

# Spectroscopic Characterization of Carbon Chains, Ions, and Cluster Ions

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**Abstract.** The current directions and experimental techniques used for the measurement of the electronic spectra of astrophysically relevant carbon chains, as well as infrared spectra of ionic complexes are outlined.



John P. Maier received his D. Phil. at Oxford in 1972 under the guidance of D.W. Turner. He completed his Habilitation in Basel in 1978 and was appointed to the Chair in Physical Chemistry in 1991. He has received several awards including the Werner-Prize (1979), the Marlow Medal (1980), and the Latsis Prize (1987).

The research activity is focused on the observation and identification of electronic and infrared spectra of radicals, ions, and ionic clusters. These reactive species are important constituents of space: in interstellar clouds, circumstellar shells, comets, planetary atmospheres, and on earth as intermediates in plasmas, flames, and chemical processes. Ionic complexes are found in the atmosphere and serve as prototype systems for the understanding of interactions present in chemical reactions and biochemical systems.

The projects aim at the development and application of spectroscopic methods to characterize these transient species. The analysis of the electronic and infrared spec-

tra leads to an understanding of their electronic and structural properties. The spectral fingerprint also provides the means of identification of such species in the hostile environments where they usually are found: at very low temperatures (10–50 K) in extraterrestrial regions and at the high temperatures (1000–2000 K) of discharges on earth.

In the case of ionic complexes, such as  $\text{NH}_4^+\text{-Ar}$  [1], infrared spectra of the mass-selected species can be obtained. After formation of the complex in a supersonic expansion and electron-impact ionization, the mass-selected species is trapped in an octopole. Vibrational transitions are excited by a tunable infrared laser. The detection is of the fragment-ion core, e.g.,  $\text{NH}_4^+$ , after predissociation. By this means, an infrared spectrum of the ionic complex in the gas-phase is observed. Rotational structure can often be resolved and the analysis provides information on the interactions between charged species and neutral moieties as well as structural data. Because the species are mass-selected, solvation processes can be followed *via* the changes in the infrared spectra, for example in the case of the  $\text{NH}_4^+\text{-Ar}_n$  clusters [1].

Particularly successful has been the identification of the electronic spectra of carbon chains. This has been achieved by a technique which combines mass spectrometry and matrix-isolation spectroscopy. Mass-selected cations or anions, which can be produced in copious amounts in ion sources are codeposited with excess of Ne on a metal surface at 5 K. This leads to trapping of isolated species in an inert surrounding of neon. The characteristic electronic transition can then be observed by absorption spectroscopy. Mass-selected neutral species are produced from an-

ions by electron detachment. By this means, a variety of carbon chains, their ions, and of the simple derivatives including hydrogen or nitrogen atoms, have been investigated and have led to a general understanding of their electronic spectra and structure [2].

*Fig. 1* shows examples of the electronic absorption spectra of carbon chains comprising an odd number of atoms, obtained by this technique. The intense transitions seen involve  $\pi\text{-}\pi$  excitation and show the typical feature of shifting by regular intervals in wavelength to the red as the length of the chain grows. This can be seen in the inset of *Fig. 1* and is readily modeled by a particle-in-a-box approach. Molecules as large as  $\text{HC}_{24}\text{H}$ , or  $\text{HC}_{23}\text{N}^-$  have been isolated and characterized in neon matrices at 5 K.

With such information in hand, the search for the electronic transitions in the gas phase can be undertaken. In the past year, this has led to the observation of the electronic transitions of carbon-chain anions,  $\text{C}_n^-$  ( $n = 4\text{--}11$ ) and radicals,  $\text{C}_{2n}\text{H}$  ( $n = 3\text{--}5$ ), in the gas phase by means of sensitive laser methods. In the case of the carbon-chain radicals, this is by means of cavity ring-down spectroscopy, which is effectively an absorption measurement using a laser light source and attaining a path length of kilometers. The species are produced at low temperatures by a supersonic expansion incorporating a discharge through acetylene. Longer chains are produced and species as large as  $\text{C}_{10}\text{H}$  have been observed [3]. Another developed technique uses a very-narrow-bandwidth laser in conjunction with modulation schemes to record the rotational structure in the electronic transitions of carbon-chain cations, e.g.,  $\text{HC}_8\text{H}^+$ , produced in a discharge cell [4]. This yields accurate

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spectroscopic constants and geometry information on these species.

In the case of anions, the production is also in a supersonic free jet within an electrical discharge, but the detection is by a mass-selected technique with laser excitation. The electronic transition of interest is probed by a tunable laser and the process is detected by detaching the electron by photons from a second laser. The absorption process is monitored from the intensity of the mass-selected neutral molecules formed as function of the wavelength of the first laser. In Fig. 2, an example for  $C_7^-$  showing the  $A^2\Pi_u - X^2\Pi_g$  electronic transition is given.

One motivation for these studies is in connection with astronomy. Carbon chains have been proposed as candidates causing some of the absorption of starlight in diffuse interstellar clouds. These absorption features, known as diffuse interstellar bands, have remained a puzzle since their first discovery over 70 years ago. Currently, a hundred or two such absorption bands are known. In Fig. 2, the astronomical observations in the region of  $C_7^-$  transitions are also shown. A striking match in the laboratory and space-measured bands is apparent for the origin band as well the ones corresponding to vibrational excitation in the upper electronic state [5]. This result provides the first compelling evidence for the identification of a molecule responsible for some of the diffuse interstellar bands.

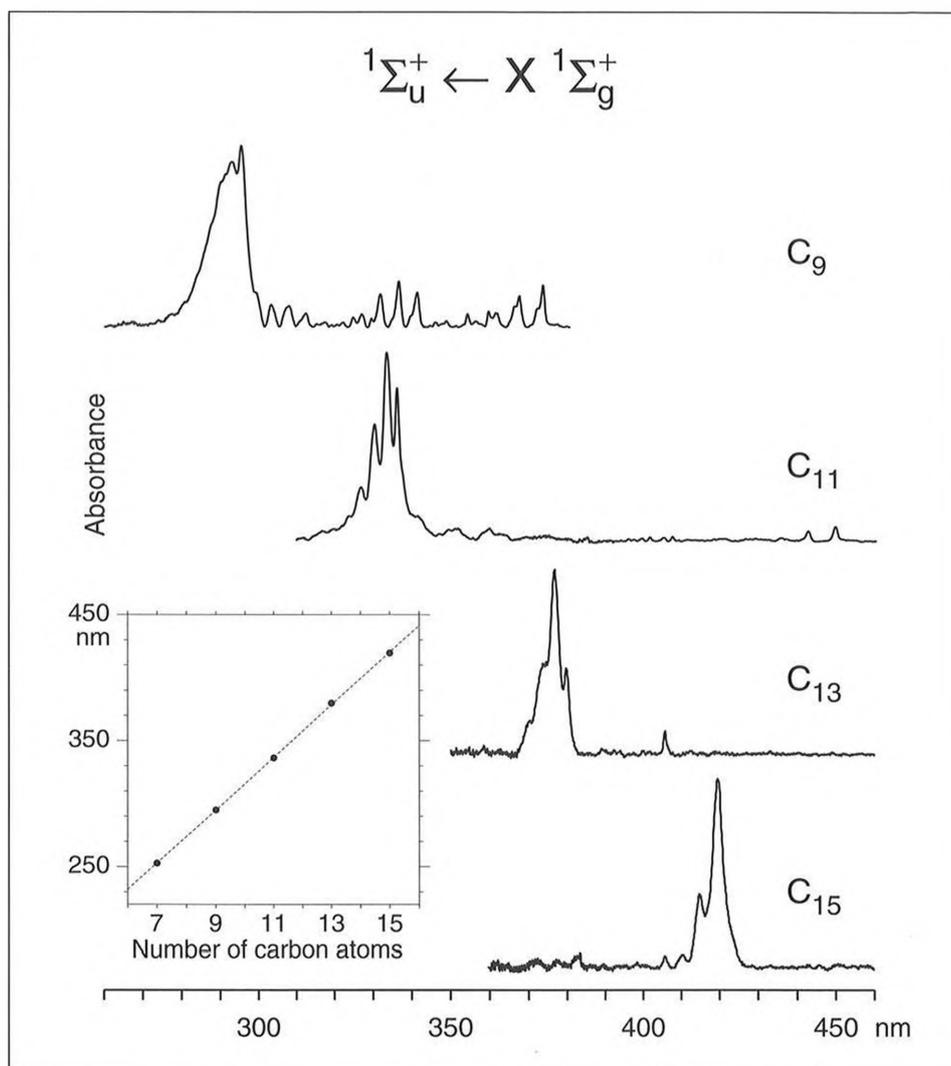


Fig. 1. Electronic absorption spectra of carbon chains with an odd number of atoms. The inset shows the dependence of the wavelength of the transition on the length of the chain.

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- [1] O. Dopfer, S.A. Nizkorodov, M. Meuwly, E.J. Bieske, J.P. Maier, *Int. J. Mass Spectr. Ion Phys.* **1997**, 167/168, 637.  
 [2] J.P. Maier, *J. Phys. Chem.* **1998**, 102, 3462.  
 [3] H. Linnartz, T. Motylewski, J.P. Maier, *J. Chem. Phys.* **1998**, 109, 3819.  
 [4] W.E. Sinclair, D. Pfluger, H. Linnartz, J.P. Maier, *J. Chem. Phys.* **1999**, 110, 296.  
 [5] M. Tulej, D.A. Kirkwood, M. Pachkov, J.P. Maier, *Astrophys. J.* **1998**, 506, L69.

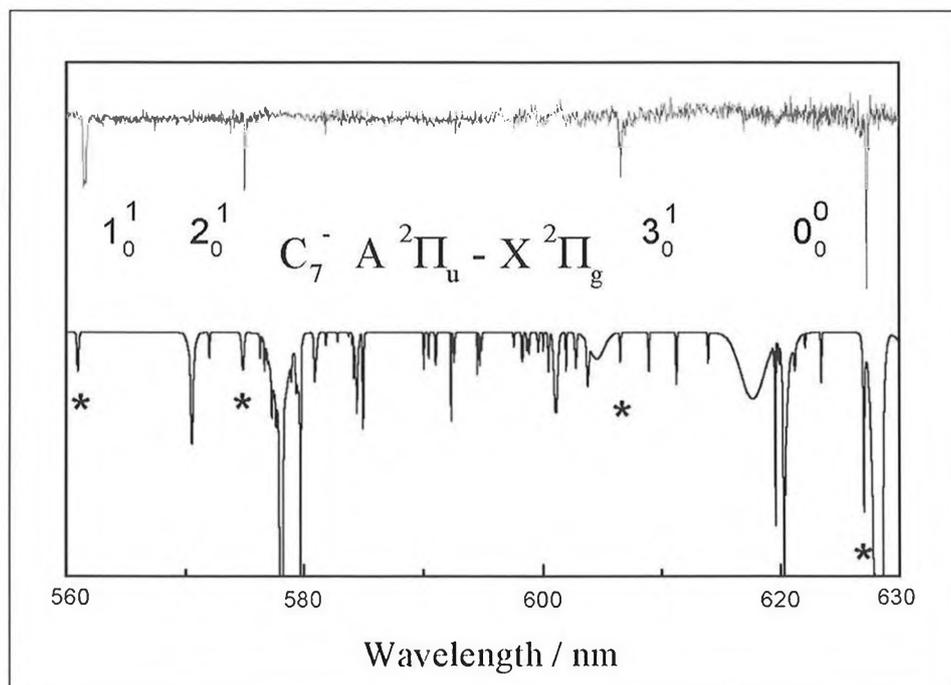


Fig. 2. The electronic spectrum of  $C_7^-$  in the gas phase,  $A^2\Pi_u - X^2\Pi_g$  transition, recorded in the laboratory by a two-color laser-excitation/electron-detachment approach (top trace). Underneath are shown the diffuse interstellar absorption features recorded by astronomers, and the matching bands are marked by asterisks.