CONF-940706--2

Laser Ionization of Molecular Clusters

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Research sponsored by the Office of Health and Environmental Research, U. S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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Abstract. Multiphoton ionization coupled with mass spectrometry was used to investigate molecular cluster distributions. Three examples will be discussed in this presentation. First, in studies of neat nitric oxide clusters, $(NO)_m$, an interesting odd-even intensity alternation was observed and will be discussed in terms of electron-pairing considerations. In a separate study, the binary clusters comprising nitric oxide and methane preferentially form a stoichiometric cluster made up of repeating units of $(NO)_2CH_4$. These presumably represent a particularly strongly bound "van der Waals" subunit. Finally, in similar studies of neat carbon disulfide clusters, $(CS_2)_m$, additional photon absorption after the two-photon ionization step stimulates a series of intracluster ion-molecular reactions leading to formation of S_m^+ and $(CS)_m^+$ polymers, as well as intermediate species such as $S_m^+(CS_2)$. This molecular cluster analogue of "laser snow" will be described in detail.

INTRODUCTION

Multiphoton ionization (MPI) has proven to be an effective method of ionizing atomic and molecular clusters for subsequent detection by mass spectrometry. When resonant MPI is used, information about intermediate states of the neutral van der Waals molecule or cluster can be obtained (1). Recently we have introduced (2) and developed (3) non-resonant MPI as a more general means of ionization. Of course, information about intermediate states is lost, but the non-resonant technique has the advantage of ionizing all of the clusters in the supersonic jet with approximately equal efficiency so that the cluster distribution can be examined. In particular, so-called "magic numbers" or especially intense peaks in the distribution provides clues to the stability of certain-sized clusters.

In previous studies we have observed extensive cluster distributions for Xe_n (4), $(NO)_m(Ar)_n$ (3) and mixed molecular clusters of the form $(NO)_mY_n$ (3,5) where Y represents other molecular partners such as N_2O, CO_2, H_2O, etc.

In the present paper we present three brief vignettes of such cluster studies. The first involves clusters of nitric oxide molecules, the second is a study of stoichometric clusters of the form $(NO)_m(CH_4)_n$, and, finally, laser induced polymerization within carbon disulfide clusters will be described.

Experimental

The experimental apparatus has been previously described (3), but a brief account is given here for completeness. The pulsed beam from a supersonic expansion is skimmed and crossed with a 266 or 240 nm laser beam in a differentially pumped chamber. Typical expansion conditions include a 100 psi backing pressure and a 0.5 mm aperture. A 30 ps (Quantel YG571C) laser beam is mildly focussed (7.5 cm FL) in the molecular beam between the extraction plates of a conventional time-of-flight mass spectrometer. The signal from a dual channel plate electron multiplier is averaged over 4,000 laser shots and displayed with a digital oscilloscope (Tektronix 11402).

Neat Nitric-Oxide Clusters

In contrast to the $(NO)_m(Ar)_n$ clusters formed in a 1% NO/Ar mixture described previously (3), when a 5% NO/Ar mixture was expanded in a supersonic jet and two-photon ionized, pure NO clusters up to about $(NO)^+_{40}$ are readily observed. The overall envelope of the distribution is a monotonically decreasing function of m. Superimposed on this envelope, however, is a very striking odd-even intensity alternation, with the odd-m clusters being more intense. For $m > 19$, *only* the odd-sized clusters are observed. Similar odd-even effects are seen in the negative ion cluster spectrum produced by Rydberg electron transfer (6).

Because NO is a free radical having an unpaired electron, even-m neutral clusters may have all of their electrons paired leading to stronger bonding than for the odd-m neutral clusters. For the ions, however, the argument reverses. Odd-m positive or negative ions may have all of their electrons paired and should be more strongly bound and hence more stable.

Relating relative bond strengths and stabilities to the intensity distributions is not trivial, however, because dynamical factors also play a role. For instance, the observed positive ion abundances reflect the original neutral distribution, the m-dependent photoionization cross section and m-dependent cluster evaporation rates. Further details may be found in reference 5.

Nitric Oxide-Methane Clusters

The cluster distribution obtained after ionizing an expansion of nitric oxide, methane and argon (5%, 5%, 90%) is quite different from that observed for any other binary molecular cluster studied by the authors or reported in the literature. From inspection of the distribution, it is immediately obvious that only some of the possible $(NO)^+_m(CH_4)_n$ clusters are observed. First, for the bulk of the distribution, only mixed clusters containing odd numbers of NO molecules are observed. This is similar to the odd-even alternation observed for pure $(NO)^+_m$ clusters, but much more extreme for low m than previously observed. The second striking feature is that for each cluster with m nitric oxide molecules only one peak is strongly observed corresponding to a set number, n, of CH_4 molecules. In each case m=2n+1, although the peak with m=2n is also observed weakly.

The implication of the fixed relationship between m and n is that a very stable configuration of mixed NO/CH_4 species must exist. Furthermore, the polymer, which can be observed out to $(NO)_{23}(CH_4)_{11}$, appears to be infinitely repeating. The repeating unit, $(NO)_2CH_4$, presumably represents a particularly stable species. No similar examples for relatively weakly-bound molecular clusters are known to the author. Similar stoichiometric hetero-clusters have been observed for mixed metal/carbon atom clusters, such as the metallo-carbohedrenes (met-cars) (7). Also, recently some novel molybdenum carbide species of formula MO_nC_{4n}(n = 1-4) have been reported (8).

Clearly, more experimental studies as well as some theoretical guidance are required before speculating about possible structures.

Intracluster Polymerization

"Laser Snow" was the whimsical name given by Professor William Happer (then at Columbia) to his observation of precipitation of white particles following resonant laser excitation of a cesium/hydrogen mixture (9). The laser beam excited the cesium atoms which then underwent a chemical reaction upon colliding with hydrogen molecules. The precipitate was analyzed and shown to be cesium hydride. Later examples of laser snow were discovered in sulfur hexafluoride, thiophenol, and carbon disulfide. Suggested applications of laser snow included isotope separation and production of ceramic powders. After arousing much interest in the late 1970s, the subject died down in the intervening years.

Recently, we have observed a modern analogue of laser snow. Although visible particles were not observed in this low pressure experiment, the mass spectrum following MPI of CS_2 clusters, revealed the presence of polymers of sulphur $(S)^+_{m=1-12}$ and carbon sulfide $(CS)^+_{m=1-4}$, the same species observed in earlier laser snow experiments with high pressure gases (10). In addition, intermediate species such as $S^+_m(CS_2)_n$ provided clues to the polymerization mechanism.

Although the original laser snow involved collisions of excited atoms or molecules with other species, the cluster mechanism eliminates the need for collisions. When one member of a cluster of CS_2 molecules is excited it finds its next-door neighbor to be a suitable reaction partner and no collision is needed. Any extra energy due to the reaction can be used to eject weakly-bound molecules from the cluster. The initially ionized molecule "eats" its way through the cluster like a molecular "Pac Man" creating bigger and bigger polymers with each bite.

Another difference from earlier laser snow experiments is that the excited specie in the reported experiments are ions. This allows for easy detection via mass spectrometry and also allows previously studied ion-molecule reactions to form the basis for the laser snow mechanism. Further details may be found in a forthcoming article (11).

These experiments provide one example of a small number of examples of "clustering within clusters" (12) or "intra-cluster chemistry" (13). Clusters provide a unique media for these chemical reactions which were previously only studied in bulk gas or crossed-beam experiments.

ACKNOWLEDGMENTS

Research sponsored by the Office of Health and Environmental Research, U. S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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