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**Ion Chemistry
New Materials**

Laser Spectroscopy of Transition Metallo-Organic Molecules

Understanding the reactivity between transition metals and organic moieties has repercussions throughout chemistry. Transition-metallo-organic (TMO) radicals are important as reaction intermediates in organometallic synthesis, homogeneous catalysis and metal surface-molecule interactions. Small TMO radicals provide a good, and relatively simple, model of the metal-carbon bond and by determining the structure of these free radicals, one can obtain important insights into chemical interactions and reactivity. By their very nature free radicals are highly reactive and resist study with conventional condensed phase methods. However, it is now possible to generate small TMO free radicals, both neutral and ionic species, in the gas phase and to probe their structures with a variety of laser-based spectroscopic techniques.

The transition-metallo-organic molecules are generated using a laser vaporisation source (the original C₆₀ source) to produce gas phase metal atoms that are reacted with various organic molecules (*e.g.* CH₄, CO, CO₂). This results in the formation of the transition-metallo-organic molecules and radicals. The gas mixture is expanded into a vacuum forming a jet-cooled molecular beam where the molecules become isolated from one another in their lowest internal energy levels. The spectroscopic aspects of this project utilise Resonance Enhanced Multi-Photon Ionisation (REMPI) spectroscopy. By varying the energy of the laser photon, the rotational and vibrational states of the TMOs can be probed. The rotational structure of each spectrum will directly elucidate molecular structures while vibrational structure will provide information about the potential energy surfaces of these molecules.

Projects in this field are currently focussed on two types of molecular systems:

(i) The Niobium Cluster–Carbonyl Interaction (Nb_n–CO)

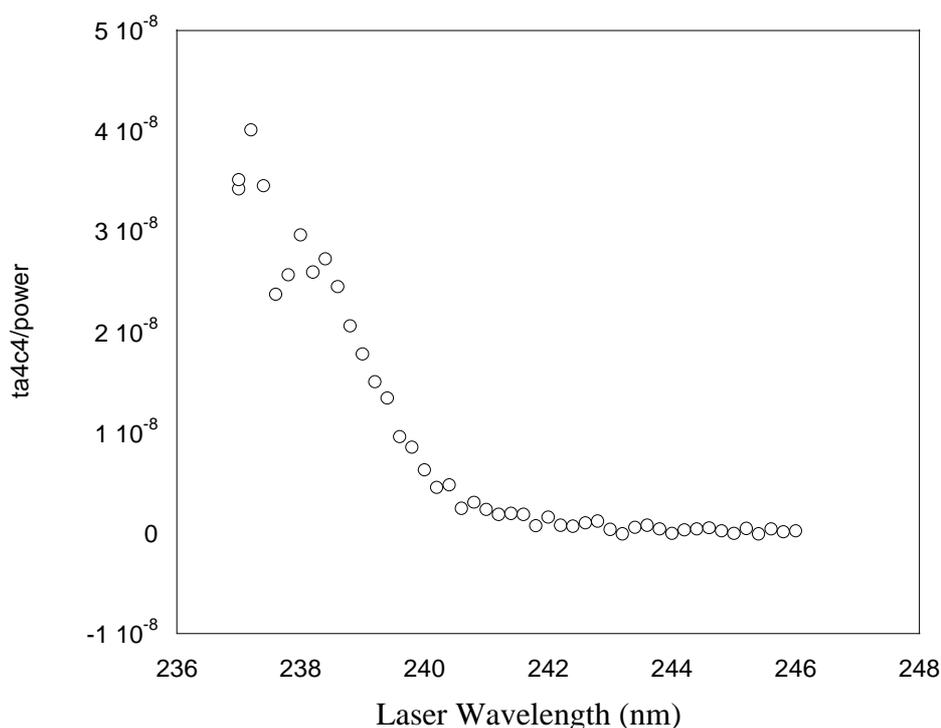
A challenge in fundamental and applied chemistry is to understand how the structure and composition of a metal surface affects catalytic activity and selectivity. The catalytic activation of CO on metal surfaces is particularly important because it is the basis of three industrially significant reactions [1]: methanation ($3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$), the water-gas shift ($\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$) and methanol synthesis ($2\text{H}_2 + \text{CO} \rightarrow \text{CH}_3\text{OH}$). For these reactions, the effects of surface additives (*e.g.* poisons and promoters) on the surface chemistry are not well understood. In particular, the importance of electronic and geometric influences needs to be clarified. Exploring the chemistry of adsorbed CO on metal clusters provides insight into these issues. Therefore, we have recently embarked on investigations of the adsorption/reaction of CO on Nb₃ and Nb₄ clusters in the gas phase.

Although it has been known for many years that CO binds to niobium clusters in the gas phase [2], there has been no experimental data concerning the structures that result. For example, does the adsorption process retain the molecular CO bond or it is dissociative as would be expected according to thermodynamic principles? We are currently using laser ionisation spectroscopy to probe the structures of a range of Nb₃–(CO)_m and Nb₄–(CO)_m clusters to answer these important questions that relate to chemical reactivity on a metal surface.

(ii) Tantalum-Carbide Nanocrystals

The electrical contacts TaC/SiC Au/TaC/SiC, Pt/TaC/SiC and W/WC/TaC/SiC are known to be ideal for high-power and high temperature devices [3]. The advantages of using tantalum-carbide as an ohmic contact to *n*-type semiconductors result from its low work function, high melting point and predicted stability with SiC.

We are currently exploring properties of tantalum-carbide clusters in the gas phase to gain an understanding of the intrinsic chemical and physical properties at the molecular level. Using the techniques described above, our laboratory can generate a series of tantalum-carbide species of the form Ta_nC_m ($n = 1-6$, $m = 0-8$) [4]. We have begun to employ one-photon ionisation experiments to determine the ionisation potentials of these clusters (as shown below for Ta_4C_4). Further spectroscopic investigation of Ta_nC_m clusters will provide information about the tantalum-carbide interface. An ideal outcome will be the understanding of how the structural, electronic, optical and chemical properties evolve with cluster size. This information will be of great interest to those designing electronic contacts containing TaC.



Ionisation spectrum of Ta_4C_4 showing onset of ionization at 241 nm

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