

Multiphoton Ionization and Dissociation of Organometallic Compounds

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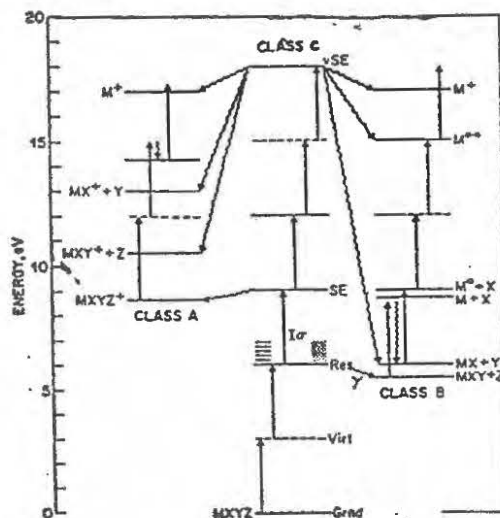
Literature Seminar

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Although there is a large amount of information concerning the synthesis and application of organometallic compounds, little is known about the electronic nature, especially the energies of excited electronic states and dynamics of the excited state [1,2]. This problem arises from the fact that many electronic spectroscopic methods are unsuitable for organometallic compounds due to continuous absorption over a large region of energy, vibrational and/or rotational coupling, the fact that many one photon absorptions/transitions are forbidden or due to the fact that many electronic excited states relax in a radiationless manner [1,2].

Within the last decade, a new spectroscopic technique has arisen, Multiphoton Spectroscopy, which is the simultaneous absorption of an integral number of photons which results in the molecule or atom being excited to a resonant electronic state. An additional absorption of another photon usually results in ionization of the molecule [1,2]. This nonlinear process was not possible until the advent of pulsed lasers which have a much larger optical power than continuous wave lasers [1,2].

Three basic types of behavior have been observed in multiphoton ionization/dissociations. The diagram below depicts the electronic states of a molecule.



In class A behavior [2], which is mostly confined to organic compounds, the molecule is excited to a SE (super excited) state via a one photon absorption from a Res (resonance) state, which in turn, was reached by a two photon absorption. After reaching the SE state, the molecule is ionized and further absorption of photons cause fragmentation of the parent ion.

Class B behavior [2] is mostly limited to organometallic compounds. Upon reaching the resonant state, the molecule dissociates a ligand instead of being ionized. The molecule continues dissociating ligands upon photon absorption until only a bare metal atom remains, which is then ionized.

Class C is unusual and so far, has only been observed in rare gases. In it, numerous photons are absorbed without reaching a resonant level. At this high energy level ionization and fragmentation appear to occur at the same time [2].

Multiphoton ionization and dissociation by a pulsed laser, coupled with a photoelectron energy analyzer has yielded a large amount of information about the excited state electronic levels of such compounds as $\text{Fe}(\text{CO})_5$ [3] and $\text{Fe}(\text{Cp})_2$, i.e. (ferrocene) [4]. Also the effect that ligands have on the electronic state populations has been examined via the chromium series $\text{Cr}(\text{C}_6\text{H}_5\text{R})(\text{CO})_3$ where $\text{R} = \text{H}, \text{CH}_3, \text{CH}_2\text{CH}_3$, and $\text{CH}_2\text{CH}_2\text{CH}_3$, Cl [5]. Studies on these compounds as well as $\text{Cr}(\text{C}_6\text{D}_6)(\text{CO})_3$ [6] has demonstrated that the rate of intramolecular vibration relaxation plays a strong role in the determination of the distribution of final states.

Di- and trinuclear compounds have only recently been examined via this spectroscopic technique coupled with mass spectroscopy [7]. It has been discovered, in addition to the expected single ionized metal ion, that many clusters form a bare metal ionized cluster. For example, with $\text{Mn}_2(\text{CO})_{10}$, not only is Mn^+ observed, but also Mn_2^+ [7]. Also, products resulting from the reaction of Mn^+ and the excited manganese parent molecule have been detected. Besides $\text{Mn}_2^+(\text{CO})_{10}$, many other di- and trinuclear compounds have been reported that also form bare ionized metal clusters [8].

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