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Final Report
Dissociation Dynamics of Nitrogen Rich Cyclic Compounds

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Abstract

The photophysics and photochemistry of the nitrogen-rich compounds diazomethane and diazirine were studied both experimentally and theoretically following excitation in the ultraviolet. These molecules are locally stable on their ground potential energy surfaces, but they contain large amounts of nuclear potential energy that can be unleashed upon photoexcitation. Methods for generating these compounds in supersonically cooled molecular beams were developed to facilitate the experimental studies. Several Rydberg states of diazomethane were characterized experimentally and assigned on the basis of theoretical calculations. Couplings among the Rydberg states and other Rydberg and valence states were analyzed experimentally and the lifetimes of the excited states were estimated. Two-photon excitation of diazirine accessed an excited valence state that dissociated promptly to give CH radicals. A unique mechanism involving isomerization to isodiazirine was proposed to explain this unexpected result. Other excited states were assigned and characterized by high-level electronic structure calculations. The diazirine ion was found to be unstable and weakly bound, as opposed to the stable cation of diazirine. On the basis of this work, a revision to the heats of formation of diazirine and diazomethane was suggested.

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Summary of Work Accomplished

Before our work began, little was known experimentally about the spectroscopy and excited state dynamics of small diazo compounds because of difficulties in preparing them in molecular beams. The molecules chosen for detailed study were diazomethane and its cyclic isomer diazirine, and their synthesis was carried out in collaboration with Dr. Karl Christe at USC. The first step was to develop procedures for the safe preparation and delivery of diazomethane and diazirine to the interaction chamber in molecular beams without significant decomposition. The next step was to develop reliable and sensitive diagnostics for these molecules by using 2+1 resonance enhanced multiphoton ionization (REMPI). In order to assign the spectroscopy and understand the excited state dynamics, we collaborated with the theoretical group of Prof. Anna Krylov at USC. Our investigations focused on the vibronic spectroscopy and state interactions in excited states of diazomethane and the photoexcitation and photodissociation dynamics of diazirine.

The electronic transitions of diazomethane in the region 6.32–7.30 eV were examined experimentally using a combination of 2 + 1 REMPI spectroscopy and photoelectron imaging. In the examined region, three Rydberg states of 3p character contribute to the transitions: $2^1A_2(3p_y \leftarrow \pi)$, $2^1B_1(3p_z \leftarrow \pi)$, and $3^1A_1(3p_x \leftarrow \pi)$. The two former states are of mostly pure Rydberg character and exhibit a resolved K structure in their spectra, whereas the $3^1A_1(3p_x \leftarrow \pi)$ state is mixed with the valence $2^1A_1(\pi^* \leftarrow \pi)$ state, which is unbound, i.e., strongly predissociative. High-level electronic structure calculations enabled us to characterize the excited electronic states and their interactions. Most of the observed 2+1 REMPI bands belong to the $2^1A_2(3p_y) \leftarrow 1^1A_1$ Rydberg transition, which is allowed only in two-photon absorption. This transition can serve as an excellent diagnostic for diazomethane. We have obtained for the first time photoelectron spectra from selected vibronic levels of this state, which aided in identifying interactions between the electronic states. Most of the electron kinetic energy (eKE) distributions showed single peaks characteristic of Rydberg states. However, several eKE distributions had two or more peaks, which derived from excitation of mixed vibronic levels involving Rydberg-Rydberg or Rydberg-valence interactions. Analyses of the REMPI vibronic spectra of diazomethane and its isotopologs together with the calculations and photoelectron images allowed us to assign many vibrational levels in the $2^1A_2(3p_y)$ neutral state and the ground state of the ion. The experimental and theoretical results agree very well and help explain differences in vibrational frequencies in the three Rydberg 3p states in terms of interactions of the Rydberg electron density with the ion core. These results were published in the *Journal of Physical Chemistry A* and were highlighted in a review article on interactions between Rydberg and valence states published in the *International Reviews of Physical Chemistry*.

We then turned our attention to studies of multiphoton ionization and dissociation in diazirine. These processes were studied experimentally with 304-325 nm two-photon excitation, and theoretically (in collaboration with Prof. Anna Krylov's group) by using the EOM-CCSD and B3LYP methods. The electronic structure calculations identified two excited valence states and four Rydberg states in the region 4.0-8.5 eV. In one-photon excitation, the strongest absorption is to the $2^1A_1(3p_x \leftarrow n)$ Rydberg state, whereas in two-photon absorption at comparable total excitation energies the first photon excites the low-lying $1^1B_2(\pi^* \leftarrow n)$ valence state, from which the strongest absorption is to the dissociative valence $1^1A_2(\pi^* \leftarrow \sigma_{NN})$ state. Thus, one- and two-photon excitation processes access different excited electronic states. The diazirine ion is calculated to be rather unstable, with a binding energy of only 0.73 eV and a geometry that resembles a weakly bound $CH_2^+ \dots N_2$ complex. In agreement with the calculated results, in the experimental studies the REMPI spectra show no ions at the parent diazirine mass but only CH_2^+ ions from dissociative photoionization. It is proposed that weak one-photon absorption to the 1^1B_2 state is immediately followed by more efficient absorption of another photon to reach the 1^1A_2 state from which competition between ionization and fast dissociation takes place. Strong signals of CH^+ ions were detected and assigned to 2+1 REMPI via the $D^2\Pi(v'=2) \leftarrow \leftarrow X^2\Pi(v''=0)$ two-photon transition of CH

fragments. The ion signals from CH fragments are the strongest in the REMPI spectrum and can serve as diagnostic for diazirine.

Velocity map CH^+ images show that CH fragments are born with substantial translational energy indicating that they arise from absorption of two photons in diazirine. It is argued that two photon processes via the 1^1B_2 intermediate state are very efficient in this wavelength range, leading predominantly to dissociation of diazirine from the 1^1A_2 state. The most likely route to $\text{CH}(\text{X})$ formation is isomerization to isodiazirine followed by dissociation to $\text{CH} + \text{HN}_2$. The unstable HN_2 molecule immediately dissociates to $\text{H} + \text{N}_2$. This mechanism agrees well with the measured maximum in the fragments' translational energy distribution, and it is similar to the proposed mechanism for formation of $\text{CH}(\text{X})$ in two-photon dissociation of the isoelectronic ketene.

In agreement with previous theoretical papers, we called for a revision of the heats of formation of diazirine and diazomethane to 77 ± 3 and 67 ± 3 kcal/mol, respectively. Ongoing experiments are focused on detecting H photofragments from diazirine and measuring their translational energy distributions in order to further elucidate mechanisms.

During this period four publications citing AFOSR sponsorship have appeared in print. In addition, two Ph.D. theses were completed:

1. Sergey Malyk (2009): "Transport and guest-host interactions in amorphous and crystalline ice".
2. Igor Fedorov (2009): "Photoelectron and ion imaging investigations of spectroscopy, photoionization, and photodissociation dynamics of diazomethane and diazirine".

Publications

S. Malyk, G. Kumi, H. Reisler, and C. Wittig, "Trapping and release of CO_2 guest molecules by amorphous ice", *J. Phys. Chem. A*, 111:13365-13370 (2007).

I. Fedorov, L. Koziol, G. S. Li, J. A. Parr, H. Reisler, and A. I. Krylov, "Vibronic structure and ion core interactions in Rydberg states of diazomethane: An experimental and theoretical investigation", *J. Phys. Chem. A*, 111:13347-13357 (2007).

I. Fedorov, L. Koziol, A. K. Mollner, A. I. Krylov and H. Reisler, "Multiphoton ionization and dissociation of diazirine: A theoretical and experimental study", *J. Phys. Chem. A*, 113:7412-21 (2009).

H. Reisler and A.I. Krylov, "Interacting Rydberg and valence states in radicals and molecules: Experimental and theoretical studies", *Int. Rev. Phys. Chem.*, 28:267-308 (2009).