Theoretical Study of Structure and Vibrational Spectra of Molecular and Ionic Clusters Existing in Vapour over Rubidium Chloride

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Abstract: The geometrical structure and the vibrational spectra of dimer Rb2Cl2, trimer Rb3Cl3, tetramer Rb4Cl4 molecules and heptaatomic Rb4Cl3+ and Rb4Cl3− ions were studied. The cluster molecules and ions had been detected in equilibrium vapour over rubidium chloride previously. The quantum chemical calculations by DFT with hybrid functional B3P86 and MP2 methods were performed. The effective core potential with Def2–TZVP (6s4p3d) basis set for rubidium atom and full electron aug–cc–pVTZ (6s5p3d2f) basis set for chlorine atom were used. The equilibrium configuration was confirmed to be rhomb of symmetry D2h for dimer Rb2Cl2, distorted cube (Td) for tetramer Rb4Cl4 and polyhedral (C3v) for heptaatomic ions Rb4Cl3+ and Rb4Cl3−. For the trimer molecule Rb3Cl3 two isomers have been revealed: hexagonal (D3h) and butterfly-shaped (C2v), the latter has lower energy and is proved to be predominant in equilibrium vapour in a broad temperature range.

Keywords: Ionic and Molecular Clusters, Rubidium Chloride, Geometrical Structure, Vibrational Spectra, DFT, MP2, Isomers

1. Introduction

Several alkali metals including rubidium may chemically combine with halogen to form different neutral and ionic clusters which exist in vapours [1–10]. These clusters are characterized by different geometrical structures, vibrational spectra, and thermodynamic properties which are mostly depend on the number of atoms composing the species [1]. The formed clusters possess specific electronic, optical, magnetic and structural properties which make them useful in different technical and scientific applications [2, 3]. These properties are also strongly depending on size and composition of the clusters. Changing the magnitude and structure of a cluster aggregate allows coming up with new materials of desired properties [11].

To investigate the structure and properties of alkali halide clusters, different experimental techniques e.g. high temperature mass spectrometry [12, 13], microwave absorption spectroscopy [14, 15] and molecular beam electric resonance [16] and theoretical methods [1, 17–21] were employed.

Different molecular and ionic associates were detected in vapour over rubidium chloride; they are dimer, trimer, and tetramer molecules and the ions Rb+(RbCl)n (n = 1–4) [22].

Previously the quantum chemical methods has been used to study tri- and pentaatomic ions Rb3Cl+ , RbCl2−, RbCl3−, Rb2Cl−, Rb2Cl− [20]. The ionic clusters were studied by density functional theory (DFT) with the Becke–Lee–Yang–Parr functional (B3LYP5), second order and fourth order Møller–Plesset perturbation theory (MP2 and MP4) using the basis sets aug–cc–pVTZ (5s4p2d1f) for Cl and cc–pVTZ (7s5p4d1f) for Rb [20]. This study aims the investigation of the structure and properties of neutral and heavier ionic clusters of rubidium chloride.

2. Methodology

The density functional theory (DFT) with hybrid functional the Becke–Perdew correlation B3P86 [23–26] and second
order Møller–Plesset perturbation theory (MP2) implemented into PC GAMESS (General Atomic and Molecular Electronic Structure System) program [27] and Firefly version 8.1.0 [28] were used for calculation of geometrical parameters and frequencies of normal vibrations. The visualization of the geometrical structure, specification of parameters, and assignment of vibrational modes in infrared spectra was done using the Chemcraft software [29] and MacMolPlt program [30]. The effective core potentials with Def2–TZVP (6s4p3d) basis set for Rb atom [31, 32] and full electron aug–cc–pVTZ basis set for Cl (6s5p3d2f) atom [31, 33] were applied in this study. The basis sets were taken from the EMSL (The Environmental Molecular Sciences Laboratory, GAMESS US) Basis Set Exchange version 1.2.2 library [34, 35].

The Open thermo software [36] was used in calculation of the thermodynamic properties including energies $\Delta E$ and enthalpies $\Delta H(0)$ of the reactions which were calculated following the through the following equations:

$$\Delta E = \sum E_{i\ prod} - \sum E_{i\ reactant}$$

$$\Delta H(0) = \Delta_e E + \Delta_e$$

Notes: Here and hereafter, $E_0$ is the total electron energy (au), $\omega_i$ is the fundamental frequency (cm$^{-1}$), $\mu_e$ is the dipole moment (D), $E_{i\ reactant}$ and $E_{i\ prod}$ are the zero point vibration energy correction, $\omega_{i\ reactant}$ and $\omega_{i\ prod}$ are the sums of the vibration frequencies of the products and reactants respectively.

### 3. Results and Discussion

#### 3.1. Monomer RbCl and dimer Rb$_2$Cl$_2$

The properties of the diatomic RbCl and dimer Rb$_2$Cl$_2$ molecules was computed using three different DFT hybrid functionals, B3LYP5, B3P86 and B3PW91 and Møller–Plesset perturbation theory (MP2) for the purpose of choosing the appropriate method to be implemented in this study and estimation of uncertainties in theoretical values. The results for diatomic molecule RbCl together with the available experimental data are shown in Table 1.

As is seen the calculated internuclear distance ($R_e$) using three DFT hybrid functionals were overrated by 0.07–0.09 Å when compared with the reference data and that of MP2 was overrated by 0.07 Å. Considering both DFT and MP2 methods, the results obtained show very little variation whereas DFT/B3P86 and MP2 give the best results regarding to the reference. The calculated values of frequencies were underestimated by 6–9 cm$^{-1}$ (2.7–3.9%) for DFT methods while MP2 result coincides with the experimental value [38]. The results for dipole moment ($\mu_e$), show high deviation from reference data for the case of MP2, overrated by 0.88 D; and overrated by 0.41–0.47 D for the DFT methods.

The adiabatic ionization energy ($IE_{\text{ad}}$) was obtained as the energy difference of the RbCl$^+$ ion and neutral molecule where the internuclear separation $R_e$(Rb–Cl) was optimized both for neutral and ionic species and vertical ionization energy ($IE_{\text{vert}}$) was obtained as the energy difference of the RbCl$^+$ ion and neutral molecule where the internuclear separation $R_e$(Rb–Cl) was optimized in neutral molecule only and accepted the same for the ion. Electron affinities ($EA$) were obtained by determining the energy difference between neutral molecule and negatively charged ion. The results obtained for $IE$ and $EA$ using both DFT and MP2 methods agree well with the reference. As the optimization procedure by MP2 was not implemented for the species with multiplicity more than 1 in the software [27, 28], the $IE_{\text{ad}}$ by MP2 method was not calculated in this study.

For the dimer molecule Rb$_2$Cl$_2$, a planar cyclic structure of $D_{2h}$ symmetry (Fig. 1a) was confirmed to be equilibrium, while linear one ($C_{2v}$) was found to be a saddle point on the potential energy surface. The calculated properties; internuclear distance, valence angle, vibrational spectra and enthalpy of the dissociation reaction are presented in Table 2. As seen the calculated values of internuclear distance are overrated by 0.04–0.09 Å compared with literature data [45] and the values of enthalpy of dissociation reaction are in agreement with the reference data [22, 46].

The absence of low frequencies in the vibrational spectra of Rb$_2$Cl$_2$ indicates the rigidity of the structure; the lowest frequency being about 50 cm$^{-1}$.

In the IR spectrum, three vibrational modes $\omega_3$, $\omega_5$, and $\omega_6$ have nonzero intensities but due to overlapping of $\omega_3$ and $\omega_6$ only two peaks could be seen which are asymmetrical stretching 171 cm$^{-1}$ and wagging 52 cm$^{-1}$ (MP2).

### Table 1. Properties of the monomer molecule RbCl.

| Property | B3LYP5 | B3P86 | B3PW91 | MP2 | Ref data |
|----------|--------|--------|--------|-----|----------|
| $R_e$(Rb–Cl) | 2.878 | 2.857 | 2.860 | 2.855 | 2.787 [37] |
| $E$ | 484.32782 | 484.42116 | 484.38973 | 483.40565 | |
| $\omega_3$ | 219 | 222 | 221 | 228 | 228 [38] |
| $\mu_e$ | 11.0 | 10.9 | 10.9 | 11.4 | 10.483 [40] |
| $IE_{\text{vert}}$ | 8.45 | 8.66 | 8.53 | 8.52 | 8.50 ± 0.03 [41] |
| $IE_{\text{ad}}$ | 8.17 | 8.38 | 8.25 | 0.49 | 0.543 ± 0.01 [44] |
| $EA$ | 0.58 | 0.67 | 0.60 | 0.49 | |

Notes: Here and hereafter, $R_e$ is the equilibrium internuclear distance (Å), $E$ is the total electron energy (au), $\omega_i$ is the fundamental frequency (cm$^{-1}$), $\mu_e$ is the dipole moment (D), $IE_{\text{vert}}$ and $IE_{\text{ad}}$ are the ionization energies, vertical and adiabatic, respectively (eV). $EA$ is the electron affinity (eV).
Based on results for the RbCl and Rb₂Cl₂ molecules, it is worth to mention that the data obtained by MP2 and DFT/B3P86 hybrid functional agree better with the available literature data therefore these two methods were chosen for further computations of heavier molecular and ionic clusters.

### Table 2. Properties of the dimer molecule, Rb₂Cl₂

| Property     | B3LYP5  | B3P86 | B3PW91 | MP2     | Ref. data |
|--------------|---------|-------|--------|---------|-----------|
| $R_a$(Rb–Cl) | 3.061   | 3.053 | 3.062  | 3.032   | 2.989 [45] |
| $\omega_1$(Rb–Cl) | 87.9   | 87.9  | 87.8   | 88.6    | 89.5 [45]  |
| $\Delta E$ | 968.71721 | 968.90454 | 968.84018 | 966.87305 |            |
| $\Delta \Delta P$ | 161.6  | 163.4 | 159.4  | 162.1   |           |
| $\omega_1$(Cl–Cl) | 159.9  | 161.6 | 157.8  | 160.1   | 164±11 [22] |
| $I_a$ | 0.94  | 0.94  | 0.94   | 0.97    |           |
| $I_b$ | 1.61  | 1.62  | 1.64   | 1.70    | 1.72      |
| $I_c$ | 1.69  | 1.69  | 1.70   | 1.65    | 1.72      |

Notes: $\alpha_a$ is the valence angle (deg), $\Delta E$ and $\Delta \Delta P(0)$ are the energy and enthalpy of the dissociation reaction Rb₂Cl₂⇌2RbCl (kJ mol⁻¹), $I_a$ are the infrared intensities (D atm⁻¹ Å⁻²). The reducible vibration representation reduces to $\Gamma = 2A_g + B_g + B_u + B_u$.

### 3.2 Trimers Rb₃Cl₁ and tetramer Rb₄Cl₂

For the trimer molecule Rb₃Cl₁, three possible geometrical configurations were considered: linear of $D_{\infty h}$ symmetry, hexagonal of $D_{3h}$ symmetry and butterfly-shaped of $C_{2v}$ symmetry. The linear configuration was found to be unstable due to presence of imaginary frequencies but the rest two configurations, (Figs. 1b and 1c) were confirmed to be equilibrium. The results are shown in Table 3.

### Table 3. Properties of trimer Rb₃Cl₁ molecule, hexagonal ($D_{3h}$) and butterfly-shaped ($C_{2v}$).

| Property     | B3P86 | MP2 | Property     | B3P86 | MP2 |
|--------------|-------|-----|--------------|-------|-----|
| $R_a$(Rb–Cl) | 1.61  | 1.72 | $R_a$(Rb–Cl) | 1.61  | 1.72 |
| $\omega_1$(Rb–Cl) | 117.9 | 119.5 | $\omega_1$(Rb–Cl) | 117.9 | 119.5 |
| $\Delta E$ | 1453.37224 | 1451.29449 | $\Delta E$ | 1453.37224 | 1451.29449 |
| $\omega_1$(A₁) | 176 | 191 | $\omega_1$(A₁) | 177 (1.79) | 185 (1.82) |
| $\omega_1$(A₂) | 126 | 127 | $\omega_1$(A₂) | 128 (0.02) | 135 (0.03) |
| $\omega_1$(B₁) | 84 | 84 | $\omega_1$(B₁) | 90 (0.25) | 102 (0.44) |
| $\omega_1$(E) | 181 | 193 | $\omega_1$(E) | 73 (0.24) | 85 (0.07) |
| $\omega_2$(A₁) | 134 | 142 | $\omega_2$(A₁) | 55 (1.21) | 57 (1.23) |
| $\omega_2$(A₂) | 21 | 23 | $\omega_2$(A₂) | 50 (0.03) | 51 (0.01) |
| $\omega_2$(E) | 46 | 48 | $\omega_2$(E) | 28 (0) | 28 (0) |
| $\omega_2$(E') | 23 | 24 | $\omega_2$(E') | 8 (0.01) | 13 (0.02) |
| $\omega_3$(A₁) | 3.94 | 3.98 | $\omega_3$(A₁) | 188 (1.25) | 200 (1.38) |
| $\omega_3$(A₂) | 0.82 | 0.78 | $\omega_3$(A₂) | 172 (0.45) | 181 (0.26) |
| $\omega_3$(E) | 1.40 | 1.45 | $\omega_3$(E) | 150 (1.03) | 162 (1.08) |
| $\omega_3$(E') | 0.50 | 0.52 | $\omega_3$(E') | 53 (0.19) | 53 (0.19) |
| $\mu$ | 9.8 | 10.4 | $\mu$ | 9.8 | 10.4 |

Notes: $\Delta E_{\text{iso}} = E(C_{2v})-E(D_{3h})$ is the relative energy of the butterfly-shaped isomer regarding the hexagonal one (kJ mol⁻¹). The reducible vibration representations for Rb₂Cl₁ or $D_{3h}$ and $C_{2v}$ symmetry reduces to $\Gamma = 3A_g + 3E' + A_u + E''$ and $\Gamma = 6A_g + 3A_u + 2E'$, respectively. For the $C_{2v}$, butterfly-shaped isomer, the values given in parentheses near the frequencies are infrared intensities (D atm⁻¹ Å⁻²).

For the hexagonal isomer ($D_{3h}$), one internuclear distance $R_a$(Rb–Cl) and one valence angle $\alpha_a$(Rb–Cl–Rb) or $\beta_a$(Cl–Rb–Cl) are needed to describe the structure; for the butterfly-shaped isomer ($C_{2v}$), four internuclear distances $R_{a1}$, $R_{a2}$, $R_{a3}$, $R_{a4}$ and two valence angles $\alpha_a$(Rb₂–Cl₁–Rb₃) and $\beta_a$(Cl₁–Rb₁–Cl₄) are used for the description. The butterfly-shaped configuration has lower energy, by 2.6 kJ mol⁻¹ (DFT) and 10.0 kJ mol⁻¹ (MP2), than hexagonal one.

The relative concentration of isomers $p(C_{2v})/p(D_{3h})$ have been estimated using the same procedure as it was described

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previously [21]. The enthalpy of the isomerization and relative energy of isomers \(\Delta_{r}E_{iso}(MP2)\) for the isomerization reaction \(\text{Rb}_3\text{Cl}_3(D_{3h}) \rightleftharpoons \text{Rb}_3\text{Cl}_3(C_{2v})\) was calculated using Eqs. (2) and (3).

The values of \(p(C_{2v})/p(D_{3h})\) were obtained for the temperature range between 700–2000 K; the plot is shown in Fig. 2. As is seen the butterfly-shaped isomer is more abundant than hexagonal one and the concentration of the former decreases with temperature increase.

Figure 1. Equilibrium geometric structures of molecules: (a) \(\text{Rb}_2\text{Cl}_2(D_{2h})\); (b) \(\text{Rb}_3\text{Cl}_3(D_{3h})\); (c) \(\text{Rb}_3\text{Cl}_3(C_{2v})\); (d) \(\text{Rb}_4\text{Cl}_4(T_d)\).

Figure 2. Temperature dependence of relative amount of the \(C_{2v}\) isomer regarding to \(D_{3h}\) isomer of trimer \(\text{Rb}_3\text{Cl}_3\) molecule.

The IR spectra of both isomers of \(\text{Rb}_3\text{Cl}_3\) molecule are shown in Fig. 3. The most intensive bands correspond to the stretching vibration modes and bending modes have lower intensities.

When comparing the properties of \(\text{Rb}_3\text{Cl}_3\) with \(\text{Rb}_3\text{F}_3\) molecule, a similarity may be noted: the same two isomers were revealed for \(\text{Rb}_3\text{F}_3\) [21] and the butterfly-shaped isomer was predominant in that case as well.

For the tetramer molecule \(\text{Rb}_4\text{Cl}_4\), the geometrical configuration considered was cube with \(T_d\) symmetry (Fig. 1d) and it was confirmed to be equilibrium. The geometrical parameters and vibrational frequencies of the tetramer molecule are presented in Table 4.

Figure 3. Theoretical IR spectra of the trimer \(\text{Rb}_3\text{Cl}_3\) molecule calculated by MP2 method: (a) hexagonal isomer (\(D_{3h}\)); (b) butterfly-shaped isomer (\(C_{2v}\)).
The reducible vibration representation reduces to $\Gamma = 2\alpha I I \omega \omega \omega \omega - \beta \alpha R$. Property $228$ Ismail Abubakari

$$7.30 \quad 7.90 \quad 0.38 \quad 0.03 \quad 0.06 \quad 0.03$$

Notes: The reducible vibration representation reduces to $\Gamma = 2A_1 + 2E + T_1 + 3T_2$. One internuclear distance $R_e(Rb-Cl)$ and one valence angle $\alpha_e(Rb-Cl-Rb)$ or $\beta_e(Cl-Rb-Cl)$ are needed to describe the structure. In the IR spectrum, three vibrational modes are active but only one peak could be observed $\omega_6(T_2)$ which is assigned to asymmetrical stretching $Rb-Cl$ vibration; other two modes have low intensities.

### 3.3. Heptaatomic Ions $Rb_2Cl_4^+$ and $Rb_2Cl_4^-$

For heptaatomic ions $Rb_2Cl_4^+$ and $Rb_2Cl_4^-$ two alternative structures were considered, polyhedral of $C_{3v}$ symmetry and two-cycled with mutually perpendicular planes of $D_{2d}$ symmetry (Fig. 4); only polyhedral structure of symmetry $C_{3v}$ was confirmed to be equilibrium. The results for both positive and negative ions are presented in Table 5. The polyhedral structure is described by two internuclear distances $R_{e1}$ and $R_{e2}$ and three valence angles, $\alpha_e(Rb_2-Cl_3-Rb_3)$, $\beta_e(Rb_1-Cl_4-Rb_3)$ and $\gamma_e(Cl_4-Rb_2-Cl_3)$. Compared to the $D_{2d}$ structure, the polyhedral configurations possesses lower energy with the energy drop of $87$ kJ mol$^{-1}$ and $83$ kJ mol$^{-1}$ for $Rb_2Cl_4^+$ and $Rb_2Cl_4^-$ respectively, according to MP2 results.

| Property | B3P86 | MP2 |
|----------|-------|-----|
| $R_e(Rb-Cl)$ | 3.191 | 3.150 |
| $\alpha_e(Rb-Cl-Rb)$ | 87.8 | 86.6 |
| $\beta_e(Cl-Rb-Cl)$ | 85.3 | 84.5 |
| $\gamma_e(Rb_1-Cl_4-Rb_3)$ | 89.2 | 89.9 |
| $-E$ | 1477.41200 | 1475.10172 |
| $\omega_e(A_1)$ | 138 (0.61) | 148 (0.82) |
| $\omega_e(A_2)$ | 116 (0.91) | 120 (0.71) |
| $\omega_e(A_3)$ | 75 (0.06) | 75 (0.07) |
| $\omega_e(A_4)$ | 37 (0.15) | 38 (0.19) |
| $\omega_e(A_5)$ | 149 (0) | 164 (0) |
| $\omega_e(E)$ | 169 (3.28) | 182 (3.30) |
| $\omega_e(T_1)$ | 125 (1.56) | 133 (1.52) |
| $\omega_e(T_2)$ | 100 (0.02) | 108 (0.06) |
| $\omega_e(T_3)$ | 51 (0.08) | 51 (0.08) |
| $\omega_e(T_4)$ | 29 (0.10) | 29 (0.12) |

Notes: $\gamma_e$ is the valence angle (deg). The reducible vibration representations reduce to $\Gamma = 4A_1 + A_2 + 5E$ for both $Rb_2Cl_4^+$ and $Rb_2Cl_4^-$. | B3P86 | MP2 |
|----------|-------|-----|
| $R_e(Rb-Cl)$ | 3.198 | 3.154 |
| $\alpha_e(Rb-Cl-Rb)$ | 84.7 | 85.1 |
| $\beta_e(Cl-Rb-Cl)$ | 83.0 | 83.8 |
| $\gamma_e(Cl_4-Rb_2-Cl_3)$ | 91.2 | 90.9 |
| $-E$ | 1913.72426 | 1911.20087 |
| $\omega_e(A_1)$ | 138 (0.04) | 146 (0.31) |
| $\omega_e(A_2)$ | 134 (1.44) | 141 (1.17) |
| $\omega_e(A_3)$ | 72 (0.15) | 74 (0.13) |
| $\omega_e(A_4)$ | 50 (0.46) | 51 (0.51) |
| $\omega_e(A_5)$ | 126 (0) | 138 (0) |
| $\omega_e(E)$ | 147 (3.74) | 157 (3.92) |
| $\omega_e(T_1)$ | 132 (1.60) | 140 (1.44) |
| $\omega_e(T_2)$ | 108 (0.06) | 120 (0.04) |
| $\omega_e(T_3)$ | 54 (0.06) | 54 (0.04) |
| $\omega_e(T_4)$ | 31 (0.26) | 31 (0.28) |

### Figure 4. Geometric structures of heptaatomic ions: polyhedral of $D_{2h}$ symmetry (a) $Rb_2Cl_4^+$ (b) $Rb_2Cl_4^-$; two cycled with the mutually perpendicular planes of $D_{2d}$ symmetry (c) $Rb_2Cl_4^+$ (d) $Rb_2Cl_4^-$. |
As is seen in Table 5 the respective geometrical parameters and vibrational frequencies of the positive and negative ions are close to each other. The IR spectra are shown in Fig. 5. In both spectra, the stretching vibrational modes have higher intensities than bending modes.

4. Conclusion

The properties of the trimer and tetramer molecules and heptaatomic ionic clusters have been investigated theoretically using DFT/B3P86 and MP2 methods. The corresponding parameters of the species calculated by two methods are generally in a good accordance to each other; while the internuclear distances Rb–Cl found with DFT/B3P86 are longer by 0.02–0.04 Å than those found with MP2 method. Among the species considered, for the Rb₃Cl₃ molecule two isomers, hexagonal C₃₅ and butterfly-shaped C₂₃, were proved to exist; the latter was evaluated to be more abundant in vapour. When compare the Rb₃Cl₃ with Rb₃F₃ studied previously, alike features may be noted (including the existence of two isomers). The results obtained for the heptaatomic ions show similarities between the respective properties of positive and negative ions.

Authors’ Contributions

All authors participate well in all steps including computation, data analysis and manuscript preparation towards production of this work.

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Appendix

Tables A1 to A5 contain the thermodynamic functions of the ionic and molecular clusters; trimer Rb₃Cl₃⁺, tetramer Rb₅Cl₄⁺, and heptaatomic Rb₇Cl₇⁺ and Rb₇Cl₇⁻. The tables include absolute temperature T in K, molar heat capacity cᵥ, Gibbs reduced free energy Φ°, and entropy S° which are given in J mol⁻¹ K⁻¹, and enthalpy increment H°(T)–H°(0) in kJ mol⁻¹.

Table A1. Thermodynamic functions of the Rb₃Cl₃, C₃ᵥ isomer.

| T    | cᵥ°   | S°   | H°(T)–H°(0) | Φ°   |
|------|-------|------|-------------|------|
| 298.15 | 130.24 | 514.540 | 33.025 | 403.718 |
| 700   | 132.51 | 626.923 | 85.999 | 504.067 |
| 800   | 132.64 | 644.626 | 99.257 | 520.555 |
| 900   | 132.71 | 660.250 | 112.524 | 535.226 |
| 1000  | 132.78 | 674.239 | 125.799 | 548.440 |
| 1100  | 132.82 | 686.896 | 139.079 | 560.461 |
| 1200  | 132.86 | 698.455 | 152.363 | 571.486 |
| 1300  | 132.89 | 709.090 | 165.649 | 581.668 |
| 1400  | 132.91 | 718.938 | 178.939 | 591.124 |
| 1500  | 132.93 | 728.108 | 192.230 | 599.955 |

Table A2. Thermodynamic functions of the Rb₅Cl₄, D₃h isomer.

| T    | cᵥ°   | S°   | H°(T)–H°(0) | Φ°   |
|------|-------|------|-------------|------|
| 298.15 | 130.23 | 516.663 | 33.245 | 405.102 |
| 700   | 132.51 | 629.039 | 86.216 | 505.873 |
| 800   | 132.63 | 646.742 | 99.474 | 522.400 |
| 900   | 132.70 | 662.368 | 112.741 | 537.100 |
| 1000  | 132.76 | 676.355 | 126.016 | 550.339 |
| 1100  | 132.84 | 689.012 | 139.296 | 562.379 |
| 1200  | 132.83 | 700.570 | 152.579 | 573.421 |
| 1300  | 132.81 | 711.205 | 165.866 | 583.616 |
| 1400  | 132.89 | 721.053 | 179.155 | 593.085 |
| 1500  | 132.92 | 730.223 | 192.446 | 601.926 |

Table A3. Thermodynamic functions of the Rb₇Cl₇, T₄ isomer.

| T    | cᵥ°   | S°   | H°(T)–H°(0) | Φ°   |
|------|-------|------|-------------|------|
| 298.15 | 178.92 | 570.693 | 43.797 | 423.724 |
| 700   | 182.18 | 725.158 | 116.611 | 558.571 |
| 800   | 182.35 | 749.497 | 134.838 | 580.950 |
| 900   | 182.47 | 770.982 | 153.079 | 600.894 |
| 1000  | 182.56 | 790.212 | 171.331 | 618.881 |
| 1100  | 182.63 | 807.615 | 189.590 | 635.256 |
| 1200  | 182.67 | 823.507 | 207.854 | 650.295 |
| 1300  | 182.69 | 838.129 | 226.123 | 664.188 |
| 1400  | 182.74 | 851.670 | 244.394 | 677.103 |
| 1500  | 182.75 | 864.278 | 262.669 | 689.165 |
Table A4. Thermodynamic functions of the RbCl^+, Cs^+ isomer.

| T       | c_0^0 | S^0 | H(T)-H(0) | Φ^0 |
|---------|-------|-----|-----------|-----|
| 298.15  | 154.80| 556.647| 38.787    | 426.489|
| 700     | 157.39| 690.161| 101.719   | 544.848|
| 800     | 157.52| 711.187| 117.465   | 564.356|
| 900     | 157.64| 729.746| 133.222   | 581.722|
| 1000    | 157.70| 746.357| 148.988   | 597.369|
| 1100    | 157.73| 761.388| 164.759   | 611.607|
| 1200    | 157.77| 775.115| 180.534   | 624.670|
| 1300    | 157.82| 787.745| 196.313   | 636.735|
| 1400    | 157.73| 790.440| 212.095   | 647.944|
| 1500    | 157.77| 810.330| 227.878   | 658.411|

Table A5. Thermodynamic functions of the RbCl^+, Cs^+ isomer.

| T       | c_0^0 | S^0 | H(T)-H(0) | Φ^0 |
|---------|-------|-----|-----------|-----|
| 298.15  | 154.92| 546.945| 38.729    | 416.983|
| 700     | 157.42| 680.513| 101.683   | 535.252|
| 800     | 157.54| 701.542| 117.431   | 554.753|
| 900     | 157.62| 720.103| 133.190   | 572.114|
| 1000    | 157.70| 736.715| 148.957   | 587.758|
| 1100    | 157.77| 751.748| 164.729   | 601.994|
| 1200    | 157.79| 765.475| 180.506   | 615.053|
| 1300    | 157.80| 778.106| 196.286   | 627.117|
| 1400    | 157.84| 789.802| 212.068   | 638.325|
| 1500    | 157.92| 800.692| 227.852   | 648.791|

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