

## Electron capture negative ion mass spectra of some freon derivatives

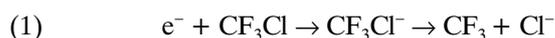
Nail L. Asfandiarov,  
Stanislav A. Pshenichnyuk,  
Vladimir S. Fal'ko,  
Jolanta Wnorowska,  
Karol Wnorowski,  
Iwona Szamrej-Foryś

**Abstract** The temperature dependence of dissociative attachment has been investigated in the temperature range 350–575 K for two freon derivatives 1,1,1-C<sub>2</sub>H<sub>3</sub>F<sub>2</sub>Cl and C<sub>2</sub>F<sub>3</sub>Cl using Electron Capture Negative Ion Mass Spectra (ECNI MS). The temperature dependence for 1,1,1-C<sub>2</sub>H<sub>3</sub>F<sub>2</sub>Cl is similar to that observed in the case of CF<sub>3</sub>Cl reported by Illenberger *et al.* In contrast, C<sub>2</sub>F<sub>3</sub>Cl exhibits quite a different spectrum and its temperature behavior. It has been suggested that  $\sigma_{\text{C-Cl}}^*$  delocalization onto two empty orbital leads to Cl<sup>-</sup> ion formation in two different resonance states.

**Key words** negative ions • electron capture • freon derivatives

### Introduction

Freon derivatives are very important objects in ecology, atmospheric physics and chemistry and many other branches. Low energy electron capture by halogenated methanes has been investigated earlier [2, 3, 6–8, 15, 16]. Low-energy dissociative attachment (DA)



exhibits a temperature effect described well and clearly in the framework of classical theory of DA [7, 11, 12]. For numerical calculation of the temperature effects it is necessary to know a number of parameters of the model: electron affinity (EA) of the molecule and halogen atom, molecular vibrational energies ( $h\omega$ ), dissociation energy (DE) and others. The results obtained are in good agreement with the experimental data [6, 7, 11, 12]. The same results may be reached by means of mixed *ab initio*-semiempirical approach of R-matrix theory [5, 16, 20]. It is clear that in the case of dissociative attachment in a low-energy electron–molecular collision the most important point is that of the formation of an intermediate negative ion, which can dissociate into a fragment ion and appropriate neutral, or lose an additional electron by autodetachment (AD). Competition between these processes determines the so-called survival probability, and governs the shape of the NI curve of effective yield (CEY), see Fig. 4 in [6]. Obviously, quantitative description of the temperature behavior of the electron capture cross section is a hard enough problem, but elaborated methodology [6, 7, 11, 12] gives the possibility to analyze DA experimental data qualitatively [17, 19]. A very similar semi-quantitative approach has been used for investigation of the temperature dependencies of DA by complex molecules of halogenated anthraquinones [1].

N. L. Asfandiarov✉, S. A. Pshenichnyuk, V. S. Fal'ko  
Institute of Physics of Molecules and Crystals,  
Russian Academy of Science,  
151 October Pr., Ufa, 450075 Russia,  
Tel.: +7 3472/ 31 19 95, Fax: +7 3472/ 31 35 38,  
e-mail: nail@anrb.ru

J. Wnorowska, K. Wnorowski, I. Szamrej-Foryś  
Chemistry Department,  
University of Podlasie,  
3 Maja Str. 54, 08-110 Siedlce, Poland

Received: 14 November 2002, Accepted: 4 February 2003

## Experimental

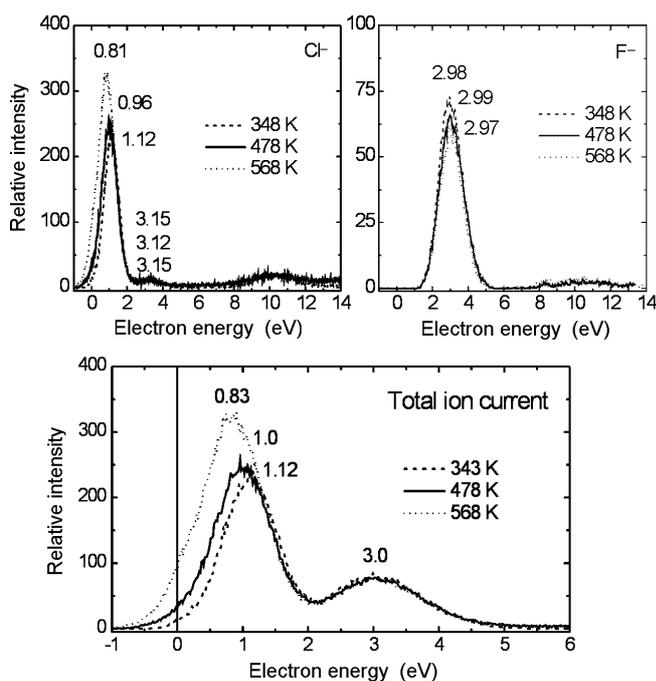
Negative ion mass spectra were obtained using a modified [9] MI-1201 mass spectrometer under the following conditions: accelerating voltage 4 kV, electron trap current  $\sim 1 \mu\text{A}$ , FWHM of electron energy distribution  $\Delta E_{1/2} = 0.35 \text{ eV}$ ,  $E_{\text{el}}$  varies in the range 0–12 eV. Vaporisation temperatures of compounds under investigation were about 300 K. Temperature dependencies of the curves of NI effective yield (CEY) were measured in the range 100–300°C. The details of ECNI MS experiments using a method developed for static mass-spectrometers have been described previously [9]. Drift time for the  $\text{SF}_6^-/\text{SF}_6$  ion ( $m/z = 146$ ) from the moment of formation in the ion source through the mass-separator system to the moment of detection by secondary electron multiplier is  $\sim 25 \mu\text{s}$ .

## Results and discussion

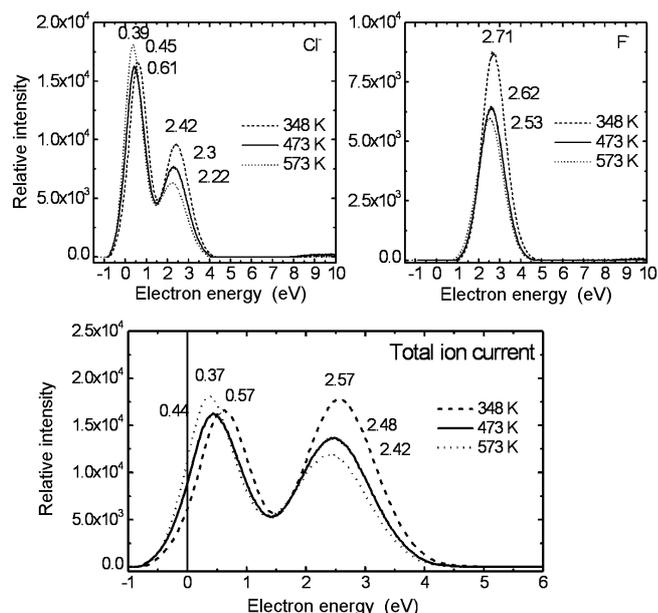
Measured negative ion curves of effective yield are presented in Figs. 1 and 2. Tabulated NI mass spectra are listed in Table 1. Abbreviation  $I^{\text{int}}$  means integrated intensity of the ion:

$$(2) \quad I^{\text{int}} = \int_{E_{\text{min}}}^{E_{\text{max}}} I(\varepsilon) d\varepsilon,$$

where  $E_{\text{min}}$  and  $E_{\text{max}}$  denote the minimum and the maximum energy of the spectrum,  $I(\varepsilon)$  stands for NI intensity as a function of electron energy  $\varepsilon$ . That value is preferable for characterisation of the NI DA abundance in the whole energy range of dissociative electron capture, whereas traditionally used value of NI intensity in the peak maximum ( $I_{\text{max}}$ ) describes the NI DA cross section as a function of electron energy. Moreover, the sum of  $I^{\text{int}}$  for all isotopes of each ion is bold faced. The last value makes it possible



**Fig. 1.** Curves of negative ion effective yield for  $\text{CH}_3\text{CF}_2\text{Cl}$ . Total ion current is a sum of CEY for all the fragment ions.



**Fig. 2.** Curves of negative ion effective yield for  $\text{C}_2\text{F}_5\text{Cl}$ . Total ion current is a sum of CEY for all the fragment ions. Only most intensive CEY's are shown; a complete spectrum listed in the Table 1.

to compare the intensities of different channels of dissociation when some of them have an isotope distribution.

Figure 1 shows that the NI curves of effective yield (CEY) of the 1,1,1- $\text{C}_2\text{H}_3\text{F}_2\text{Cl}$  exhibit a typical temperature dependence as in the case of  $\text{CF}_3\text{Cl}$  [6, 7, 12, 15]. The first resonant state (RS1) at the energy of about 1 eV shifts toward low energy with increasing temperature, and its relative intensity increases as well. The second RS ( $E_{\text{el}} \sim 3 \text{ eV}$ ) keeps its energy and relative intensity. Following the conclusions of the Illenberger [6], we interpret them as the shape resonance (single particle resonance) with an additional electron in the  $\sigma^*$  orbital of the C-Cl bond (lowest unoccupied orbital of the molecule, LUMO), and the electron excited resonance (two particles resonance) where the incoming electron excites one of the electrons in the target molecule.

The temperature dependence of the shape resonance can be explained clearly by means of a simple semi-classical approach [6, 11, 12]. The potential energy surfaces  $V^0$  and  $V^-$  of the neutral  $\text{CH}_3\text{CF}_2\text{Cl}$  and the anion  $\text{CH}_3\text{CF}_2\text{Cl}^-$  as a function of the dissociative bond length  $r_{\text{C-Cl}}$  are shown in Fig. 3. Appropriate Morse curve  $V_0(r) = E_0 + DE\{1 - \exp[-\beta(r - r_0)]\}^2$  for the neutral, adopted to reproduce the experimental data, has the following parameters:  $E_0 = 0 \text{ eV}$ ;  $r_0 = 3.31 a_0$  for the equilibrium bond length,  $DE_0 = 3.76 \text{ eV}$  [6] for the dissociation energy,  $\beta_0 = 0.7935 a_0^{-1}$ , and for anion:  $E^- = -0.37 \text{ eV}$ ,  $r^- = 4.59 a_0$ ,  $DE^- = 0.52 \text{ eV}$ ,  $\beta^- = 0.8464 a_0^{-1}$ . The reduced mass of the Cl atom is  $\mu = 22.75 \text{ a.m.u.} = 4.147 \times 10^4 m_e$ . According to the model, the vibrational energy in the molecule  $\hbar\omega_0 = \beta_0(\mu/2DE_0)^{1/2} = 55.7 \text{ meV}$ , which looks as a reasonable value. So, the temperature dependence of the CEY's for the  $\text{CH}_3\text{CF}_2\text{Cl}$  shown in Fig. 1 can be rationalized in the framework of a simple semi-classical model elaborated in [6, 7, 12, 15]. Indeed, using the classical approximation [4] we can evaluate the energy of the transition from the molecular term in the right turning point to the anion term,

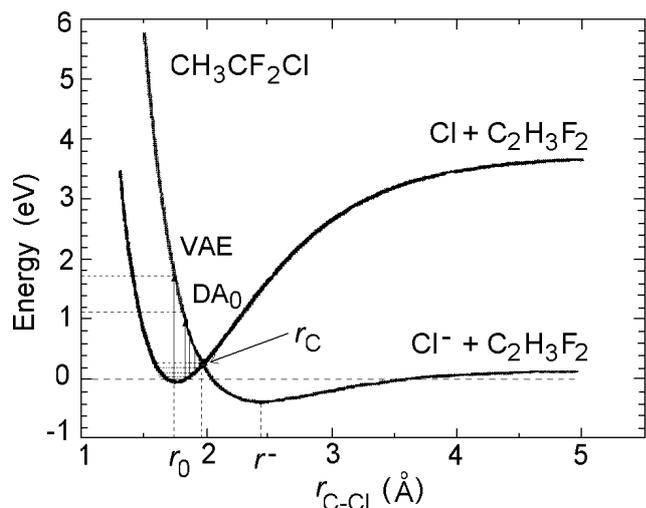
**Table 1.** NI mass spectra of 1,1,1-C<sub>2</sub>H<sub>3</sub>F<sub>2</sub>Cl and C<sub>2</sub>F<sub>5</sub>Cl derivatives.

Temperature (K)	m/z	Structure	$E_{\max}$ (eV)	$I_{\max}$	$I^{\text{int}}$	$I^{\text{int}}$ , sum of all isotopes	$I^{\text{int}}$ (%)	$I^{\text{int}}$ , sum of all isotopes
<b>1,1,1-C<sub>2</sub>H<sub>3</sub>F<sub>2</sub>Cl</b>								
$T = 343$	35	Cl <sup>-</sup>	1.12	246	15,286	<b>20,273</b>	55.31	<b>73.35</b>
	37			80	4987		18.04	
	19	F <sup>-</sup>	2.98	73	7365	<b>7365</b>	26.65	<b>26.65</b>
$T = 478$	35	Cl <sup>-</sup>	0.96	258	17,939	<b>23,792</b>	58.73	<b>77.89</b>
	37			84	5853		19.16	
	19	F <sup>-</sup>	2.98	65.4	6755	<b>6755</b>	22.11	<b>22.11</b>
$T = 568$	35	Cl <sup>-</sup>	0.81	328	25,645	<b>34,012</b>	64.12	<b>85.04</b>
	37			107	8367		20.92	
	19	F <sup>-</sup>	2.94	62	5985	<b>5985</b>	14.96	<b>14.96</b>
<b>C<sub>2</sub>F<sub>5</sub>Cl</b>								
$T = 348$	135	(M-F) <sup>-</sup>	3.48	4.5	242	<b>321</b>	0.007	<b>0.01</b>
	137			1.5	79		0.002	
	119	(M-Cl) <sup>-</sup>	2.76	5.25	261	<b>261</b>	0.007	<b>0.007</b>
	35	Cl <sup>-</sup>	0.61	16,625	1,186,450	<b>1,573,541</b>	34.20	<b>45.37</b>
	37			5424	387,091		11.16	
	35	Cl <sup>-</sup>	2.42	9625	843,200	<b>1,109,302</b>	24.31	<b>32.24</b>
	37			3140	275,102		7.93	
	19	F <sup>-</sup>	2.71	8753	776,730	<b>776,730</b>	22.39	<b>22.39</b>
$T = 473$	135	(M-F) <sup>-</sup>	3.3	4	239	<b>317</b>	0.008	<b>0.011</b>
	137			1.5	78		0.003	
	119	(M-Cl) <sup>-</sup>	2.6	3.7	223	<b>223</b>	0.007	<b>0.007</b>
	35	Cl <sup>-</sup>	0.45	16,250	1,174,330	<b>1,557,467</b>	38.45	<b>50.99</b>
	37			5302	383,137		12.54	
	35	Cl <sup>-</sup>	2.3	7700	688,175	<b>912,699</b>	22.53	<b>29.88</b>
	37			2512	224,524		7.35	
	19	F <sup>-</sup>	2.62	6435	583,747	<b>583,747</b>	19.11	<b>19.11</b>
$T = 573$	135	(M-F) <sup>-</sup>	0.2	2.6	151	<b>201</b>	0.005	<b>0.007</b>
	137			0.8	50		0.002	
	135	Cl <sup>-</sup>	3.3	3.6	219	<b>292</b>	0.007	<b>0.009</b>
	137			1.2	73		0.002	
	119	(M-Cl) <sup>-</sup>	0.56	1.1	89	<b>369</b>	0.003	<b>0.003</b>
	119			2.5	3.7		280	
	35	Cl <sup>-</sup>	0.39	18,025	1,247,500	<b>1,654,509</b>	41.88	<b>55.54</b>
	37			5881	407,009		13.66	
	35	Cl <sup>-</sup>	2.22	6300	573,650	<b>760,809</b>	19.26	<b>25.54</b>
	37			2055	187,159		6.28	
	19	F <sup>-</sup>	2.53	5978	562,800	<b>562,800</b>	18.89	<b>18.89</b>

the arrow DA in Fig. 3. That value is equal to  $DA_0 = 1.1$  eV. When the first excited vibrational level in the target molecule is populated the energy of the appropriate transition will be  $DA_1 = 0.73$  eV. Such a simplification of the semi-classical approach [6, 7, 11, 12, 15], nevertheless, gives qualitative agreement with the experimental observations.

In contrast, the experimental CEY's for C<sub>2</sub>F<sub>5</sub>Cl we have obtained have a quite different temperature behavior, see Fig. 2. First, the Cl<sup>-</sup> channel exhibits two resonant states, at  $\sim 0.6$  eV and  $\sim 2.4$  eV, with high intensity. Second, the F<sup>-</sup> channel at 2.7 eV has comparable intensity, see Fig. 2 and Table 1. Third, the second RS shifts left with increasing

the temperature in parallel with the RS1. And at last, the intensity of both the channels Cl<sup>-</sup> and F<sup>-</sup> in the second RS decreases as the temperature is raised, in contrary to the Cl<sup>-</sup> intensity in the RS1. These facts allow supposing that RS2 is a shape resonance with an additional electron captured into the second empty orbital (LUMO+1) of the target molecule. The view of the LUMO and LUMO+1 of the C<sub>2</sub>F<sub>5</sub>Cl and CH<sub>3</sub>CF<sub>2</sub>Cl according to the results of semiempirical PM3 calculations are presented in Fig. 4. It is easy to see that the  $\sigma_{\text{C-Cl}}^*$  bond contributes to the LUMO in the case of the CH<sub>3</sub>CF<sub>2</sub>Cl and Cl<sup>-</sup> ion formation is allowed in RS1 only. The  $\sigma_{\text{C-Cl}}^*$  bond contributes to both



**Fig. 3.** Schematic representation of the terms of the  $\text{CH}_3\text{CF}_2\text{Cl}$  molecule and anion as a function of C-Cl bond length. See notation in text. (VAE – vertical attachment energy.)

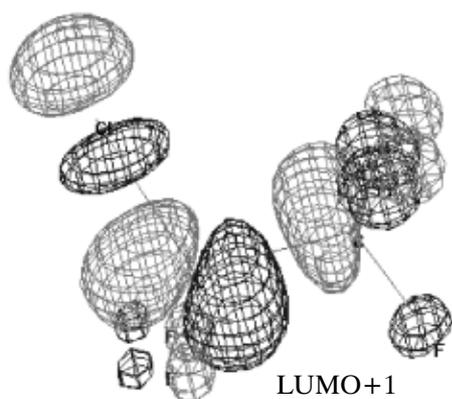
the LUMO and LUMO+1 in the case of  $\text{C}_2\text{F}_5\text{Cl}$ , therefore  $\text{Cl}^-$  formation is possible in the RS1 and RS2, too. That effect is called “principle of orbital correlation” [10], an analog of the well-known Woodward–Hoffmann rules in concert chemical reactions.

For the analysis of the CEY’s temperature dependencies of the  $\text{C}_2\text{F}_5\text{Cl}$  let us consider terms of the molecule and anion. The low-energy RS1 is modeled well enough when appropriate fitting parameters are used. The molecular term (marked by  $V_0$  in Fig. 5):  $E_0 = 0$  eV;  $r_0 = 3.31 a_0$ ;  $\beta_0 = 0.926 a_0^{-1}$ ;

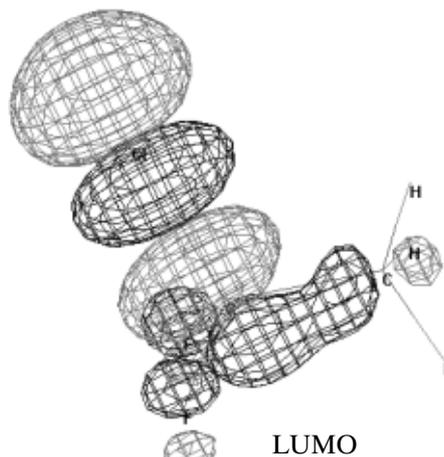
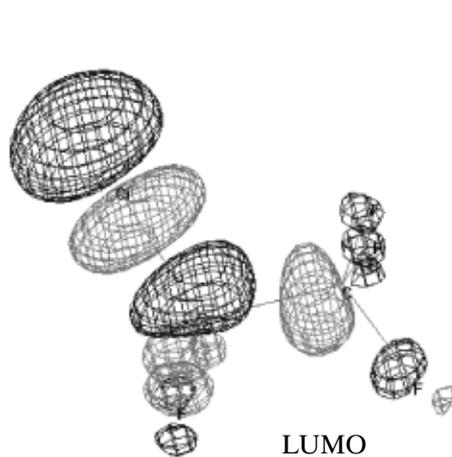
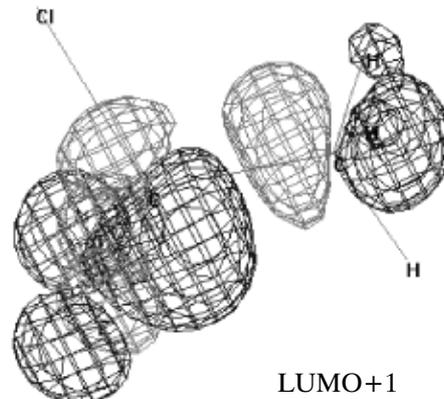
$DE = 3.72$  eV. Vibrational energy in the molecule  $\hbar\omega = 59.3$  meV. The anion dissociative term ( $\text{Cl}^-$  channel formation) was described using the repulsive potential [16]  $U_1^{\text{rep}} = A \cdot \exp[-2\delta(r-r_0)] + D$  with the following parameters ( $U_1^{\text{rep}}$  in Fig. 5):  $D = 0.11$  eV for the asymptotic ( $D = DE_0 - EA(\text{Cl}) = 3.72 - 3.61$  eV);  $A = 1.4$  eV;  $\delta = 2.38 a_0^{-1}$ ;  $r_0 = 3.31 a_0$ . Supplementary term  $V^-$  of the channel  $(\text{M-Cl})^-$  formation, see Table 1, is described by the Morse curve:  $E^- = 0.6$  eV;  $DE^- = 1.91$  eV for dissociation energy of the C-Cl bond in the anion which is equal to the difference between  $DE_0 = 3.72$  eV and electron affinity of the  $\text{C}_2\text{F}_5$  fragment  $EA(\text{C}_2\text{F}_5) = 1.81 \pm 0.14$  eV [18];  $r^- = 4.63 a_0$  for the equilibrium bond length in the anion;  $\beta = 0.436 a_0^{-1}$ . Vibrational quantum of the anion  $\hbar\omega = 16.6$  meV seems as a reasonable estimation. Dissociation with  $(\text{M-Cl})^-$  formation is forbidden by energy in the first resonance ( $DE^- > E_{\text{max}}(\text{RS1})$ ), but it is observed in the second resonance with very low intensity, see Table 1. It may be explained by taking into consideration the repulsive term  $U_3^{\text{rep}}$  shown in Fig. 5.

The terms obtained give the possibility to analyze the temperature dependencies of the RS1 in  $\text{C}_2\text{F}_5\text{Cl}$ . The dissociative repulsive term,  $U_1^{\text{rep}}$ , leading to the  $\text{Cl}^-$  formation exhibits similar behavior as the same term in the case of  $\text{CF}_3\text{Cl}$  [6, 12, 15] and  $\text{CH}_3\text{CF}_2\text{Cl}$ . Therefore, an increase in DA cross section with a shift of the RS1 maximum to lower energies is quite clear. An additional channel of  $(\text{M-Cl})^-$  formation is forbidden by energy in the first resonance, see Table 1. However, in the high-temperature spectrum (573 K) we detect a weak signal of  $\text{C}_2\text{F}_5^-$  in the low-energy region. It is a very strange phenomenon because a simple

$\text{C}_2\text{F}_5\text{Cl}$ , PM3



$\text{CH}_3\text{CF}_2\text{Cl}$ , PM3



**Fig. 4.** Two lowest normally empty MO of  $\text{C}_2\text{F}_5\text{Cl}$  (left), and  $\text{CH}_3\text{CF}_2\text{Cl}$  (right) according to semiempirical PM3 calculations.  $\sigma_{\text{C-Cl}}^*$  bond contributes to both of them in the first case, and  $\sigma_{\text{C-Cl}}^*$  bond contributes only to the LUMO in the second one.

energetic estimation shows that this is impossible. Consider the target eight-atom molecule  $C_2F_5Cl$  as a statistical ensemble with  $3N-6 = 18$  interacting degrees of freedom. The internal vibrational energy of that system is about  $E_{vib} \sim 18$  kT. At a temperature of 573 K  $E_{vib} \sim 0.9$  eV. Total internal energy of the temporary anion is equal to  $E^{total} = E_{vib} + E_{el}$ ;  $E_{el}$  means electron energy. So, it is obvious, that the channel for  $(M-Cl)^-$  formation can be achieved at the energy  $\sim 1$  eV if all degrees of freedom will contribute to energy fluctuation on the dissociative vibrational mode, see Fig. 5. Unfortunately, we cannot exclude an influence of the possible impurities on the hot spectrum; therefore we have not definitive conclusion for this phenomenon.

Consider the second resonant state RS2 at the energy  $\sim 2.5$  eV. This RS exhibits three dissociation channels  $Cl^-$ ,  $F^-$ , and  $(M-Cl)^-$ , see Fig. 2 and Table 1. All of them have the same temperature behavior: a decrease in DA cross section with a shift of the RS2 maximum to lower energies. The energy shift is about 0.2 eV when the temperature increases from 348 K to 573 K. The intensity of RS2, in contrary to the case of RS1, decreases to a considerable extent. That effect cannot be explained in the framework of the simple classical model [7, 11, 12]. According to our estimations, by the model of united atom approximation [13, 14] mean lifetime towards autodetachment of the  $C_2F_5Cl^-$  in RS1 is  $\tau_a^1 \approx 4$  fs, and in RS2  $\tau_a^2 \approx 6$  fs. The details of the calculations were described earlier [13]. The above values are very close to the previous ones for the dissociation lifetime in the case of  $CF_3Cl$  ( $\tau_a \approx 3$  fs) [6, 11, 12]. It means that the dissociation probability  $\sigma_{DA}$  for the second resonant state should be slightly higher than for the first RS, as it follows from:

$$(3) \quad \sigma_{DA} = \sigma_C \cdot \exp(-\tau_D / \tau_{AD}),$$

where  $\sigma_C$  means total electron capture cross section;  $\tau_D$  means dissociation lifetime. The last formula is very approximate, but quantitatively right. That fact explains relative ion intensities in RS1 and RS2, but decreasing of ion intensity in RS2 with the temperature rising is still unclear. The effect of negative temperature dependence of RS2 in  $C_2F_5Cl$  may be considered as an indication of classical model [7, 11, 12] limitation.

At the end, the parameters used for fitting of the  $U_2^{rep}$  and  $U_3^{rep}$  presented in Fig. 5 are listed.  $U_2^{rep}$  corresponds to the  $Cl^-$  formation in RS2:  $D = 0.11$  eV,  $A = 2.65$  eV,  $\delta = 0.529 a_0^{-1}$ ;  $r_0 = 3.31 a_0$ .  $U_3^{rep}$  corresponds to the  $C_2F_5^-$  formation in RS2:  $D = 1.91$  eV,  $A = 0.85$  eV,  $\delta = 0.4 a_0^{-1}$ ;  $r_0 = 3.31 a_0$ .

## Conclusion

The present data on ECNI MS of two freon derivatives show quite different temperature dependencies. The  $CH_3CF_2Cl$  has NI CEY the same as the one for the  $CF_3Cl$  investigated earlier. The first RS, exclusively  $Cl^-$  formation, is a shape resonance with an additional electron captured on the  $\sigma_{C-Cl}^*$  orbital. This resonance has a positive dependence of the DA cross section with temperature. Energy shifts toward low electron energy,  $\Delta E \approx 0.3$  eV, when the temperature is varying from 348 to 568 K. The second RS, predominantly  $F^-$  formation, is an electron excited Feshbach

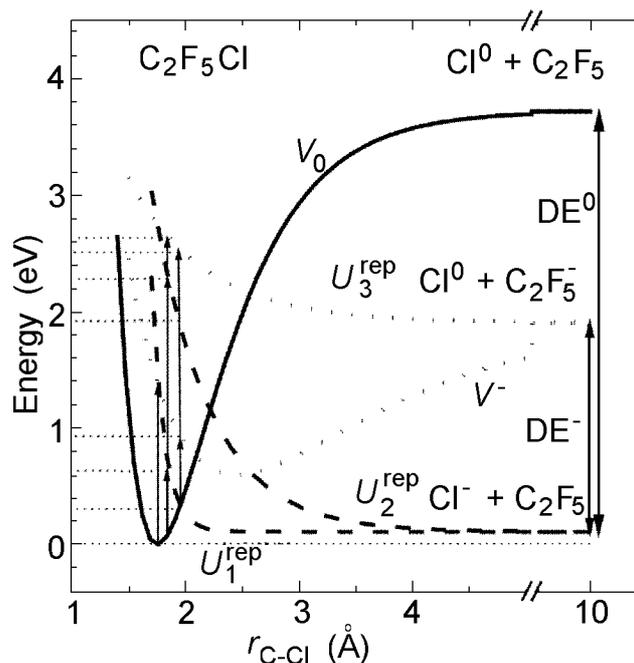


Fig. 5. Schematic representation of the terms of the  $C_2F_5Cl$  molecule and anion as a function of C-Cl bond length. See notation in text.

resonance which is not sensitive to the temperature variation.

Substitution of the  $CH_3$  group by the  $CF_3$  group leads to the dramatic changes in CEY temperature dependence. The first RS in  $C_2F_5Cl$  keeps growing and shifting into low-energy region with increasing temperature. The second RS for DA in the  $C_2F_5Cl$  molecule is of resonance shape, too. Both, the ions  $Cl^-$  and  $F^-$  formed in this resonance decrease their intensities and the maxima shift to the left by about 0.2 eV when the temperature increases from 348 to 573 K. The supposition has been made that  $\sigma_{C-Cl}^*$  delocalization into two empty orbitals leads to  $Cl^-$  ion formation in two different resonance states. The temperature dependencies observed for the RS1 in  $CH_3CF_2Cl$  and  $C_2F_5Cl$  are described qualitatively in the framework of a semi-classical model elaborated by the Illenberger group. Decreasing of RS2 intensity in  $C_2F_5Cl$  spectra with rising temperature is unclear in the framework of this model. The final decision of this problem requires additional experimental and theoretical investigations.

**Acknowledgments** Work has been supported by the Russian Foundation for Basic Research, grant No. 00-02-16578, the Polish State Committee for Scientific Research under grant No. 3 T09A010 18, and NATO grant JSTC.RCLG.979570.

## References

- Asfandiarov NL, Fal'ko VS, Lukin VG *et al.* (2001) Violation of frozen shell approximation in dissociative electron capture by halogenated anthraquinones. *Rapid Commun Mass Spectrom* 15:1869–1878
- Christophorou LG (ed.) (1994) *Electron–molecule interactions and their applications*, Vols 1–2. Academic Press, New York
- Chutjian A, Alajian SH (1985) s-Wave threshold in electron attachment: observations and cross sections in  $CCl_4$  and  $SF_6$  at ultra low electron energies. *Phys Rev A* 31:2885–2892

4. Elyashevich MA (2001) Atomic and molecular spectroscopy. Editorial URSS, Moscow
5. Fabrikant II, Hotop H (2001) Low-energy behavior of exothermic dissociative electron attachment. *Phys Rev A* 63:022706–1–022706–10
6. Hahndorf I, Illenberger E, Lehr L, Manz J (1994) Temperature effects of dissociative electron attachment to  $\text{CF}_3\text{Cl}$ . *Chem Phys Lett* 231:460–466
7. Illenberger E, Scheunemann HU, Baumgärtel H (1979) Negative ion formation in  $\text{CF}_2\text{Cl}_2$ ,  $\text{CF}_3\text{Cl}$  and  $\text{CFCl}_3$  following low-energy (0–10 eV) impact with near monoenergetic electrons. *Chem Phys* 37:21–31
8. Illenberger E, Smirnov BM (1998) Electron attachment to gas and condensed phase molecules. *Usp Fiz Nauk* 168:731–766 (in Russian)
9. Khvostenko VI (1981) Negative ion mass spectrometry in organic chemistry. Nauka, Moscow
10. Khvostenko VI, Rafikov SR (1975) Basic rules of negative ion formation in dissociative electron attachment by polyatomic molecule. *Dokl Akad Nauk* 220:892–894 (in Russian)
11. Lehr L, Manz J, Miller WH (1997) A classical approach to resonant low-energy electron scattering off molecules: application to the  $a_1$ -shape resonance of  $\text{CF}_3\text{Cl}$ . *Chem Phys* 214:301–312
12. Lehr L, Miller WH (1996) A classical approach to dissociative electron attachment DA: application to temperature effects in the DA cross section of  $\text{CF}_3\text{Cl}$ . *Chem Phys Lett* 250:515–522
13. Nafikova EP, Asfandiarov NL, Fokin AI, Lomakin GS (2002) Application of the united atom model for estimating the lifetime of negative molecular ions relative to electron autodetachment. *J Exp Theor Phys* 95:605–610
14. Nafikova EP, Fal'ko VS, Fokin AI, Lomakin GS, Lukin VG, Pshenichnyuk SA, Asfandiarov NL (2001) Modeling of shape resonance electron scattering by molecules. In: *Int Symp on Electron–Molecule Collisions and Swarms*, 14–16 July 2001, Lincoln, USA, pp 170–171
15. Pearl DM, Burrow PD (1994) Dissociative attachment in selected monochloroalkanes. *J Chem Phys* 101:2940–2947
16. Pearl DM, Burrow PD, Fabrikant II, Gallup GA (1995) Dissociative attachment in hot  $\text{CH}_3\text{Cl}$ : experiment and theory. *J Chem Phys* 102:2737–2743
17. Rosa A, Barszczewska W, Nandi D *et al.* (2001) Unusual temperature dependence in dissociative electron attachment to 1,4-chlorobromobenzene. *Chem Phys Lett* 342:536–544
18. Sullivan SA, Beauchamp JL (1976) NIST Chemistry WebBook. <http://webbook.nist.gov/chemistry/>
19. Sunagawa T, Shimamori H (2001) Temperature dependence of low-energy electron attachment to  $\text{CHCl}_3$ . *Int J Mass Spectrom* 205:285–291
20. Wilde RS, Gallup GA, Fabrikant II (1999) Semiempirical R-matrix theory of low energy electron- $\text{CF}_3\text{Cl}$  inelastic scattering. *J Phys B: At Mol Opt Phys* 32:663–673