

# INTERACTIONS OF LOW-ENERGY ELECTRONS WITH Ir(ppy)<sub>3</sub> IN THE GAS PHASE

A.V. Kukhta<sup>1</sup>, I.N. Kukhta<sup>1</sup>, S.M. Kazakov<sup>2</sup>, V.A. Andreev<sup>2</sup>

<sup>1</sup> Institute of Molecular and Atomic Physics, Nat. Acad. Sci. of Belarus,  
70 Nezalezhnastsi Ave., Minsk 220072, Belarus  
e-mail: kukhta@imaph@bas-net.by

<sup>2</sup> Chuvash State University, 15 Moskovski Ave., Cheboxary 428015, Russia

Pump-probe processes in the femtosecond domain with a probe VUV and dressing optical pulses are considered: ionization of the Li atom with the continuum coupled to the excited 3d state and ionization of the He atom with the coupled flat continua. In the first case, spectra and angular distributions of the photoelectrons were calculated and analyzed for two linearly polarized collinear fields by numerical solution of the non-stationary Schrödinger equation. The spectrum and the angular distributions are controlled by the time delay between the pulses and the two-photon detuning. In the second case, we concentrated on the modulation of the He ionization signal as function of the angle between the field polarization vectors. Within the second order time-dependent perturbation theory for the Gaussian field envelopes, a partly analytical solution was found and used.

## Introduction

Iridium organic complexes have become of great practical and scientific interest during recent years. These molecules can phosphoresce at room temperature with a high quantum yield. The highest electroluminescence quantum efficiency up to 100% [1] has been achieved with this material. It is also promising for applications in efficient organic solar cells and sensors. The Ir complexes are highly photo- and thermally stable and can be easily studied in the gas phase while being prepared by thermovacuum evaporation. In this paper the relative efficiency of excitation into singlet and triplet states in the energy region between 1.5 and 9 eV, their dependence on projectile electron energies for the scattering of monoenergetic electrons with tunable energies from 0 to 50 eV at an angle of 90°, for the widely known electroactive organic material tris(2-phenylpyridine)iridium (Ir(ppy)<sub>3</sub>) in the gas phase are presented.

## Experimental

A special electron spectrometer was used for the energy loss spectra measurements [2]. It contains a four electrode electron gun to prepare and to collimate the electron beam and 127° electrostatic analyzer with channeltron to analyze the energies of the scattered electrons. A quasimonoenergetic electron beam of 1.5 mm in diameter is formed in 10<sup>-6</sup> Torr vacuum; the electron beam current did not exceed 10 μA; the full-energy resolution determined using elastic scattering peak was about 0.3 eV. The organic vapor density in the collision cell was less than 10<sup>-3</sup> Torr to avoid multiple collisions and secondary processes. Optically allowed transitions are characterized by a forward peaked behavior, while spin-forbidden transitions show a more isotropic angular behavior, resulting in a relative enhancement of triplet signal at high scattering angles. The 90° scattering angle is good for both singlet and triplet transition measurements. The incident electron beam current was measured with a 35 mm Faraday cup. The length of the collision range inside

the chamber was 5 mm. Optical absorption spectra were recorded using a spectrophotometer Cary 500 Scan UV-VIS-NIR (Varian Ltd). Ir(ppy)<sub>3</sub> was obtained from American Dyes Source and purified in our Institute by vacuum sublimation. The chemical structure of this molecule is presented in Fig. 1.

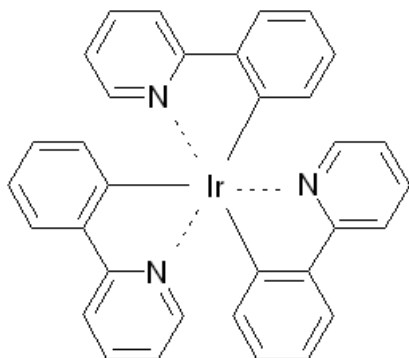


Fig. 1. Molecular structure of Ir(ppy)<sub>3</sub>

### Theoretical calculations

For interpretation of the electron energy loss spectra (EELS) and optical absorption spectra the calculations for both compounds were performed using the Gaussian-03 program package [3] and the density functional theory (DFT) techniques. Time-dependent density functional theory (TDDFT) has shown a better agreement with experiments in large conjugated organic molecules, so it has become the most widely used tool for theoretical evaluation of the excited state energies. The Los Alamos Lab (LANL2DZ) basis sets were employed for the ligands and the Ir atom. The geometry of Ir(ppy)<sub>3</sub> was fully optimized without symmetry constraints using an exchange correlation (B3PW91) approximation. This assumption was justified by a good agreement of the calculated mean bond-lengths of Ir-C (2.02155 – 2.02308 Å) and Ir-N (2.12767 – 2.12877 Å) with experimental values (2.024 and 2.132 Å, respectively [4]) as well as with the absorption spectra. The spectrum of the vertical electronic transitions in this molecule was found to be very rich, so the ground state and 150 singlet excited electronic states as well as oscillator strengths  $f$  (for singlet

states only) were calculated using the dipole transition matrix elements and TDDFT calculations. The spectra of the vertical electronic transitions for these molecules have been simulated using a newly developed program in the following way. The contours of the calculated absorption peaks were calculated using the gaussian distribution  $\epsilon(E_n) = \epsilon_{\max} \exp[-(E_n - E)^2/0.1]$  with a half width of about 0.45 eV for every transition. The absorption spectrum was obtained as a sum of the bands for all transitions.

### Results and discussion

Figure 2 presents the differential electron energy loss spectra measured for this compound at different incident electron energies (14, 20, 30, and 50 eV) in the energy region from 0 to 9 eV, and Fig. 3 shows the photoabsorption spectrum of a toluene solution as well as two EELS in the corresponding energy interval with the background subtracted and normalized using intense low energy inelastic peaks, and the calculated spectrum of the singlet transitions. The spectral backgrounds in Fig.2 are higher at higher loss energies due to the secondary electron emission from the electron gun electrodes.

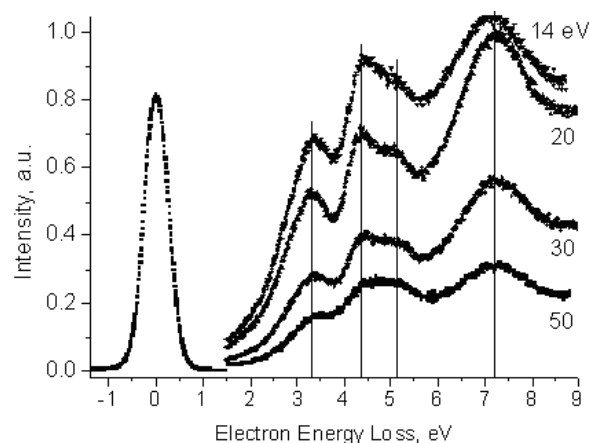


Fig. 2. Electron energy loss spectra at different incident electron energies (near curve in eV).

The measured EELS contain strongly pronounced peaks at 3.3 eV (with a prolonged low-energy shoulder), 4.4 eV and 7.2 eV, and a distinguishable shoulder at 5.2 eV.

The rise of the incident electron energy results in the intensity increase of the high energy maxima as compared to a peak at 3.3 eV. But, the relative intensity of the 4.4 eV band decreases with energy compared to a shoulder at 5.2 eV, pointing to an essential contribution of triplet transitions. No intense triplet transition can be observed in spite of the presence of heavy Ir atom [5]. This is probably due to the nature of charge transfer transitions. Almost for all organic molecules a resolved triplet band can be observed in the low energy part of the EELS. But, for  $\text{Ir}(\text{ppy})_3$  such a peak is absent. Nevertheless, low energy shoulder (Fig. 3) is higher at 14 eV incident electron energy than at 50 eV pointing to the presence of the triplet transitions in the middle of the shoulder (approximately at 2.5-2.7 eV).

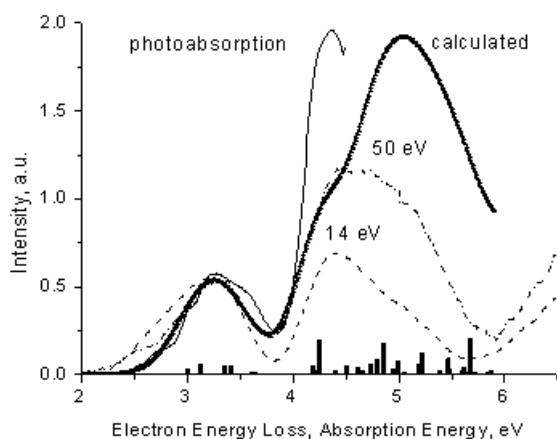


Fig. 3. Spectrum of optical absorption, electron energy loss spectra at 14 and 50 eV, and the calculated spectra; the bars represent the computed transition with height equal to the corresponding oscillator strengths.

The absorption spectrum of this compound (Fig. 3) shows intense bands appearing in the ultraviolet part of the spectrum between 2.5 and 4.5 eV (240 and 350 nm). In the long wavelength shoulder of the absorption spectrum three distinguished features at 2.55, 2.7 and 3 eV are clearly observed. It should be noted that energy shifts for molecules in the condensed phase are present. A remarkable point in Fig. 3 is the close correspondence between the EELS and the optical absorption spectra. The energy positions as

well as the relative intensities are very similar in both cases. In the low energy band of EELS the corresponding multiple structures are not resolved and the band appears to be broader and slightly higher than in the optical spectrum. The intensity of the band at 4.4 eV is less than in the optical absorption spectrum due to the rather low incident electron energy (less than 100 eV) and to an uncertainty in background current determination. Thus, in EELS we can observe the same transitions as in the optical spectroscopy which can be assigned accordingly. The 7.2 eV peak can be apparently attributed to the ionization energy.

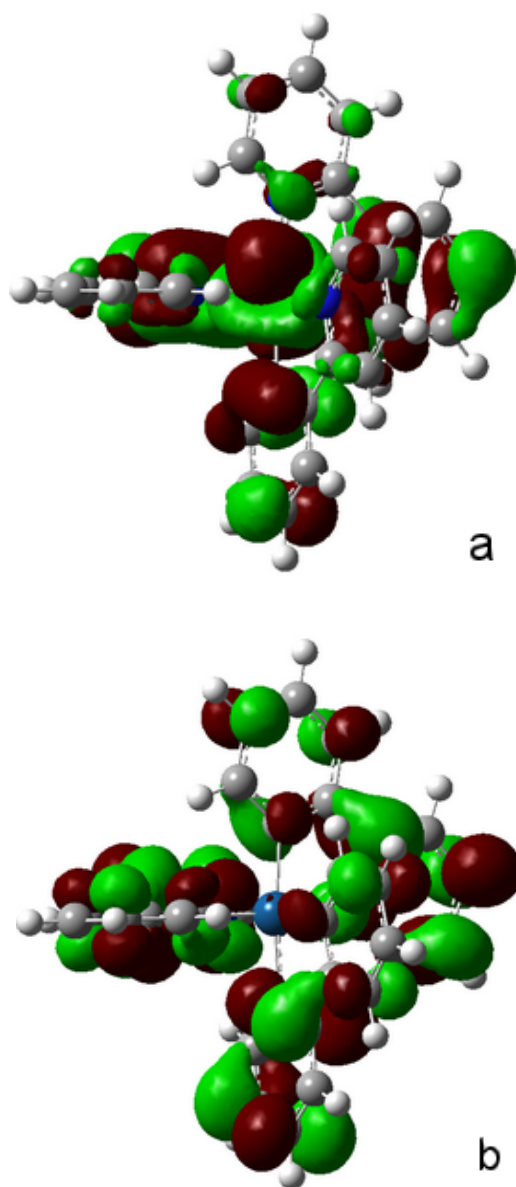


Fig. 4. HOMO (a) and LUMO (b) of  $\text{Ir}(\text{ppy})_3$

The calculated spectrum of the singlet transitions (Fig. 3) is also very close to the EELS and photoabsorption spectrum. The low energy peak is in a rather good agreement with EELS and the optical absorption. The second intense peak corresponds not to the 4.4 eV peak, but to a feature at 5.1 eV with a long shoulder, confirming the presence of triplet transitions in EELS in this region. The probabilities of transitions also show a rather good correspondence to EELS and to the photoabsorption data though the low energy shoulder of 3.3 eV band in EELS is slightly higher than in the calculated spectrum. The lowest triplet level is located at 2.6 eV. The calculated orbitals show that this molecule has a propeller like configuration. The highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals (see Fig. 4) confirm charge transfer from Ir atom to ligands. It was already found [4] that in this molecule the highest occupied orbital has an Ir(5d) character, but with an almost equal admixture of ligand  $\pi^*$  orbitals. The spin densities in the cations show about 0.6 electron on the metal center. The lowest excited orbitals are totally of the  $\pi^*$  ligand character, as also reflected in the spin densities in the anion. Due to the resonance between the d-orbital of the central iridium atom and the  $\pi$ -orbital of the ligand molecules all of the low lying allowed and spin-forbidden transitions are categorized as charge transfer from the metal atom towards

the molecular macrocycle transitions, although the metal orbitals have a significant mixture of ligand character. Strong coupling of iridium and ligands leads to a mixing of singlet and triplet states. This, in turn, leads to a high intensity of such transitions and a nearly 100% conversion of the inter-system crossing from singlet to triplet excited states and allows strong radiative transitions from triplet to singlet ground states. Therefore, very strong phosphorescence with a radiative lifetime of about 2  $\mu$ s and larger is possible even at room temperatures. The bands in the high-energy region have been assigned to the spin-allowed  $^1(\pi-\pi^*)$  transitions of the phenylpyridyl ligand..

### Conclusion

Some direct singlet-triplet transitions in the region 2.5-2.8 eV and near 4.4 eV are observed. No intense singlet-triplet transition can be observed in spite of the presence of the heavy Ir atom, apparently owing to its charge transfer nature. No essential differences between the optical and electron impact excitation of Ir(ppy)<sub>3</sub> have been found, and phosphorescence can be observed mainly owing to intercombination singlet-triplet transitions. The optical spectrum calculated using density functional theory techniques is in a rather good accordance with electron energy loss and optical absorption spectra.

### References

1. M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, S. R. Forrest, Appl. Phys. Lett. 75, 4 (1999).
2. A.V. Kukhta, S.M. Kazakov, D.V. Murtazaliev, D.V. Ritchik, Chem. Phys. Lett. 373, 492 (2003).
3. Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., Gaussian, Inc., Wallingford CT, 2004.
4. P.J.Hay, J.Phys.Chem.:A 106, 1634 (2002).

## **ВЗАЄМОДІЯ ПОВІЛЬНИХ ЕЛЕКТРОНІВ З Ir(ppy)<sub>3</sub> У ГАЗОВІЙ ФАЗІ**

**А.В. Кухта<sup>1</sup>, І.Н. Кухта<sup>1</sup>, С.М. Казаков<sup>2</sup>, В.А. Андрєєв<sup>2</sup>**

<sup>1</sup> Інститут молекулярної і атомної фізики НАН Білорусі,  
Проспект Незалежності, 70, Мінськ 220072, Білорусь,  
e-mail: kukhta@imaph@bas-net.by

<sup>2</sup> Чуваський державний університет,  
Московський проспект, 15, Чебоксари 428015, Росія

Представлено відносні ефективності збудження синглетних і триплетних станів у області енергій від 1,5 до 9 еВ, їх залежності від енергії первинних електронів при розсіянні моноенергетичних електронів регульованої енергії від 0 до 50 еВ на кут 90° для відомих електроактивних органічних молекул три(2-фенілпіридин)іридій Ir(ppy)<sub>3</sub> у газовій фазі. Спостережено деякі прямі синглет-триплетні переходи у області 2,5–2,8 еВ та поблизу 4,4 еВ. Незважаючи на присутність важкого атома Ir, інтенсивні синглет-триплетні переходи не спостерігалися, що, ймовірно, пояснюється природою переходу, пов'язаною з обміном заряду. З використанням методу теорії функціоналу густини досліджено спектр синглетних переходів і положення триплетних переходів.