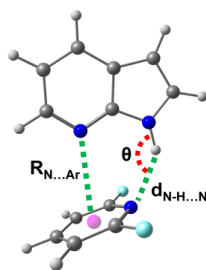


**$n \rightarrow \pi^*$  INTERACTION: TOO WEAK BUT CAN COMPETE WITH STRONG HYDROGEN BONDING INTERACTION**

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In this work, we have investigated a subtle competition between a very weak  $n \rightarrow \pi_{Ar}^*$  and a very strong hydrogen bond (N-H...N) interactions present in the complexes of 7-azaindole (7-AI) with a series of 2,6-substituted fluoropyridines (FP) and observed how the weak interaction modulates the overall structural motif of these complexes in the presence of the strong interaction. We have studied these complexes using resonant two photon ionization (R2PI) and IR-UV double resonance spectroscopy combined with *ab initio* calculations. Comparison of the experimental and theoretical IR spectra in the N-H stretching region reveals that the observed structure of the complexes of 7-AI and 2,6-substituted fluoropyridines is the one having a fine interplay between N-H...N hydrogen bond and  $n_{(7-AI)} \rightarrow \pi_{Ar}^*$  (FP) interactions. The current study provides indirect experimental proof in favour of the  $n \rightarrow \pi_{Ar}^*$  interaction. It has been found that the strength of the N-H...N interaction in these complexes decreases with increasing fluorination in the fluoropyridine ring while the proximity between the nitrogen atom in 7-azaindole and the aromatic ring of fluoropyridine increases through  $n \rightarrow \pi_{Ar}^*$  interaction. Comparison of the binding energy values as well as structural parameters of these complexes calculated at the B3LYP level with those obtained at the MP2, M05-2X, and B97-D levels of theory clearly indicates that the dispersion effect is mostly responsible for this attractive  $n \rightarrow \pi_{Ar}^*$  interaction [1]. This conclusion is also supported by localized molecular orbital-energy decomposition analysis (LMO-EDA). The present study has great significance in understanding the structures of the biomolecules as well as materials as these interactions are very often present there simultaneously.



7-AI...2,6-FP

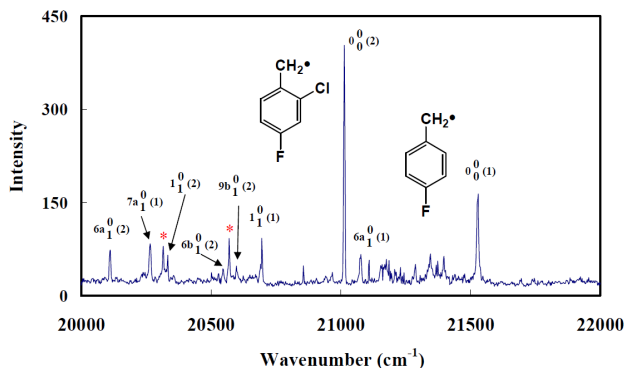
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## VIBRONIC EMISSION SPECTROSCOPY OF BENZYL-TYPE RADICALS GENERATED BY CORONA DISCHARGE

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Benzyl radical is a prototypical aromatic free radical and has been the subject of numerous spectroscopic studies. On the other hand, ring-substituted benzyl radicals, benzyl-type radicals, have received less attention due to the difficulties associated with production in corona discharge and analysis of spectra. We report vibronic emission spectra of hetero halogen di-substituted benzyl radicals generated by corona discharge of corresponding toluene derivatives using a pinhole-type glass nozzle, from which visible vibronic emission spectra were recorded using a long-path monochromator. The spectra show nice features of strongest origin band and a series of vibronic bands in the lower energies originating from the vibrationless  $D_1$  state. From the analysis of the spectra observed, we determined the energies of the  $D_1 \rightarrow D_0$  electronic transition and vibrational mode frequencies in the ground electronic state.[1] On the other hand, all substituted benzyl radicals show the origin bands shifted to red region with respect to the parental benzyl radical at  $22002 \text{ cm}^{-1}$ . The shifts of multi-substituted benzyl radicals can be well estimated using the method developed from mono-substituted benzyl radicals as well as the positions of nodal point and mutual orientation of substituents, which could be useful for scientists to set a proper scanning range of their spectrometers for the spectroscopic observation of transient molecules. In this presentation, we will discuss the substituent effect on electronic transition energy [2,3] and the experimental technique developed in this laboratory.



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**REMPI SPECTROSCOPY OF HALOGEN CONTAINING REAGENTS:  
ENERGETICS, STATE INTERACTION AND PHOTOFRAGMENTATION OF  
RYDBERG AND ION-PAIR STATES**

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Mass resolved REMPI signals as a function of laser excitation wavenumber for number of halogen containing molecules have been recorded to derive ion dependent REMPI spectra. Signals are formed via resonance excitation to Rydberg or Ion-pair states followed by state interaction and/or fragmentation. Spectra analysis in terms of deperturbation, line-positions, line-intensities, line-widths as well as signal laser power dependences were performed. Quantitative and qualitative evaluation, relevant to the parent molecules or fragment energetics, state interaction and photofragmentation processes were derived. Specific examples will be given.

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## FRANCK-CONDON FACTORS CALCULATION FOR VIBRATIONAL PROGRESSION IN PAH MOLECULES

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UV photoionization of polycyclic aromatic hydrocarbons (PAHs) is followed by the structural alteration of cation and gives rise to the vibrational progression in photoelectron spectrum (PES). The PES of a molecule is typically associated with a broadening due to the Franck-Condon overlap of vibrational states. We have done photoelectron spectroscopy experiments with two PAHs namely pyrene and fluorene at GASPHASE photoemission beam line at the Elettra-Sincrotrone Trieste laboratory, Trieste, Italy. The observed vibrational progressions are well reproduced with the help of our Franck-Condon factors calculation for  $D_0 \leftarrow S_0$  transitions using Density functional theory methods within harmonic approximation in GAUSSIAN09. Our calculation compare well with our experimental results for pyrene and fluorene [1]. All the studied PAHs in the present work, showed C-C trans-annular stretching in plane mode with  $a_g$  symmetry as the dominant mode of vibration corresponding to  $\sim 1400$   $\text{cm}^{-1}$  band which is also observed in Unidentified Infrared (UIR) bands of interstellar medium (ISM) [2]. UV photo absorption is the dominant excitation mechanism for PAHs in ISM and de-excitation *via* IR fluorescence is observed in stellar UIR bands. The formation of vibrationally excited cations during the process of UV photoionization will influence the IR bands seen in ISM. The appearance of band at  $1400$   $\text{cm}^{-1}$  in our Franck-Condon simulated spectrum for the all small PAHs, indicates PAHs as a possible carrier for UIR band.

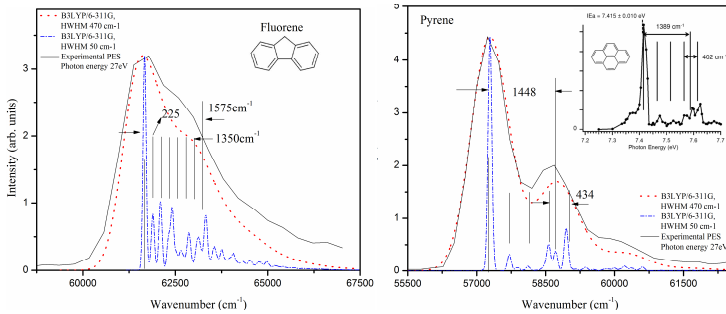


Figure: Experimental PES (shifted) comparison with theoretical vibrational progression showing C-C stretch as dominant mode for fluorene (left) and pyrene (right).

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**SPECTROSCOPIC AND DFT STUDY OF DIPOL MOMENTS OF D<sup>0</sup> ORGANOMETALLICS IN S<sub>0</sub> AND T<sub>1</sub> STATES EXEMPLIFIED FOR ZR COMPLEX**

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Triple states, based on organometallic compounds, are of special fundamental and commercial interest. Rare ligand-to-metal charge-transfer (LMCT) excited states, based on d<sup>0</sup>-metal complexes, were revealed to be highly emissive and long-lived [1]. We have obtained first group 4 metal  $\pi$ -complex (rac-C<sub>6</sub>H<sub>10</sub>(IndH<sub>4</sub>)<sub>2</sub>ZrCl<sub>2</sub>), having high phosphorescence quantum yield ( $\Phi$  up to 0.41) and lifetime (10<sup>-7</sup>–10<sup>-5</sup> s.) in liquids at room temperature [3], and also unique photosensor properties.

The present work provides an experimental and theoretical strategy for estimate of electric dipole moments of d<sup>0</sup> organotransition metal complexes in the ground and emissive ligand-to-metal charge transfer states in gas phase and in various organic solutions. Notably, the solvent effects show a clear trend. The absorption and luminescence maxima and the energies of the 0-0 transition of the representative zirconocenes undergo long-wave shifts with increase of polarity of the solvent. With the use of large selection of aprotic organic solvent (where solvolysis of solutes does not occur), it is shown that solvent dependence can provide a quantitative measure of the change in dipole moment upon photoexcitation. Using photophysical measurements and quantum-chemical calculations at different levels of theory (DFT B3LYP, MP2), we estimated electric dipole moments for Zr(IV) complexes in the ground state and phosphorescent excited state in a series of organic solvents being typical for catalysis and organometallic synthesis (e.g., as shown on Fig. 1).

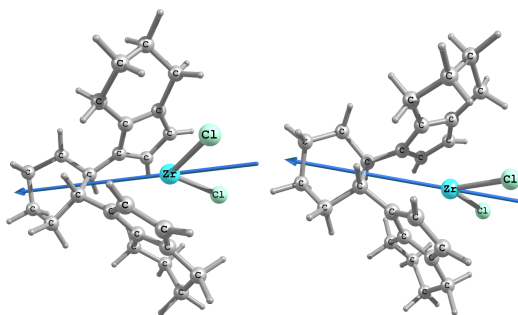


Figure 1. Schematic representations for the simulated structures and dipole moments of target rac-C<sub>6</sub>H<sub>10</sub>(IndH<sub>4</sub>)<sub>2</sub>ZrCl<sub>2</sub> in S<sub>0</sub> (DFT-3-21G\*\*) and T<sub>1</sub> (DFT-3-21G\*\*) electronic states.

The authors gratefully acknowledge long-standing collaboration of the colleagues at IPCP RAS and MSU and also financial support from Russian Academy of Sciences and RFBR (projects 14-03-32014, 12-03-00984, and 12-03-33104). The study was conducted in the framework of SEC “Chemistry of High Energy” of Lomonosov Moscow State University.

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## ENERGY TRANSFER: IMPACT OF WEAK INTERACTIONS UNRAVELLED BY PHOTOPHYSICAL AND THEORETICAL METHODS

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Triplet energy transfer (TET) is the most common and important type of energy transfer involved in chemical and biochemical processes. Electron-exchange resonant (Dexter) energy transfer involves exchange of electrons between donor and acceptor and only occurs when their FMOs overlap. In this work, we will overview our unusual spectral-luminescent data (some preliminar results can be found in [1-5]) on TET in condensed media and reveal the key intermediates obtained quantum-chemically. Fine interactions between the energy donors and acceptors affecting TET were revealed by spectroscopic methods and the intriguing data will be discussed in depth. The representative TET systems under our on-going study are (i) unsaturated hydrocarbons (olefins and dienes) and group 4 organometallics, (ii) olefins and amines (e.g., as shown on Fig. 1). Notably, radiationless triplet energy transfer to unsaturated hydrocarbons in these systems obeys the Perrin equation, occurs at radii, being close to the diameter of interacting molecules, and is well described by electron-exchange resonant (Dexter) mechanism of interaction. In view of the experimental data, inner- and outer-sphere coordinative interactions between some components of the mentioned systems are rationalized and studied in detail at different levels of theory.

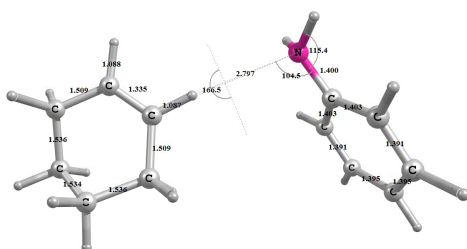


Figure 1. *H*-complex formed by the triplet energy donor aniline and the energy acceptor cyclohexene (calc.). Quantum-chemical study was conducted with ab initio [MP2(full)/DGDZVP, MP2(fc)/SDD, MP2(full)/6-31G\*\*] and DFT [B3LYP/DGDZVP and B3LYP/6-311+G\*\*] methods applying programs Gaussian 03, 09.

These spectroscopic and theoretical findings also provide a new example of TET use for studying intermolecular interactions, in particular, the first example of systematic study of weak complex formation/ fine interactions *controlling overall electron-exchange resonant energy transfer process*. Organometallic reactions have proven difficult to be studied by direct measurements, evaluation of rate constants being a historical quest. Accordingly, a combined spectroscopic and theoretical approach may be promising for mechanistic study of key organometallic reactions, e.g., catalysis.

The authors thank colleagues for a long-standing collaboration and financial support from Russian Academy of Sciences and RFBR (projects 12-03-00984, 12-03-33104). The study was conducted in the framework of SEC “Chemistry of High Energy” of Lomonosov Moscow State University.

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