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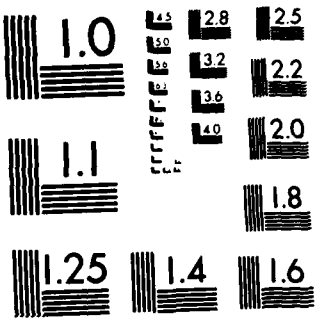

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

We have employed lasers to study elementary chemical reactions and to examine the structure of molecular ions. Specifically, we have: (i) investigated the effect of atomic reagent approach geometry on the outcome of chemical reaction, (ii) examined ion unimolecular fragmentation kinetics using a novel multiphoton ionization technique, (iii) studied the molecular CO_2^+ ion using double-resonance spectroscopy, and (iv) developed a new method for determining the vibrational structure of molecular ions.

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A. Chronological Bibliography of Publications Supported by AFOSR-81-0053*

1) D. Proch, D. M. Rider, and R. N. Zare, "Unimolecular Fragmentation Kinetics by Multiphoton Ionization," Chem. Phys. Lett., 81, 430-434 (1981).

2) Charles T. Rettner and Richard N. Zare, "Effect of Atomic Reagent Approach Geometry on Reactivity: Reactions of Aligned Ca($^1P_1$) with HCl, Cl_2 and CCl_4," J. Chem. Phys. 77, 2416-2429 (1982).

3) R. N. Zare, "Optical Preparation of Aligned Reagents," Berichte der Bunsen-Gesellschaft 86, 422-425 (1982).

4) Mark A. Johnson, Joëlle Rostas, and Richard N. Zare, "Optical-Optical Double Resonance on Cooled Molecular Ions: Rotational Assignments in the Perturbed CO_2^+ $\tilde{B}$-$\tilde{X}$ System," Chem. Phys. Lett. 92, 225-231 (1982).

5) S. L. Anderson, D. M. Rider, and R. N. Zare, "Multiphoton Ionization Photoelectron Spectroscopy: A New Method for Determining Vibrational Structure of Molecular Ions," Chem. Phys. Lett. 93, 11-15 (1982).

* Reprints or preprints of these publications have already been sent.

B. Summary

Much progress has been made during this first year of funding. A number of new experimental methods have been successfully developed and implemented in studies of chemical reaction dynamics and the structure of molecular ions. These studies have included: (i) an investigation of ion unimolecular fragmentation kinetics using multiphoton ionization, (ii) an examination of the effect of reagent approach geometry on the outcome of chemical reactions, (iii) a two-laser double-resonance study of the molecular ion CO_2^+, and (iv) the development of a new method for determining the vibrational structure of molecular ions. These projects will be discussed in turn:

(i) Unimolecular Fragmentation Kinetics of Molecular Ions

When a compound is ionized in a mass spectrometer, extensive fragmentation may occur, producing the mass spectrum characteristic of that species. Such spectra usually contain sharp peaks corresponding to the different masses of the fragment ions. However, diffuse peaks are also occasionally observed. As was first pointed out by Hipple et al.,[1] these may be attributed to the production of "metastable" ions which fragment en route to the ion detector. In a time-of-flight mass spectrometer, an ion will then arrive at a time somewhere between the time appropriate to the fragment and the parent species. This produces broad asymmetrically distorted peaks, the shapes of which are determined by the unimolecular fragmentation rates and the geometry of the mass spectrometer. Of the many techniques employed to study this phenomenon, the most informative are those in which the

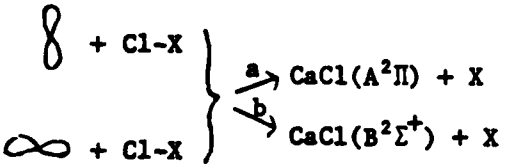
reactant ions are created with a well-characterized distribution of internal energy and in which this distribution can be readily controlled. This usually calls for the use of vacuum ultraviolet photoionization.[2] Unfortunately, the number of such studies is very limited because of the difficulty of producing and manipulating sufficiently intense tunable VUV radiation. To overcome these problems, we have developed a method involving photoionization with multiple visible or near UV photons. This multiphoton ionization (MPI) technique has many advantages,[3] in particular, large numbers of ions can be produced with well-known energies using only conventional optics.

Initial studies have been concerned with the parent aniline ion, $C_6H_7N^+$, which eliminates HCN to yield $C_6H_5^+$. Thus in the laser MPI mass spectrum of aniline we observe a broad asymmetric peak at m/e = 66 which we have analyzed to give the unimolecular decomposition rate of the $C_6H_7N^+$ species for a number of well-known energies. Rates of the order of 2×10^6 s^{-1} are obtained.

(ii) Reactions of Aligned $Ca(^1P_1)$ Atoms

Although reagent approach geometry plays a pivotal role in most theories of bimolecular reactions, there have been only a few direct experimental studies of such effects. These have dealt exclusively with control of molecular reagent approach geometry, typically employing electric-field oriented symmetric top molecules. We have examined the role of atomic reagent approach geometry, preparing aligned atomic oribtals. Specifically, we have investigated the reactions of aligned $Ca(^1P_1)$ atoms with HCl, Cl_2, and CCl_4. Aligned calcium p orbitals are prepared by excitation of a ground

state calcium atomic beam via the transition $Ca\,^1S_0 - {}^1P_1$ using linearly polarized light at 422.7 nm. These atoms react with a target gas to yield electronically excited CaCl(A,B) products, allowing us to make comparisons of the sort



(1)

where X = H, Cl or CCl_3 and  represents a directed calcium p orbital. We find a range of behavior. For the HCl reagent, the orbital alignment does not effect the total yield of excited state products but it does alter the course of the reaction. It is found that the direction of the atomic p orbital correlates with the corresponding pσ or pπ molecular orbital of the CaCl products in the $Ca(^1P_1)$ + HCl reaction. For Cl_2, perpendicular approach to the p orbital is favored by both channels while the CCl_4 reagent displays no significant sensitivity to orbital alignment. Our findings can be rationalized using an electron-jump model in which the symmetry of the reagents is preserved during a reactive encounter.

In addition to these experimental studies with aligned atomic reagents, we have examined in detail the possibilities for optical preparation of aligned molecular reagents. Starting with a quantum description of the optical absorption process, we have derived expressions for the degree of alignment caused when diatomic and symmetric top molecules undergo an electric-dipole-allowed transition induced by the absorption of plane polarized light.

(iii) Double-Resonance Spectroscopy of CO_2^+

Since our pioneering study of the collisional ionization reaction[4]

$$N_2 + e \rightarrow N_2^+ + 2e \qquad (2)$$

we have continued to be interested in the quantum-state-specific detection of molecular ions. In particular we have recently employed the combined techniques of free-jet expansion cooling and population labeling optical-optical double resonance spectroscopy[5] to the highly perturbed CO_2^+ $\tilde{B}$-$\tilde{X}$ band system. The 290 nm region of this spectrum is complicated by intramolecular perturbation in the $\tilde{B}^2\Sigma_u^+(000)$ state and is characterized by irregular rotational structure, extra lines, and anomalous intensities. As a result, the spectrum has frustrated unambiguous rotational assignment since the first high resolution spectrum was obtained more than forty years ago.[6]

CO_2^+ ions are prepared by electron impact on a free-jet of neutral CO_2 which emerges from a 0.1 mm nozzle backed by a pressure of 1 atmosphere. The expansion cooling serves to considerably simplify spectra by effectively eliminating sequence overlap. The population labelling method is as follows: two pulsed dye lasers are employed, a weak probe and a powerful pump laser. The probe laser is fixed on an unknown line in the 290 nm $\tilde{B}(000)$-$\tilde{X}(000)$ spectrum and the population in the lower level of this transition is monitored by detecting the resulting fluorescence. The pump laser is then scanned through the known $\tilde{A}(202)$-$\tilde{X}(000)$ system around 278 nm. When both lasers excite a common lower level, population driven out of the lower level by the pump laser is observed as a depletion in the fluorescence signal generated by the probe and thus assigns the lower level quantum

number of the previously unassigned probe transition. In this manner, we have systematically assigned 29 lines in the $\tilde{B}^2\Sigma_u^+(000)$-$\tilde{X}^2\Pi_{g_{\frac{3}{2}}}(000)$ excitation spectrum of CO_2^+. The term values so-obtained provide the first complete description of the perturbations at play in the $^{12}CO_2^+$ $\tilde{B}^2\Sigma_u^+(000)$ level.

(iv) Vibrational Structure of Molecular Ions

When a molecule is photoionized, in the absence of fragmentation, excess energy is partitioned between internal energy of the photoion and translational energy of the ion-electron system. Thus energy analysis of the photoelectron (photoelectron spectroscopy) reveals the energy content of the ion and can thus be of great value in determining the vibrational and electronic structure of molecular ions.[7] For molecules with more than a few atoms however, with single-photon ionization it is sometimes very difficult to observe and interpret vibrational structure because of spectral congestion and because of the Franck-Condon Principle which favors the appearance of only a limited number of vibrational modes. By using multiple photons to ionize via a resonant intermediate state, we have recently shown that many of these problems can be overcome. We have employed resonant two-photon ionization of the chlorobenzene molecule (C_6H_5Cl) to demonstrate this approach. In resonant two-photon ionization, a molecule can be excited through a number of real intermediate vibronic levels. Since each of these will have a different set of Franck-Condon factors and selection rules for ionization, we find that multiphoton ionization photoelectron spectroscopy provides a means of obtaining additional vibrational information about polyatomic ions.

For chlorobenzene, we have excited a number of different levels of the $^1B_2$ intermediate state. Each of these yields a markedly different photoelectron spectra, allowing us to assign the vibrational frequencies of the first five in-plane modes of the chlorobenzene cation, identifying three modes which were previously unobserved.

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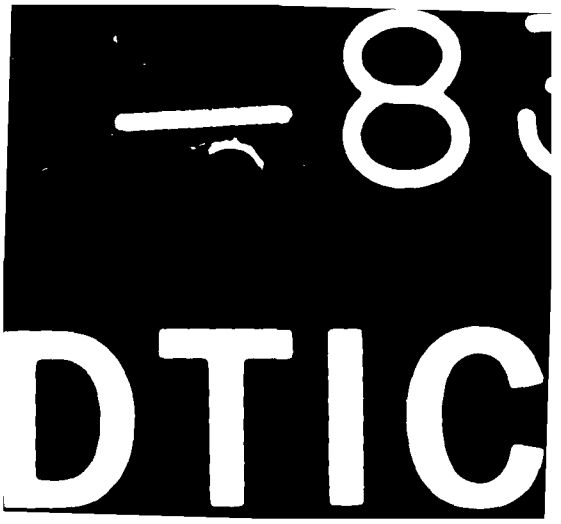
7) See for example, J. W. Rabalais, "Principles of Ultraviolet Photoelectron Spectroscopy," (Wiley, New York, 1977).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