К Юбилею ученого

Щеголева Людмила Николаевна



Новосибирск, 2024



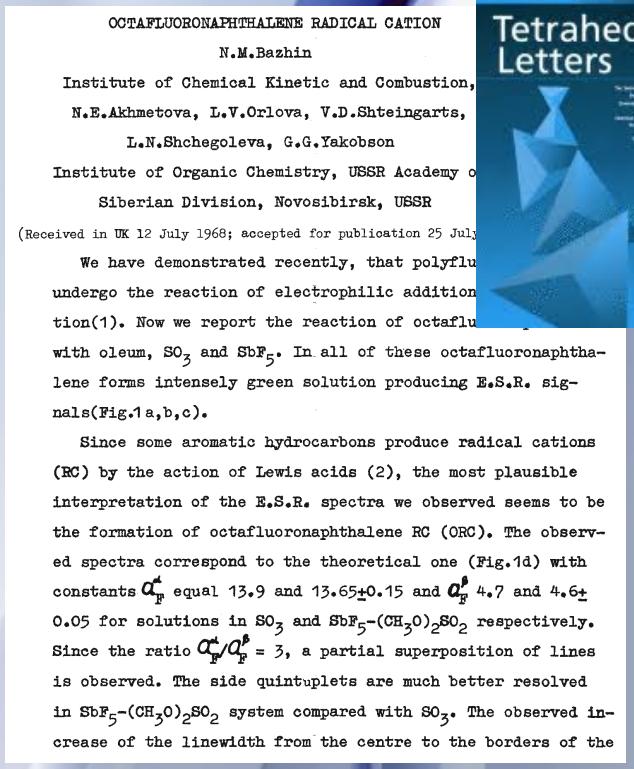
В НИОХ СО РАН (тогда НИОХ СО АН СССР) Щёголева Людмила Николаевна пришла в 1967 году после окончания Новосибирского государственного университета (ФЕН) по специальности химия и была принята на должность стажёра-исследователя в Лабораторию галоидных соединений (ЛГС), возглавляемую Г.Г. Якобсоном.



В 1974 году избрана по конкурсу на должность младшего научного сотрудника, в 1986 году переведена на должность научного сотрудника, а в 1987 – на должность старшего научного сотрудника.



Сотрудники лаборатории галоидных соединений. Слева направо: 1-й ряд - Е.В. Войцеховская, З.Я. Присяжная, О.И. Осина, Н.Д. Хлыстова, Т.Д. Петрова, Н.Я. Силкина, И.Г. Жигулева; 2-й ряд - В.С. Черток, Л.Н. Щеголева, К.В. Дворникова, Л.С. Кобрина, В.Е. Платонов, А. Герасимова, Т.И. Савченко, Т.А. Бирюкова, С.М. Руденкова; 3-й ряд - С. Круподер, А.М. Максимов, В.В. Бардин, В.Н. Ковтонюк, В.М. Карпов, В.М. Власов, В.Ф. Коллегов.



OCTAFLUORONAPHTHALENE RADICAL CATION

N.M.Bazhin

Institute of Chemical Kinetic and Combustion,

N.E.Akhmetova, L.V.Orlova, V.D.Shteingarts,

L.N.Shchegoleva, G.G.Yakobson

Institute of Organic Chemistry, USSR Academy o

Siberian Division, Novosibirsk, USSR

(Received in UK 12 July 1968; accepted for publication 25 July

We have demonstrated recently, that polyflu undergo the reaction of electrophilic addition tion(1). Now we report the reaction of octaflu with oleum, SO_3 and SbF_5. In all of these octafluoronaphthalene forms intensely green solution producing E.S.R. signals(Fig.1a,b,c).

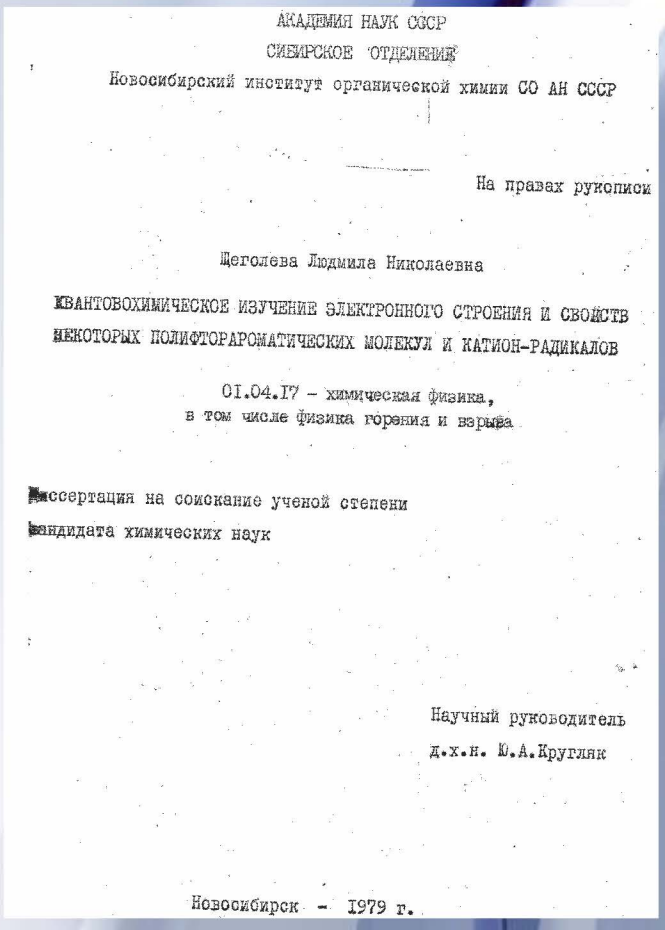
Since some aromatic hydrocarbons produce radical cations (RC) by the action of Lewis acids (2), the most plausible interpretation of the E.S.R. spectra we observed seems to be the formation of octafluoronaphthalene RC (ORC). The observed spectra correspond to the theoretical one (Fig.1d) with constants a_F^{α} equal 13.9 and 13.65±0.15 and a_F^{β} 4.7 and 4.6± 0.05 for solutions in SO_3 and SbF_5-$(CH_3O)_2SO_2$ respectively. Since the ratio a_F^{α}/a_F^{β} = 3, a partial superposition of lines is observed. The side quintuplets are much better resolved in SbF_5-$(CH_3O)_2SO_2$ system compared with SO_3. The observed increase of the linewidth from the centre to the borders of the

С первых лет работы в ЛГС и по настоящее время её основная научная тематика связана с полифторароматическими соединениями и их ион-радикалами. Первой опубликованной в институте стала работа в Tetrahedron Letters (Bazhin N.M., Akhmetova N.E., Orlova L.V., Shteingarts V.D., Shchegoleva L.N., Yakobson G.G. OCTAFLUORONAPHTHALENE RADICAL CATION // Tetrahedron Letters. 1968. Т. 9. № 42. С. 4449-4452), посвящённая катион-радикалу октафторнафталина.





Советско-японский семинар по химии фтора



АКАДЕМИЯ НАУК СССР
СИБИРСКОЕ ОТДЕЛЕНИЕ
Новосибирский институт органической химии СО АН СССР

На правах рукописи

Щеголева Людмила Николаевна

КВАНТОВОХИМИЧЕСКОЕ ИЗУЧЕНИЕ ЭЛЕКТРОННОГО СТРОЕНИЯ И СВОЙСТВ НЕКОТОРЫХ ПОЛИФТОРАРОМАТИЧЕСКИХ МОЛЕКУЛ И КАТИОН-РАДИКАЛОВ

01.04.17 – химическая физика,
в том числе физика горения и взрыва

Диссертация на соискание ученой степени
кандидата химических наук

Научный руководитель
д.х.н. Ю.А.Кругляк

Новосибирск – 1979 г.

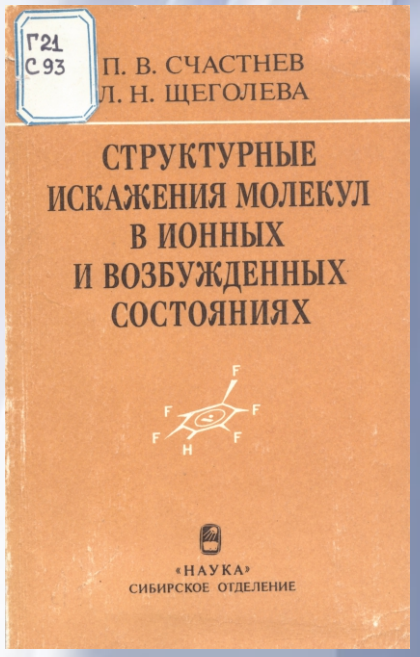
Дальнейшие исследования, в том числе в рамках заочной аспирантуры под руководством д.х.н. Ю.А. Кругляка (Институт теоретической химии, г. Киев), сложились в диссертационную работу на соискание учёной степени кандидата химических наук «Квантовохимическое изучение электронного строения и свойств некоторых полифторароматических соединений и катион-радикалов», которая была защищена в 1980 г.

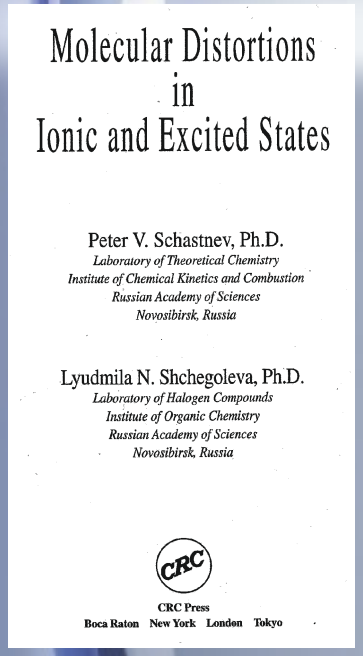
Одним из официальных оппонентов кандидатской диссертации Людмилы Николаевны стал Петр Вячеславович Счастнев, знакомство с которым переросло в многолетнее и плодотворное сотрудничество.





Было опубликовано шесть совместных статей и монография (Счастнев П.В., Щёголева Л.Н. Структурные искажения молекул в ионных и возбуждённых состояниях. Новосибирск: ВО Наука, 1992). Позднее монография была переведена на английский язык и издана CRC Press в 1995 г.





Изменение заряда молекулярной системы всегда влечёт за собой изменение её геометрии. Вертикальный захват или испускание электрона приводит к ион-радикалу, имеющему геометрию нейтрального предшественника. Последующая релаксация ион-радикала может сохранять симметрию нейтральной молекулы. Однако во многих случаях происходят структурные искажения с понижением симметрии. В результате потенциальная поверхность системы уже не является одноямной, многоямное строение поверхности потенциальной энергии может проявляться в спектральных и химических свойствах ион-радикала.



Дружный коллектив ион-радикальщиков



В 1990 году Л.Н. Щёголевой присвоено звание «Заслуженный ветеран СО АН СССР».

В 1995 году Л.Н. Щёголева переведена в Лабораторию физических методов исследования, которую возглавлял В.И. Маматюк.

VI Voevodsky Conference. Physics and Chemistry of Elementary Chemical Processes. Novosibirsk. 2002: Potential energy surfaces and reactivity of halobenzene radical ions.





Людмила Николаевна с учениками, Высоцким В.П. и Берговой И.В. (справа)

В 2002 г. Под руководством Щёголевой Л.Н. защищена диссертация Береговой И.В. на соискание учёной степени кандидата физико-математических наук «Поверхности потенциальной энергии и мономолекулярный распад анион-радикалов фтор- и хлорпроизводных бензола».

РОССИЙСКАЯ АКАДЕМИЯ НАУК
СИБИРСКОЕ ОТДЕЛЕНИЕ
НОВОСИБИРСКИЙ ИНСТИТУТ ОРГАНИЧЕСКОЙ ХИМИИ
им. Н. Н. Ворожцова

На правах рукописи

ЩЕГОЛЕВА Людмила Николаевна

СТРУКТУРНЫЕ ИСКАЖЕНИЯ ИОН-РАДИКАЛОВ АРОМАТИЧЕСКИХ И НЕНАСЫЩЕННЫХ МОЛЕКУЛ

02.00.04 - Физическая химия

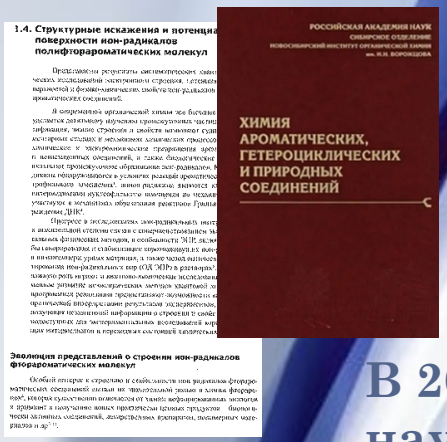
Диссертация на соискание ученой степени
доктора химических наук

Новосибирск – 2007

В 2007 г. Щёголевой Л.Н. защищена диссертация на соискание учёной степени доктора химических наук «Структурные искажения ион-радикалов ароматических и ненасыщенных молекул».



Всероссийская конференция"Современные проблемы органической химии", Новосибирск, 2007. Представлен стендовый доклад: Береговая И.В., Щеголева Л.Н. Анион-радикалы фторбензолов: структурная нежесткость и мономолекулярный распад.



Л.Н. Щеголева, И.В. Береговая
Структурные искажения и потенциальные поверхности ион-радикалов полифторарароматических молекул // Химия ароматических, гетероциклических и природных соединений (НИОХ СО РАН 1958-2008) / Новосибирск, 2009, стр. 147-170.

В 2008 году избрана по конкурсу на должность ведущего научного сотрудника.
С 1997 по 2019 годы Людмила Николаевна была руководителем шести грантов РФФИ.

В 2022 году Л.Н. Щёголева переведена в новую лабораторию, созданную в НИОХ СО РАН и возглавленную Л.А. Шундриным – Лабораторию электрохимически активных соединений и материалов, где работает по настоящее время.



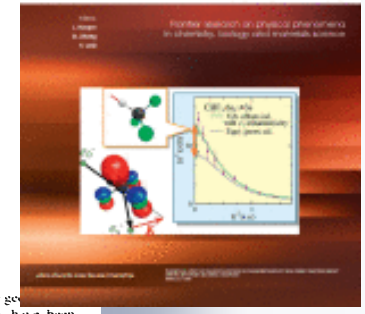


Со старыми друзьями и единомышленниками – квантовыми химиками из Иркутска. Узкий семинар с квантовыми химиками на Байкале.

Наиболее значимыми работами Людмила Николаевна Щеголева считает:

Chemical Physics 82 (1983) 343–353
North-Holland Publishing Company

CHEMICAL PHYSICS



GEOMETRICAL AND ELECTRONIC STRUCTURE OF FLUORO-SUBSTITUTED BENZENE RADICAL ANIONS BASED ON QUANTUM CHEMICAL ANALYSIS OF HYPERFINE INTERACTIONS

L.N. SHCHEGOLEVA, I.I. BILKIS
Institute of Organic Chemistry, Novosibirsk 630090, USSR

and

P.V. SCHASTNEV
Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, USSR

Received 11 July 1983

The INDO method has been employed to calculate the isotropic and anisotropic hyperfine interactions for some geometrical structures of the $C_6F_6^-$, $C_6HF_5^-$, 1,2,4,5-$F_4C_6H_2^-$ radical anions. The π and σ states of planar radical anions have been considered together with three types of non-planar structures: (a) with out-of-plane distortions of the benzene ring following the "chair" pattern; (b) with neighbouring fluorine atoms displaced in opposite directions from the ring plane due to their electrostatic repulsion; (c) with symmetric (of e_{2u} type) displacement of CF bonds due to the interaction between the ground π- and lowest exited σ-electron states within the pseudo-Jahn–Teller effect. It is the last model that describes all experimental data on magnetic resonance parameters. This model is also preferable for energy reasons. Most likely, this type of non-planar structures reflects the basic features of the real geometry of the above radical anions whose ground state may be termed as pseudo-π-electronic since the unpaired electron occupies an orbital that is a linear combination of the π and σ orbitals of the corresponding planar structure with a prevailing π component.

1. Introduction

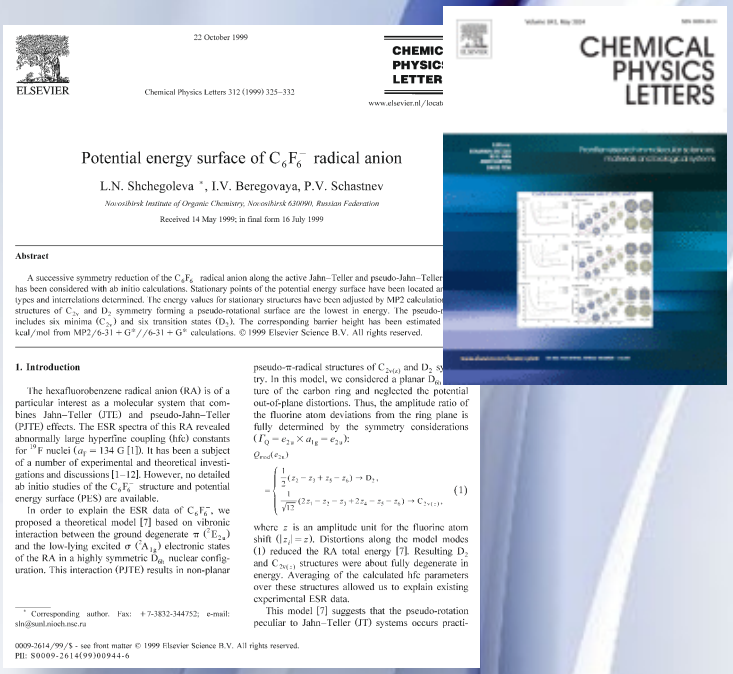
ESR spectra of radical anions (RAs) for some fluoro-substituted benzenes generated in an adamantane matrix were first described by Williams et al. [1]. The highly sensitive optical detection method made it possible to take ESR spectra of these particles in solutions [2]. The spectral characteristics [1,2] practically coincide which proves similar RA structures in both systems. The extremely high isotropic hyperfine interactions (ihfi) constants with ^{19}F nuclei observed in $C_6F_6^-$, C_6HF^-, $C_6H_2F_4^-$ run counter to the idea of their planar π-electron structure which fact prompts the assumption [1] of a planar σ-electron character of the RAs. The a_F values obtained from INDO calculations [1] of the RA σ states performed for the optimized geometry and planar structure agree with the experimental ones in order of magnitude; sometimes, however, they differ by a factor larger than two. This model describes also fairly well the constant $a(^{13}C) = a_C = 12.1$ G measured for $C_6F_6^-$ [3]. According to the calculations, the σ state is not the ground one. However, since an increase in the number of fluorine substituents reduces the energy difference between the π and σ states, it has been assumed [1] that actually the terms may invert.

As shown by analysis [4,5], the anisotropic ESR spectrum taken for $C_6F_6^-$ disagrees with the assumption of its σ structure. If the σ state were realized, the basic contribution to the anisotropic hyperfine interaction (ahfi) with fluorine nuclei would be made by the $2p_\sigma^F$ AO spin density and thus, providing the RA rotates in the ring plane, the parallel and perpendicular ahfi components would be interrelated as $A_\parallel < A_\perp$. Experiment, however, shows an inverse relation. It has been proposed [4] that the ihfi and ahfi constants for

0301-0104/83/0000–0000/$03.00 © 1983 North-Holland

GEOMETRICAL AND ELECTRONIC STRUCTURE OF FLUORO-SUBSTITUTED BENZENE RADICAL ANIONS BASED ON QUANTUM CHEMICAL ANALYSIS OF HYPERFINE INTERACTIONS
Shchegoleva L.N., Bilkis I.I., Schastnev P.V.
Chemical Physics. 1983. Т. 82. № 3. С. 343-353.

(самая цитируемая статья по РИНЦ)



22 October 1999

Chemical Physics Letters 312 (1999) 325–332

Potential energy surface of $C_6F_6^-$ radical anion

L.N. Shchegoleva *, I.V. Beregovaya, P.V. Schastnev

Novosibirsk Institute of Organic Chemistry, Novosibirsk 630090, Russian Federation

Received 14 May 1999; in final form 16 July 1999

Abstract

A successive symmetry reduction of the $C_6F_6^-$ radical anion along the active Jahn–Teller and pseudo-Jahn–Teller has been considered with ab initio calculations. Stationary points of the potential energy surface have been located a types and interrelations determined. The energy values for stationary structures have been adjusted by MP2 calculatio structures of C_{2v} and D_2 symmetry forming a pseudo-rotational surface are the lowest in energy. The pseudo- includes six minima (C_{2v}) and six transition states (D_2). The corresponding barrier height has been estimated kcal/mol from MP2/6-31 + G*//6-31 + G* calculations. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The hexafluorobenzene radical anion (RA) is of a particular interest as a molecular system that combines Jahn–Teller (JTE) and pseudo-Jahn–Teller (PJTE) effects. The ESR spectra of this RA revealed abnormally large hyperfine coupling (hfc) constants for ^{19}F nuclei (a_F = 134 G [1]). It has been a subject of a number of experimental and theoretical investigations and discussions [1–12]. However, no detailed ab initio studies of the $C_6F_6^-$ structure and potential energy surface (PES) are available.

In order to explain the ESR data of $C_6F_6^-$, we proposed a theoretical model [7] based on vibronic interaction between the ground degenerate π ($^2E_{2u}$) and the low-lying excited σ ($^2A_{1g}$) electronic states of the RA in a highly symmetric D_{6h} nuclear configuration. This interaction (PJTE) results in non-planar pseudo-π-radical structures of $C_{2v(z)}$ and D_2 sy try. In this model, we considered a planar D_{6h} ture of the carbon ring and neglected the potential out-of-plane distortions. Thus, the amplitude ratio of the fluorine atom deviations from the ring plane is fully determined by the symmetry considerations ($\Gamma_Q = e_{2u} \times a_{1g} = e_{2u}$):

$$Q_{\mathrm{tw}2}(e_{2u}) = \begin{cases} \frac{1}{2}(z_1 - z_2 + z_3 - z_4) \to D_2, \\ \frac{1}{\sqrt{12}}(2z_1 - z_2 - z_3 + 2z_4 - z_5 - z_6) \to C_{2v(z)}, \end{cases} \quad (1)$$

where z is an amplitude unit for the fluorine atom shift ($|z_i| = z$). Distortions along the model modes (1) reduced the RA total energy [7]. Resulting D_2 and $C_{2v(z)}$ structures were about fully degenerate in energy. Averaging of the calculated hfc parameters over these structures allowed us to explain existing experimental ESR data.

This model [7] suggests that the pseudo-rotation peculiar to Jahn–Teller (JT) systems occurs practi-

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PII: S0009-2614(99)00944-6

CHEMICAL PHYSICS LETTERS

POTENTIAL ENERGY SURFACE OF C6F6- RADICAL ANION

Shchegoleva L.N., Beregovaya I.V., Schastnev P.V.

Chemical Physics Letters. 1999. Т. 312. № 2-4. С. 325-332.



QUANTUM CHEMISTRY

Potential Energy Surface as a Key to Understanding the Structure and Properties of Short-Living Radical Ions of Cyclic Organic Molecules

Lyudmila N. Shchegoleva* and Irina V. Beregovaya

The review proposed summarizes the results of investigations on the adiabatic potential energy surfaces (PESes) for the radical ions of some derivatives of highly symmetric organic molecules such as benzene and cyclohexane. The results obtained show that the main feature of the PESes of highly symmetric Jahn–Teller ions, namely conical intersection, may persist for their low-symmetric derivatives. Hence, their PESes have a pseudorotational shape resulting from the intersection avoidance. A distinctive feature of radical anions of fluorine containing aromatic compounds is the planar structure disturbance due to the vibronic coupling of the ground π and low excited σ states. The data on the PES structure including positions and relative energies of its extrema, curvatu their vicinity, and stationary point interrelations provid foundation for understanding the spectral properties and tivity of radical ionic species. Examples of applying PES study results to experimental data interpretation are

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Introduction

Investigation of the reaction intermediates is actual topical problem of modern organic chemistry.[1] Knowledge of their structure and properties is necessary to reveal the elementary stages and realize the mechanisms of chemical reactions. Various chemical and biological processes pass through the intermediate formation of radical ions. These active species arise at the irradiation of neutral precursors, and so play a key role in photo- and radiation chemistry. One-electron reduction or oxidation is an efficient method for activating the molecule to undergo further transformations changing crucially its reactivity. Some examples are the $S_{RN}1$ nucleophilic substitution,[2] reductive dehalogenation of fluorinated arenes,[3] and electrosynthesis of nitroaryl radicals.[4]

Up-to-date improvement of appropriate experimental techniques provides a possibility of recording and studying radical ions having more and more short-life-times.[5] Theoretical ideas about the structure and physicochemical properties of these particles are also evolving. A number of recent theoretical works were devoted to the processes of ionization and dissociative electron capture (see Refs. 6–8 and those herein). However, systematic theoretical studies on the inherent properties of organic radical ions are virtually absent. The present review is an attempt to close partially this gap in literature.

We showed earlier that various structure distortions with symmetry lowering are typical for organic radical ions and lead to a complex multihole PES architecture and structure flexibility of the ions.[9] Symmetry reduction of a polyatomic molecular system is inevitable when its electronic state is degenerate (the Jahn–Teller effect, JTE) but may also occur in systems in a non-degenerate state due to the pseudo-Jahn–Teller effect (PJTE). We do not consider the JTE and PJTE in detail here as there are some recent reviews and a monograph.[10–12]

Radical ions of the highly symmetric cyclic organic mo are the JT ions. Consequently, their PESes are the surfa conical intersection with the point of the electron torres co corresponding to a highly symmetric ion structure wit degenerate ground electronic state. The crossing avoi occurs through pseudorotation. At the same time, the sym change of the ion ground electron state takes place.

The concept of pseudorotation relates to the structure fl systems characterized by internal nuclear motions which a small vibrations about one equilibrium structure but large amplitude motions connecting several equilibrium structures close or equal in energy.[13] A sequence of deformations in ring systems give the impression of a rotation of the whole molecule.

The present review summarizes the results of relatively recent investigations on the adiabatic PESes for the radical ions of the benzene and cyclohexane families, which show that the main feature of the PESes of JT ions, namely conical intersection, may also persist in their low-symmetric derivatives. Unlike the JT case, the pseudorotation coordinate in low-symmetric ions has no analytical expression. This term describes the moving on a bottom of a cyclic trough along the intrinsic reaction coordinate (IRC) connecting the trough stationary structures.

The aim of this review was to demonstrate that the various spectral and chemical properties of some cyclic organic radical ions may be realized through the investigations of their adiabatic PESes in the frame of relatively simple quantum chemical

L. N. Shchegoleva, I. V. Beregovaya
Laboratory of physical research methods, N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Science, 9 Lavrentiev Ave., Novosibirsk 630090, Russia
E-mail: sln@nioch.nsc.ru

Contract grant sponsor: Russian foundation for Basic Researches; contract grant number: 13-03-00427.

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International Journal of QUANTUM CHEMISTRY

POTENTIAL ENERGY SURFACE AS A KEY TO UNDERSTANDING THE STRUCTURE AND PROPERTIES OF SHORT-LIVING RADICAL IONS OF CYCLIC ORGANIC MOLECULES

Shchegoleva L.N., Beregovaya I.V.

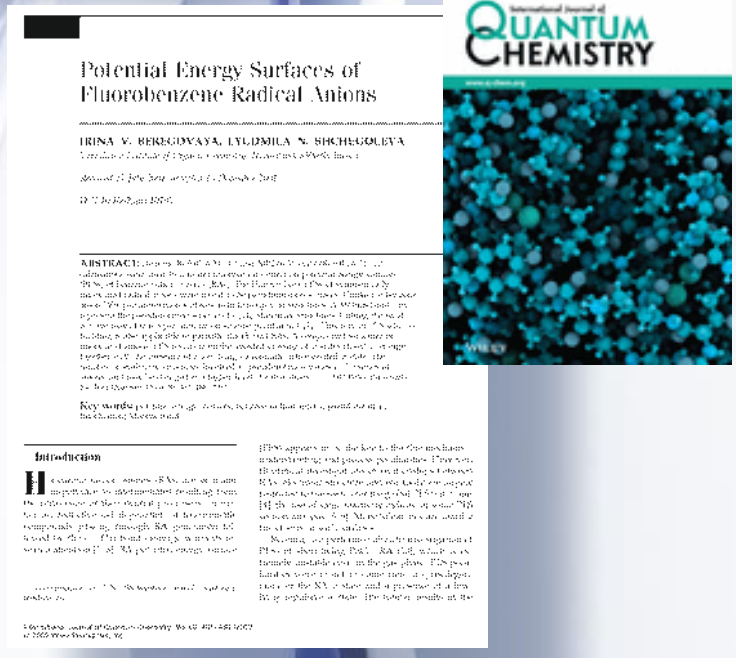
International Journal of Quantum Chemistry. 2016. Т. 116. № 3. С. 161-173.



INTRAMOLECULAR DYNAMICS OF 1,2,3-TRIFLUOROBENZENE RADICAL ANIONS AS STUDIED BY OD ESR AND QUANTUM-CHEMICAL METHODS

Barlukova M.M., Bagryansky V.A., Molin Y.N., Beregovaya I.V., Vysotsky V.P., Shchegoleva L.N.

The Journal of Physical Chemistry A: Dynamics, Kinetics, Environmental Chemistry, Spectroscopy, Structure, Theory. 2005. Т. 109. № 19. С. 4404-4409.



Potential Energy Surfaces of Fluorobenzene Radical Anions

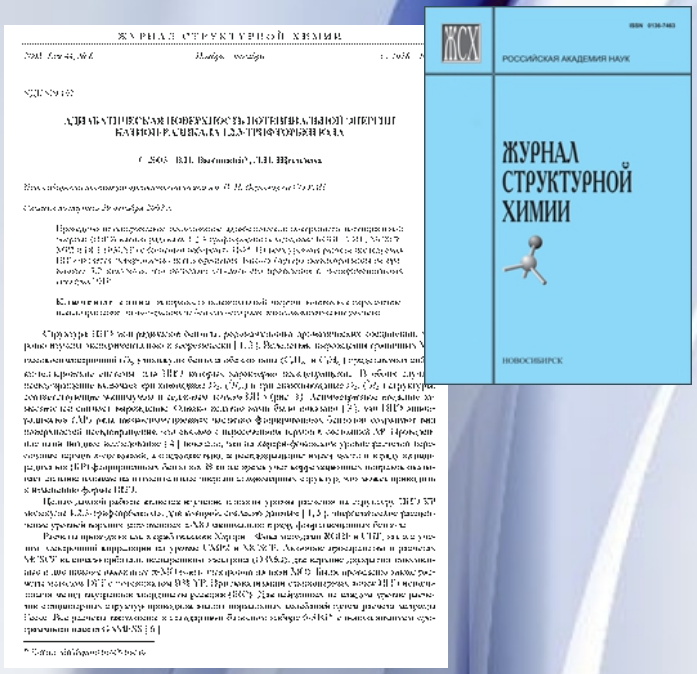
IRINA V. BEREGOVAYA, LYUDMILA N. SHCHEGOLEVA

Introduction

POTENTIAL ENERGY SURFACES OF FLUOROBENZENE RADICAL ANIONS

Beregovaya I.V., Shchegoleva L.N.

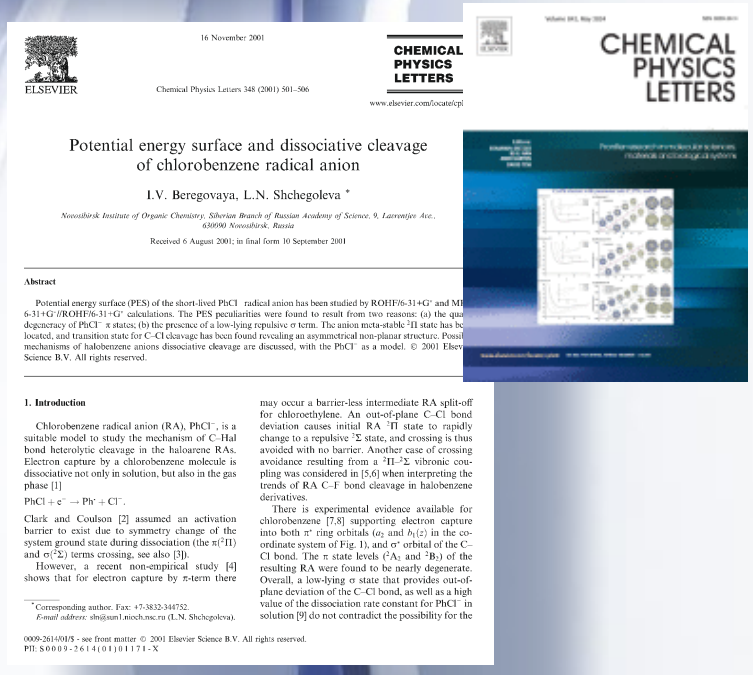
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