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IONIZATION PROBES OF MOLECULAR STRUCTURE AND CHEMISTRY

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The development of new techniques for the study of chemical systems is vital for progress in understanding commercially and environmentally important chemical reactions such as combustion, atmospheric ozone depletion, chemical etching in semiconductor manufacture, etc. Lasers provide one of the most powerful tools in probing the courses of chemical reaction in difficult and complicated environments such as those mentioned above. The very high light flux obtainable from current tunable lasers enables the user to obtain a diagnostic response from molecules present in extremely small concentrations. To interpret this response, however, requires a fundamental knowledge of the spectroscopy and photophysics of molecules and chemical systems of interest. Based upon this understanding, it is possible to devise spectroscopic techniques which enable the study of the ephemeral unstable molecules which play important roles in the chemical pathways vital to technology and the environment. It is the goal of our research program to understand the photophysics involved with molecule-laser interactions and to devise new spectroscopic analysis techniques which both tell us more about the molecules and enable their detection in difficult environments.

With high powered pulsed lasers, an almost inevitable end product of the molecule-laser interaction is ionization of the molecule via the absorption of one or several photons. This fact provides an opportunity for detection because it is very easy to collect and count ions. The challenge is to extract information from the ionization event, which typically does not convey the spectral signatures which allow the detailed characterization possible in other spectroscopic transitions. In order to get this information, we are presently exploiting the very high Rydberg states which are present just below the energy of each ionic state as referenced to the neutral ground state. By creating and then field ionizing these Rydberg states, we are able to extract the states of the molecular ion from the continuum absorption. When we detect the resulting ion in a mass spectrometer, we call the technique Mass Analyzed Threshold Ionization (MATI) spectroscopy. The information obtained from the experiment is equivalent to having an infrared spectrum of the ion responsible for each parent mass peak in a mass spectrometer sampling a mixture. The identity and structure of each species can be determined.

The bulk of our effort in the last year has been involved with understanding the detailed mechanism of this technique and with extending it to allow different light sources.

THE MECHANISM OF MATI

Traditional wisdom holds that MATI (and ZEKE, an earlier variant which detects electrons) works by the creation of Rydberg states where the excited electron is in an orbit with a very high principle quantum number n (typically 150-250). These orbitals are practically macroscopic in size and the electron is removed from the core with a very small voltage. However, for the experiments to proceed, the large excited state must live for the order of microseconds. There has been much recent discussion in the community involved with this type of spectroscopy as to the reason for the longevity of the observed states. Transitions from valence orbitals of molecules cannot end up in very high angular momentum states because of conservation rules. However, low angular momentum Rydberg states are not predicted to last very long. High angular momentum electrons with circular orbits are predicted to last much longer and are assumed to be the ones observed. The question is: How do the electrons gain angular momentum? This has been attributed to small stray fields in the spectrometer, and this may be the case for very dilute samples. We have taken a different line, and argue the case that most MATI or ZEKE experiments take place under conditions where many Rydbergs and ions are

created in a single laser shot. This changes the picture considerably.

The focal volume of a laser is quite small, typically 10-20 microns in size. The Rydberg orbits are comparable in size, typically 1-5 microns. This means that if several Rydberg states and/or ions are created in the focal volume there is going to be considerable interaction between them. It is interesting that the field created by an ion at a distance of one micron is 14 V/cm, much higher than the pulsed fields used to theoretically "field ionize" the high Rydberg states. What we would like to claim is that there are many Rydberg-Rydberg and Rydberg-ion interactions which govern the lifetimes and stabilities of the states which give the field ionization signal in MATI.

Intellectually understanding that these interactions must be considered is easy. Devising some experiments which study them is considerably more difficult. Fortunately our MATI apparatus is designed to operate with very low voltages in the ionization region (it is unique in that respect) and we can get some idea about the ion-Rydberg interactions by observing the shapes of the mass peaks produced by our reflectron mass spectrometer as a function of the voltages applied when the laser is fired and when the ions are extracted from the focal region. We have found that the mass peak shapes vary considerably with laser intensity and sample density in a way that is consistent with charge-transfer and ion-ion interaction effects. We have also found that there are considerable effects of clusters in the signal at higher sample densities. These create prompt ions at the monomer mass which undoubtedly contribute to the mini-plasma effects which are observed. Hopefully, the understanding of these phenomena will enable us to sort out the photophysical effects observed in MATI spectra and enable us to design even more effective spectrometers.

MATI WITHOUT A LASER

The MATI technique we have developed using lasers is a very valuable high resolution method, and is particularly useful when studying a system which is fairly well characterized. Although laser vacuum ultraviolet generation is certainly an option, so far we have used a pump-probe ionization scheme which allows rotational and vibrational selectivity in the intermediate state. To use this one needs to have some information about the bound states of the molecule under study and these have to be stable.

If the bound states of the system are unknown or unstable and if the ionization potential of the system is not known, it can be difficult to do any experiments with lasers. To scan a very large region requires frequent dye changes and survey studies are time consuming. It would be much better to have a light source which could be tuned across a very large range of energies in the vacuum ultraviolet so that one photon excitation could be done wherever the ionization limit is found. To this end we have assembled a MATI apparatus which uses a vacuum ultraviolet lamp as a light source. This instrument uses a high pressure argon arc invented here many years ago in conjunction with a vacuum monochromator to produce a tunable VUV source with relatively high intensity (about 10^{11} photons/sec-Å).

Doing MATI with a continuous light source at first seems difficult since in most instruments the pulsed nature of the source is used to effect the separation of the Rydbergs and ions, and to enable the use of a time-of-flight mass spectrometer. In this instrument we use the unidirectional velocity characteristics of a supersonic beam to carry the molecules through the light focus, creating the Rydberg states. Separation of Rydbergs and ions is then accomplished by their different subsequent flights in electric fields until their injection into a quadrupole mass

- spectrometer.

The spectral resolution of the instrument will be an order of magnitude less than one using lasers. However the broad tunability will much more than make up for this lack in such studies as those involving clusters or chemical reactions where the exact identity of the molecules are not known. When interesting spectra are located, the laser instrument can then be used to investigate them at higher resolution. We also hope to use this CW machine to investigate the photophysics of MATI under conditions of very sparse excitation. At any given time there will only be one Rydberg or ion in the apparatus and interactions can be neglected.

The apparatus we have just completed is spectrally limited by the use of magnesium fluoride windows and lenses. However if this proves to be a valuable technique, the concept can be transferred to a synchrotron light source where the light flux will be much higher and the tuning range essentially unlimited.

CARBON DIOXIDE PHOTOPHYSICS

We have continued our investigations into the multiphoton photophysics of CO_2 . In previous work we found that transitions can take place in molecules even above the ionization limit at relatively low intensities if the laser is resonant with a transition in the ionic core. In those experiments it was clear that the ionization was proceeding through autoionizing states above the threshold. We called this phenomenon Resonance Enhanced Above Threshold Absorption (REATA) and wanted to examine how it depends on the character of the autoionizing state used as an intermediate resonance. We therefore have extended the previous work by investigating REATA through the 6f Rydberg state, where the 4-photon level is above the A state of the ion and therefore the mixed A and B electronic states of CO_2^+ are not expected to play the same role as in the 4f or 5f cases studies previously.

The previous REATA results, with REMPI photoelectron terminations at the five photon level on the C state of CO_2^+ , were only observed in REMPI-PES through 4f and 5f Rydberg states. A 21.4 eV state was also observed in REMPI-PES through the nf Rydberg states. In both of these cases, the four photon level falls in regions of Rydberg states which converge to the mixed A and B electronic states of CO_2^+ and peculiarities associated with these unusual mixed electronic states may mean that REATA is not a phenomenon which could be generally expected.

Sharp autoionizing state resonances are observed as 4-photon resonances to the blue of the 3-photon 4f and 5f resonances, which are diagnostic for autoionization playing an important role. The 6f Rydberg state resonance lies above the photon energy where mixed Rydberg states converging to the A and B states have their resonances. No similar sharp structure is observed to the blue of the main 6f envelope even though the 4-photon level is in an area of Rydberg structure leading to the ionic B state.

REMPI-PES spectra through the 6f intermediate Rydberg state have peaks consistent with photoelectron terminations on the C state of CO_2^+ , which indicates that the REATA process is still operative, even when the four-photon level falls above the mixed A and B electronic states of CO_2^+ and the "sharp structure" is absent from the REMPI ion spectra. The vibrational structure of the photoelectron spectra are different, however, indicating that the character of the intermediate embedded in the continuum is playing an important role in the ionization dynamics. Also at the 4f and 5f resonances the photoelectron spectra are very wavelength dependent in a way which helps to understand the photoionization dynamics at the 4-photon level.

In a collaborative effort with M. White at Brookhaven National Laboratory, we have

examined the 1+1 ionization spectrum of CO_2 through the 4f state using laser generated vacuum UV light. It is found that there is a region of greatly enhanced ionization in the middle of the spectrum which has rotational resolution when only the CO_2^+ signal is measured. Analysis of this structure promised to give much insight into the nature of the state and into dissociation mechanisms of the molecule. This is all the more important since there is only one other rotationally resolved state of the molecule seen in absorption.

BUDGET

The funding request is not changed from the one submitted at the time of the renewal proposal. There has been no change in any other Federal funding for the principle investigator.

PUBLICATIONS

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