



# Isotope effect in cross-section of $(M-H/D)^-$ negative ions formation from $CF_3COOH$ and $CF_3COOD$



P.V. Shchukin<sup>a,\*</sup>, G.P. Mikhailov<sup>b</sup>, M.V. Muftakhov<sup>a</sup>

<sup>a</sup> Institute of Molecule and Crystal Physics, Ufa Research Centre of Russian Academy of Sciences, Prospect Octyabrya, 151, Ufa, Russia

<sup>b</sup> Ufa State Aviation Technical University, K. Marx St., 12, Ufa, Russia

## ARTICLE INFO

### Article history:

Received 20 November 2014

Received in revised form 13 February 2015

Accepted 17 February 2015

Available online 25 February 2015

### Keywords:

Trifluoroacetic acid

Resonance electron capture

Negative ions

Isotope effect

Predissociation

Tunneling

## ABSTRACT

In the present paper the processes of resonant electron attachment by trifluoroacetic acid molecules ( $CF_3COOH$ ) and its deuterated analog ( $CF_3COOD$ ) leading to formation of fragment negative ions have been investigated by negative ion mass spectrometry. Inverse or small direct isotope effect was detected for majority of negative ions. It is expressed both in difference between cross-section of ion formation, and in resonance peak displacement over energy scale for isotopically substituted ions from  $CF_3COOH$  and  $CF_3COOD$ . Isotope effect of maximal magnitude  $\sigma_{(H)}/\sigma_{(D)} \approx 19$  was registered for  $(M-H/D)^-$  ions at electron energy 0.73 eV, and formation of these ions was explained by the mechanism of tunneling predissociation.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

In resonance electron capture experiments the isotope effect was originally observed as a decrease of formation cross section of  $D^-$  ions from deuterium  $D_2$  as compared with the formation cross-section of  $H^-$  from hydrogen  $H_2$  [1]. This phenomena was theoretically explained by Demkov [2] in terms of a competition between the electron autodetachment and dissociative decay proceeding in negative ions. Thus, in the case of compound containing a heavy isotope, the dissociation of molecular ions proceeds slowly, therefore the yield of fragment ions decreases, and efficiency of autodetachment process is conversely, increases. As a result, the ratio of the yield intensities of identical ions in mass spectra of isotopically substituted compounds can reach two orders of magnitude.

The extensive studies of isotope effect in dissociative electron attachment to organic molecules have been carried out in 60–70 s of the last century in the course of elaboration of theoretical concepts for resonance electron–molecular interactions. Among the applications of those investigations was the approach to the problem of estimation of molecular negative ions lifetime with respect to electron autodetachment (autoionization). For example, from the observation of strong isotope effect for  $H^-/D^-$  ions formation from

molecular hydrogen and deuterium [3] it was concluded that  $H_2^-$  autoionization lifetime should be comparable with the time spend by electron when transiting through the extent of the molecule. On the contrary, experiments with ammonia revealed weak isotope effect in the process of formation of  $NH_2^-$  and  $ND_2^-$  ions [4,5] and indicated that the lifetime of  $NH_3^-$  molecular ions exceeds the period of intramolecular vibrations, or these values were comparable, at least. Isotope effect was also measured for fragment ions from other compounds, including water [6], formaldehyde [7], and methane molecules [8]. In particular, the latter one revealed inverse isotope effect attributed to the difference in absolute electron capture cross-section for isotopically substituted samples. Among the recent studies of the isotope effect in the cross section of dissociative electron attachment the investigations of acetylene [9], uracil [10], and isomers of aminobutanoic acid [11] are worth mentioning.

In the present work the isotope effect in cross section of fragment ions formation from trifluoroacetic acid  $CF_3COOH$  and its deuterated analog  $CF_3COOD$  have been investigated. Trifluoroacetic acid represents a good model for studying electron–molecular reactions in carboxyl-containing objects, including such biologically relevant substances as amino acids. Special attention was paid to examination of reaction of formation  $(M-H/D)^-$  ions in 1 eV energy region, characteristic for OH-containing molecules. As shown previously [12], these ions are formed as a result of predissociative process which requires the long lifetime of the molecular ions with respect to fragmentation, exceeding the period of interatomic vibrations. This circumstance in conjunction with the competition

\* Corresponding author. Tel.: +7 347 2848869; fax: +7 347 2359522.

E-mail address: [pavel@anrb.ru](mailto:pavel@anrb.ru) (P.V. Shchukin).

from electron autodetachment was expected to lead to the strong isotope effect.

## 2. Experimental

The experiments were performed using the magnetic mass spectrometer, model MI-1201V (Sumy, Ukraine). The apparatus was modified to analyze negative ions under resonance capture of energy-controlled electrons [13] with the possibility to operate with positive ions under electron ionization being remained. Depending on the tasks to be solved, the experiments were carried out at different temperatures of the ionization chamber and appropriate electron beam energy resolution. These values are indicated in figure captions. The electron energy scale was calibrated using the maximum of the effective yield curves of  $\text{SF}_6^-/\text{SF}_6$  ( $\sim 0$  eV). The resonance peak of  $\text{SF}_6^-/\text{SF}_6$  ( $\sim 0$  eV) ions was used also for estimation electron energy distribution.

Samples of compounds were purchased from Sigma Aldrich. Among the difficulties in experiment with deuterated sample was the occurrence of uncontrolled reactions of H–D-exchange in the ionization chamber and resulting in H-acid production inside the device. To control this process and measure the ratio of H- and D-acids in the reaction area, the device was switched over to the conventional regime of electron ionization at 70 eV, and the efficiency of ions yield at  $m/z$  45/ $\text{COOH}^+$  and  $m/z$  46/ $\text{COOD}^+$ , dominating in positive ion mass spectra of  $\text{CF}_3\text{COOH}$  and  $\text{CF}_3\text{COOD}$ , accordingly, was evaluated. Assuming the possible isotope effect in the positive ions formation cross section to be negligible, measuring the peak intensities of the above ions we were able to determine the density ratio of H/D-acids inside the ionization chamber and thereby to control the total amount of sample vapor introduced from liquid/gas inlet system.

## 3. Results and discussion

The negative ion mass spectrum of  $\text{CF}_3\text{COOH}$  consists of peaks of at least seventeen fragment ions which are formed within 0–13 eV energy range. Effective yield curves as functions of the captured electron energy are shown in Fig. 1. The obtained spectrum is in good agreement with the previous studies [14–16], however several types of negative ions were registered for the first time. Judging from the observed elemental composition of fragment ions from trifluoroacetic acid, it can be concluded that these ions are generated not only due to simple bond cleavage reactions but also in rearrangement processes, with some ions ( $\text{F}_2\text{H}^-$ ,  $\text{CF}_3\text{H}^-$  and  $\text{FOH}^-$ ) having cluster structure. Variation in the different ions yield intensities reaches four orders of magnitude. Mass spectrum is dominated by the group of ions  $\text{CF}_3\text{COO}^-$ ,  $\text{CF}_2\text{COO}^-$  and  $\text{CF}_2^-$ , formed in the range 0–3 eV. Yield of other negative ions is lower and in some cases barely exceeds 0.1% of most abundant  $\text{CF}_3\text{COO}^-$  ions. The ion composition of deuterated  $\text{CF}_3\text{COOD}$  acid mass spectrum is similar to the  $\text{CF}_3\text{COOH}$  spectrum, demonstrating minor deviations in intensities of some resonance peaks and shifts of their positions in the energy scale. The measured values of isotope effect  $\sigma_{(\text{H})}/\sigma_{(\text{D})}$  in cross section of fragment negative ions formation from  $\text{CF}_3\text{COOH}/\text{CF}_3\text{COOD}$  are shown in Table 1. (The most accurate values were obtained for  $\text{CF}_3\text{H}^-/\text{CF}_3\text{D}^-$  and  $\text{HO}^-/\text{DO}^-$  ions due to the felicitous observation of some abundant H-containing ions during the experiments with deuterated acid. High accuracy of measured isotope effect values is also characteristic to intensive  $\text{CF}_3\text{COO}^-$ ,  $\text{CF}_2\text{COO}^-$  and  $\text{CF}_2^-$  ions that were analyzed additionally.) The obtained data show that the strongest isotope effect demonstrate the  $(\text{M}-\text{H})^-$  ions (with the structure  $\text{CF}_3\text{COO}^-$  being the same for both acids) and  $\text{H}^-/\text{D}^-$  ions. The other ion pairs demonstrate no noticeable difference in the formation cross section.

**Table 1**

Isotope effect in dissociative cross-section of negative ion formation from  $\text{CF}_3\text{COOH}/\text{CF}_3\text{COOD}$ .

Ions	$\sigma_{(\text{H})}/\sigma_{(\text{D})}$ ( $E_{\text{max}}$ , eV)
$\text{CF}_3\text{CO}_2^-$	19 (0.73 eV) 3.7 (>1.3 eV)
$\text{CF}_2\text{CO}_2^-$	0.92 (1 eV)
$\text{CF}_3\text{H}^-/\text{CF}_3\text{D}^-$	0.8 (1.1 eV)
$\text{CF}_3^-$	3.5 (2.3 eV) 1.1 (7.3 eV)
$\text{CF}_2\text{H}^-/\text{CF}_2\text{D}^-$	1.9 (5 eV) 1.6 (6.5 eV)
$\text{CF}_2^-$	0.9 (1.5 eV)
$\text{FCO}_2^-$	1.1 (1.1 eV) 1.4 (4.9 eV) 1.2 (7.5 eV)
$\text{FCO}^-$	1.3 (1.7 eV) 1.1 (6.7 eV) 1 (10.5 eV)
$\text{HCO}_2^-/\text{DCO}_2^-$	1.7 (5 eV) 1.4 (7.5 eV)
$\text{CO}_2^-$	1.6 (10.7 eV) 1.5 (2 eV) 1.3 (5 eV)
$\text{F}_2\text{H}^-/\text{F}_2\text{D}^-$	4.3 (7.5 eV) 1 (5 eV) 1.3 (7 eV)
$\text{FOH}^-/\text{FOD}^-$	1.2 (7 eV)
$\text{F}^-$	1.3 (1.5 eV) 1.5 (7.6 eV)
$\text{HO}^-/\text{DO}^-$	1.9 (7.2 eV)
$\text{O}^-$	2.5 (5 eV) 1.3 (10.5 eV)
$\text{H}^-/\text{D}^-$	>8 (7.6 eV)

Effective  $(\text{M}-\text{H})^-$  ion formation in proximity of 1 eV was registered earlier for many OH-containing compounds [12,17]. As it was shown, these ions are formed due to hydrogen loss from the carboxyl group and have  $\text{R}-\text{COO}^-$  structure characterized by high electron affinity. Fig. 2 shows effective yield curves of  $(\text{M}-\text{H})^-/\text{CF}_3\text{COOH}$  negative ions obtained with higher electrons energy resolution of  $\Delta E_{1/2} \sim 0.1$  eV. The curve demonstrates distinct peak at 0.73 eV with a small shoulder at 0.35 eV, and wide structureless shoulder extended to higher energies up to 2.2 eV. Taking into account that electron-excited states associated with two-particle resonances occur in trifluoroacetic acid at energies higher than  $\approx 4.51$  eV (275 nm) [18], these resonance states are expected to correspond to one-particle resonances.

The experiment with temperature variation showed that the observed small shoulder at 0.35 eV in  $(\text{M}-\text{H})^-$  effective yield curve revealed temperature dependence (see Fig. 3). It points to the fact that electron captured here by vibrationally excited molecules, the number of which grows with increasing temperature. The ratio of the populations of excited and ground states with  $E_{\text{H}}$  and  $E_0$  energies, respectively, given by the following expression (Boltzmann distribution) [19]:

$$\frac{N_{\text{H}}}{N_0} = \exp\left(-\frac{\Delta E}{k_{\text{B}}T}\right)$$

where  $\Delta E = E_{\text{H}} - E_0$ ,  $k_{\text{B}}$  – is the Boltzmann's constant,  $T$  – is the temperature. Based on the Arrhenius plot displaying the logarithm of the intensity of the peak at 0.35 eV ions versus inverse temperature  $1/T$ , we estimated the difference between the ground and excited vibrational levels of molecules to be  $\Delta E \sim 0.1$  eV. Analysis of the vibrational spectrum of trifluoroacetic acid shows that probably it corresponds to excitation of  $\nu_{\text{CF}_3}$  (0.097 eV) vibrational mode [20].

It was suggested earlier [14] that resonance peak of  $(\text{M}-\text{H})^-$  negative ions in trifluoroacetic acid near 1 eV is associated with shape resonances where electron capture into a virtual  $\pi^*$  molecular orbital localized mainly at the carboxyl group. The same

Download English Version:

<https://daneshyari.com/en/article/1192941>

Download Persian Version:

<https://daneshyari.com/article/1192941>

[Daneshyari.com](https://daneshyari.com)