THEORETICAL STUDY OF THE STRUCTURE AND STABILITY OF THE Na₂Cl⁺, NaCl₂, Na₃Cl₂, AND Na₂Cl₃ IONS

T. Pogrebnoy, A. M. Pogrebnoi, and L. S. Kudin

The geometrical parameters, normal vibration frequencies, and thermochemical characteristics of the Na₂Cl⁺, NaCl₂, Na₃Cl₂, and Na₂Cl₃ ions in saturated vapors over sodium chloride were calculated by the ab initio methods including electron correlation. According to calculations, the Na₂Cl⁺ and NaCl₂ triatomic ions have a linear equilibrium Dfh configuration. The pentaatomic ions can exist in the form of the D₅h linear isomer, Cᵥ planar cyclic isomer, or D₃h bipyramidal isomer. At ~1000 K the Na₃Cl₂⁺ and Na₂Cl₃⁻ ions exist predominantly in the form of the linear isomers. The energies and enthalpies of the ion–molecule reactions involving the above ions were calculated. The formation enthalpy of the ions ΔfH₀(0 K) was determined: 230 ± 2 kJ/mol (Na₂Cl⁺), –96 ± 4 kJ/mol (Na₃Cl₂⁺), –616 ± 2 kJ/mol (NaCl₂⁻), and –935 ± 4 kJ/mol (Na₂Cl₃⁻).

Keywords: ions in vapors over sodium chloride, ab initio calculation, geometrical configuration, isomers, geometrical parameters, vibrational spectra, ion molecular reactions, formation enthalpy of ions.

The M₂X⁺, MX₂⁻, M₃X₂⁻, and M₂X₃⁻ type ions (M is an alkali metal; X is halogen) in vapors over alkali metal halides were recorded in mass spectrometric studies [1, 2]. Experimental data about the structure and spectra of these ions are unavailable. Previously, ab initio studies were carried out to investigate the structure and properties of the ions in vapors over lithium [3] and sodium [4] fluorides. The aim of this work was to determine the characteristics of the Na₂Cl⁺⁺, NaCl₂⁻, Na₃Cl₂⁻, and Na₂Cl₃⁻ ions, namely, the geometrical parameters, normal vibration frequencies, and IR band intensities, as well as the dissociation energies and enthalpies of these ions, leading to the elimination of the NaCl molecule.

DETAILS OF CALCULATIONS

Calculations were carried out using the GAMESS program [5] (PC GAMESS version [6]). The following ab initio methods were used: density functional theory with the Becke–Lee–Yang–Parr functional B3LYP5 (DFT), second (MP2) and fourth (MP4) order Möller–Plesset perturbation theory, and the configuration interaction method including single and double excitations (CISD) and a correction for quartic excitations (CISD + Q). The electron shells of the sodium and chlorine atoms are described with the McLean–Chandler (12s9p)/[6s5p] basis sets complemented with the d type polarization functions and s and p type diffusion functions on both atoms [5]. In MP2, MP4, CISD, and CISD + Q calculations, the Na 1s and Cl 1s,2s,2p
orbits were “frozen.” Geometry optimization of the ions and normal vibration frequency calculations (in the harmonic approximation) were carried out by the methods implemented in the GAMESS program.

RESULTS AND DISCUSSION

**NaCl +** and **NaCl**

**Table 1** presents the calculated characteristics of the NaCl + and NaCl ions obtained in the DFT, MP2, and CISD approximations. According to calculations in all approximations used, the $D_{sh}$ linear configuration is the equilibrium configuration of the ions (Fig. 1). The internuclear distances and vibration frequencies obtained in the MP2 approximation agreed with the results of CISD calculations. The DFT method gave overestimated internuclear distances and underestimated vibration frequencies relative to CISD. These differences were moderate and did not exceed 0.02 Å for $R_e$ and ~10% for $\omega$. Let us compare the characteristics of the NaCl + and NaCl ions. The CISD calculated values of $R_e$ are 0.007 Å larger for the negative ion and, accordingly, the stretching symmetric vibration frequency $\omega_1$ in the negative ion is slightly smaller than in the positive ion. At the same time, the frequencies of the $\omega_2$ antisymmetric stretching vibrations and the $\omega_3$ deformation vibrations are higher for the negative ion.

We calculated the ion dissociation energies $\Delta E$, leading to the elimination of the NaCl molecule,

$$\text{NaCl}^+ = \text{Na}^+ + \text{NaCl},$$

$$\text{NaCl} = \text{Cl}^- + \text{NaCl}.$$  

The values of $\Delta E$ obtained by the DFT method nearly coincided with the results of the CISD + Q calculations. At the same time, MP2 gave higher values of $\Delta E$ than CISD + Q. However, as shown previously [4, 7], the results of CISD + Q calculations cannot serve as a reliability criterion of $\Delta E$ calculations in view of the size inconsistency of the CISD + Q method. Therefore, the energies of the ion–molecule reactions were refined in MP4 calculations (see below). Nevertheless, analysis of the energies $\Delta E$ given in Table 1 shows that the negative ion is more stable against decomposition than the positive ion. Thus, according to MP2 calculations, for NaCl, $\Delta E$ is ~20 kJ/mol higher than for NaCl +.

**Table 1.** Characteristics of the NaCl + and NaCl Ions as Calculated in Various Theoretical Approximations

<table>
<thead>
<tr>
<th>Property</th>
<th>NaCl +, $D_{sh}$</th>
<th>NaCl, $D_{sh}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DFT</td>
<td>MP2</td>
</tr>
<tr>
<td>$R_e$</td>
<td>2.487</td>
<td>2.481</td>
</tr>
<tr>
<td>$-E^*$</td>
<td>784.620021</td>
<td>783.553242</td>
</tr>
<tr>
<td>$\nu_1$ (Σg)</td>
<td>222</td>
<td>231</td>
</tr>
<tr>
<td>$\nu_2$ (Σu)</td>
<td>325</td>
<td>333</td>
</tr>
<tr>
<td>$\omega_3$ (Πu)</td>
<td>57</td>
<td>45</td>
</tr>
<tr>
<td>$A_2$</td>
<td>109</td>
<td>110</td>
</tr>
<tr>
<td>$A_3$</td>
<td>128</td>
<td>135</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>199.4</td>
<td>203.1</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>1.8</td>
<td>1.7</td>
</tr>
</tbody>
</table>

*Calculation in the CISD + Q approximation.

Note. The equilibrium internuclear distances $R_e$ (Na–Cl) are given in Å; the total energy $E$, in au; the normal vibration frequencies $\omega$, in cm$^{-1}$; the IR band intensities $A_i$, in km/mol; the energies of ion dissociation with elimination of the NaCl molecule $\Delta E$, in kJ/mol; the zero-point energy corrections $\Delta E$, in kJ/mol.