Interpretation of resonance states of the molecular negative perfluoropropylene ion

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An algorithm for interpreting resonance states of molecular negative ions has been suggested. This algorithm, using quantum-chemical calculations, allows one to select vacant MO that can be excited in a series of resonances, the energy gap between which coincides with the difference between the corresponding ionization energies. The resonance states of the molecular negative perfluoropropylene ion at energies of electrons from 0.5 to 12.0 eV are formed according to the mechanism of electron-excited Feschbach resonance. Spectral parameters of these resonances have been established.

Key words: perfluoropropylene, negative ion, resonance states.

Recently, interest to studying the formation of negative ions (NI) has been steadily increasing. This is explained by the fact that the data obtained in studying NI characterize vacant molecular orbitals (VMO) of a molecule. The combination of this information with data of photoelectron spectroscopy makes it possible to obtain a sufficiently complete pattern of the electronic structure of a molecule, which determines various chemical applications.

The interpretation of resonance states (RS) of molecular negative ions is a rather difficult problem. In this work, the series of Feschbach resonances related to the excitation of one of the electrons of a molecule and the capture of an electron attacking by the same VMO is interpreted. Similar series, which are observed experimentally by the coincidence of the energy gap between RS (ΔE_{RS}) with the difference between the corresponding ionization energies (ΔIE) (which will be denoted as the series $\Delta E_{RS} \approx \Delta IE$), were first studied in the middle eighties.[1]

The series $\Delta E_{RS} \approx \Delta IE$ found in perfluoropropylene (Fig. 1) is considered in this work. It has been suggested

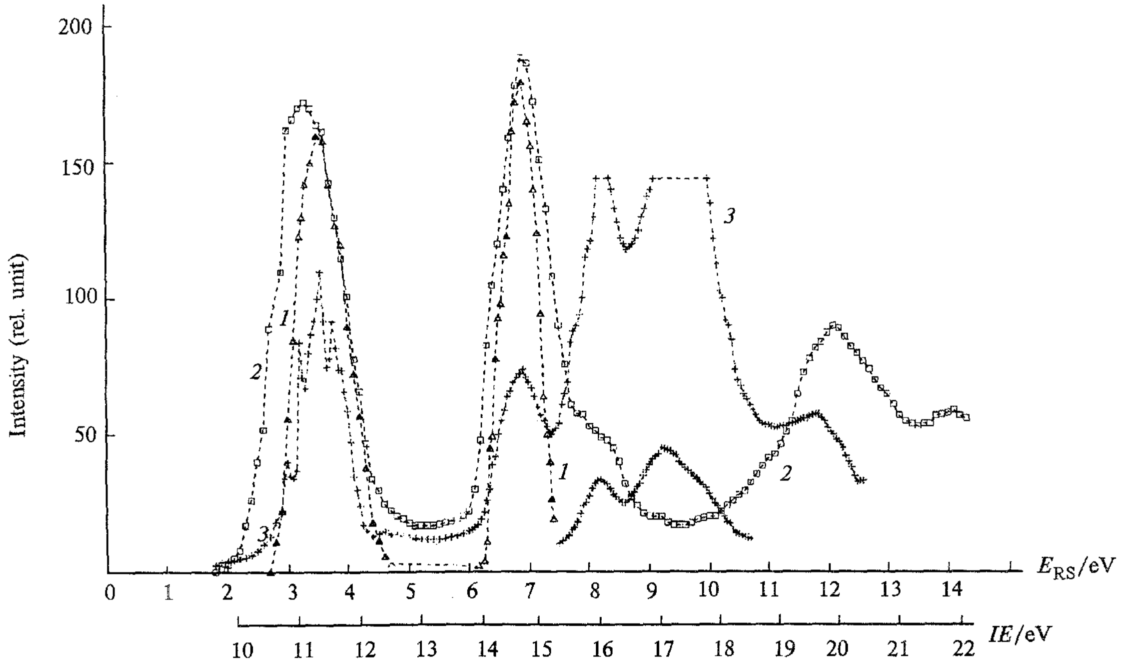

Fig. 1. Comparison between energies of resonance states (E_{RS}) and ionization energies (IE) of perfluoropropylene (the energy scale of the photoelectronic spectrum is shifted for revealing the fulfillment of the condition $\Delta E_{RS} \approx \Delta IE$). Curves: *1*, efficient yield of the $(M - F)^{\neg -}$ NI (see Ref. 7); *2*, efficient yield of the $F^{\neg -}$ NI (see Ref. 7); *3*, photoelectronic spectrum of perfluoropropylene.[8]

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previously[1] that for the $\Delta E_{RS} \approx \Delta IE$ series the mechanism of formation of RS is the excitation of the sequence of occupied MO (OMO) followed by localization of an excited electron of a molecule and an attacking electron on some VMO, which is the same in a given series of Feschbach RS.

When the excitation and capture of an electron occur on the same VMO, it is easy to obtain by standard quantum-chemical methods that the energy gap between RS is equal to the difference in the corresponding ionization energies plus the $\Delta^{2\nu}{}_{i,i-1}$ value, which is expressed by the Coulomb ($J_{i\nu}$) and exchange ($K_{i\nu}$) integrals for MOs active in a given electronic configuration. For the RS series in which an unpaired electron (hole) occupies the *i*- or ($i-1$)-, ($i+1$)th, *etc.* OMO, we consider that the ν VMO is occupied by an electron pair. Then[2]

$$\Delta^{2\nu}{}_{i,i-1} = \Delta E_{RS} - \Delta IE = -2(J_{i\nu} - J_{i-1,\nu}) + (K_{i\nu} - K_{i-1,\nu}). \quad (1)$$

To calculate Coulomb and exchange integrals entering Eq. (1), it is necessary to calculate arbitrary excited configurations, which cannot be performed by modern quantum-chemical methods (in particular, by the semiempirical MNDO method[3]). Therefore, we used the upper bound of these integrals according to the Pipek algorithm.[4]

According to this algorithm, the coordinate space occupied by a molecule is divided into nonoverlapping spheres that surround each of its atoms, and the wave function is assumed to be constant inside any sphere. The integral expressed as a linear combination of such wave functions is estimated by the theorem of mean, using Mulliken population densities on atoms of a molecule and mean interatomic distances known from calculation of the ground state by the MO LCAO method. For the four-centered integral,[4] the formula of the upper bound has the form:

$$\left\langle \varphi_i\varphi_j \middle| 1/r \middle| \varphi_k\varphi_l \right\rangle^2 \le \|L\|^2 \cdot \left| \sum_a Q_a^i \cdot \sum_a Q_a^j \right| \cdot \left| \sum_b Q_b^k \cdot \sum_b Q_b^l \right|, \quad (2)$$

where $Q_a{}^i$ and $Q_a{}^j$ are high population densities according to Mulliken on the *a* atom for φ_i and φ_j MO, respectively; $Q_b{}^k$ and $Q_b{}^l$ are the same for the *b* atom and φ_k and φ_l MO, respectively; $\|L\|^2$ is the maximum eigenvalue of the matrix

$$L_{ab} = \begin{cases} \alpha_a/\rho_a, & a = b,\ \alpha_a = 1.2 \\ \left|\mathbf{R}_a - \mathbf{R}_b\right|^{-1}, & a \ne b. \end{cases} \quad (3)$$

(Here ρ_a is the covalent radius of the *a* atom; $\mathbf{R}_a$, $\mathbf{R}_b$ are the radii-vectors of the *a* and *b* atoms.)

It follows from Eqs. (1)—(3) that the $\Delta^{2\nu}{}_{i,i-1}$ value is minimum, when the corresponding Coulomb integral $J_{\nu\nu}$ for the ν VMO is minimum. Therefore, for the $\Delta E_{RS} \approx \Delta IE$ series, RS in which the Coulomb repulsion of a pair of outer electrons is minimum are realized of the set of hypothetically possible electron-excited Feschbach RS with an electron pair on the same VMO.

Table 1. Mean values of $\Delta^{-2\nu}{}_{i,i-1}$, their dispersions *D*, and Coulomb integrals $J_{\nu\nu}$ (upper bound) for five higher OMO (23—27) and ν VMO of perfluoropropylene

VMO ν	$\Delta^{-2\nu}{}_{i,i-1}$	*D*	$J_{\nu\nu}$/eV
28	−4.500	40.310	9.672
29	−1.427	6.301	1.879
30	−2.149	11.079	2.754
31	−1.372	15.048	4.054
32	1.283	7.119	2.186
33	0.295	29.700	7.646
34	−1.561	11.289	3.187
35	−1.286	11.028	3.784
36	−2.728	14.121	2.888

The excitation and capture of an electron to different VMO are not considered in this work. The existence of a molecular NI with such an electron configuration is possible only when there is a considerable dipole moment, whose field can retain an outer electron in the NI, in the corresponding excited state of a neutral molecule. This mechanism of RS formation has been considered previously.[5]

We have developed a program for estimating the $\Delta^{2\nu}{}_{i,i-1}$ value with the Pipek algorithm.[6] When ΔE_{RS} coincides with ΔIE, this program allows one to determine which VMO are able to participate in a given electronic configuration. The results of calculations by this program for the perfluoropropylene molecule are presented in Table 1 and show that the second VMO is most likely active in the considered $\Delta E_{RS} \approx \Delta IE$ series.

To check this assumption, we built the correlation diagrams, which confirm both the maintenance of the state symmetry

$$\Gamma(M^{\neg -}) = \Gamma(A^{\neg -}) \otimes \Gamma(B) \otimes \Gamma(C)$$

(A, B, and C are the reaction products of $M^{\neg -} \rightarrow A^{\neg -} + B + C$; Γ is the irreducible representation of the given fragment in the symmetry group of the molecule) and the fulfillment of correlations with respect to nodal properties of wave functions of the molecular NI and fragments.

It should be mentioned that the fact that Rydberg MO were not taken into account in MNDO calculations exert no effect on the shapes of correlation diagrams, because Rydberg orbitals are fully symmetric and, hence, inclusion of them into the basis does not change nodal properties of MO.

Let us consider processes of formation of fragmentary NI in the resonance capture of an electron in perfluoropropylene. This capture has already been studied previously.[7] However, only thermochemical parameters of reactions of NI formation were obtained in addition to experimental curves of the efficient yield of NI, and RS found were not interpreted.

Let us interpret RS using the algorithm described. It has been mentioned above that there is the $\Delta E_{RS} \approx \Delta IE$ series for the compound described. (The photoelectron

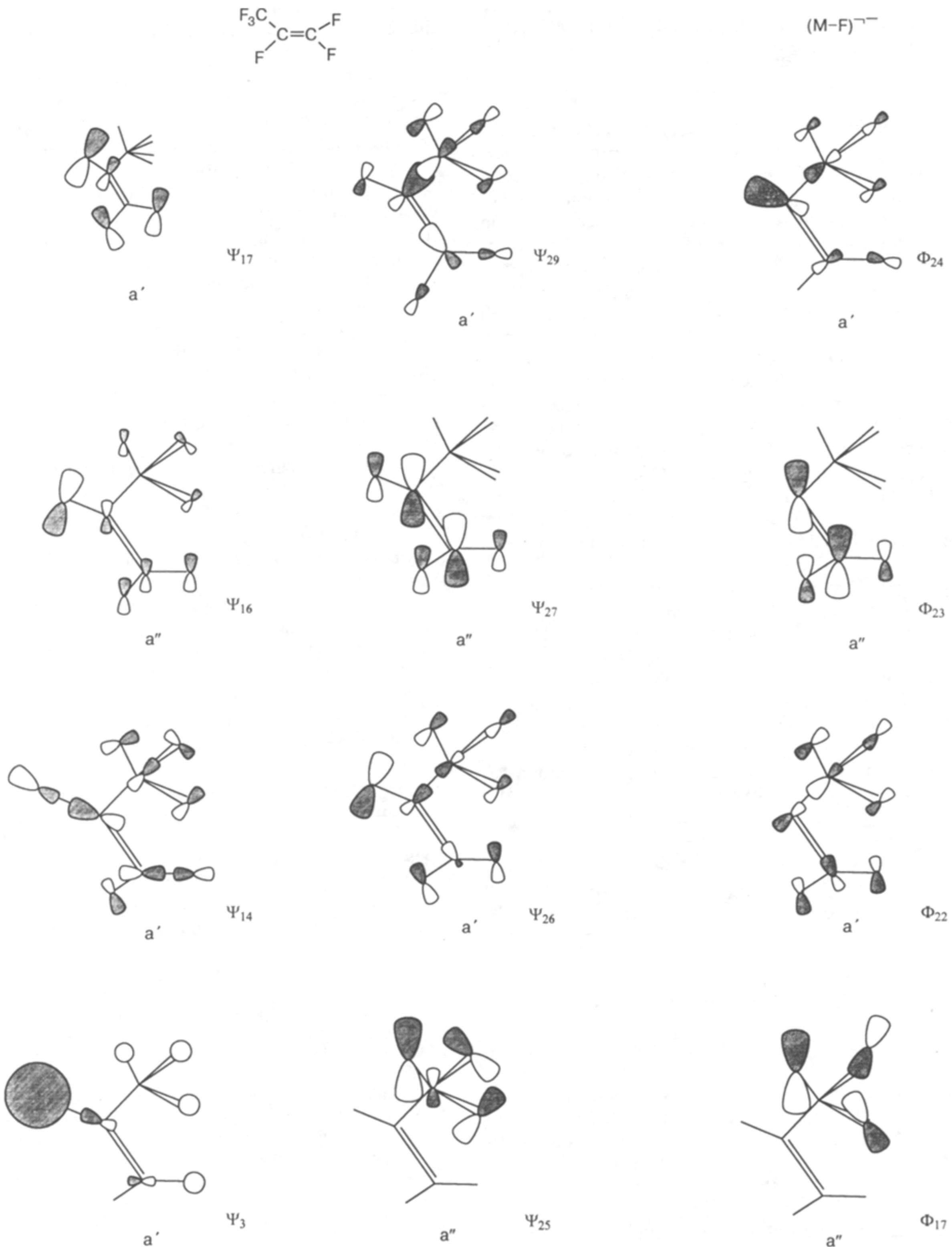

Fig. 2. Correlation diagram for the process of $(M - F)^{\neg-}$ NI formation from perfluoropropylene.

spectrum of perfluoropropylene has been published previously.[8]) This series is presented in Fig. 1. It is noteworthy that there are no $(M - F)^{\neg-}$ NI in RS with an energy of 8.2 eV.

This fact can be explained by plotting correlation diagrams and checking the principle of orbital correlation. The correlation diagram for the process

$$M^{\neg -} \rightarrow (M - F)^{\neg -} + F^{\cdot}$$

can be plotted for two electronic configurations: (1) the RS is formed *via* the mechanism of form resonance, with localization of a captured electron on the second VMO (however, this electronic configuration does not explain the existence of the $\Delta E_{RS} \approx \Delta IE$ series); (2) an electron is captured *via* the mechanism of electron-excited Feschbach resonance. In this case, two electrons occupy the second VMO, and an unpaired electron (which appeared in the system in capturing) occupies either the upper OMO or the preceding OMO. The part of the correlation diagram for the formation of the $(M - F)^{\neg -}$ NI with the second electronic configuration of two configurations indicated above is presented in Fig. 2. The second VMO Ψ_{29}, which is active in the series, correlates with the doubly occupied higher Φ_{24} MO of the ion, and the higher Ψ_{27} OMO correlates with the Φ_{23} orbital of the ion. In addition, the Ψ_{16} MO, which resembles the $2p_z$ AO of the F atom in nodal properties, correlates with the Φ_{23} MO. Finally, Ψ_{17}, Ψ_{14}, and Ψ_3 VMO correspond to AO of F.

When an unpaired electron occupies the second Ψ_{26} VMO, it correlates with the occupied Φ_{22} orbital of the ion. The latter also correlates with the Ψ_{14} OMO (see Fig. 2); then Ψ_{17}, Ψ_{14}, and Ψ_3 OMO correspond to atomic orbitals of F. When the appearance of an unpaired electron on the third Ψ_{25} OMO is assumed, it is impossible to find an orbital whose nodal properties simultaneously resemble those of the Φ_{17} orbital of the ion and one of the AO of the F atom among all remaining MO. This explains the absence of the $(M - F)^{\neg -}$ ion in the RS with an energy of 8.2 eV (see Fig. 1).

It should be noted in consideration of the formation of the $F^{\neg -}$ ion that Ψ_{17}, Ψ_{14}, and Ψ_3 OMO with even numbers of electrons should correlate with its orbitals. Depending on which of the F atoms is detached (belonging to the symmetry plane of a molecule or not), the highest OMO of the $(M - F)^{\neg\cdot}$ radical will be of the a′ or a″ type. When the F atom, which is not in the symmetry plane of the molecule, is detached from the CF_3 group, there is no symmetry plane in the radical, *i.e.*, only an approximate symmetry in the C_s group can be considered. Since the positions, which are known from the experiment, of the two first RS for $F^{\neg -}$ and $(M - F)^{\neg -}$ NI coincide, the corresponding states established above should coincide for them as well. Taking into account that the RS at 8.2 eV, in which only $F^{\neg -}$ NI are observed, correlates with IE_3 (see Fig. 1), the electronic configuration of the molecular NI in it is that of electron-excited Feschbach resonance with an electron pair on the second VMO and an unpaired electron on the Ψ_{25} OMO of perfluoropropylene (see Fig. 2).

It is likely that for the $F^{\neg -}$ NI the first RS with an energy of 3.25 eV is related to detachment of F atoms, which are not in the symmetry plane of the molecule. In this case, the singly occupied MO of the $(M - F)^{\neg\cdot}$ radical has an approximate a″ symmetry and correlates to the higher Ψ_{27} OMO of the molecule. It is likely that the RS at 6.8 eV is formed due to the detachment of F atoms from the symmetry plane of the molecule. Then the singly occupied MO of the radical is assigned to the a′ type and correlates with the Ψ_{26} OMO of the molecule. It is noteworthy that for the $(M - F)^{\neg -}$ NI the consideration of different variants of the detachment of the F atom is insignificant, because it results only in the inversion of the doubly occupied MO, which does not change the shape of the correlation diagram.

In addition, Fig. 1 shows that vibrational structures of the first band of the photoelectronic spectrum and the first RS in the curve of the efficient yield of the $(M - F)^{\neg -}$ NI obtained[7] by the method of difference of retardation potentials are identical. This is an additional argument in favor of the suggested interpretation of RS, because a vibrational structure in the electron-excited Feschbach resonance is mainly determined by an unpaired electron, which occupies the higher OMO. The series of electron-excited Feschbach resonances considered in this work begins from the RS at 3.2 eV. The participation of Rydberg MO in the formation of RS is hardly possible for this energy. Since two remaining RS with energies of 6.9 and 8.2 eV enter the $\Delta E_{RS} \approx \Delta IE$ series, the mechanism of their formation is probably similar. Therefore, one can draw the conclusion that Rydberg MO most likely do not participate in the formation of these two RS.

Thus, we have suggested a scheme for interpreting resonance states of molecular negative ions. This scheme, using quantum-chemical calculations, allows one to distinguish vacant MO that are able to be active in a series of resonances with energy gaps coinciding with the difference in the ionization energies corresponding to these resonances. It is shown that the resonance states of the molecular negative ion of perfluoropropylene for energies of electrons from 0.5 to 12 eV are formed *via* the mechanism of electron-excited Feschbach resonance.

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