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# Structure and Vibrational Spectra of Cluster Ions over Rubidium Iodide by Computational Chemistry

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**Abstract**—The properties of  $\text{Rb}_2\text{I}^+$ ,  $\text{RbI}_2^-$ ,  $\text{Rb}_3\text{I}_2^+$  and  $\text{Rb}_2\text{I}_3^-$  ions were studied using two quantum chemical methods, DFT and Møller–Plesset perturbation theory of the 2<sup>nd</sup> order. The effective core potential with Def2-QZVP basis set for rubidium atom and SDB-aug-cc-pVTZ basis set for iodine atom were used. According to the results, the equilibrium geometric structure of the triatomic ions was found to be linear of  $D_{\infty h}$  symmetry. For the pentaatomic ions, the three isomeric forms were found: the linear ( $D_{\infty h}$ ), the kite-shaped ( $C_{2v}$ ), and the bipyramidal ( $D_{3h}$ ), both for the positive and negative ions. For all species, the equilibrium geometric parameters and vibrational spectra have been determined.

**Index Terms**—rubidium iodide; positive and negative cluster ions; quantum chemical computation; geometric structure; vibrational spectra.

## INTRODUCTION

The cluster ions  $\text{Rb}_2\text{I}^+$ ,  $\text{RbI}_2^-$ ,  $\text{Rb}_3\text{I}_2^+$ , and  $\text{Rb}_2\text{I}_3^-$  have been observed experimentally in saturated vapour over rubidium iodide by mass spectrometric technique [1]. At present the experimental data on the structure and spectra of the ions considered are absent.

These theoretical quantum chemical methods have been proved to be useful tools in attaining the characteristics of ions and molecules [2] especially when experimental methods are not available. Previously the quantum chemical calculations had been carried out for some similar cluster ions, e.g. [3–5].

The aim of this work is to determine the equilibrium geometric structure of the ions  $\text{Rb}_2\text{I}^+$ ,  $\text{RbI}_2^-$ ,  $\text{Rb}_3\text{I}_2^+$ , and  $\text{Rb}_2\text{I}_3^-$ ; to compute the normal vibrational frequencies, and to find out possible isomeric configurations. It had been shown that the ions under consideration occur not in the vapors over rubidium iodide only but emit from the heated solid electrolyte  $\text{RbAg}_4\text{I}_5$  [1] forming intensive ion beams. The determination of the thermochemical characteristics of the cluster ions requires their geometric parameters and vibrational frequencies.

## CALCULATION DETAILS

The calculations were performed using the GAMESS (General Atomic and Molecular Electronic Structure System) software [6], Firefly version 8.0 [7]. Two quantum chemical methods, DFT (Density Functional Theory) and MP2 (Møller–Plesset perturbation theory of the 2<sup>nd</sup> order) have been applied. The effective core potentials with Def2-QZVP basis set for Rb atom [8] and SDB-aug-cc-pVTZ basis set for I atom [9] were taken from the EMSL (The Environmental Molecular Sciences Laboratory, U.S.) Basis Set Library [10, 11] and used in the calculations.

The optimization of the geometric parameters of the ions and the calculations of vibrational frequencies in the harmonic approximation were carried out by the methods implemented in the GAMESS software.

## CALCULATION RESULTS AND DISCUSSION

### Diatomic molecule *RbI*

The equilibrium internuclear distance, the normal vibration frequency, and the dipole moment are given in Table 1 for the RbI molecule. The calculated values are compared with the reference data.

TABLE 1. PROPERTIES OF DIATOMIC MOLECULE RbI.

Quantity	DFT	MP2	Experimental
$R_e(\text{Rb-I})$ , Å	3.256	3.250	3.177 [12, 13]
$\omega_e$ , $\text{cm}^{-1}$	131	133	138.5 [12]
$\mu_e$ , D	11.7	12.1	11.48 [13]

As is seen in Table 1, the results obtained by both methods, MP2 and DFT, agree well with each other. Note that MP2 method gives a shorter distance and higher frequency than DFT method. Compared with the reference data [12, 13], the internuclear distances calculated are overrated about 0.07–0.08 Å and the frequencies are underrated by 4–5%. We expect the similar uncertainties in the values of  $R_e$  and  $\omega_i$  for the tri- and

pentaatomic ions. It is worth to mention here that the data obtained by the MP2 method seem more reliable as they are closer to the experimental values.

### Triatomic ions $Rb_2I^+$ and $RbI_2^-$

The equilibrium structure of both ions is found to be linear of  $D_{\infty h}$  point group symmetry. The calculated characteristics of the triatomic ions  $Rb_2I^+$ , and  $RbI_2^-$  are listed in Table 2. Here and hereafter, are given the equilibrium internuclear distances  $R_e(Rb-I)$  in Å, total electronic energy  $E$  in a.u., frequencies of normal vibrations  $\omega_i$ , in  $cm^{-1}$  and nonzero intensities  $I_i$  in IR spectra in  $D^2 \cdot amu^{-1} \cdot \text{Å}^{-2}$ . The theoretical values obtained by the two methods are generally in an agreement with each other.

TABLE 2. PROPERTIES OF TRIATOMIC IONS  $Rb_2I^+$ ,  $RbI_2^-$  OF LINEAR SYMMETRY

Quantity	$Rb_2I^+$		$RbI_2^-$	
	DFT	MP2	DFT	MP2
$R_e(Rb-I)$	3.397	3.380	3.461	3.435
$E$	-59.53183	-59.27598	-47.11584	-46.89523
$\omega_1 (\Sigma_g^+)$	80	83	64	67
$\omega_2 (\Sigma_u^+)$	115	121	117	124
$\omega_3 (\Pi_u)$	14	17	22	23
$I_2$	0.91	0.87	0.79	0.75
$I_3$	0.72	0.75	0.58	0.60

Comparison between the positive and negative ions shows that the internuclear distance in the  $Rb_2I^+$  ion is shorter by approximately 0.06 Å than in  $RbI_2^-$  whereas the symmetric valence frequency  $\omega_1$  is 16  $cm^{-1}$  (20%) higher, respectively. The deformational frequency  $\omega_3$  of the  $RbI_2^-$  ion is higher than that of the  $Rb_2I^+$  that indicates the more rigid bond is in the negative ion.

### Pentaatomic ions $Rb_3I_2^+$ , and $Rb_2I_3^-$

Several probable geometric configurations of nuclei were considered: linear of  $D_{\infty h}$  symmetry point group, planar cyclic ( $C_{2v}$ ), and bipyramidal ( $D_{3h}$ ). These configurations are shown in Fig. 1, appropriate geometric parameters are indicated.

For each configuration the geometric parameters were optimized, and the frequencies of normal vibrations were calculated. The quantities obtained, namely the equilibrium internuclear distances, valence angles (in degrees), frequencies of normal vibrations, and nonzero intensities in IR spectra are listed in Tables 3–5. In the first column along with the frequencies, the symmetry species of the vibration modes are given.

It is noticeable for the linear configuration (Table 3) the close similarity of the properties of the pentaatomic positive and negative ion, i.e. both internuclear separations (terminal and bridged), each type of vibration mode of the ion  $Rb_3I_2^+$  approximate those of the  $Rb_2I_3^-$ . The results reveal both of these ions to be nonrigid regarding the deformation along the vibration modes  $\omega_5 (\Pi_g)$  and  $\omega_7 (\Pi_u)$ . Moreover for the  $Rb_3I_2^+$ ,

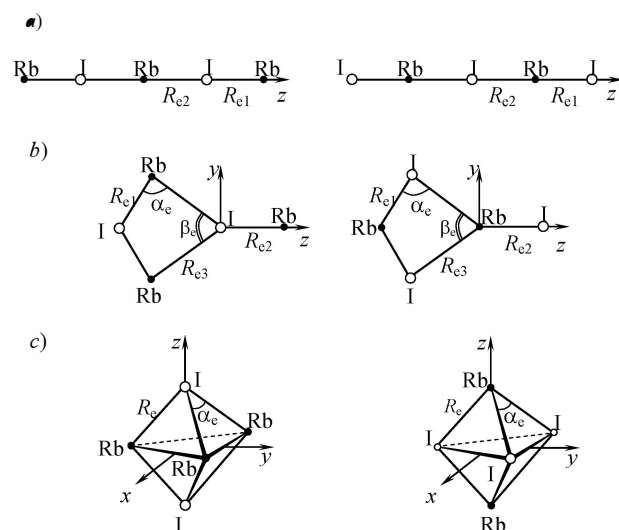


Fig. 1: Geometric configurations of the pentaatomic ions  $Rb_3I_2^+$  and  $Rb_2I_3^-$  with  $D_{\infty h}$  (a),  $C_{2v}$  (b), and  $D_{3h}$  (c) symmetry.

the magnitude of  $\omega_7 (\Pi_u)$  found by the MP2 method was imaginary. The further optimization led to a slightly distorted bent configuration of the  $Rb_3I_2^+$  ion without any energy gain. We accepted the linear configuration for this ion and estimated the  $\omega_7 (\Pi_u) \approx 5 cm^{-1}$  using the similarity to the  $Rb_2I_3^-$  ion. Alike case had been occurred for the  $Cs_2Cl_3^-$  ion [14].

TABLE 3. PROPERTIES OF  $Rb_3I_2^+$  AND  $Rb_2I_3^-$  IONS OF LINEAR SYMMETRY

Quantity	$Rb_3I_2^+$		$Rb_2I_3^-$	
	DFT	MP2	DFT	MP2
$R_{e1}(Rb-I)$	3.353	3.343	3.401	3.384
$R_{e2}(Rb-I)$	3.500	3.464	3.524	3.489
$E$	-95.13670	-94.72374	-82.72104	-82.34335
$\omega_1 (\Sigma_g^+)$	114	120	116	122
$\omega_2 (\Sigma_g^+)$	43	46	39	42
$\omega_3 (\Sigma_u^+)$	120	128	120	127
$\omega_4 (\Sigma_u^+)$	92	96	76	79
$\omega_5 (\Pi_g)$	9	13	16	19
$\omega_6 (\Pi_u)$	18	23	22	22
$\omega_7 (\Pi_u)$	2	(5)	2	5
$I_3$	1.77	1.64	1.65	1.54
$I_4$	0.02	0.05	0.01	0.01
$I_6$	0.90	0.93	0.94	1.05
$I_7$	0.28		0.10	0.03

The properties of the cyclic or kite-shaped structure are given in Table 4. Three nonequivalent internuclear distances,  $R_{e1}$ ,  $R_{e2}$ , and  $R_{e3}$ , and two valence apex angles  $\alpha_e$  and  $\beta_e$  (Fig. 1, b) specify this geometric configuration. The value of  $h_1$  is the relative energy of the cyclic isomer regarding to the linear:

$h_1 = E(C_{2v}) - E(D_{3h})$ . The relative energies  $h_1$  (as well as  $h_2$  for the bipyramidal isomer in Table 5) are given in  $\text{kJ}\cdot\text{mol}^{-1}$ . As is seen, the magnitude of  $h_1$  is not high; it is positive in the DFT method but negative in MP2 for both ions. Actually the cyclic configuration is comparable by energy to the linear isomer.

The shortest distance in the cycle  $R_{e1}(\text{Rb}-\text{I})$  is almost the same for the  $\text{Rb}_3\text{I}_2^+$  and  $\text{Rb}_2\text{I}_3^-$  within one method of calculation, whereas the other two distances,  $R_{e2}$  and  $R_{e3}$ , are shorter for the positive ion by 0.02–0.08 Å. The valence apex angle  $\angle\text{I}-\text{Rb}-\text{I}$ , i.e.  $\alpha_e$  in the  $\text{Rb}_3\text{I}_2^+$  ion or  $\beta_e$  in  $\text{Rb}_2\text{I}_3^-$ , is close to  $90^\circ$  while another angle  $\angle\text{Rb}-\text{I}-\text{Rb}$  ( $\beta_e$  in the  $\text{Rb}_3\text{I}_2^+$  ion or  $\alpha_e$  in  $\text{Rb}_2\text{I}_3^-$ ) is acute,  $80$ – $85^\circ$ . The vibrational spectra for both ions are similar regarding the magnitudes of the frequencies and the IR intensities.

The third geometric configuration, the bipyramidal one, considered here, was found to be isomeric as well. Due to the

TABLE 4. PROPERTIES OF  $\text{Rb}_3\text{I}_2^+$  AND  $\text{Rb}_2\text{I}_3^-$  IONS WITH CYCLIC SHAPE,  $C_{2v}$  SYMMETRY

Quantity	$\text{Rb}_3\text{I}_2^+$		$\text{Rb}_2\text{I}_3^-$	
	DFT	MP2	DFT	MP2
$R_{e1}(\text{Rb}-\text{I})$	3.408	3.381	3.410	3.384
$R_{e2}(\text{Rb}-\text{I})$	3.430	3.416	3.466	3.438
$R_{e3}(\text{Rb}-\text{I})$	3.724	3.656	3.800	3.704
$E$	-95.13631	-94.72579	-82.71950	-82.34439
$\alpha_e$	92.5	90.7	80.4	81.6
$\beta_e$	82.6	84.8	92.3	92.4
$h_1$	1.0	-5.4	4.1	-2.7
$\omega_1(A_1)$	104	109	101	108
$\omega_2(A_1)$	100	104	97	102
$\omega_3(A_1)$	57	64	46	50
$\omega_4(A_1)$	31	29	32	32
$\omega_5(B_1)$	26	27	33	33
$\omega_6(B_1)$	9	14	12	11
$\omega_7(B_2)$	101	107	109	112
$\omega_8(B_2)$	50	61	52	61
$\omega_9(B_2)$	17	19	19	18
$I_1$	0.30	0.44	0.20	0.26
$I_2$	0.72	0.56	0.69	0.63
$I_3$	0.14	0.11	0.09	0.06
$I_4$	0.03	0.48	0.04	0.04
$I_5$	0.45	0.03	0.36	0.38
$I_6$	0.00	0.00	0.03	0.04
$I_7$	0.47	0.47	0.54	0.52
$I_8$	0.27	0.11	0.22	0.22
$I_9$	0.05	0.06	0.01	0.02

TABLE 5. PROPERTIES OF  $\text{Rb}_3\text{I}_2^+$  AND  $\text{Rb}_2\text{I}_3^-$  IONS WITH BIPYRAMIDAL SHAPE,  $D_{3h}$  SYMMETRY

Quantity	$\text{Rb}_3\text{I}_2^+$		$\text{Rb}_2\text{I}_3^-$	
	DFT	MP2	DFT	MP2
$R_e(\text{Rb}-\text{I})$	3.588	3.556	3.602	3.544
$\alpha_e$	84.9	86.1	94.4	93.8
$E$	-95.14134	-94.73456	-82.72250	-82.35255
$h_2$	-12.2	-28.5	-3.8	-24.2
$\omega_1(A_1')$	91	94	92	98
$\omega_2(A_1')$	50	54	52	54
$\omega_3(A_2'')$	82	84	72	80
$\omega_4(E')$	81	82	84	91
$\omega_5(E')$	38	39	29	31
$\omega_6(E'')$	61	64	58	68
$I_3$	0.76	0.67	0.58	0.61
$I_4$	1.34	1.50	1.42	1.34
$I_5$	0.24	0.28	0.10	0.12

high symmetry of the point group,  $D_{3h}$ , only two geometric parameters,  $R_e(\text{Rb}-\text{I})$  and the apex angle  $\alpha_e$ , specify this structure (Fig 1, c; Table 5).

The internuclear distances  $R_e(\text{Rb}-\text{I})$  are equal for the ions  $\text{Rb}_3\text{I}_2^+$  and  $\text{Rb}_2\text{I}_3^-$  within uncertainties of the calculations. The bond angle  $\alpha_e$  at the top of the bipyramid is acute for positive ion and obtuse for negative one, i.e. the  $\text{Rb}_3\text{I}_2^+$  bipyramid is somewhat extended along the  $C_3$  axis, and the  $\text{Rb}_2\text{I}_3^-$  bipyramid is, on the contrary, compressed.

The relative energy  $h_2 = E(D_{3h}) - E(D_{3h})$  of the bipyramidal isomer is negative as for the  $\text{Rb}_3\text{I}_2^+$  as  $\text{Rb}_2\text{I}_3^-$  ions according to the both methods used. Therefore the bipyramidal isomer is energetically more stable than the linear one. A note is to be made, that the MP2 level gives more negative values of  $h_2$ . The vibrational spectra for both ions are similar regarding the magnitudes of the frequencies and IR intensities.

## CONCLUSION

The two quantum chemical approaches, DFT and MP2, have been applied to determine the properties of  $\text{Rb}_2\text{I}^+$ ,  $\text{RbI}_2^-$ ,  $\text{Rb}_3\text{I}_2^+$ , and  $\text{Rb}_2\text{I}_3^-$  ions. Both methods provides with the comparable results about the equilibrium geometric parameters and vibrational spectra of the species. As a rule the internuclear separation  $\text{Rb}-\text{I}$  obtained by the MP2 method is shorter by 0.02 – 0.03 Å, and, correspondingly, the valence vibrational frequencies are higher than those by DFT. We consider the results by MP2 method as more reliable than by DFT.

According to the results, the properties of the positive and negative ions were found to be similar. It concerns as triatomic species as all three considered isomers of the pentaatomic ions. The bipyramidal structure of both  $\text{Rb}_3\text{I}_2^+$  and  $\text{Rb}_2\text{I}_3^-$  appeared to be more stable by the energy than the linear and kite-shaped configurations. However the lower energy does not imply that

the pyramidal isomer should be the most abundant in the saturated vapor over rubidium iodide. To come to the final conclusion about relative concentration of the isomers, entropy factor should be taken into account. The analysis of the previous results [3, 4, 14] allows us to accept the linear structure of the pentaatomic ions, both positive and negative, as the dominant isomer occur in saturated vapor over rubidium iodide.

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