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Halogenomethanes molecules fragmentation at interaction with ions

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The mechanism of fragmentation of isolated molecules of carbon tetrachloride CCl_4 and the simplest chlorofluorocarbons CFC-12 (CCl_2F_2), CFC-13 ($CClF_3$) at the single electron capture by H^+, He^{2+} and Ar^{6+} ions keV energy has been studied. It is shown that the main process during the ionization of the molecules under study is the process of elimination of atomic chlorine. The formation of an undissociated molecular ion M^+ is observed only for CF_3Cl and CCl_2F_2 molecules, for which the process of elimination of atomic fluorine is significantly less probable than chlorine. The parameters of molecules and singly charged halogenomethane ions were calculated using the multiconfiguration method of self-consistent field in total active space (CASSCF). For the experimentally observed main channels of fragmentation of these ions, reaction paths are considered within the framework of the CASSCF method.

Keywords: electron capture, chlorofluorocarbons, halogenomethane, fragmentation of molecular ions, mass spectrometry, multi-configuration self-consistent field method.

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Introduction

It is believed that contamination of the stratosphere with various halocarbons leads to depletion of the ozone layer due to the interaction of ozone with halogen atoms formed during fragmentation of these molecules, in particular, when they interact with ultraviolet radiation, for example [1–5]. This problem was reflected in 1987 Montreal Protocol on Substances that Deplete the Ozone Layer among which specially highlighted simplest chlorofluorocarbons and carbon tetrachloride [2], which are gases of anthropogenic origin [6].

The lifetime in the stratosphere of chlorofluorocarbons and carbon tetrachloride is many years (CCl_3F — 45 years, CCl_2F_2 — 100 years, $CClF_3$ — 640 years and CCl_4 — 265 years [2]). It is believed that the removal of these substances from the atmosphere occurs mainly in the stratosphere due to UV photolysis and chemical reactions, for example, with excited atomic oxygen $O(^1D)$ [5]. Ref. [7] proposes to take into account the processes of dissociative adhesion of slow electrons ($E_{el} < 20$ eV) leading to fragmentation of halogenomethane molecules.

In particular, chain reactions involving Cl atoms are responsible for the destruction of ozone molecules in the stratosphere, when they collide with ozone atoms, chlorine monoxide and an oxygen molecule are formed. Chlorine monoxide, in turn, can react with atomic oxygen producing atomic chlorine, which leads to a cycle in which ozone is destroyed to molecular oxygen, and chlorine atoms return to the stratosphere. One chlorine atom destroys 10^5 molecules of $_3$ on average. Chlorine is removed when it enters the troposphere and it is removed by rains with HCl. Atomic fluorine is a part of a similar chain of ozone depletion, but the chain is quickly interrupted with the formation of HF due to the chemical activity of fluorine [4,8].

The practical significance of halogenomethanes has stimulated a large number of studies that investigated the fragmentation of these molecules in interaction with radiation [8–12], electrons [7,13–18] and ions [19–21] penetrating into the upper layers of the Earth atmosphere. This paper studied the mechanism of fragmentation of isolated carbon tetrachloride molecules CCl_4 and chlorofluorocarbons CCl_2F_2, $CClF_3$ in the process of capturing one electron from them by H^+, He^{2+} ions and Ar^{6+} keV energy. The parameters of molecules and single-charged halomethane ions were calculated using the multi-configuration method of a self-consistent field in the full active space (CASSCF), and the reaction paths of the main experimentally observed fragmentation channels of these ions were considered using the CASSCF method.

1. Experimental method

The experimental setup described in detail in Ref. [19] was used to conduct the study. A collimated monokinetic beam of H^+, He^{2+} and Ar^{6+} ions with energy of $10.2z$ keV (where z — the charge of the incoming ion) crossed the effusion gas jet molecules. The interaction of the ion beam and the molecular jet occurred in the region of a homogeneous electric field with a strength of 150 V/cm. This electric field pulled the ions formed in the collision with the incoming ions into the ion-optical system of the time-of-flight mass analyzer. The fragment ions of the target molecule were accelerated by the analyzer optics to the energy of $2.5q$ keV, where q is the charge of the

Table 1. Ionization potentials, bond lengths and dipole moments of molecules CCl_4, CF_2Cl_2 and CF_3Cl in optimal geometry

Molecules and ions	IP_v (eV)	IP [23] (eV)	R(C−Cl) (nm)	R(C−F) (nm)	μ (D)
CCl_4 ($^1A_1$)	11.99	11.47 ± 0.01	0.1793		0.00
CCl_4^+ ($^2B_1$)			0.1735 (Cl2&Cl3)* 0.1852 (Cl4&Cl5)		
CF_2Cl_2 ($^1A_1$)	11.99	12.0 ± 0.2	0.1758	0.1327	0.26
$CF_2Cl_2^+$ ($^2B_1$)			0.1788	0.1283	
$CF_2Cl_2^+$ ($^2B_2$)			0.1794	0.1300	
$CF_2Cl_2^+$ (2^2B_2)			0.1670	0.1447	
CF_3Cl ($^1A_1$)	12.61	12.6 ± 0.4	0.1787	0.1320	0.14
CF_3Cl^+ (^2E)			There is no optimal geometry		
CF_3Cl^+ ($^2A_2$)			0.1679	0.1371	

Note. * — numbering of atoms on the insert Fig. 2.

fragment ion. The ions that passed the mass analyzer were accelerated additionally by a voltage of 12 kV and were recorded by a detector, whose signals were used as „stop" signals of time-of-flight mass analyzer. A high and uniform efficiency of recording of ions of different mass and charge was achieved through the additional acceleration. Calculations performed during the designing of the analyzer showed that this ion-optical system can ensure 100% collection of recoil ions with initial energies of less than 5 eV. The incoming ions after the collision were analyzed by charge by an electrostatic analyzer and recorded by a detector, the signals of which were used as the „start" signals of the time-of-flight mass analyzer.

2. Quantum chemical calculation method

The parameters of neutral halogenomethane molecules were calculated using the GAMESS-US (2023) [22] multi-configuration method of the complete active space self-consistent field CASSCF(n, k) (n-active electrons localized on k-active molecular orbitals). The number of active electrons decreases by one during the ionization process, and the wave function of a single-charged ion is described by the CASSCF($n − 1$, k) method. The calculations were performed in a full-electron correlation-matched cc-pVTZ atomic basis.

The active space was used for 16 active electrons distributed over 13 active molecular orbitals $[7b_110a_111a_15b_28b_13a_212a_16b_2—13a_17b_29b_114a_14a_2]$ when calculating the parameters of the CF_2Cl_2 molecule having the symmetry group C_{2v}. The optimal geometric parameters of the molecular ion $CF_2Cl_2^+$ were calculated both in the ground state $^2B_1$ and in the two lower electronic states $^2B_2$ and 2^2B_2 (Table 1).

The active space was used for 18 active electrons distributed over 13 active molecular orbitals $[5e1a_26e9a_17e10a_1—11a_112a18e]$ when calculating the parameters of the CF_3Cl molecule having the symmetry group C_{3v}. The optimal geometric parameters of the molecular ion CF_3Cl^+ were calculated both in the ground state ^2E and in the excited state $^2A_2$ (Table 1). It turned out that the ground state ^2E of the CF_3Cl^+ ion does not have an optimal geometry and, as a result, a barrier for the fragmentation process with the separation of the neutral chlorine atom.

The active space was used for 14 active electrons distributed over 11 active molecular orbitals $[2t_16a_17t_2—7a_18t_2]$ when calculating the parameters of CCl_4 molecule having a symmetry group T_d.

The calculated ionization potentials for all studied molecules are in good agreement with those recommended in the NIST database [23] (Table 1). The value of the ionization potential for the molecule of CCl_4 was obtained by averaging over three components of the term $^2T_1$ and is therefore slightly overestimated.

The IRC (Intrinsic Reaction Coordinate) algorithm in the space of mass-weighted coordinates was used to calculate the paths of halogen atom separation reactions for CCl_4 and $CCl_2F_2^+$ ions. The calculation of fragmentation paths of $CClF_3^+$ ion was performed using partial geometry optimization due to averaging over electronic states ^2E and $^2A_2$ with the same weights when optimizing molecular orbitals (state-averaged CASSCF).

3. Results and discussion

Figure 1 shows typical time-of-flight mass spectra of fragment ions formed during the capture of one electron by He^{2+} ions in halogenomethane molecules. During
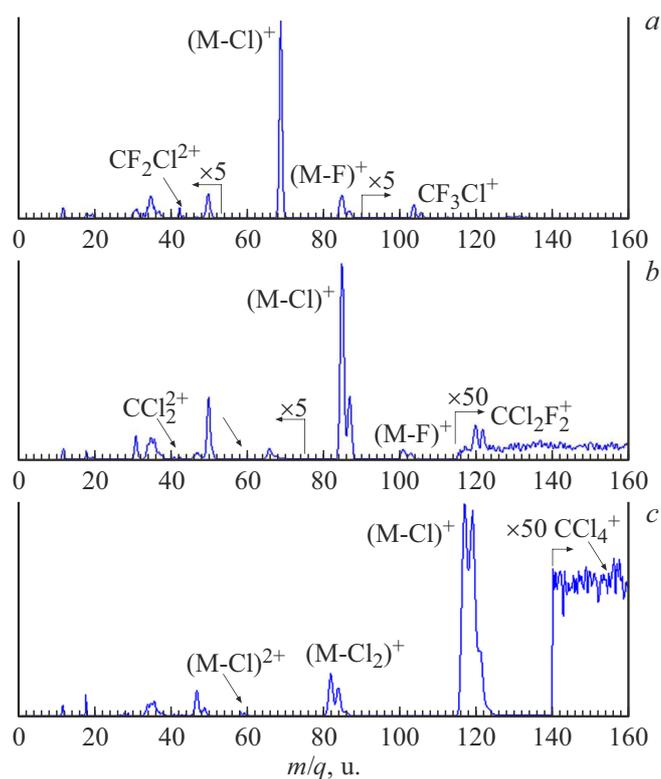
Figure 1. Mass spectra of ion fragments formed in the process of capture of one electron by He^{2+} ions from halogenomethane molecules: a — CF_3Cl, b — CCl_2F_2, c — CCl_4.

Figure 2. Dependence of the relative energy of the molecular ion of CCl_4^+ along the path of the chlorine atom separation reaction. The energy reference point is the total energy of the CCl_4^+ ion in the optimal geometry of the neutral molecule. A straight red line is the energy effect of the reaction.

the formation of the mass spectra, the „start" signals were the recording signals of incoming $Ion^{(z-1)}$ ions that captured one electron. Thus, the fragment ions forming these mass spectra are formed in the processes of single-electron capture and capture with ionization. In particular, the capture process with ionization manifests itself in the appearance of peaks of the corresponding two-charged ion fragments in the mass spectra. Tables 2−4 show the relative cross sections of the formation of fragment ions when one electron is captured by H^+, He^{2+}, Ar^{6+} ions in molecules of CCl_4, CCl_2F_2 and $CClF_3$. The total capture cross section of one electron σ_{zz-1} is assumed to be 100%. In addition, the tables show the ionization cross sections of the studied molecules by electron impact $\sigma_{ion}(e^-)$ from the database [23]. As can be seen from the above data, the main process during ionization of the studied molecules is the process of separation of the chlorine atom from them to form the molecular ion $(M-Cl)^+$. The formation of an undissociated molecular ion M^+ is observed only for CF_3Cl and CCl_2F_2 molecules. The process of separation of the fluorine atom from these molecules is significantly less likely than in case of chlorine.

Quantum chemical calculations show that the process of separation of the chlorine atom has practically no barrier for all the considered molecules and all the corresponding reactions are exothermic. The energy effects of the reactions ΔE, shown in Table 5, are defined as the difference in

the energies of the initial ion in the geometry of a neutral molecule, which corresponds to the process of vertical ionization, and the energies of the system after fragmentation. Previously, such energy effects were estimated as a result of quantum chemical calculations [24], which turn out to be less than those obtained in this paper. This discrepancy is explained by the use of a more complete atomic basis set and a more advanced calculation method.

The calculated dependence of the relative energy of the molecular ion CCl_4^+ on the path of the chlorine atom separation reaction is shown in Fig. 2. The total energy of the CCl_4^+ ion in the optimal geometry of the neutral molecule is taken as the energy reference point and determines the vertical ionization potential of the molecule of CCl_4 (Table 1). Calculations show that, for example [25] the symmetry of the ion decreases in the optimal geometry from T_d in a neutral molecule to C_{2v} as a result of the Jahn−Teller effect (Table 1). The molecular ion is located at a local minimum with a depth of about 0.05 eV in the optimal geometry. The calculated energy of the appearance of CCl_3^+ ions is in satisfactory agreement with experimental data (Table 5).

The calculated relative energy dependences for the three lower electronic states of the molecular ion of $CCl_2F_2^+$ along the path of the separation reaction of one halogen atom are shown in Fig. 3. The total energy of $CF_2Cl_2^+$ ion in the ground state $^2B_1$ in the optimal geometry of a neutral molecule is taken as the relative energy reference point when considering fragmentation paths and determines the vertical ionization potential of the CF_2Cl_2 molecule (Table 1). The ion in these states retains the symmetry of C_{2v} in the optimal geometry. Fragmentation from the ground state $^2B_1$ leads to the formation of CF_2Cl^+ ion and a neutral chlorine atom. There is a minimum with a depth of about 0.12 eV on the surface of the potential energy at

Table 2. Relative cross sections of ion fragmentation processes formed in case of capture of one electron by ions of H^+, He^{2+}, Ar^{6+} in molecules of CCl_4

Fragment of ion	$\langle MW \rangle^*$ (u.)	$\sigma_{10}(H^+)$ %	$\sigma_{21}(H^{2+})$ %	$\sigma_{65}(Ar^{6+})$ %	$\sigma_{ion}(e^-)$ [23] %
CCl_3^+	118.37	57.25	73.41	69.53	73.58
CCl_2^+	82.92	14.80	11.48	11.71	13.59
CCl_3^{2+}	59.19	1.31	0.83	4.73	
CCl^+	47.46	12.16	6.15	7.28	8.31
Cl^+	35.45	12.65	6.52	5.80	4.40
C^+	12	1.84	1.60	0.95	0.12

Note. * — the average value of the molecular weight of the fragment, taking into account the isotopic composition.

Table 3. Relative cross sections of ion fragmentation processes formed by capture of one electron by ions of H^+, He^{2+}, Ar^{6+} from molecules of CF_2Cl_2

Fragment of ion	$\langle MW \rangle^*$ (u.)	$\sigma_{10}(H^+)$ %	$\sigma_{21}(H^{2+})$ %	$\sigma_{65}(Ar^{6+})$ %	$\sigma_{ion}(e^-)$ [23] %
$CF_2Cl_2^+$	120.91	0.2	0.3	0.2	0.21
$CFCl_2^+$	101.92	8.2	6.3	6.3	8.21
CF_2Cl^+	85.46	62.6	78.6	69.0	71.57
CCl_2^+	82.92	1.4	0.1	0.4	0.11
Cl_2^+	70.91	0.1	0.1	0.1	0.21
$CFCl^+$	66.46	2.7	1.2	2.9	2.68
CF_2^+	50	8.3	4.3	7.1	6.33
CCl^+	47.46	2.1	1.0	1.3	1.88
CCl_2^{2+}	41.46	0.5	0.3	1.2	
Cl^+	35.45	9.1	4.6	6.6	4.99
CF^+	31	3.9	1.9	3.9	3.70
F^+	19	0.2	0.3	0.3	0.11
C^+	12	0.8	1.1	0.5	

Table 4. Relative cross sections of ion fragmentation processes formed during capture of one electron by ions H^+, He^{2+}, Ar^{6+} from molecules of CF_3Cl

Fragment of ion	$\langle MW \rangle^*$ (u.)	$\sigma_{10}(H^+)$ %	$\sigma_{21}(H^{2+})$ %	$\sigma_{65}(Ar^{6+})$ %	$\sigma_{ion}(e^-)$ [23] %
CF_3Cl^+	104.46	1.08	1.50	1.22	0.64
CF_2Cl^+	85.46	24.19	15.80	13.74	17.09
CF_3^+	69	54.34	69.13	55.72	72.01
$CFCl^+$	66.46	0.27	0.35	0.78	0.21
CF_2^+	50	6.90	2.79	9.25	4.63
CCl^+	47.46	0.45	0.33	0.37	0.36
CF_2Cl^{2+}	42.73	0.95	0.77	2.97	
Cl^+	35.45	7.63	5.20	8.71	2.92
$CFCl^{2+}$	33.23	0.25	0.30	1.26	0.50
CF^+	31	2.83	1.70	4.77	1.28
F^+	19	0.44	0.70	0.60	0.14
C^+	12	0.68	1.43	0.61	0.21

a distance of $r(C - Cl) \approx 0.338$ nm due to the polarization of the outgoing neutral chlorine atom.

Calculations show that the process of separation of a fluorine atom is not realized on the surface of the potential energy of the ground electronic state $^2B_1$, but is possible on the surfaces of the potential energy of the lower electronically excited states $^2B_2$ and 2^2B_2 (Fig. 3). The initial optimal geometry (C_{2v}) of the $CF_2Cl_2^+$ ion in the electronic state $^2B_2$ represents a local minimum. The process of separation of the fluorine atom passes through the transition state point

Table 5. Energies of the appearance of fragment ions and the energy effect of fragmentation reactions

Parent ion	Fragment of ion	AE (eV)	AE (eV) [23]	ΔE (eV)	ΔE (eV) [24]
CCl_4^+ ($^2B_1$)	CCl_3^+	11.99	11.28	2.64	1.97
$CCl_2F_2^+$ ($^2B_1$)	$CClF_2^+$	11.99	12.7	1.88	1.19
$CCl_2F_2^+$ ($^2B_2$)	CCl_2F^+	13.55	14.2	0.25	
$CCl_2F_2^+$ (2^2B_2)	CCl_2F^+	14.81		0.25	
CF_3Cl^+(^2E)	CF_3^+	12.6	12.7	1.78	0.84
CF_3Cl^+($^2A_2$)	CF_2Cl^+	15.6	15.4	0.57	
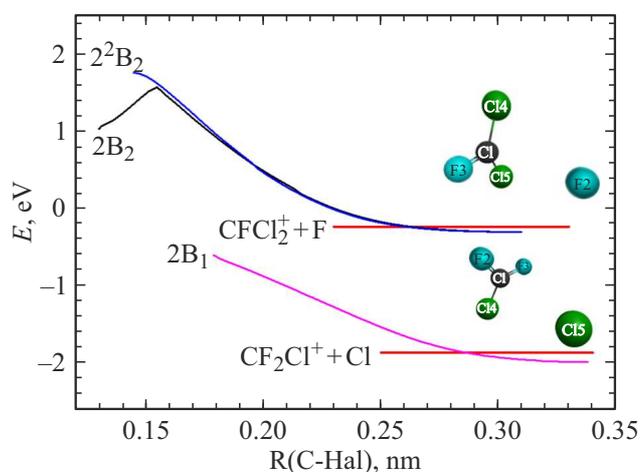
Figure 3. Dependence of the relative energy of the molecular ion $CF_2Cl_2^+$ along the path of the halogen atom separation reaction (Cl or F). Energy reference point is the total energy of the $CF_2Cl_2^+$ ion in the optimal geometry of a neutral molecule. Straight red lines — the energy effect of the reaction.

with a distance of $r(C - F) \approx 0.155$ nm. The process of ion fragmentation with the same symmetry, but in the excited state 2^2B_2 leads to barrier-free separation of the fluorine atom. The calculated energies of the appearance of $CFCl_2^+$ ions in the processes discussed above are in good agreement with experimental data (Table 5).

The calculated relative energy dependences for the two lower electronic states of the molecular ion of $CClF_3^+$ along the path of the separation reaction of one halogen atom are shown in Fig. 4. The total energy of the ground state of the CF_3Cl^+ ^2E ion in the geometry of a neutral molecule is taken as the relative energy reference point and determines the vertical ionization potential of the CF_3Cl molecule (Table 1). In this case, the ground state ^2E of the CF_3Cl^+ ion does not have an optimal geometry and fragments with the separation of the chlorine atom. There is a minimum with depth of about 0.18 eV on the reaction path at a distance of $r(C - Cl) \approx 0.314$ nm.

The process of separation of a fluorine atom along the surface of the potential energy of the ground state of the CF_3Cl^+ ion is not realized. This process can occur along the surfaces of the potential energy of excited states, Fig. 4 shows the first excited state $^2A_2$, in which, as shown by the calculation, unlike the ground state ^2E ion of CF_3Cl^+ has the optimal geometry belonging to the symmetry group of C_{3v}. A decrease of the bond length C−Cl and an elongation of the bonds C−F is observed when the optimal geometry is formed (shortening occurs) (Table 1). As the system develops along the reaction path, one of the bonds C−F elongates, which results in a decrease of the symmetry of the system to C_s. The path of the fluorine atom separation reaction passes through the quasi-intersection point of the potential energy surfaces of the two lower terms $^2A''$ at a distance of $r(C - F) = 0.1651$ nm, as a result of which at distances less than this value the potential energy of the system is determined by the term $2^2A''$ and by the term $1^2A''$ at larger distances.
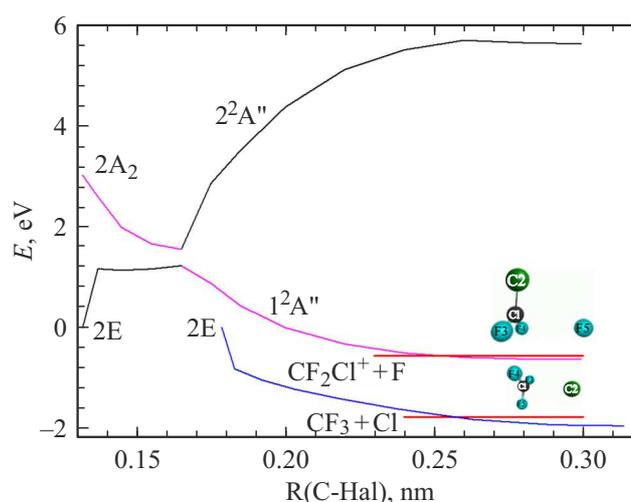
Figure 4. Dependence of the relative energy of the molecular ion of CF_3Cl^+ along the path of the halogen atom separation reaction (Cl or F). The energy reference point is the total energy of the CF_3Cl^+ ion in the optimal geometry of the neutral molecule. Straight red lines — the energy effect of the reaction.

Conclusion

Capture of one electron from molecules of carbon tetrachloride CCl_4 and the simplest chlorofluorocarbons CCl_2F_2 and $CClF_3$ by ions of H^+, He^{2+} and Ar^{6+} is accompanied by the separation of the chlorine atom. The process has practically no barrier, and all relevant reactions are exothermic. The formation of an undissociated molecular ion M^+ is observed only for CF_3Cl and CCl_2F_2 molecules. The process of separation of the fluorine atom from these molecules is significantly less likely than in case of chlorine. Quantum chemical calculations show that the process of separation of the fluorine atom most likely occurs during the formation of molecular ions in excited electronic states. The energy characteristics of the processes obtained by the multi-configuration CASSCF method are in good agreement with the available experimental data.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] IPCC. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Eds. S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor, H.L. Miller. (Cambridge University Press, Cambridge, United Kingdom NY., USA, 2007), 996 p.

[2] World Meteorological Organization. *Scientific Assessment of Ozone Depletion: 2010. Global Ozone Research and Monitoring Project*, Report N 52. Geneva, (2011).

[3] X. Fang, S. Park, T. Saito, R. Tunnicliffe, A.L. Ganesan, M. Rigby, S. Li, Y. Yokouchi, P.J. Fraser, C.M. Harth, P.B. Krummel, J. Mühle, S. O'Doherty, P.K. Salameh, P.G. Simmonds, R.F. Weiss, D. Young, M.F. Lunt, A.J. Manning, A. Gressent, R.G. Prinn. Nature Geoscience, **12**, 89 (2019). https://doi.org/10.1038/s41561-018-0278-2

[4] F.S. Rowland. Annu. Rev. Phys. Chem., **42**, 731 (1991).

[5] M.K. Vollmer, D. Young, C.M. Trudinger, J. Mühle, S. Henne, M. Rigby, S. Park, S. Li, M. Guillevic, B. Mitrevski, C.M. Harth, B.R. Miller, S. Reimann, B. Yao, L.P. Steele, S.A. Wyss, C.R. Lunder, J. Arduini, A. McCulloch, S. Wu, T.S. Rhee, R.H.J. Wang, P.K. Salameh, O. Hermansen, M. Hill, R.L. Langenfelds, D. Ivy, S. O'Doherty, P.B. Krummel, M. Maione, D.M. Etheridge, L. Zhou, P.J. Fraser, R.G. Prinn, R.F. Weiss, P.G. Simmonds. Atmos. Chem. Phys., **18**, 979 (2018). https://doi.org/10.5194/acp-18-979-2018

[6] S.J. Walker, R.F. Weiss, P.K. Salameh. J. Geophys. Res., **105** (C6), 14285 (2000).

[7] D. Chakraborty, D. Nandi. Phys. Rev. A, **102**, 052801 (2020). DOI: 10.1103/PhysRevA.102.0528

[8] E. Kokkonen, K. Jänkälä, M. Patanen, W. Cao, M. Hrast, K. Bučar, M. Žitnik, M. Huttula. J. Chem. Phys., **148**, 174301 (2018). https://doi.org/10.1063/1.5026720

[9] W. Zhang, G. Cooper, T. Ibuki, C.E. Brion. Chem. Phys., **137**, 391 (1989).

[10] A.F. Lago, A.C.F. Santos, G.G.B. de Souza. J. Chem. Phys., **120**, 9547 (2004).

[11] D.A. Shaw, D.M.P. Holland, I.C. Walker. J. Phys. B: At. Mol. Opt. Phys., **39**, 3549 (2006).

[12] A.C.F. Santos, D.N. Vasconcelos, M.A. MacDonald, M.M. Sant'Anna, B.N.C. Tenório, A.B. Rocha, V. Morcelle, V.S. Bonfim, N. Appathurai, L. Zuin. J. Phys. B: At. Mol. Opt. Phys., **54**, 015202 (2021). https://doi.org/10.1088/1361-6455/abc9cc

[13] G. Allcock, J.W. McConkey. J. Phys. B: Atom. Molec. Phys., **11**, 741 (1978). DOI: 10.1088/0022-3700/11/4/021

[14] K. Leiter, K. Stephan, E. Märk, T.D. Märk. Plasma Chem. Plasma Process., **4** (4), 235 (1984).

[15] R. Martinez, F. Castaño, M.N. Sánchez Rayo. J. Phys. E: At. Mol. Opt. Phys., **25**, 4951 (1992).

[16] B.G. Lindsay, K.F. McDonald, W.S. Yu, R.F. Stebbings, F.B. Yousif. J. Chem. Phys., **121**, 1350 (2004). DOI: 10.1063/1.1761055

[17] B. Sierra, R. Martínez, C. Redondo, F. Castaño. Int. J. Mass Spectr., **246**, 105 (2005). DOI: 10.1016/j.ijms.2005.08.006

[18] M. Tarana, K. Houfek, J. Horáček, I.I. Fabrikant. Phys. Rev. A, **84**, 052717 (2011). DOI: 10.1103/PhysRevA.84.052717

[19] V.V. Afrosimov, A.A. Basalaev, B. Fastrup, E. Horsdal-Pedersen, M.N. Panov, A.V. Tulub, D.S. Yakovlev. J. Phys. B: At. Mol. Opt. Phys., **36**, 1991 (2003).

[20] D. Wang, Y. Fan, Z. Zhao, G. Min, X. Zhang. J. Phys. B: At. Mol. Opt. Phys., **49**, 165201 (2016). DOI: 10.1088/0953-4075/49/16/165201

[21] N. Das, S. De, P. Bhatt, C.P. Safvan, A. Majumdar. J. Chem. Phys., **158**, 084307 (2023). DOI: 10.1063/5.0135440

[22] G.M.J. Barca, C. Bertoni, L. Carrington, D. Datta, N. De Silva, J.E. Deustua, D.G. Fedorov, J.R. Gour, A.O. Gunina, E. Guidez, T. Harville, S. Irle, J. Ivanic, K. Kowalski, S.S. Leang, H. Li, W. Li, J.J. Lutz, I. Magoulas, J. Mato, V. Mironov, H. Nakata, B.Q. Pham, P. Piecuch, D. Poole, S.R. Pruitt, A.P. Rendell, L.B. Roskop, K. Ruedenberg, T. Sattasathuchana, M.W. Schmidt, J. Shen, L. Slipchenko, M. Sosonkina, V. Sundriyal, A. Tiwari, J.L. Galvez Vallejo, B. Westheimer, M. Włoch, P. Xu, F. Zahariev, M.S. Gordon. J. Chem. Phys., **152** (15), 154102 (2020). https://doi.org/10.1063/5.0005188

[23] *NIST Mass Spectrometry Data Center, NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology*, Eds. P.J. Linstrom, W.G. Mallard (Gaithersburg MD, 20899), https://doi.org/10.18434/T4D303

[24] A.V. Tulub, K.V. Simon. J. Struct, Chem. **48** (Suppl.) S79 (2007).

[25] N.S. Ham. Uspekhi khimii, **XXXII** (8), 1010 (1963) (in Russian).

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