===== **SHORT COMMUNICATIONS** =====

trans-Difluoro(pentafluorophenyl)xenonium(IV) in Acetonitrile: A Quantum-Chemical Study

S. G. Semenov and Yu. F. Sigolaev

St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: sigal@svs.ru

*trans*-Difluoro(pentafluorophenyl)xenonium tetrafluoroborate synthesized in 1999 by low-temperature reaction of difluoro(pentafluorophenyl)borane with xenon tetrafluoride [1] is the first organoxenon compound having a $C-Xe^{IV}$ bond. The present communication reports on the results of quantum-chemical study on *trans*-difluoro(pentafluorophenyl)xenonium cation (**I**) solvated in liquid acetonitrile.

Using the C-PCM/B3LYP/[6-311G($3d_5f_7,p$) & Xe 3-111G(d_5)] method, which was applied previously in the quantum-chemical study of (pentafluorophenyl)xenonium ion (**II**) and fluoro(pentafluorophenyl)xenon molecule [2], we calculated the geometric parameters of adduct MeCN·**I** and compared the results with those obtained in [2] for analogous MeCN·**II** adduct in liquid acetonitrile. The frequencies and energies of zero-point normal vibrations of the solvated cation were determined with the use of 6-311G(d_5,p) basis set. The calculations were performed using Gaussian software [3].

The equilibrium bond lengths (Å) and bond angles (deg) are given below. The C–Xe bond in MeCN·**I** is shorter by 0.015 Å than the corresponding bond in MeCN·**II**, whereas the N–Xe bond is longer by 0.034 Å. The equivalent Xe–F bonds are oriented at an angle of 62° with respect to the pentafluorophenyl fragment. The carbon–carbon bond lengths in this fragment indicate its aromatic character. The charges on the Xe, F, and C[1] atoms (+2.01, –0.55, and –0.32 a.u.; calculated by the NPA method [4]) suggest strong polarization of bonds at the xenon(IV) atom. The charge on Xe in MeCN·**I** is twice as high as that in MeCN·**II**, while the magnetic shielding constant of the [129]Xe nuclei is twice as low. The calculated [129]Xe chemical shift (δ_{Xe} 2182 ppm) approaches the experimental value (δ_{Xe} 2101 ppm [1]).

The equilibrium Xe–F bond shortens to 0.035 Å due to interaction between the xenon atom, on the one hand, and pentafluorophenyl radical and coordinated acetonitrile molecule, on the other. The wave number characterizing the antisymmetric stretching vibrations of the F–Xe–F group increases by 47 cm^{-1}, and the intensity of the corresponding IR band decreases by 33%, as compared to the calculated IR parameters of XeF_2 molecule in acetonitrile.
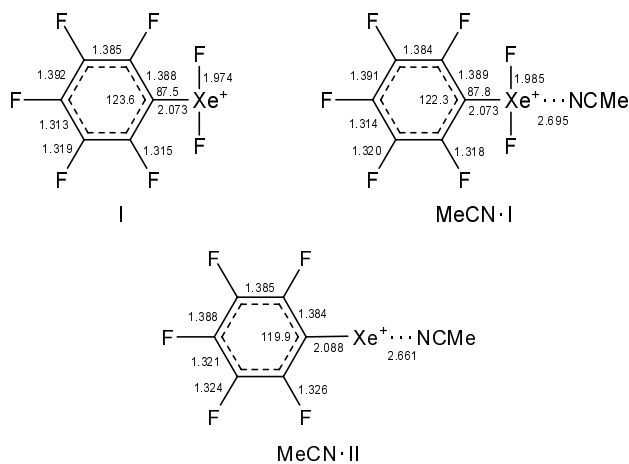
Specific mode of solvation of cation **I** in liquid acetonitrile leads to reduced energy of the system adduct–acetonitrile relative to the sum of the energies of the systems cation **I**–acetonitrile and MeCN–acetonitrile (by 7 kcal/mol), as well as to extended interatomic distance Xe–F (by 0.010 Å). The charge on the ligand in adduct MeCN·**I** is not large (+0.05 a.u.); however, strong electrostatic effect of cation **I** on the coordinated MeCN molecule leads to reduction in the calculated wave number (by 18 cm^{-1}) of the strong IR band with its maximum at 2253 cm^{-1} (which is typical of pure acetonitrile), and 4.6-fold increase in its intensity.

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