

Study of the Metastable Decay of Single Size Benzene Clusters by an Ion Stopping Technique

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A method has been developed which allows to stop single sized cluster ions in a superionic jet. This cluster will stay isolated in space for a long time and photochemical processes can be studied without perturbation from the other clusters in the jet. This allows to uniquely identify the parent complex, and the metastable decay of this complex can be analyzed.

Introduction

Molecular clusters are attractive objects of research. Such clusters are typically prepared up to high complexity by rapid adiabatic expansion in a hypersonic jet. Although this is a highly efficient method, it suffers from the major problem that all clusters are produced simultaneously whereas, for purposes of understanding the microscopic behavior of such clusters, it would be highly desirable to study individual clusters, a problem as yet unsolved.

For the mass selection and individual preparation of single molecular clusters the often proposed mass selection of the corresponding ions is not satisfactory since the very process of ionization produces mixtures of clusters, i.e. one has pollution of the ion being measured by decomposition of larger sized cluster ions. Highly sophisticated ionization-neutralization methods have been successfully employed for metal atoms but not for molecular clusters [1].

We present here a new method for the separation and storing in space of ion clusters. We produce and dilute the clusters in a hypersonic jet and make use of the unique property of such jets that all masses are accelerated to about the same velocity, the velocity being the more uniform the higher the driving pressure of the jet. These clusters are then laser ionized in the absence of a field, after which a retarding electric pulse is applied. This means that all cluster ions will receive a change of momentum which is proportional to the electric force times the pulse-width. By correctly

adjusting this pulse, clusters of a single mass can be brought to a dead stop whereas the other clusters will leave the region of ionization.

In this way ion clusters of a single mass are selected and brought to a standstill. After a variable time delay the stopped ions are extracted into the time-of-flight mass spectrometer. A minimum time delay before extracting has to be preserved to ensure that all ions which are not stopped have left the critical region.

With this new method, ions of a single cluster size can be selected and, because they stay confined in space, they can be used as targets for a further laser absorption or for studying ion molecule reactions with a collision gas.

We present here just one application of this technique, the determination of the metastable decay of large molecular cluster ions after laser ionization. If no metastable decay occurs after stopping of the ions, only a single mass peak will be observed in the mass spectrum. From the observation of peaks of smaller masses the channels for metastable decay can be detected, and from the measurement of the relative peak heights after different delay times before extracting the ions, decay times for these processes can be determined. Here measurements up to 20 microseconds could be performed. For shorter decay times this new method can also be applied. For this stop pulse has to be delayed and from the analysis of the peak heights in dependence on the delay time the metastable decay leading to a cluster of a certain size before stopping can be analyzed.

In this work we used this new technique to study benzene clusters where we could separate clusters of up to eight benzene molecules and demonstrate the metastable decay of these large clusters.

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Experimental

The supersonic experiment was described previously [2]. The benzene complexes are produced in a supersonic jet. For this benzene at 10 °C with a vapor pressure of 65 mbar seeded in Helium with a backing pressure of up to 4 bars is expanded through a pulsed nozzle (Bosch fuel injection valve) into the vacuum. The jet is skimmed 35 mm downstream of the nozzle by a skimmer with an opening of 1 mm and enters the main chamber. The benzene complexes are then ionized at the center of the ion extraction optics at a total distance of 10 cm from the nozzle with a frequency doubled dye laser (Coumarin 307) pumped with the third harmonic of an Nd:YAG laser (Quanta Ray DCR1-A). The laser beam is focussed perpendicular onto the supersonic jet and the ions are extracted colinearly to the jet into a reflectron time of flight mass spectrometer. The ion optics consist of a repeller plate with a central opening of 1.5 mm through which the supersonic jet enters and an extractor plate with a central opening of 4 mm through which the ions are extracted into the reflectron time of flight mass spectrometer (RETOF). The distance between the two plates is 8 mm. To avoid lense effects from these openings, a grid of 90% transmission was mounted onto the plates. The extraction plate and the repeller plate are at ground potential when the clusters are ionized. By applying a proper electric pulse at the repeller plate the ions could either be stopped or extracted into the RETOF. To stop the various sized cluster ions a negative electric pulse of 300 Volts and a variable pulse-width from 50 ns to 500 ns is applied which could also be delayed to the laser pulse. For the extraction of the ions a positive voltage of 900 Volts is applied to the repeller at a variable delay up to 20 μ s relative to the laser pulse. The extraction voltage then was maintained for 3 μ s to ensure that all ions between the repeller and extractor plates are extracted during this time into the RETOF.

Results

When one expands a gas in a seeded supersonic expansion, the molecules and the clusters formed in the jet will obtain a velocity which is nearly the same for all molecules in the jet and is near to the speed of the carrier gas, if the seed ratio is sufficiently low. We have measured this velocity distribution in a previous

experiment [3], where we used a high speed chopper which allowed to select a two microsecond wide start time window for a time of flight determination of the speed distribution of benzene clusters in the jet. This distribution is shown in Fig. 1 a, where benzene is seeded in helium at a stagnation pressure of two bar. The complexes and the bare molecule nearly obtained the same speed and only a small velocity slip for the larger clusters is seen. This picture is changed dramatically if one plots the momentum distribution of the clusters, which is shown in Figure 1 b.

The peaks of the different sized clusters are separated and do not overlap. When these benzene clusters are ionized, the momentum is nearly not changed. If one now applies an electric field E for a short period of time Δt , the momentum of the clusters will change by

$$\Delta p = q E \Delta t,$$

where q is the charge of the cluster.

One now can adjust this electric pulse so that it just compensates the momentum of one of the clusters.

After some time all clusters beside the stopped ones will have left the space between the plates of the ion optics. If one applies an electric field after that time to extract the ions, only a single mass peak should be detected in the time of flight mass spectrometer. This is shown in Figure 2. The upper curve shows the mass spectrum if the ions are extracted immediately after ionization. From this spectrum there is no way to determine the neutral cluster distribution as the metastable decay of larger clusters contributes to the peak size of smaller clusters.

When one applies a proper electric pulse, a selected benzene cluster (B_n) can be stopped. The extraction pulse was applied 10 μ s after stopping the ions. The spectra are normalized to the largest peaks within each spectrum. The largest mass observed in each spectrum corresponds to the mass of the stopped ion. In addition to this B_n peak also the B_{n-1} peak can be seen, which increases in intensity with increasing n . For B_7 and B_8 also the B_{n-2} peaks can be seen but show a much smaller intensity.

Discussion

In this experiment the clusters are ionized by non-resonant multiphoton absorption as a worst test case. In this process more energy than necessary for reaching the ionization threshold is absorbed and will partially be removed by the electron or leads to excited

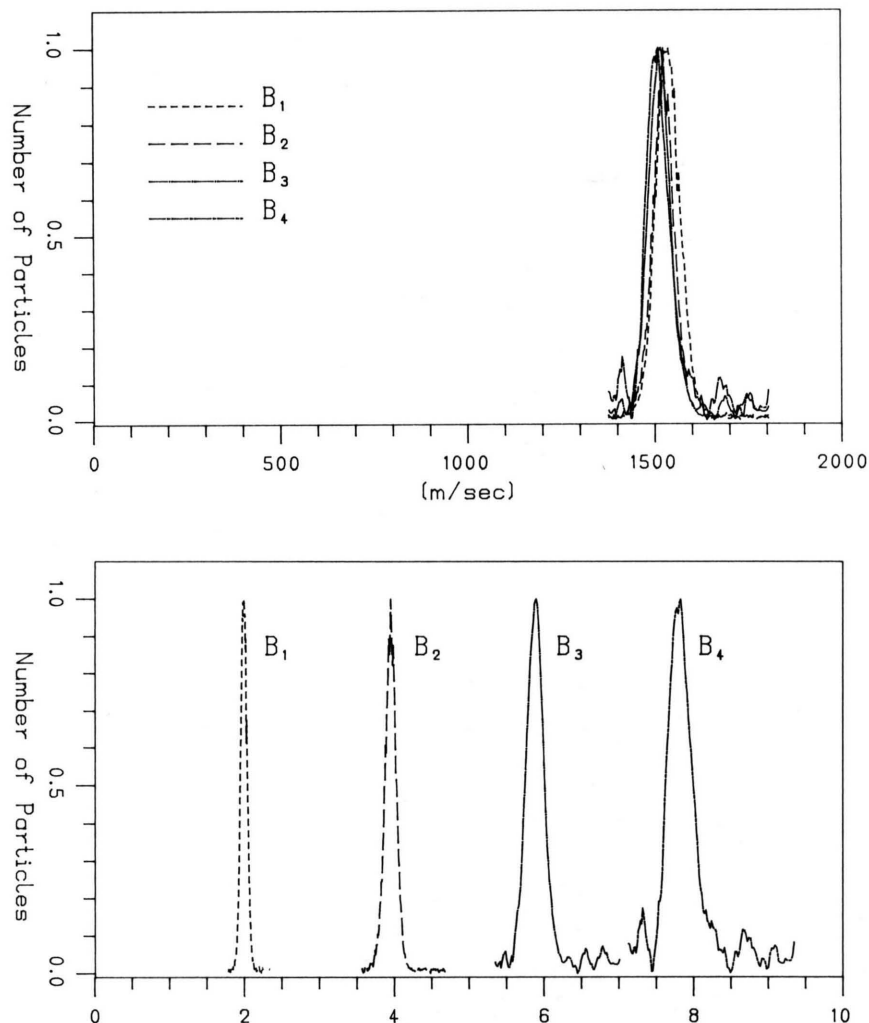


Fig. 1 a. Velocity distribution of benzene clusters in a supersonic jet. – Benzene at 60 mbar is seeded in He at 2 bar. The jet is chopped to obtain a start window of 2 μ s, and the velocity is measured from the flight time to the place of laser ionization. The speed was found to be around 1500 m/sec for all clusters with a width of about 60 m/sec. The larger clusters B_2 , B_3 and B_4 show a small velocity slip in the order of 20 m/sec with respect to the monomer B_1 .

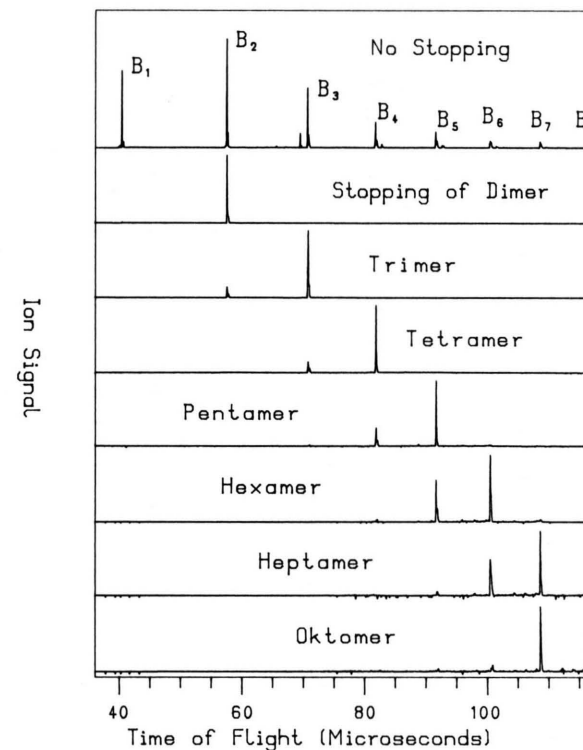


Fig. 2. Metastable decay of benzene complexes determined from mass spectra of size selected cluster ions. – The upper curve shows the mass spectrum when all ions are extracted immediately after laser ionization. The ionization laser frequency coincided with the absorption band of the S_1 6_0^1 dimer transition and therefore the dimer peak is the largest one. The small peak in front of the trimer (B_3) arises from contamination of the background oil vapor. – The lower mass spectra are obtained by stopping the various clusters immediately after the ionizing laser pulse and extracting after 10 μ s. The main peak then arises from the stopped parent and the lower mass peaks are metastable decay products. The metastable peaks increase with cluster size at otherwise equal experimental conditions.

Fig. 1 b. Momentum distribution in the jet. – The momentum distribution is evaluated from the velocity measurement of Figure 1 a. The individual clusters are well separated and the distributions do not overlap.

cluster ions. This excess energy then can flow into the intermolecular bond and leads to metastable decay on a microsecond time scale [4].

The mass spectra obtained with this new technique from selected single sized clusters show peaks at smaller masses, which arise from this metastable decay in the time between the end of the stopping pulse and the start of the extraction, i.e. from 500 ns to 10 μ s in this case. For the dimer no metastable decay is detected but for the larger clusters the abstraction of a benzene molecule is observed as the main decay channel.

This metastable decay becomes slower with the size of the cluster, and similarly also the abstraction of two or more benzene molecules is observed. This indicates that for the same multiphoton excitation conditions more excess energy is stored for a longer time in the complexes, which leads to a stronger metastable decay on this long time scale.

Conclusion

The preparation of single sized molecular clusters in a jet experiment is crucial for studying the metastable decay of such complexes. With this new technique individual cluster ions can be prepared in a dead-stop and stored for further examination. The cluster can undergo different reactions like metastable decay, and the reaction channels can be followed by a mass analysis of the products in a RETOF. The time delay for stopping a size selected cluster relative to the excitation laser pulse can be varied, which from analysis of the mass spectra then covers the time range up to the stop pulse, whereas the processes on a larger time scale can be analyzed by varying the time delay of the extraction of the ion into the RETOF. This new method therefore permits one to study primary photochemical processes and the metastable decay from the nanosecond to the microsecond time regime.

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