Registration Method for Metastable Decompositon of Benzene–Ar$_n$ and Toluene–Ar$_n$ Cluster Ions in RETOF Instruments

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A simple method for the study of metastable organic molecule – noble gas cluster cations in a RETOF mass spectrometer, based on the change in the direction of the flight path of charged particles, is presented.

In recent years, studies combining supersonic molecular beam and mass resonance enhanced multiphoton ionization spectroscopy technologies in the investigation of weakly-bound clusters of organic molecules between each other and with a gas-carrier have been actively promoted.[1–3]

The main attention of investigators is directed at the properties of charged clusters. However, the ionization of clusters by various methods is accompanied by an excitation of the charged associate of weakly-bound molecules and atoms. This may lead to the redistribution of surplus energy in the inner degree of freedom and to the formation of stable cluster cations, to the appearance of rapidly-decaying cluster ions immediately in the ionization area. Furthermore, cluster ions start to produce metastable cations the lifetime of which is comparable with the time gate between the ionization and detection times.[4,5]

Different methods devised to identify the unimolecular decomposition pathways of cluster ions reveal diverse and usually unique information about their structure, properties and intracluster ion-molecule reactions. Using an energy analyser, the parent masses and the daughter masses of the metastable decay process (or unimolecular decomposition) can be identified. The most productive methods are based on an energy and intensity analysis of metastable cluster ions produced by two-photon ionization in a reflectron time of flight (RETOF) mass spectrometer and by electron impact in a nozzle system coupled to a VG–ZAB–E mass spectrometer.[6]

It is well known[7,8] that the shapes and positions of metastable peaks on the TOF spectra are strongly influenced by formation conditions of neutral clusters through adiabatic expansion of the gas-carrier, by the geometry of the acceleration region, mass selected and field-free drift region, by a typical set of voltages on the electric sectors and, last, by any kinetic energy released during the decomposition process.

In ref. 7 the reflecting field of the RETOF mass spectrometer was used as an energy analyser. In order to detect metastable ions the authors avoided complete time focusing for ions with differing kinetic energies by using a slightly altered set of voltages on braking and reflecting fields. But this method gives decreased typical mass resolution achieved in the instrument,[8] completely shifting a time scale in comparison with an adjusted set of voltages. Stable ion peaks were suppressed by a suitable voltage. As a result, considerable difficulties were encountered in understanding complete metastable mass spectra.

The present work offers a simple method for the study of metastable cluster cations in a RETOF mass spectrometer based on the change in the direction of the flight path of charged particles immediately before entering the reflecting field, by means of the deflecting plates which leads to an angular as opposed to a time shifting of the cluster ion beam. Such an approach is devoid of the aforementioned shortcomings and enables us to obtain stable, blended stable-metastable and 'pure' metastable mass spectra, which is attributed to dissociation processes. The time-of-flight of stable and metastable ions for all possible dissociation processes and boundary conditions, including an anisotropic Maxwellian distribution function, were calculated.

The experiments were performed on an apparatus which combines a supersonic nozzle system and a RETOF instrument (BRUKER, TOFl). The RETOF instrument (Fig. 1) has been described in detail in previous works.[1,2,7] A supersonic nozzle system is used to generate neutral clusters of the following types: (organic molecule)$_n$, (organic molecule)$_n$ – (inert gas)$_m$, by an expansion of a mixture noble gas – organic vapour through a 140 μm pulsed nozzle (5 Hz repetition rate, Bosch fuel injector valve). The expansion chamber is separated from a molecular beam chamber by a skimmer (1 mm diameter) which selects the central part of the molecular beam and is placed 2 cm downstream of the nozzle.

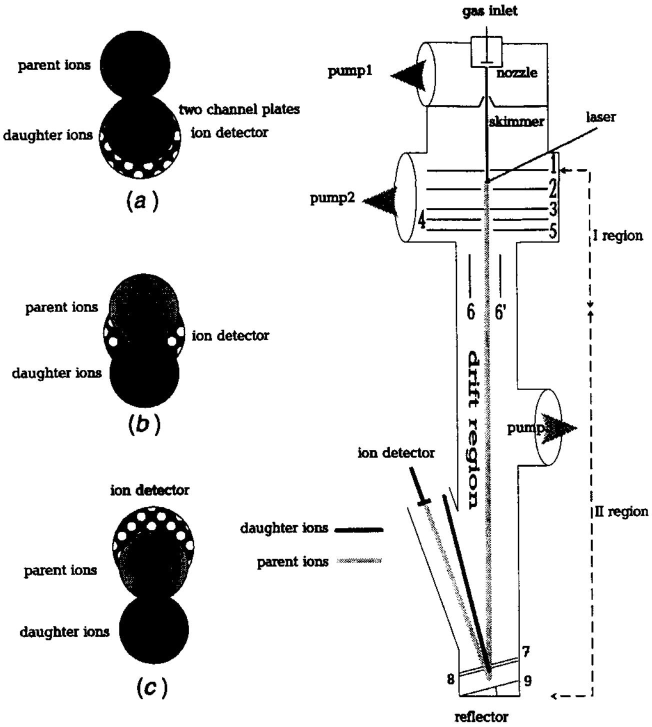

Fig. 1 Schematic representation of time-of-flight mass spectrometer TOFl and drift paths of parent and daughter ions charged in the ionization point by laser beam. The laser beam from a double-frequency dye laser (Lambda Physik FL 3001, XeCl excimer laser Lambda Physik LPX110 was used as a pumping laser with pulse energy of 160 mJ impulse^{-1}) was focused at the centre of a molecular beam at a distance of 7 mm from the repulsive plate 1 (U_{rep}). The orifice diameter of plate 1 was 2 mm, the distance to the accelerating plate 2 (U_{acc}) was 12 mm. Plates 3 and 5 were grounded. The voltage on plate 4 was $U_{\mathrm{col}} = -630$ V, orifice diameter 5 mm. The distances between plates 2,3,4 and 5 were equal to 14, 8 and 8 mm, respectively. The reflector has three main plates, number 7 (grounded), 8 (U_{br}), and 9 (U_{ref}) with distances of 20 and 135 mm between them, respectively. The drift region was 1100 mm, the distance from the reflectron to the detector (two microchannel plates) was 660 mm.

Computer simulation was performed only in region I (cylindrical symmetry) and in region II (cartesian three-dimensional grid) (see text).

(*a*) reciprocal location of ion detector and beam cross sections of parent and daughter ions at voltages of deflecting plates 6–6′ (ΔU from -22 to $+23$V) suitable for preferential registration of daughter ions; (*b*) simultaneous registration of parent and daughter ions; (*c*) suitable voltage on deflecting plates for preferential registration of parent ions.

The collimated neutral cluster beam enters the ion source of the mass spectrometer in a collinear configuration where it is ionized in a two-photon absorption process. A typical set of voltages is $U_{\mathrm{rep}} = 966$ V, $U_{\mathrm{acc}} = 520$ V, $U_{\mathrm{br}} = 393$ V, $U_{\mathrm{ref}} = 766$ V. Time-of-flight mass spectra were acquired on a SONY/Tektronix RTD710A transient digitizer (200 MHz, 10 bits vertical resolution), averaged over 10 to 1000 laser shots, and transferred *via* A/D input to a MOTOROLA 68020 MVME 133A–20 computer, where the individually selected mass peaks were integrated and stored. The resulting mass spectra were then corrected for baseline variations and normalized.

All calculations were conducted in a modified electrostatic lens analysis and design program SIMION V4.0.[9] The grid was divided into two regions: one with cylindrical symmetry and the other three-dimensional with $l = 50$ mm, $R = 32$ mm (1 mm between grid points) and $l = 130$ cm, $h,w = 60$ cm (1 cm between grid points), respectively. The ion source chamber (cylindrical symmetry) has three adjustable electrodes: $U_{\mathrm{rep}}, U_{\mathrm{f}}$ and U_{acc}. Trajectory calculations begin at $t = 0$ ionization by a laser pulse at the starting point. Upon immediate exit of the nozzle, the flow is quite complex.

Molecular velocities prior to ionization were modeled according to Maxwell's distribution, eqn. (1),

$$f(v) = n\left[\frac{m}{2\pi kT_{\parallel}}\right]^{1/2}\left[\frac{m}{2\pi kT_{\perp}}\right]\exp\left[-\frac{m}{2kT_{\parallel}}(v_{\parallel} - u)^2 - \frac{m}{2kT_{\perp}}v_{\perp}^2\right] \tag{1}$$

where u is the hydrodynamic flow speed, $T_{\parallel} = 6$ K is the local temperature along the current, $T_{\perp} = 1$ K is the local temperature perpendicular to the current and $v_{\parallel}$ and $v_{\perp}$ are the magnitudes of the velocity vectors parallel and perpendicular to the flow streamline, respectively. This treatment will suffice to accommodate a majority of buffer gases used in most nozzle beam studies.[10]

Since in this work clusters of benzene and toluene between themselves and with a gas-carrier were the objects of study, $T_{\parallel}$ was chosen to be the maximum temperature, taken from data for the time-of-flight experiment.[5,11]

The total effective width of the cluster ion beam at the entrance to the detector depends on the time-space focusing near the source, on the widening imposed by the reflecting system and on the pulse widening caused by the deviation of its plane from perpendicular to the RETOF axis. The kinetic energy of ions which decomposed during the time of flight to the reflectron decreases proportionally to the lost mass. The trajectories of such ions differ from those of the parent ions and do not cross with the detector plane. In ref. 7 the reflecting system of electrostatic lenses was employed as the analyser of kinetic energy. The present investigation used deflecting plates which on changing the direction of the flight path exerted no effect on the cross section of the pulse plane in space, but provided for the entrance of ions with different kinetic energies into the detector. Aberrations caused by the deflecting plates are negligible, since the distance between the plates is far greater than the beam diameter and the plates are quite long. The widening of the beam in the direction of the flight path, resulting from inaccuracy of angular focusing, is insignificant and can be neglected. However, in the perpendicular direction this shifting is sufficient enough for stable registration of newly-formed ions. Fig. 2 shows the angular distribution of parent and daughter ion beams. Fig. 3 represents the experimental spectra in the region of simultaneous registration of $C_6H_6^+$–Ar_n clusters and $C_6H_6^+$–Ar_{n-1} daughter ions ($\lambda = 258.9$ nm). Calculated positions of daughter ion-clusters of the studied row for one of the conformations and a typical set of voltages for the RETOF instrument are indicated. Time of delay between the opening of the gas valve and molecular beam ionization was chosen with a specific purpose. The highest numerical density of clusters was observed in the middle section of the gas pulse, *i.e.* in the region most distant from the fronts. An assignment of each line in the spectra was conducted according to an analysis of 500 trajectories independently grouped with Maxwell's distribution. A similar numerical and physical experiment was performed for the toluene–Ar (gas-carrier) system ($\lambda = 260.03$nm). The high numerical density of clusters in the middle section of the gas pulse, wide cluster inner energy spectrum and high intensity of laser beam lead to the formation of $C_6H_5CH_3^+$–Ar_{n-2} daughter ions. Results are shown in Fig. 4.

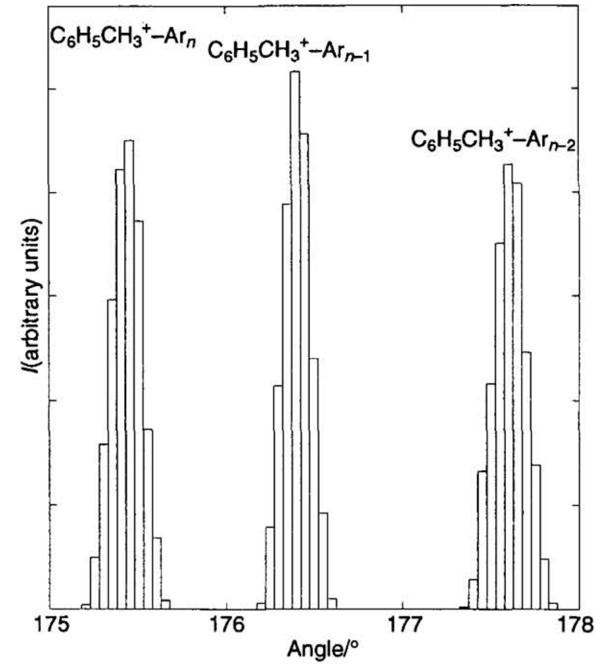

Fig. 2 Angular distribution of parent $C_6H_5CH_3^+$–Ar_n ion and daughter $C_6H_5CH_3^+$–Ar_{n-1} and $C_6H_5CH_3^+$–Ar_{n-2} ion trajectories. The angle is measured from the ion path before entering the reflectron fields. Each histogram includes 500 independent trajectories.

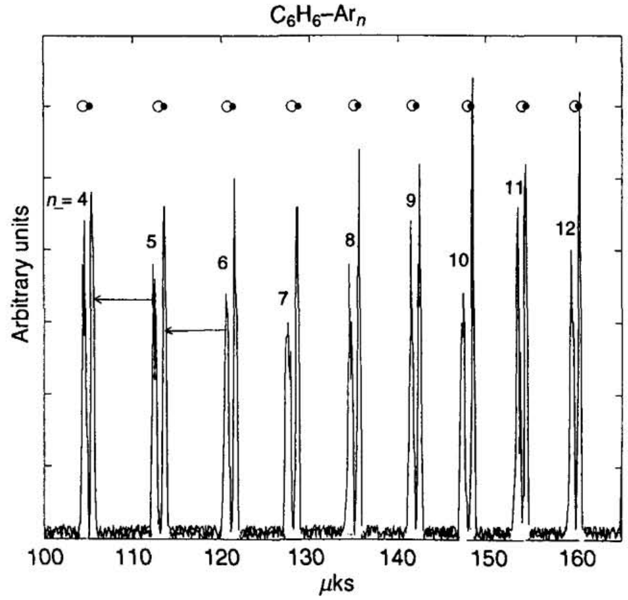

Fig. 3 Time-of-flight spectrum of $C_6H_6^+$–Ar_n clusters during a trajectory shift sufficient for the simultaneous registration of parent and daughter ions (blended stable – metastable mass spectra). Computed stable and metastable peak positions are indicated by open and closed circles, respectively. The numbers show the number of Ar atoms in stable clusters. Arrows indicate the direction of the shift of metastable ions from the parent ion on the time scale.

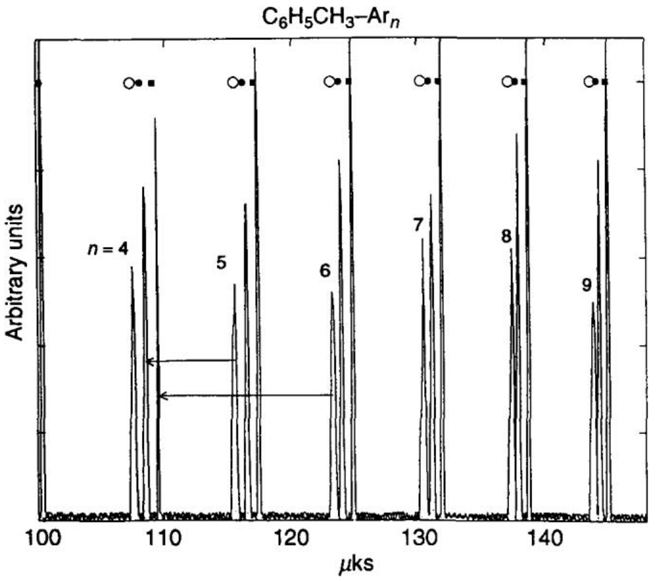

Fig. 4 Time-of-flight spectrum of $C_6H_5CH_3^+$–Ar_n clusters. The trajectory shift before the reflectron entrance was chosen with the purpose of simultaneous registration of two paths of daughter ion formation. Computed positions of stable $C_6H_5CH_3^+$–Ar_n ions are shown by open circles, daughter ions of the $C_6H_5CH_3^+$–Ar_{n-1} type by closed circles and daughter ions of the $C_6H_5CH_3^+$–Ar_{n-2} type by closed squares. Arrows indicate the shift direction of metastable ions on the time-of-flight scale from the parent ion.

Therefore, a simple method of obtaining mass spectra for metastable decay of organic molecular-rare gas clusters has been investigated. The results of numerical simulation based on the trajectory analysis of ion flights in RETOF instrument fields are in good agreement with the experimental data. The suggested method does not introduce significant distortions into the mass spectra of initial ions and does not reduce the high resolution of the RETOF mass spectrometer. Specifically chosen conditions of molecular impulse beam formation and its ionization allow registration of various metastable decomposition paths.

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