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Pogrebnaya, Tatiana P.

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## Calculation of the Thermodynamic Characteristics of Ions in Vapor over Sodium Fluoride

T. P. Pogrebnaya, A. M. Pogrebnoi, and L. S. Kudin

Ivanovo State University of Chemical Technology, Ivanovo, Russia

e-mail: pgamtp@mail.ru

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**Abstract**—The geometric parameters, normal vibration frequencies, and thermochemical characteristics of the ions present in vapor over sodium fluoride,  $\text{Na}_2\text{F}^+$ ,  $\text{Na}_3\text{F}_2^+$ ,  $\text{NaF}_2^-$ , and  $\text{Na}_2\text{F}_3^-$ , were calculated ab initio by the Hartree–Fock method and taking into account electron correlation. The main equilibrium configuration of all ions was found to be the linear configuration of  $D_{\infty h}$  symmetry. Pentaatomic ions could also exist as two isomers, planar cyclic of  $C_{2v}$  symmetry and bipyramidal of  $D_{3h}$  symmetry. Their energies were higher than that of the  $D_{\infty h}$  isomers, and their contents in vapor were negligibly low. The energies and enthalpies of dissociation of the ions with the elimination of the NaF molecule were calculated. The enthalpies of formation of the ions were obtained.

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### INTRODUCTION

The  $\text{Na}_2\text{F}^+$ ,  $\text{Na}_3\text{F}_2^+$ , and  $\text{NaF}_2^-$  ionic associates were experimentally observed in saturated vapor over sodium fluoride by high-temperature mass spectrometry [1–3]. The authors measured the equilibrium constants of ion-molecular reactions, determined their enthalpies, and calculated the enthalpies of formation of the ions.

The determination of the thermochemical characteristics of ions from the mass spectrometry data requires information about their structure and vibrational frequencies. In [1–3], these data were either obtained by calculations within the framework of the ionic model [4–6] or estimated by the comparative method.

The current level of nonempirical calculations allows more reliable information to be obtained about the geometry and vibrational frequencies of the ions under consideration and thereby refine their thermochemical characteristics.

The first ab initio calculations of the thermochemical characteristics of the triatomic  $\text{M}_2\text{F}^+$  and  $\text{MF}_2^-$  ions ( $\text{M} = \text{Li}$  and  $\text{Na}$ ) were performed by the Hartree–Fock (HF) method in [7–9]. In [10], the  $\text{Li}_2\text{F}^+$  and  $\text{Li}_3\text{F}_2^+$  ions were studied theoretically taking electron correlation into account.

In this work, we performed a nonempirical study of the  $\text{Na}_2\text{F}^+$ ,  $\text{Na}_3\text{F}_2^+$ ,  $\text{NaF}_2^-$ , and  $\text{Na}_2\text{F}_3^-$  ions with the inclusion of electron correlation. Our goals were:

(1) to determine the stablest equilibrium geometric configuration, geometric parameters, and normal vibration frequencies of the ions;

(2) reveal possible isomers among the alternative structures of the  $\text{Na}_3\text{F}_2^+$  and  $\text{Na}_2\text{F}_3^-$  pentaatomic ions;

(3) determine the enthalpies of dissociation of the ions;

(4) calculate the thermodynamic functions of the ions and repeat experimental data processing [1, 3] according to the third law of thermodynamics; and

(5) determine the enthalpies of formation of the ions.

### METHOD OF CALCULATIONS

The calculations were performed using the Hartree–Fock–Roothaan approximation, Möller–Plesset second- (MP2) and fourth-order (MP4) perturbation theory, the density functional theory method DFT B3LYP5, and the configuration interaction method including single and double excitations (CISD) and taking into account corrections for quartic excitations (CISD + Q). The frozen core in MP2, MP4, and CISD calculations contained the 1s Na and F orbitals; all the virtual orbitals were included.

The calculations were performed using the GAMESS package [11], the McLean–Chandler (12s9p)/[6s5p] basis set for Na [12], and the valence triple-zeta (10s6p)/[5s3p] basis set for F [13] augmented by the diffuse *s*- and *p* functions with the exponents  $\xi(s) = 0.125$  [14] and  $\xi(p) = 0.074$  [15]. In addition, these basis sets were augmented by the polarization six-

**Table 1.** Characteristics of the  $\text{Na}_2\text{F}^+$  and  $\text{NaF}_2^-$  ions and the energies of dissociation of the ions with the elimination of the NaF molecule

Property	$\text{Na}_2\text{F}^+, D_{\infty h}$				$\text{NaF}_2^-, D_{\infty h}$			
	HF	MP2	DFT	CISD	HF	MP2	DFT	CISD
$R_e$	2.018	2.049	2.028	2.033	2.040	2.079	2.058	2.057
$-E$	423.125462	423.574600	424.299743	423.571476	360.916725	361.477408	362.113934	361.466575
$\omega_1 (\Sigma_g^+)$	298	282	290	290	322	303	311	314
$\omega_2 (\Sigma_u^+)$	528	504	517	518	493	466	481	484
$\omega_3 (\Pi_u)$	117	115	115	118	124	120	123	122
$A_2$	2.66	2.56	2.58	2.60	2.78	2.61	2.57	2.69
$A_3$	4.70	4.64	4.36	4.62	4.88	4.62	4.34	4.74
$\Delta E$	262	255	255	254	263	257	257	245
$-\Delta\epsilon$	3.0	3.1	3.2	3.2	3.2	3.0	3.2	3.1

Note:  $R_e(\text{Na-F})$ , Å, is the equilibrium internuclear distance;  $E$ , au, is the total energy;  $\omega_i$ ,  $\text{cm}^{-1}$ , is the normal vibration frequency;  $A_i$ ,  $\text{D}^2/(\text{amu } \text{Å}^2)$ , is the IR band intensity;  $\Delta E$ , kJ/mol, is the reaction energy; and  $\Delta\epsilon$ , kJ/mol, is the correction for the zero-point vibrational energy.

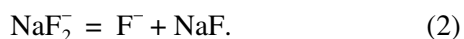
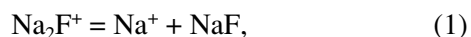
component  $d$  functions with the exponents  $\xi(d) = 0.175$  (Na) [16] and  $\xi(d) = 0.9$  (F) [15].

Equilibrium geometric parameter and vibrational frequency calculations were performed analytically in the Hartree–Fock approximation and numerically at the other levels using the options provided by the GAMESS package.

## RESULTS AND DISCUSSION

*The  $\text{Na}_2\text{F}^+$  and  $\text{NaF}_2^-$  ions.* The calculated characteristics of the triatomic isoelectronic  $\text{Na}_2\text{F}^+$  and  $\text{NaF}_2^-$  ions obtained in the HF, MP2, DFT B3LYP5, and CISD approximations are listed in Table 1. According to these results, the equilibrium configuration of both ions is a linear configuration of  $D_{\infty h}$  symmetry (figure). The theoretical  $R_e(\text{Na-F})$  internuclear distances, normal vibration frequencies  $\omega_i$ , and intensities of IR spectral bands  $A_i$  obtained in different approximations satisfactorily agree with each other. Hartree–Fock calculations give  $R_e$  values systematically underestimated (by 0.009–0.015 Å) and stretching vibration frequencies, overestimated (by  $\approx 2\%$ ) compared with the values obtained at the highest level of approximation (CISD). Conversely, the MP2 method systematically exaggerates  $R_e$  (by 0.01–0.02 Å) and, accordingly, underestimates stretching vibration frequencies (by 1–3%). DFT calculations give  $R_e$  and  $\omega_i$  molecular constants closest to those obtained in CISD calculations.

We calculated the energies  $\Delta E$  of dissociation of the ions with the elimination of the NaF molecule,



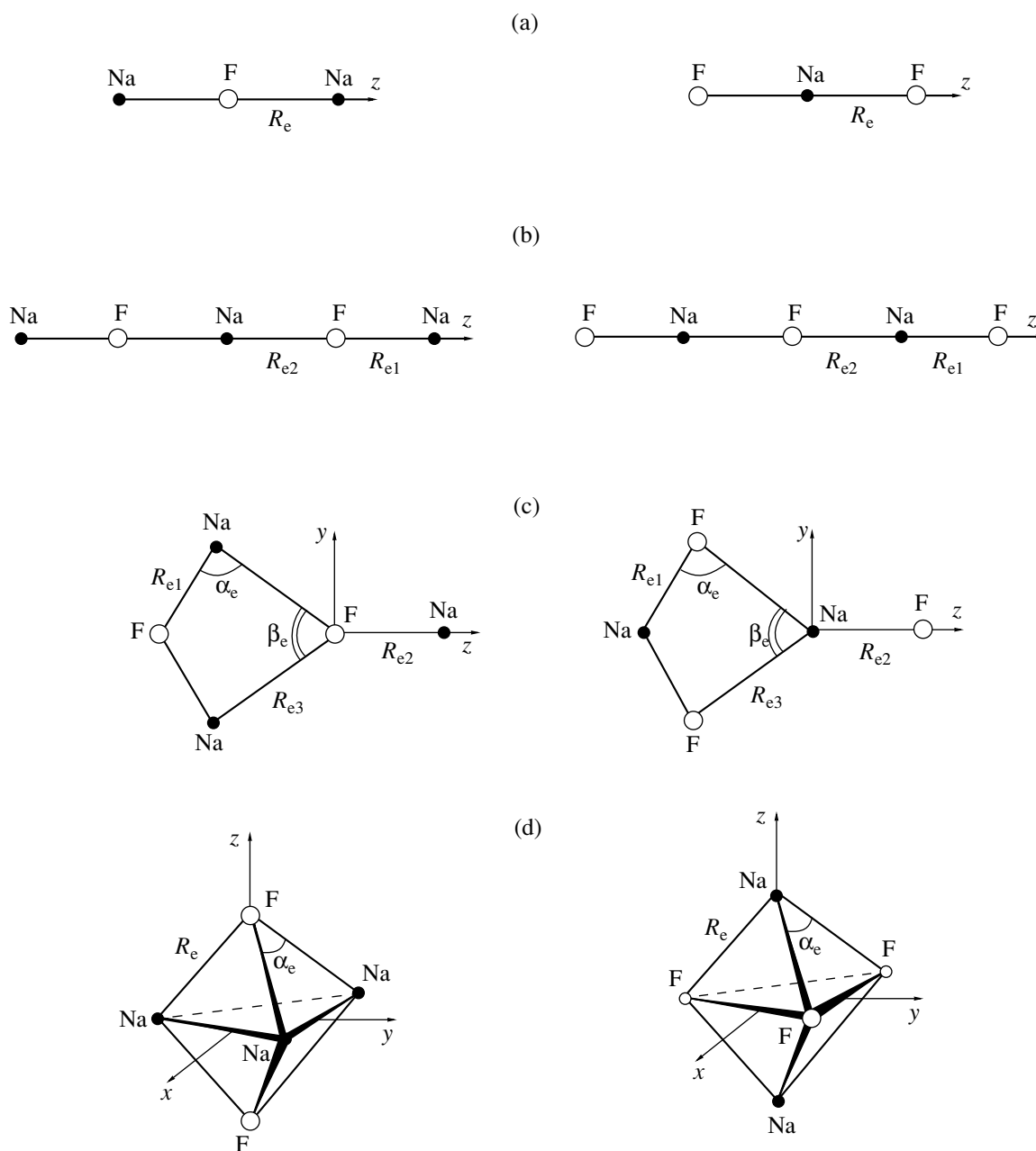
For both ions, the HF method gives dissociation energies higher than those calculated with the inclusion of electron correlation. The  $\Delta E$  values obtained for the  $\text{Na}_2\text{F}^+$  ion in the MP2, DFT, and CISD + Q approximations virtually coincide. At the same time, the CISD + Q method gives the  $\Delta E$  value for  $\text{NaF}_2^-$  which is lower by 12 kJ/mol than that obtained in the MP2 and DFT approximations, probably, because the CISD method is not dimensionally consistent, and the Davidson correction for four-fold excitations [17] includes dimensional consistency not very accurately. For this reason, we refined the  $\Delta E$  values using many-body fourth-order perturbation theory (see below).

Note that, earlier [7–9], the dissociation energies of  $\text{Na}_2\text{F}^+$  and  $\text{NaF}_2^-$  were calculated by the HF method with the double-zeta basis set for F. The energies obtained were 284 ( $\text{Na}_2\text{F}^+$  [8]) and 264 kJ/mol ( $\text{NaF}_2^-$  [9]). The  $\Delta E$  values calculated in this work by the HF method with the triple-zeta basis set were 262 and 263 kJ/mol, respectively; that is, the extension of the basis set for the fluorine atom substantially changed the theoretical  $\Delta E$  value for the  $\text{Na}_2\text{F}^+$  ion. As was mentioned above, the contribution of the electron correlation energy is also fairly substantial and should be taken into account in calculations of  $\Delta E$ .

The correction for the zero-point vibrational energy is

$$\Delta\epsilon = (1/2)hc(\Sigma\omega_{i, \text{prod}} - \Sigma\omega_{i, \text{init}}),$$

where  $\Sigma\omega_{i, \text{prod}}$  and  $\Sigma\omega_{i, \text{init}}$  are the sums of the vibrational frequencies of reaction products and initial substances, respectively. All approximations give approximately equal  $\Delta\epsilon$  values of  $\approx -3$  kJ/mol for both reactions (1) and (2).



Geometric configurations of the (a)  $\text{Na}_2\text{F}^+$  and  $\text{NaF}_2^-$  triatomic and (b)  $\text{Na}_3\text{F}_2^+$  and  $\text{Na}_2\text{F}_3^-$  pentaatomic ions of  $D_{\infty h}$  symmetry, (c) pentaatomic ions of  $C_{2v}$  symmetry, and (d) pentaatomic ions of  $D_{3h}$  symmetry.

Let us compare the characteristics of the  $\text{Na}_2\text{F}^+$  and  $\text{NaF}_2^-$  isoelectronic ions. The  $R_e(\text{Na}-\text{F})$  distance is larger by  $\approx 0.03 \text{ \AA}$  and the antisymmetric stretching vibration frequency  $\omega_2 (\Sigma_u^+)$  lower by approximately 10% in the  $\text{NaF}_2^-$  negative ion. At the same time, the totally symmetrical vibration frequency  $\omega_1 (\Sigma_g^+)$  of the negative ion is higher by 7–8%. The  $A_2$  and  $A_3$  intensities of IR spectral bands are approximately equal for the two ions. The stabilities of both positive and negative triatomic ions with respect to decomposition reac-

tions (1) and (2) are also approximately equal, of 255 and 257 kJ/mol, respectively, according to MP2 and DFT calculations.

*The  $\text{Na}_3\text{F}_2^+$  and  $\text{Na}_2\text{F}_3^-$  ions.* Several geometric configurations were considered for the pentaatomic ions,<sup>1</sup> including linear of  $D_{\infty h}$  symmetry, planar cyclic of  $C_{2v}$

<sup>1</sup> Note that the  $\text{Na}_2\text{F}_3^-$  negative ion was not observed experimentally, but  $\text{M}_2\text{X}_3^-$  ions were recorded for the other alkali metal halides, for instance, KF [1], KCl [18], and CsI [19].

**Table 2.** Characteristics of the  $\text{Na}_3\text{F}_2^+$  and  $\text{Na}_2\text{F}_3^-$  ions and the energies of dissociation of the ions with the elimination of the NaF molecule

Property	$\text{Na}_3\text{F}_2^+, D_{\infty h}$			$\text{Na}_2\text{F}_3^-, D_{\infty h}$		
	HF	MP2	DFT	HF	MP2	DFT
$R_{e1}$	1.995	2.025	2.005	2.013	2.050	2.030
$R_{e2}$	2.064	2.094	2.073	2.070	2.101	2.081
$-E$	684.565088	685.349712	686.529348	622.356625	623.252688	624.343794
$\omega_1 (\Sigma_g^+)$	512	489	498	482	458	467
$\omega_2 (\Sigma_g^+)$	178	167	172	181	168	173
$\omega_3 (\Sigma_u^+)$	542	521	531	524	501	512
$\omega_4 (\Sigma_u^+)$	347	332	339	378	358	366
$\omega_5 (\Pi_g)$	90	92	90	92	89	91
$\omega_6 (\Pi_u)$	140	141	140	142	134	138
$\omega_7 (\Pi_u)$	28	30	28	28	29	30
$A_3$	4.85	4.66	4.71	4.78	4.50	4.52
$A_4$	0.11	0.12	0.13	0.29	0.31	0.29
$A_6$	7.41	7.09	6.69	7.50	7.04	6.62
$A_7$	0.92	0.91	0.95	0.96	0.96	0.94
$\Delta E$	205	201	199	206	202	199
$-\Delta \epsilon$	3.4	3.6	3.6	3.8	3.7	3.7

Note: The  $E$  and  $\Delta E$  values were also calculated in the CISD + Q approximation, which gave  $E = -685.335710$  au and  $\Delta E = 180$  kJ/mol for  $\text{Na}_3\text{F}_2^+$  and  $E = -623.226503$  au and  $\Delta E = 169$  kJ/mol for  $\text{Na}_2\text{F}_3^-$  (see text); see Table 1 for notation.

symmetry, and bipyramidal of  $D_{3h}$  symmetry (figure). For each configuration, geometric parameters were optimized and normal vibration frequencies, IR spectrum band intensities, and energy stability calculated. The most stable structure had a linear configuration of  $D_{\infty h}$  symmetry.

The calculated characteristics of pentaatomic ions of  $D_{\infty h}$  symmetry obtained in the HF, MP2, and DFT B3LYP5 approximations are listed in Table 2. We see that the equilibrium internuclear distances, vibrational frequencies, and IR spectrum band intensities obtained using different approximations satisfactorily agree with each other. HF calculations give  $R_e$  values for both terminal and bridge bonds smaller by  $\approx 0.01$  Å than those obtained using the DFT method. Conversely, MP2 calculations exaggerate  $R_e$  by  $\approx 0.02$  Å compared with DFT values. Accordingly, the theoretical stretching vibration frequencies of both ions,  $\omega_1$ ,  $\omega_2$ ,  $\omega_3$ , and  $\omega_4$ , are higher by 2–4% in HF and lower by 2–3% in MP2 calculations than those obtained using the DFT method. The Na–F bridge bond is longer than the terminal bond by 0.07 and 0.05 Å in positive and negative ions, respectively.

The  $\Delta E$  energies of ion decomposition with the elimination of the NaF molecule were calculated for the linear configurations of the  $\text{Na}_3\text{F}_2^+$  and  $\text{Na}_2\text{F}_3^-$  ions,



The  $\Delta E$  values calculated by the HF method were exaggerated by 3–7 kJ/mol compared with calculations in the MP2 and DFT approximations. The corrections for zero-point energies obtained using these three approximations were approximately equal, of  $-3.6$  kJ/mol for  $\text{Na}_3\text{F}_2^+$  and  $-3.7$  kJ/mol for  $\text{Na}_2\text{F}_3^-$ .

In addition, the CISD + Q approximation was used to calculate the total energies of the  $\text{Na}_3\text{F}_2^+$  and  $\text{Na}_2\text{F}_3^-$  ions and the energies of reactions (3) and (4). For the  $\text{Na}_3\text{F}_2^+$  ion at  $R_{e1} = 2.005$  Å and  $R_{e2} = 2.073$  Å,<sup>2</sup> we obtained  $E = -685.335710$  au and  $\Delta E(3) = 180$  kJ/mol. The results for  $\text{Na}_2\text{F}_3^-$  at  $R_{e1} = 2.026$  Å and  $R_{e2} = 2.079$  Å (optimized at the CISD level) were  $E = -623.226503$  au and  $\Delta E(4) = 169$  kJ/mol. We see that the energies of reactions (3) and (4) obtained in the CISD + Q approximation were substantially lower (by 20 kJ/mol for  $\text{Na}_3\text{F}_2^+$  and 30 kJ/mol for  $\text{Na}_2\text{F}_3^-$ ) than the energies calculated at the HF and MP2 levels. Compared with the triatomic ions, the pentaatomic ions are characterized

<sup>2</sup>The  $R_{e1}$  and  $R_{e2}$  internuclear distances were optimized using the DFT approximation.

**Table 3.** Characteristics of the  $\text{Na}_3\text{F}_2^+$  and  $\text{Na}_2\text{F}_3^-$  ions of  $C_{2v}$  symmetry (planar cycle)

Property	$\text{Na}_3\text{F}_2^+$			$\text{Na}_2\text{F}_3^-$		
	HF	MP2	DFT	HF	MP2	DFT
$R_{e1}$	2.019	2.052	2.034	2.019	2.052	2.035
$R_{e2}$	2.045	2.079	2.056	2.059	2.097	2.076
$R_{e3}$	2.259	2.289	2.270	2.293	2.330	2.316
$\alpha_e$	96.5	96.1	95.8	103.4	103.7	104.3
$\beta_e$	83.5	83.6	83.3	87.4	87.7	87.9
$h_1$	29.2	25.7	27.6	33.0	29.5	32.0
$\omega_1 (A_1)$	439 (0.36)	419 (0.85)	432 (0.97)	429 (0.79)	407 (0.62)	397 (0.78)
$\omega_2 (A_1)$	428 (3.53)	408 (2.88)	419 (2.66)	412 (2.87)	394 (2.88)	379 (2.61)
$\omega_3 (A_1)$	213 (0.56)	207 (0.51)	209 (0.51)	217 (0.96)	207 (0.83)	200 (0.93)
$\omega_4 (A_1)$	169 (0.16)	161 (0.16)	161 (0.16)	167 (0.20)	159 (0.24)	159 (0.15)
$\omega_5 (B_1)$	176 (3.42)	169 (3.21)	168 (3.06)	176 (3.53)	169 (3.24)	171 (3.08)
$\omega_6 (B_1)$	61 (0.10)	59 (0.10)	65 (0.09)	61 (0.07)	59 (0.08)	74 (0.06)
$\omega_7 (B_2)$	443 (2.23)	423 (2.08)	431 (2.03)	453 (2.34)	433 (2.17)	419 (2.14)
$\omega_8 (B_2)$	204 (1.70)	202 (1.62)	201 (1.57)	185 (1.67)	181 (1.58)	166 (1.59)
$\omega_9 (B_2)$	98 (0.10)	95 (0.11)	96 (0.10)	107 (0.18)	103 (0.18)	108 (0.09)
$\mu_e$	11.38	11.45	11.18	11.4	11.6	11.0

Note: Geometric parameters:  $R_e$  in Å and  $\alpha_e$  and  $\beta_e$  in degrees (see figure); relative isomer energies  $h_1$  in kJ/mol, normal vibration frequencies  $\omega_i$  in  $\text{cm}^{-1}$ , and dipole moment  $\mu_e$  in D. Parenthesized values are the intensities of IR spectrum bands in  $\text{D}^2/(\text{amu} \text{Å}^2)$ .

**Table 4.** Characteristics of the  $\text{Na}_3\text{F}_2^+$  and  $\text{Na}_2\text{F}_3^-$  ions of  $D_{3h}$  symmetry (bipyramid)

Property	$\text{Na}_3\text{F}_2^+$			$\text{Na}_2\text{F}_3^-$		
	HF	MP2	DFT	HF	MP2	DFT
$R_e$	2.164	2.198	2.181	2.165	2.201	2.185
$\alpha_e$	88.3	88.1	88.0	93.4	93.4	93.5
$h_2$	31.2	24.2	26.8	31.3	25.9	32.6
$\omega_1 (A_1')$	394 (0)	369 (0)	376 (0)	368 (0)	349 (0)	360 (0)
$\omega_2 (A_1')$	258 (0)	242 (0)	246 (0)	265 (0)	252 (0)	246 (0)
$\omega_3 (A_2'')$	314 (4.23)	298 (3.97)	298 (3.81)	295 (4.27)	282 (3.98)	292 (3.64)
$\omega_4 (E')$	321 (3.62)	309 (3.42)	310 (3.29)	338 (3.51)	324 (3.33)	346 (2.97)
$\omega_5 (E')$	174 (0.59)	167 (0.55)	168 (0.52)	181 (0.93)	171 (0.84)	166 (0.90)
$\omega_6 (E'')$	230 (0)	223 (0)	219 (0)	223 (0)	217 (0)	226 (0)

Note: See Table 3 for notation and units.

by a larger difference between the  $\Delta E$  values calculated in the CISD + Q and the other approximations, which can be caused by a stronger influence of dimensional inconsistency of the CISD + Q method. For this reason, the dissociation energies of the ions were refined using fourth-order many-body perturbation theory MP4.

The results obtained in calculations of two alternative structures of the  $\text{Na}_3\text{F}_2^+$  and  $\text{Na}_2\text{F}_3^-$  ions (planar cyclic of  $C_{2v}$  symmetry and bipyramidal of  $D_{3h}$  symme-

try) are listed in Tables 3 and 4. According to these results, both structures have no imaginary frequencies; that is, both configurations correspond to potential energy surface minima and are isomers. The relative energies of the isomers  $h_1$  and  $h_2$  are the differences of the total energies of the ions of different symmetries,

$$h_1 = E(C_{2v}) - E(D_{\infty h}),$$

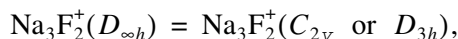
$$h_2 = E(D_{3h}) - E(D_{\infty h}).$$

In addition to the  $h_1$  and  $h_2$  values given in Tables 3 and 4, the relative isomer energies were also calculated in the CISD + Q approximation using fixed geometric parameters obtained in the DFT approximation. The  $h_1$  and  $h_2$  values were 25.3 and 22.8 kJ/mol for the  $\text{Na}_3\text{F}_2^+$  positive ion and 28.8 and 23.1 kJ/mol for the  $\text{Na}_2\text{F}_3^-$  negative ion; that is, the bipyramidal isomer of both ions was more stable energetically than the cyclic isomer.

We calculated the relative contents of both isomers of the  $\text{Na}_3\text{F}_2^+$  positive ion in equilibrium vapor over the temperature range 1000–1200 K (this corresponded to the temperatures of measurements). The calculations were performed by the equation

$$\Delta_r H^\circ(0 \text{ K}) = -RT \ln(p_{\text{iso}}/p_{\text{lin}}) + T\Delta\Phi^\circ(T),$$

where  $\Delta_r H^\circ(0 \text{ K})$  is the enthalpy of the isomerization reaction



$p_{\text{iso}}/p_{\text{lin}}$  is the ratio of the pressure of ions of  $C_{2v}$  or  $D_{3h}$  symmetry to that of ions with a linear geometric configuration of  $D_{\infty h}$  symmetry, and  $\Delta\Phi^\circ(T)$  is the reduced Gibbs energy of the isomerization reaction. The  $\Delta_r H^\circ(0 \text{ K})$  values were calculated from the relative isomer energies  $h$  according to CISD + Q calculations taking into account corrections for zero-point energy. The reduced Gibbs energies were obtained in the rigid rotator–harmonic oscillator approximation from the molecular constants found in DFT calculations. At 1000 K, the fractions of the cyclic and bipyramidal  $\text{Na}_3\text{F}_2^+$  isomers were 1.1 and 0.05%, respectively. The relative fractions of both isomers slightly increased as the temperature grew. Although bipyramidal isomers were stabler energetically, their content in vapor was substantially lower than that of ions of  $C_{2v}$  symmetry because of the influence of the entropy factor.

The geometric parameters and vibrational frequencies of the  $\text{Na}_2\text{F}_3^-$  negative ion were close to those of the positive ion (Tables 3, 4), and the  $h$  value was slightly higher than for  $\text{Na}_3\text{F}_2^+$ . This leads us to conclude that the contents of the isomeric forms of the  $\text{Na}_2\text{F}_3^-$  ion in vapor were also negligibly low.

*The enthalpies of ion-molecular reactions and enthalpies of formation of the ions.* The ion dissociation energies were refined by calculating the  $\Delta E$  values at the level of fourth-order perturbation theory with the inclusion of single, double, triple, and quadruple excitations (SDTQ-MP4). Unlike CISD + Q, this method is dimensionally consistent. In addition, the correction for the basis set superposition error was included by the counterpoise method [20]. According to this method, the energies of the dissociation products are calculated with the same basis set as that used in calculations of the complex ion energy. For instance, the energy of

reaction (1) corrected for the basis set superposition error was determined by the equation

$$\Delta E_c(1) = E(\text{Na}^+/\text{Na}_2\text{F}^+) + E(\text{NaF}/\text{Na}_2\text{F}^+) - E(\text{Na}_2\text{F}^+),$$

where  $E(\text{Na}^+/\text{Na}_2\text{F}^+)$  and  $E(\text{NaF}/\text{Na}_2\text{F}^+)$  are the energies of the  $\text{Na}^+$  ion and  $\text{NaF}$  molecule, respectively, calculated with the same basis set as that used in calculations of the  $\text{Na}_2\text{F}^+$  ion energy. The  $\Delta E_c$  values for reactions (2)–(4) were calculated similarly. In calculations of reaction product energies, the missing basis functions were centered at the distances equal to the equilibrium distances in the complex ion of  $D_{\infty h}$  symmetry. This approach to our problem is quite acceptable, because the complex ions of  $D_{\infty h}$  symmetry contain fragments whose structures slightly differ from those of free particles (dissociation products).

The energies of ion-molecular reactions calculated at the SDTQ-MP4 level with and without taking into account basis set superposition errors ( $\Delta E_c$  and  $\Delta E$ , respectively) are listed in Table 5. We see that the compensation error was of 6–8 kJ/mol for the dissociation of triatomic ions and 10–11 kJ/mol for pentaatomic ions.

The enthalpies of reactions  $\Delta_r H^\circ(0 \text{ K})$  were calculated using zero-point energies  $\Delta\varepsilon$  determined by the DFT method (Tables 1, 2),

$$\Delta_r H^\circ(0 \text{ K}) = \Delta E_c + \Delta\varepsilon.$$

The enthalpies of reactions  $\Delta_r H^\circ(0 \text{ K})$  and the enthalpies of formation of ions  $\Delta_f H^\circ(0 \text{ K})$  obtained in this work were compared with the literature data (Table 5). In mass spectrometric studies [1–3], the equilibrium constants of ion-molecular reactions were determined and the second and third laws of thermodynamics were used to determine the enthalpies of heterophase reactions of type (1), where  $\text{NaF}$  was in the condensed state. Experimental studies of negative ions were complicated by exceedingly low ion current intensities, especially for the  $\text{F}^-$  ion [1]. For this reason, only the lower boundary of the enthalpy of dissociation (2) was obtained for the  $\text{Na}_2\text{F}_2^-$  ion in [1].

We repeated the processing of the experimental data from [1, 3] with the use of the thermodynamic functions calculated from the molecular constants obtained in the CISD approximation for triatomic ions. The thermodynamic functions and enthalpies of formation of  $\text{Na}^+$ ,  $\text{F}^-$ , and  $\text{NaF}$  were taken from [21]. The enthalpies of heterophase reactions were recalculated to gas phase conditions using the enthalpy of sublimation of sodium fluoride  $\Delta_s H^\circ(\text{NaF}, 0 \text{ K}) = 280.700 \text{ kJ/mol}$  [21].

We see from Table 5 that the  $\Delta_r H^\circ(0 \text{ K})$  and  $\Delta_f H^\circ(0 \text{ K})$  values calculated in this work for  $\text{Na}_2\text{F}^+$  triatomic positive ions are in agreement with the experimental data [1, 3]. The calculation results more closely agree with the values obtained using the second law of thermodynamics. The discrepancies between our values and the values obtained according to the third law of thermodynamics decrease as a result of reprocessing with new thermodynamic functions. Agreement



**Table 5.** Energies and enthalpies of ion-molecular reactions and enthalpies of formation of ions, kJ/mol, (I) obtained in this work in the SDTQ-MP4 approximation and (II) reported in the literature

Reaction	$\Delta E$	$\Delta E_c^a$	$\Delta_r H^\circ(0\text{ K})$		$\Delta_f H^\circ(0\text{ K})$	
			I	II	I	II
$\text{Na}_2\text{F}^+ = \text{Na}^+ + \text{NaF}$	256	250	$247 \pm 2$	$248 \pm 6$ [3] <sup>b</sup> $243 \pm 20$ [1] <sup>b</sup> $242 \pm 20$ [2] <sup>b</sup> $256 \pm 4$ [1–3] <sup>c</sup> $251 \pm 4$ [1, 3] <sup>d</sup>	$63 \pm 2$	$62 \pm 6$ [3] $67 \pm 20$ [1] $56 \pm 5$ [2] $59 \pm 4$ [1–3] $52^{e\%}$ [1]
$\text{NaF}_2^- = \text{F}^- + \text{NaF}$	258	250	$247 \pm 2$	$\geq 247 \pm 8$ [1] <sup>c</sup> $\geq 245 \pm 8$ [1] <sup>d</sup>	$-791 \pm 2$	$\geq -789 \pm 8$ [1] $-802^e$ [1]
$\text{Na}_3\text{F}_2^+ = \text{Na}_2\text{F}^+ + \text{NaF}$	202	192	$189 \pm 4$	$195 \pm 8$ [3] <sup>d</sup> $201 \pm 8$ [2]	$-420 \pm 4$	$-431 \pm 13$ [2] $-435^e$ [1] $-430^f$ [1, 3]
$\text{Na}_3\text{F}_2^+ + \text{Na}^+ = 2\text{Na}_2\text{F}^+$	-54	-56	$-56 \pm 4$	$-60 \pm 8$ [2] <sup>b</sup> $-50$ [2] <sup>c</sup> $-49$ [1] <sup>c</sup> $-50$ [1] <sup>d</sup>		
$\text{Na}_2\text{F}_3^- = \text{NaF}_2^- + \text{NaF}$	203	192	$188 \pm 4$	–	$-1273 \pm 4$	$-1283^e$ [1]

<sup>a</sup>  $\Delta E_c$  are the energies of ion-molecular reactions calculated taking into account basis set superposition errors.

<sup>b</sup> Calculated using the second law of thermodynamics.

<sup>c</sup> Calculated using the third law of thermodynamics.

<sup>d</sup> Experimental data reprocessing according to the third law of thermodynamics with the use of the thermodynamic functions obtained in this work.

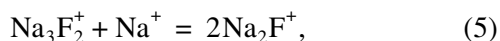
<sup>e</sup> Calculations by the ionic model.

<sup>f</sup> Calculations of the enthalpy of the reaction  $\text{Na}_3\text{F}_2^+ = \text{Na}^+ + 2[\text{NaF}]$  according to the third law of thermodynamics with the use of the thermodynamic functions obtained in this work. The relative ion current intensities were taken from the mass spectrometric data (one measurement from [1] and two measurements from [3]).

Note: The thermodynamic functions were calculated from the molecular constants obtained in the CISD approximation for triatomic ions and in the DFT approximation for pentaatomic ions. The errors in the theoretical enthalpy values were estimated by comparing the  $\Delta E$  energies obtained in the MP2, DFT, and MP4 calculations.

between our values for the negative triatomic ion and estimates made in [1] on the basis of the experimental data and calculations according to the ionic model is also quite satisfactory.

For the  $\text{Na}_3\text{F}_2^+$  pentaatomic ion, the ion-ion reaction



was studied experimentally in [1]. For this reaction, equilibrium constants were obtained over a wide temperature range (1021–1200 K) and the data were processed according to the second and third laws of thermodynamics. Reaction (3) was not directly studied in [1], but the enthalpy of reaction (3) can be easily found as the sum of the enthalpies of reactions (1) and (5). We calculated the enthalpy of reaction (5) using the total energies of the  $\text{Na}^+$ ,  $\text{Na}_2\text{F}^+$ , and  $\text{Na}_3\text{F}_2^+$  ions calculated at the SDTQ-MP4 level with the geometric parameters optimized in the MP2 approximation; the correction for zero-point energy was 0.2 kJ/mol. The enthalpy of reaction (5) obtained this way,  $-56 \pm 4$  kJ/mol, was in agreement with the experimental data [1, 2]. The sum of the

enthalpies of reactions (1) and (5) is  $251 + (-60) = 191$  kJ/mol according to the experimental data [1, 2]. This is also in agreement with the enthalpy of reaction (3) obtained in this work,  $\Delta_r H(0\text{ K}) = 189 \pm 4$  kJ/mol.

Gusarov [1] estimated the enthalpy of formation of the negative pentaatomic ion on the basis of the ionic model,  $\Delta_f H^\circ(\text{Na}_2\text{F}_3^-, 0\text{ K}) = -1283$  kJ/mol. This value is lower by 10 kJ/mol than that obtained in this work ( $-1273 \pm 4$  kJ/mol). The enthalpies of formation of the other ions estimated in [1] within the framework of the ionic model also do not contradict our results. Note that they are systematically lower by approximately 10 kJ/mol for all ions in comparison with our data.

## CONCLUSIONS

To summarize, all the theoretical approximations used in this work (HF, MP2, DFT B3LYP5, and CISD) give the parameters of the  $\text{Na}_2\text{F}^+$ ,  $\text{Na}_3\text{F}_2^+$ ,  $\text{NaF}_2^-$ , and  $\text{Na}_2\text{F}_3^-$  ions with an accuracy acceptable for thermodynamic function calculations. The optimum method for

geometric parameter, vibrational frequency, and IR band intensity calculations (from the point of view of the accuracy of the results and requirements on computer resources) is the DFT method.

The energies and enthalpies of reactions can be calculated using the MP2, DFT, and MP4 methods. HF calculations exaggerate reaction energies by ~20 kJ/mol. At the same time, the CISD + Q method underestimates these values by 20–30 kJ/mol because of dimensional inconsistency. The theoretical enthalpies of ion-molecular reactions and enthalpies of formation of ions obtained in this work are in agreement with the results of mass spectrometric measurements.

The isoelectronic positive and negative ions  $\text{Na}_2\text{F}^+$ ,  $\text{NaF}_2^-$  and  $\text{Na}_3\text{F}_2^+$ ,  $\text{Na}_2\text{F}_3^-$  have closely similar parameters. Their equilibrium configurations ( $D_{\infty h}$  symmetry) and vibrational spectra (vibrational frequencies and IR spectrum band intensities) are similar. Their dissociation energies with the elimination of the NaF molecule are approximately equal, 250 kJ/mol for triatomic and 192 kJ/mol for pentaatomic ions. The  $\text{Na}_3\text{F}_2^+$  and  $\text{Na}_2\text{F}_3^-$  pentaatomic ions have two isomers each, cyclic of  $C_{2v}$  symmetry and bipyramidal of  $D_{2h}$  symmetry. The contents of the isomeric forms in vapor are low.

The characteristics of the  $\text{Na}_2\text{F}^+$  and  $\text{Na}_3\text{F}_2^+$  positive ions are closely similar to those of the  $\text{Li}_2\text{F}^+$  and  $\text{Li}_3\text{F}_2^+$  ions studied in [10] by the HF and CISD methods. The  $\text{Li}_2\text{F}^+ - \text{Na}_2\text{F}^+$  and  $\text{Li}_3\text{F}_2^+ - \text{Na}_3\text{F}_2^+$  ions have the same equilibrium configurations ( $D_{\infty h}$  symmetry) and similar vibrational spectra. The enthalpies of dissociation of the lithium ions are slightly higher than those of their sodium counterparts, compare 288 and 247 kJ/mol for  $\text{Li}_2\text{F}^+$  and  $\text{Na}_2\text{F}^+$  and 215 and 189 kJ/mol for  $\text{Li}_3\text{F}_2^+$  and  $\text{Na}_3\text{F}_2^+$ , respectively. The  $\text{Li}_3\text{F}_2^+$  ion can exist as a cyclic isomer of  $C_{2v}$  symmetry, but the bipyramidal structure is a saddle point. For  $\text{Na}_3\text{F}_2^+$ , both alternative configurations are isomers.

Similar characteristics of positive and negative ions,  $\text{Na}_2\text{F}^+ - \text{NaF}_2^-$  and  $\text{Na}_3\text{F}_2^+ - \text{Na}_2\text{F}_3^-$ , lead us to suggest that the properties of the other isoelectronic pairs of alkali metal halide ions,  $\text{K}_2\text{Cl}^+ - \text{KCl}_2^-$  and  $\text{K}_3\text{Cl}_2^+ - \text{K}_2\text{Cl}_3^-$ ;  $\text{Rb}_2\text{Br}^+ - \text{RbBr}_2^-$  and  $\text{Rb}_3\text{Br}_2^+ - \text{Rb}_2\text{Br}_3^-$ , and  $\text{Cs}_2\text{I}^+ - \text{CsI}_2^-$  and  $\text{Cs}_3\text{I}_2^+ - \text{Cs}_2\text{I}_3^-$ , should also be similar.

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