MASS-SELECTIVE MATRIX-ISOLATION SPECTROSCOPY: FT-IR SPECTRA OF CYANOACETYLENE AND TETRACYANOETHYLENE IONS AND THEIR IONIC FRAGMENTS

A. M. SMITH-GICKLHORN, M. FRANKOWSKI, M. LORENZ, V. E. BONDYBEY, *Institut für Physikalische und Theoretische Chemie, Lichtenbergstraße 4, D-85747 Garching, Germany*; and R. KOŁOS, *Institute of Physical Chemistry of the Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland*.

Recent spectroscopic results from a new setup for the deposition of mass-selected ions in neon matrices are presented. Gaseous precursor substances are ionized in a homebuilt electron impact source, the ions extracted and deflected by 90° into a quadrupole mass filter with unity mass resolution up to 500 amu. The mass-selected cations are deposited simultaneously with an excess of electrons, to maintain overall sample neutrality and prevent buildup of space charges, and neon gas onto a reflective substrate held at 7 K.

Fourier-transform infrared spectra from such samples using cyanoacetylene and tetracyanoethylene reveal new infrared transitions for several cations. The strong infrared signal observed for the asymmetric stretch of CNC^+ and the appearance of the corresponding band for $^{13}CNC^+$ in its natural isotopic abundance, demonstrates the sensitivity and usefulness of the apparatus. A combination band of CNC^+ is also observed, revealing its low-frequency bend. Using this setup, the infrared spectra of cyanoacetylene ions[a] ($H(D)C_3N^+$ and $C_3N_2^+$) and tetracyanoethylene ions and ionic fragments[b] ($C_6N_4^+$, $C_6N_4^-$, $C_6N_3^+$, $C_5N_3^+$, and $C_3N_2^+$) are observed for the first time. The assignment of the numberous observed vibrations of these ions are well-supported by our density-functional calculations.

Using this apparatus and the sensitive LIF techique, the assignment of a rich emission spectrum with origin near 440 nm is confirmed to be due to mass 88 or C_5N_2 **neutral** [c] as subsequently verified by a cavity ringdown measurement of Linnartz, Maier et al.

[a] A.M. Smith-Gicklhorn, M. Lorenz, R. Kołos and V.E. Bondybey *J. Chem. Phys.* **115**, 7534-7542 (2001).
[b] A.M. Smith-Gicklhorn, M. Frankowski, and V.E. Bondybey *Phys. Chem. Chem. Phys.* In Press.
[c] A.M. Smith-Gicklhorn, M. Lorenz, M. Frankowski, R. Kołos and V.E. Bondybey *Chem. Phys. Lett.* **351**, 85-91 (2002).