemical processes involving oxygen species do occur. CO is hypothesized to originate from the oxidation of methane by water.

To conclude this section, we have shown a quite large number of gas-phase chemical reactions relevant to nonequilibrium processes of astronomical interest which deserve detailed study and characterization. We have also outlined how the photoloc technique, or any other variant, can be succesfully used for their study.

35

References

[1] D. Morrison and G. K. Schmidt, *Astrobiology Roadmap* (National Aeronautics and Space Administration, Ames Research Center, Moffett Field, California, 1999).

[2] P. Thaddeus, Annu. Rev. Astron. Astrophys. **10**, 303 (1972).

[3] E. Herbst, Annu. Rev. Phys. Chem. **46**, 27 (1995).

[4] P. Essenwanger and H. P. Gush, Can. J. Phys. **62**, 1680 (1984).

[5] R. Hilbig and R. Wallenstein, IEEE J. Quantum Electronics **QE-17**, 1566 (1981).

[6] E. E. Marinero, C. T. Rettner, R. N. Zare, and A. H. Kung, Chem. Phys. Lett **95**, 486 (1983).

[7] C. T. Rettner, E. E. Marinero, R. N. Zare, and A. H. Kung, J. Phys. Chem. **88**, 4459 (1984).

[8] C. R. Vidal, *Tunable Lasers* (Springer-Verlag Topics in Applied Physics, Berlin, 1987), Vol. 59, pp. 57–113.

[9] G. Hilber, A. Lago, and R. Wallenstein, J. Opt. Soc. Am. B **4**, 1753 (1987).

[10] T. Okada, T. Aoi, M. Maeda, K. Muraoka, and M. Akazari, Japanese J. App. Phys. Part I **27**, 1550 (1988).

[11] J. P. Marangos, N. Shen, H. Ma, M. H. R. Hutchinson, and J. P. Connerade, J. Opt. Soc. Am. B **7**, 1254 (1990).

[12] C. E. M. Strauss and D. J. Funk, Opt. Lett. **16**, 1192 (1991).

[13] P. C. Hinnen, S. E. Werners, S. Stolte, W. Hogervorst, and W. Ubachs, Phys. Rev. A **52**, 4425 (1995).

[14] E. Reinhold, W. Hogervorst, W. Ubachs, and L. Wolniewicz, submitted to J. Chem. Phys. (1999).

[15] E. Reinhold, A. de Lange, W. Hogervorst, and W. Ubachs, J. Chem. Phys. **109**, 9772 (1998).

[16] E. Reinhold, W. Hogervorst, and W. Ubachs, Chem. Phys. Lett. **296**, 411 (1998).

[17] P. P. Sorokin and J. H. Glownia, Chem. Phys. Lett. **234**, 1 (1995).

[18] P. C. Hinnen and W. Ubachs, Chem. Phys. Lett. **240**, 351 (1995).

[19] P. P. Sorokin and J. H. Glownia, Astrophys. J. **473**, 900 (1996).

[20] K. Tsukiyama, S. Shimizu, and T. Kasuya, J. Mol. Spec. **155**, 352 (1992).

[21] K. Tsukiyama, J. Ishii, and T. Kasuya, J. Chem. Phys. **97**, 875 (1992).

[22] H. Suzuki, M. Nakata, Y. Ogi, and K. Tsukiyama, J. Mol. Spec. **191**, 142 (1998).

[23] W. M. McClain and R. A. Harris, *Excited States* (Academic Press Inc., New York, 1977), pp. 1–56.

[24] R. L. Swofford and A. C. Albrecht, Annu. Rev. Phys. Chem. **29**, 421 (1978).

[25] S. H. Lin, Y. Fujimura, H. J. Neusser, and E. W. Schlag, *Multiphoton Spectroscopy of Molecules, Quantum Electronics - Principles and Applications* (Academic Press, London, 1984).

[26] E. E. Marinero, R. Vasudev, and R. N. Zare, J. Chem. Phys. **78**, 692 (1983).

[27] K.-D. Rinnen, D. A. V. Kliner, R. N. Zare, and W. M. Huo, Isr. J. Chem. **29**, 369 (1989).

[28] W. M. Huo, K.-D. Rinnen, and R. N. Zare, J. Chem. Phys. **95**, 205 (1991).

[29] *Chemistry and Physics of Molecules and Grains in Space*, Faraday Discuss. **109**, 1 (1998).

[30] R. I. Hall, I. Čadež, M. Landau, F. Pichou, and C. Schermann, Phys. Rev. Lett. **60**, 337 (1988).

[31] P. J. Eenshuistra, J. H. M. Bonnie, J. Los, and H. J. Hopman, Phys. Rev. Lett. **60**, 341 (1988).

[32] J. D. Buck, D. C. Robie, A. P. Hickman, D. J. Bamford, and W. K. Bischel, Phys. Rev. A **39**, 3932 (1989).

[33] D. C. Robie, L. E. Jusinski, and W. K. Bischel, Appl. Phys. Lett. **56**, 722 (1990).

[34] F. Fernández-Alonso, B. D. Bean, and R. N. Zare, J. Chem. Phys. **111**, 2490 (1999).

[35] F. Fernández-Alonso, B. D. Bean, J. D. Ayers, and R. N. Zare, in preparation .

[36] F. W. Taylor, *Planetary Systems, The Long View* (Editions Frontieres, Château de Blois, 1998), pp. 225–230.

[37] G. Herzberg, *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules* (Krieger Publishing Co., Malabar, reprinted in 1989).

[38] R. J. Glinski, J. T. Lauroesch, M. D. Reese, and M. L. Sitko, Astrophys. J. **490**, 826 (1997).

[39] C. W. H. C. A. Barth, I. A. Stewart and A. L. Lane, Icarus **17**, 457 (1972).

[40] T. P. Softley, W. E. Ernst, L. M. Tashiro, and R. N. Zare, Chem. Phys. **116**, 299 (1987).

[41] A. L. Broadfoot, B. R. Sandel, D. E. Shemansky, and complete this entry, Space Science Rev. **21**, 183 (1977).

[42] A. L. Broadfoot, M. J. S. Belton, P. Z. Takacs, and complete this entry, Science **204**, 979 (1979).

[43] B. R. Sandel, D. E. Shemansky, A. L. Broadfoot, and complete this entry!, Science **206**, 966 (1979).

[44] P. Zalicki and R. N. Zare, J. Chem. Phys. **102**, 2708 (1995).

[45] *Astrobiology Advanced Systems Measurement Systems Workshop*, NASA Ames Research Center (see www.???.???) June 17 (1998).

[46] W. Klemperer, Annu. Rev. Phys. Chem. **46**, 1 (1995).

[47] W. Klemperer, Proc. R. Institution 209 (1997).

[48] L. E. Snyder and D. Buhl, Nature **228**, 267 (1970).

[49] S. S. Prasad and S. P. Tarafdar, Astrophys. J. **267**, 603 (1983).

[50] A. D. R. Gredel, S. Lepp and E. Herbst, Astrophys. J. **347**, 289 (1989).

[51] A. Sternberg and A. Dalgarno, Astrophys. J. Suppl. Series **99**, 565 (1995).

[52] R. Genzel, *Molecular Clouds (ed. by R. A. James and T. J. Millar)* (Cambridge University Press, New York, 1991), pp. 75–96.

[53] M. Elitzur and W. D. Watson, IEEE J. Quantum Electronics **236**, 172 (1980).

[54] D. J. Hollenbach, T. Takahashi, and A. G. G. M. Tielens, Astrophys. J. **377**, 192 (1991).

[55] V. Escalante, A. Sternberg, and A. Dalgarno, Astrophys. J. **375**, 630 (1991).

[56] C. Letzelter, M. Eidelsberg, F. Rostas, J. Breton, and B. Thieblemont, Chem. Phys. **114**, 273 (1987).

[57] B. E. Fort and C. F. Merrow, J. Chem. Phys. **95**, 3252 (1991).

[58] W. R. Sheldon, *Planetary Systems, The Long View* (Editions Frontieres, Château de Blois, 1998), pp. 81–83.

[59] M. R. Walter, *Earth's Earliest Biosphere,* (Princeton University Press, Princeton, 1983), pp. 187–213.

[60] R. P. Wayne, *Chemistry of Atmospheres. An Introduction to the Chemistry of the Atmospheres of Earth, the Planets, and their Satellites* (Clarendon Press, Oxford, 1991).

[61] M. Ogawa, J. Chem. Phys. **54**, 2550 (1971).

[62] D. A. Shaw, D. M. P. Holland, M. A. Hayes, M. A. MacDonald, A. Hopkirk, and S. M. McSweeney, Chem. Phys. **198**, 381 (1995).

[63] Y.-F. Zhu and R. J. Gordon, J. Chem. Phys. **92**, 2897 (1990).

[64] Y. Matsumi, N. Shafer, K. Tonokura, M. K. Y.-L. Huang, and R. J. Gordon, J. Chem. Phys. **95**, 7311 (1991).

[65] M. Koshi, M. Yoshimura, and H. Matsui, Chem. Phys. Lett. **176**, 519 (1991).

[66] D. J. Bamford, M. J. Dyer, and W. K. Bischel, Phys. Rev. A **36**, 3497 (1987).

[67] M. A. Hines, H. A. Michelsen, and R. N. Zare, J. Chem. Phys. **93**, 8557 (1990).

[68] P. J. H. Tjossem and K. C. Smyth, J. Chem. Phys. **91**, 2041 (1990).

[69] B. Buijsse, W. J. van der Zande, A. T. J. B. Eppink, D. H. Parker, B. R. Lewis, and S. T. Gibson, J. Chem. Phys. **108**, 7229 (1998).

[70] K. Tonokura, N. Shafer, Y. Matsumi, and M. Kawasaki, J. Chem. Phys. **95**, 3394 (1991).

[71] F. Fernández-Alonso, Ph.D. thesis, Stanford University, 1999.

[72] R. J. Jensen, R. D. Guettler, and J. L. Lyman, Chem. Phys. Lett. **277**, 356 (1997).

[73] R. N. Zare and D. R. Herschbach, Proc. IEEE **51**, 173 (1964).

[74] R. N. Zare, *Angular Momentum. Understanding Spatial Aspects in Chemistry and Physics* (John Wiley & Sons, New York, 1988).

[75] N. C. Blais and D. G. Truhlar, Chem. Phys. Lett. **102**, 120 (1983).

[76] N. C. Blais and D. G. Truhlar, Chem. Phys. Lett. **162**, 503 (1989).

[77] Y.-S. M. Wu and A. Kuppermann, unpublished results (1999).

[78] Y.-S. M. Wu, A. Kuppermann, and J. B. Anderson, Phys. Chem. Chem. Phys. **1**, 929 (1999).

[79] W. R. Simpson, T. P. Rakitzis, S. A. Kandel, T. Lev-On, and R. N. Zare, J. Phys. Chem. **100**, 7938 (1996).

[80] T. P. Rakitzis, S. A. Kandel, T. Lev-On, and R. N. Zare, J. Chem. Phys. **107**, 9392 (1997).

[81] I. Sims and I. W. M. Smith, Annu. Rev. Phys. Chem. **46**, 109 (1995).

[82] B. R. Rowe, G. Dupeyrat, J. B. Marquette, and P. Gaucherel, J. Chem. Phys. **80**, 4915 (1984).

[83] J. B. B. R. Rowe Marquette, Int. J. Mass Spectrom. Ion Proc. **80**, 239 (1987).

[84] M. Brouard, D. W. Hughes, K. S. Kalogerakis, and J. P. Simons, J. Phys. Chem. A **102**, 9559 (1998).

[85] J. August, M. Brouard, M. P. Docker, A. Hodgson, C. J. Milne, and J. P. Simons, Ber. Bunsenges. Phys. Chem. **92**, 264 (1988).

[86] S. Klee, K.-H. Gericke, and F. J. Comes, Ber. Bunsenges. Phys. Chem. **92???**, 264??? (1988???).

[87] M. Brouard, M. T. Martínez, J. O'Mahony, and J. P. Simons, Chem. Phys. Lett. **150**, 6 (1988).

[88] M. Brouard, M. T. Martínez, C. J. Milne, and J. P. Simons, Chem. Phys. Lett. **165**, 423 (1990).

[89] M. Y. Marov, V. I. Shematovich, D. V. Bisikalo, and J.-C. Gérard, *Nonequilibrium Processes in the Planetary and Cometary Atmospheres: Theory and Applications, Astrophysics and Space Science Library, vol. 217* (Kluwer Academic Publishers, Dordrecht, 1997).

[90] S. J. Clemett, Ph.D. thesis, Stanford University, 1996.

[91] D. S. Mckay, E. K. Gibson Jr., K. L. Thomas-Keprta, H. Vali, C. S. Romanek, S. J. Clemett, X. D. F. Xiller, C. R. Maechling, and R. N. Zare, Science **273**, 924 (1996).