Time-of-flight mass spectroscopic detection of new elemental and mixed small atomic clusters in the laser evaporation of carbon nitride

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New, positively-charged elemental and mixed atomic carbon–nitrogen clusters have been detected by time-of-flight mass spectroscopy in the laser evaporation of carbon nitride $C_3N_{4.25}$.

Many elemental and mixed atomic clusters of carbon and nitrogen — promising materials in the production of high-energy density materials — demonstrate relative stability, according to recent *ab initio* calculations.[1,2] Meanwhile, up to date experimental studies on the structural, physical and chemical properties of these clusters are very rare because production of the clusters by laser vaporisation source techniques is impeded by a lack of nitrogen-rich carbonaceous targets.[3–6] In this case, current mass spectroscopic studies of the gas-phase evaporation products of carbon–nitrogen materials, usually related to the laser deposition of superhard carbon nitride (β-C_3N_4) thin films,[7,8] can also provide a clearer understanding of the nature of nitrogen and nitrogen–carbon atomic clusters.

In this work positively charged products from the laser evaporation of carbon nitride $C_3N_{4.25}$ (a polymeric material with a *symm*-heptazine monomer produced by thermal decomposition of mercuric rhodanide[9]) were studied by time-of-flight mass spectroscopy. The sample was prepared from a purified powder of polymer carbon nitride (PCN) pressed at 50 bar to a pellet (diameter 0.7 cm, thickness 0.4 cm, bulk density 1.6 g cm^{-3}).

Time-of-flight studies were carried out using a commercial quadrupole MX-7304 mass spectrometer modified for time-of-flight mass analysis (Figure 1). Operation conditions for the linear mass spectrometer were maintained by pumping the vacuum chamber with a high-vacuum discharge pump up to 10^{-7} Torr. The pulsed second harmonic output of a Q-switched Nd:YAG laser [laser wavelength λ = 532 nm, pulse energy E = 4.5±0.3 mJ, pulse duration (FWHM) τ = 10±1 ns, pulse repetition rate f = =0.92±0.05 Hz] attenuated by neutral calibrated filters and a $LiNbO_3$ polariser was focused by a lens (F = 28 cm) onto the surface of a PCN target at a slight angle (10–15°). A small part (8%) of the laser radiation energy was directed by a beam splitter onto a photodiode and a pyroelectric plate to synchronise the detection system and to control the laser energy per pulse.

Primary positive ions generated from the PCN target were extracted and accelerated by a pulsed voltage (–100 V, pulse width 0.1–10 μs) applied to a grid placed at a distance of 4 cm in front of the target with a ground graphite ring supporting the target. The cluster ion beam, with an adjustable mechanical momentum of the ions, was mass-analysed during drift in a field-free region (45 cm) to the input of a secondary electron multiplier with a time constant of 3 ns. After discrimination of noise and pre-amplification separate bursts of positive pulses of amplitude +4 V corresponding to individual cluster ions were digitised for 320 μs by a pulse counter connected to a PC *via* an interface. The digital signal was averaged over 100 laser shots and was then recorded.

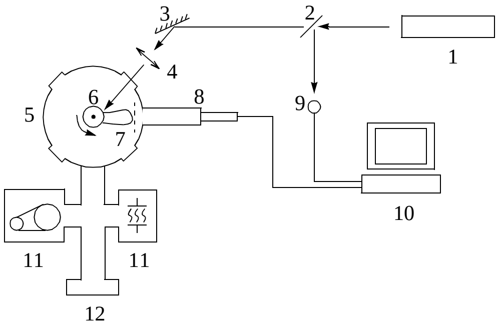

Figure 1 Scheme for the linear time-of-flight mass spectrometer: 1 – laser, 2 – beam splitter, 3 – mirror, 4 – focusing lens, 5 – vacuum chamber, 6 – polymer carbon nitride target supported on a ground graphite ring, 7 – extracting/accelerating grid and ion drift tube of mass analyser, 8 – secondary electron multiplier, noise discriminator and pre-amplifier, 9 – photodiode and pyroelectric plate, 10 – computer with pulse counter and interface, 11 – prevacuum pump and high-vacuum discharge pump, 12 – thermocouple and ionisation gauges.

The time-of-flight spectra of positive cluster ions were obtained during laser evaporation of the PCN target with laser power density 0.3 GW cm^{-2}. The calibration curve for the cluster ion mass *versus* flight time obtained for the cluster source conditions allowed the determination of ion mass values to an accuracy of 0.1% and reproducibility 0.3%. Maximum initial kinetic energies of ions measured by retarding potential technique were equal to $0.5 << eU \approx 100$ eV. Corresponding temperature of the cluster ion source $T < 6000$ K was favourable for preferable formation of singly charged ions.

Cluster ion masses were calculated using equation (1) for the acceleration and drift of singly charged ions:

$$M = \frac{eU\tau(t - 0.5\tau)}{l(L + l)m_0} \tag{1}$$

where M is the cluster ion mass (a.m.u.) related to its charge ($Z = 1$), e is the charge of an electron (C), U is the accelerating voltage (V), l is the distance from the target to the accelerating grid (m), L is the drift tube length (m), m_0 is one twelfth part of the carbon atom mass (carbon unit of mass, kg), t is the flight time (s) and τ is the accelerating electric pulse width (s). According to the formula the maximum mass of a cluster ion detected with the mass analyser is proportional to the accelerating pulse width and increases from 200 to 1700 a.m.u., with growth of the latter in the range 1–10 μs.

Pulsed acceleration of cluster ions to equal momentum is favourable in the resolution of high molecular mass ions due to the linear dependence of ion mass on flight time, as compared with monoenergetic ion beams which are described by a square root dependence. In this case, mass resolution of the cluster ion beam over the whole mass range was independent of cluster ion mass and was limited only by time resolution of the detection system t_c = 1.25±0.05 μs (counting cycle of the pulse counter). Then mass resolution of the nearest peaks in the mass spectra of positive clusters with a difference in mass of Δ a.m.u. was provided by their detection within the next counting cycle:

$$t(N + \Delta) - t(N) = \frac{Llm_0}{eU\tau}\Delta \geq 2t_c \tag{2}$$

Taking into account equation (2), the numerical expression for mass resolution of the cluster ion beam is of the form Δ (a.m.u.) = 1.2τ (μs) which corresponds to resolution of the two nearest peaks for mixed carbon–nitrogen cluster ions (with Δ = 2 a.m.u.) by using an accelerating electric pulse of width $\tau < 2$ μs.

The abundances of the cluster ions detected were multiplied by coefficient $M^{0.5}$, thus accounting for the dependence $E/M^{0.5}$ of the ion-electron conversion efficiency of a secondary electron

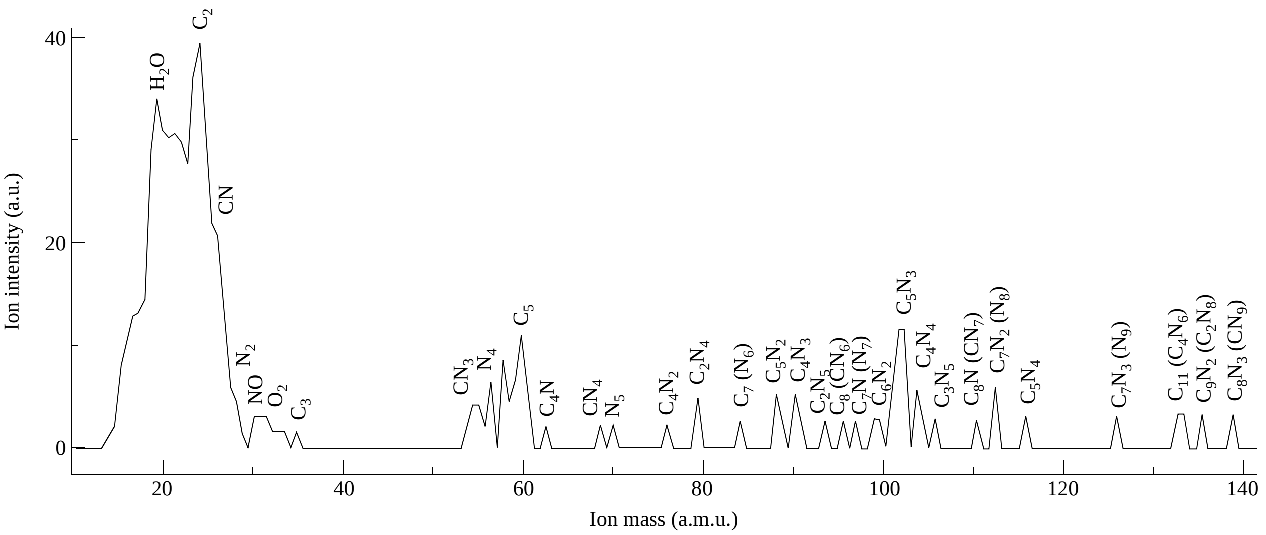

Figure 2 Time-of-flight spectrum of positive cluster ions (in the range 10–140 a.m.u.) generated from the polymer carbon nitride target.

multiplier on cluster ion mass (where E is the kinetic energy and M is the mass of the corresponding ion[10]).

The time-of-flight spectrum obtained for the PCN target and recorded at an accelerating pulse width of 1 µs and laser power density 0.3 GW cm^{-2} (Figure 2) exhibits a variety of elemental and mixed carbon–nitrogen atomic positive cluster ions as well as molecular ions H_2O^+, N_2^+, NO^+ and O_2^+. Most of the cluster ions appear in the 50–140 a.m.u. mass range due to the enhanced stability of their cyclic structure (for example, five-membered ring[11]) which is more favourable compared with a linear structure due to saturation of the valences.

An unambiguous interpretation of chemical composition for the detected cluster ions $C_{k-7x}N_{m+6x}$ is possible only at the index values $k < 7$ and $m < 6$. Thus, in the mass range 50–110 a.m.u. new mixed carbon–nitrogen atomic positive cluster ions CN_4^+, $C_2N_4^+$, $C_4N_3^+$, $C_5N_3^+$, $C_3N_5^+$ and $C_5N_4^+$ were identified. The chemical composition of the cluster ions with mass in the 110–140 a.m.u. range (also including masses 84, 96 and 98 a.m.u.) can be interpreted by many alternative combinations of carbon and nitrogen atoms [for example, an ion of mass 84 a.m.u. can be identified as C_7^+ (ref. 12) as well as N_6^+ (ref. 3)] (Figure 2). Unfortunately, an accurate identification of these $C_{k-7x}N_{m+6x}$ cluster ions with index values $k > 7$ or $m > 6$ (over 84–140 a.m.u. mass range) by an analysis of the natural isotopic distribution of carbon and nitrogen atoms was impossible, due to the discrimination of the low-intensity signals of isotopically-substituted cluster ions by the detection system of the mass spectrometer.

Thus, time-of-flight mass spectroscopic detection of clusters generated by a laser vaporisation technique from the unique nitrogen-rich target of polymeric carbon nitride $C_3N_{4.25}$ carried out in this work shows the existence of several new elemental and mixed carbon–nitrogen small cluster ions incorporating up to 5 nitrogen atoms.

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