Investigation of free volumes in phthalocyanines and perylene

O. Melikhova¹, J. Čížek¹, P. Hruška¹, T. Vlasák¹, P. Fitl², M. Novotný³

Introduction. Filing of nanostructured metal films with functional organic layer represents a novel approach for the development of miniature gas sensors. Using co-deposition phthalocyanine could be incorporated into so called black metals, which exhibit extremely high specific surface area due to their fractal-like porous structure with percolated cavities. For design of gas sensors based on black metals filled with phthalocyanine sensitive layer it is important to characterize the free volume structure of the functional organic layers. In the present work positron annihilation spectroscopy was employed for characterization of the size distribution and local chemical environment of free volumes in perylene, phthalocyanine and its complexes with metals. The size distribution of free volumes was determined from the pick-off annihilation lifetimes of ortho-positronium. The local chemical environment of positron annihilation sites was characterized by the coincidence Doppler broadening spectroscopy.

Samples



- (a) H-phthalocyanine C₃₂H₁₈N₈ (H₂Pc),
- (b) Titanyl phthalocyanine C₃₂H₁₆N₈OTi (TiOPc),
- (c) Zinc phthalocyanine C₃₂H₁₆N₈Zn (ZnPc),
- (d) Nickel phthalocyanine-tetrasulfonic acid tetrasodium salt $C_{32}H_{12}N_8Na_4NiO_{12}S_4$ (NiTSPc). (e) Perylene $C_{30}H_{12}$

Methods of characterization.

• A ²²Na positron source with activity of 1 MBq deposited on 5 µm thick Kapton foil was encapsulated in the studied powder. The positron source was placed in the center of a small cylindrical chamber with a diameter of 8 mm and height of 5 mm. Subsequently, the chamber was completely filled with the measured powder and closed. Dimensions of the chamber ensure that virtually all positrons are thermalized inside the chamber and, thereby, annihilate in the studied powder.

Positron lifetime (LT) spectroscopy :

•A digital spectrometer with time resolution of 145 ps [1]

•The source contribution with lifetime of 403(2) ps and relative intensity of 8(1)% was always subtracted from LT spectra.

- At least 10⁷ positron annihilation events were accumulated in each LT spectra.
- Decomposition of LT spectra into individual components was performed using the LT code [2]

Coincidence Doppler broadening (CDB) spectroscopy:

•A digital spectrometer [3] equipped with two HPGe detectors.

•The resolution of the CDB spectrometer was 0.9 keV at the energy of the positron annihilation photo-peak (511 keV).

•Results of CDB spectroscopy are presented as ratio curves with respect to a well annealed AI (99.999%) reference.

Results

Results of LT investigations: τ_1 , I_1 - lifetime and relative intensity of the component arising from positron annihilations; I_{Ps} – intensity of the Ps contribution consisting of a p-Ps component with lifetime fixed at 125 ps and intensity ¼ I_{Ps} and an o-Ps component with the mean lifetime τ_{o-Ps} and intensity ¾ I_{Ps} . The o-Ps contribution was considered as a continuous distribution of positron lifetimes with standard deviation (width of the distribution) σ_{o-Ps}

sample	τ ₁ (ps)	I ₁ (%)	τ _{o-Ps} (ns)	I _{Ps} (%)	σ _{o-Ps} (ns)
H ₂ Pc	327.9(5)	92.8(8)	1.91(2)	7.2(8)	0.386(5)
ZnPc	356.3(5)	95.1(5)	2.04(2)	4.9(5)	0.412(5)
NiTSPc	343.4(4)	93.0(6)	1.94(2)	7.0(6)	0.393(4)
TiOPc	345.9(5)	95.0(6)	2.05(3)	5.0(6)	0.410(6)
Perylene	309.2(4)	96.4(9)	1.49(4)	3.6(9)	0.305(8)





The correlation between the lifetimes τ_{o-Ps} and $\tau_1 \rightarrow$

There is a good correlation between the lifetime τ_1 which is a measure of the open volume at positron annihilation sites and τ_{o-Ps} representing a measure of the free volume probed by Ps. It indicates that Ps is formed in similar regions as those where positrons are annihilated.



 \leftarrow (a) Size distribution of free volumes H(R), where R is the free volume hole radius which was calculated from LT data using the Tao-Eldrup model [4,5]. All phthalocyanines studied exhibit similar size distribution of free volumes characterized by a mean value of ~ 0.34 nm. In particular, the size distribution of free volumes of H₂Pc and NiTSPc is almost the same despite that fact that the central ring of H₂Pc is empty while in NiTSPc it is filled by a Ni metal ion. It indicates that Ps is formed in free volumes along phthalocyanine molecules but not in the central ring even for H₂Pc which has the central ring without any metal ion.

← (b) Size distribution of free volumes multiplied by the intensity of the Ps contribution I_{Ps} The Ps yield in H_2 Pc and NiTSPc is higher than in TiOPc and ZnPc indicating that in the latter samples a higher fraction of electrons created in spur formed during positron thermalization is caught by ions. Perylene contains free volumes of significantly smaller size compared to phthalocyanines and the Ps yield in perylene is the lowest one among the samples studied.

Summary

Investigations of phthalocyanine and its complexes with metals (TiO, Ni, Zn) revealed that positrons do not penetrate into the center region of the phthalocyanine molecule and are, thereby, insensitive to metal ion filling the central ring. Positron annihilations occur predominantly in the regions along the molecule with electrons belonging to C and N. Presence of tetrasulfonic acid group leads to a change of the momentum distribution measured by CDB due to a contribution of positrons annihilated in the vicinity of O. Ps was formed in all phthalocyanine samples and also in perylene in free volumes located among the molecules. The mean radius of free volumes in phthalocyanine samples is ≈0.34 nm. Perylene contains smaller open volumes with the mean radius of ≈0.30 nm.

(a) CDB ratio curves (related to Al reference) for the samples studied; (b) comparison of the CDB ratio curves with pure element references. The shape of the ratio curves for all phthalocyanine samples is very similar to that measured for graphite which testifies that positrons are annihilated predominantly in the vicinity of C atoms. The ratio curve for oxygen (Al_2O_3) exhibits more pronounced peak at $p\approx 9\times 10^3$ m₀c since O contains two more 2p electrons compared to C. Hence remarkable increase of the peak at $p\approx 9\times 10^{-3}$ m₀c for NiTSPc is caused by positrons annihilated in the vicinity of oxygen. The ratio curve for N is expected to be located somewhere between those for C and O since N has one more electron with respect to C. Hence, positrons phthalocyanines are likely annihilated also in the vicinity of N atoms. Ito and Suzuki [6] reported that momentum distributions measured by CDB for phthalocyanines containg Co, Cu and Zn ions are practically the same indicating that positrons do not probe the central ring of the molecule containing metal ion. This is in accordance with the results obtained in present work.

Acknowledgement

This work was supported by the Czech Science Agency (project 18-09347S).

References

[1] F. Bečvář, J. Čížek, I. Procházka, J. Janotová, Nucl. Instrum. Methods Phys. Res. A 539, 372 (2005).
[2] J. Kansy, Nucl. Instrum. Methods Phys. Res. A 374, 235 (1996).
[3] J. Čížek, M. Vlček, I. Procházka, Nucl. Instr. Meth. Phys. Res. A 623, 982 (2010).
[4] S.J. Tao, J. Chem. Phys. 56, 5499 (1972).
[5] M. Eldrup, D. Lightbody, J.N. Sherwood, Chem. Phys. 63, 51 (1981)
[6] Y. Ito, T. Suzuki, Rad. Phys. Chem. 58, 743 (2000).

¹Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, 18000, Prague 8, Czech Republic ²Department of Physics and Measurements, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic ³Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Prague 8, Czech Republic

ICPA18