

# An ab initio investigation of the potential energy function and rotation–vibration energies of $\text{H}_2\text{O}\cdot\text{Na}^+$

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The ab initio MCSCF molecular energy, gradient, and Hessian have been evaluated analytically at nine points for the ground electronic state of the  $\text{H}_2\text{O}\cdot\text{Na}^+$  complex. A potential energy surface has been fitted to these data and the vibrational and rotational energies have been calculated using an approximate vibrational Hamiltonian and a nonrigid inverter Hamiltonian. The vibrational and rotational energies may assist in the experimental search for the gas-phase spectra of the complex.

## 1. Introduction

Ion hydration strongly affects physicochemical and chemical processes occurring in water solutions and is therefore of great importance in physical chemistry, biochemistry and molecular biology [1,2]. Since the pioneering work of Bernal and Fowler on molecular models for aqueous solutions [3], this phenomenon has been the subject of a number of experimental and theoretical investigations, see ref. [4] and references therein. One of the goals of these studies has been to provide a model for the ion–water interaction that would give information about energy and structural changes associated with hydration.

Most previous studies are based on classical electrostatic models involving a large number of parameters fitted to physical, thermochemical, and occasionally ab initio data [4–6]. A substantial part of these data has been accumulated from spectral analysis of hydration in condensed phases. Their accuracy is limited and may not be adequate for a correct description of the hydration processes in the gas-

phase. Obviously, an ideal way of overcoming this limitation would be to record high-resolution gas-phase spectra of the hydrated ionic species. So far no such spectrum has been reported and the problem remains a challenge for high-resolution molecular spectroscopy. However, work along these lines has started by attempting to record spectra of  $\text{H}_2\text{O}\cdot\text{Na}^+$  [7]. Our aim is to assist the experimental effort by performing a fully theoretical study of the rovibrational dynamics of the complex and to provide a sound prediction of its spectral characteristics.

The  $\text{H}_2\text{O}\cdot\text{Na}^+$  complex has six vibrational degrees of freedom. A complete theoretical study, including the evaluation of the ab initio potential energy surface and the solution of the rovibrational eigenproblem, therefore represents a considerable numerical task. According to a previous normal coordinate analysis [8] based on a Hartree–Fock surface [9], the dynamical problem can be approximately separated into two subproblems, one pertaining to the three high-frequency modes of water and the other to the three low-frequency modes associated with hydration. In addition, all modes seem to be opposed

by only slightly anharmonic potentials. Based on these facts, we have made two important simplifications. Firstly, the accurate *ab initio* determination of the energy surface is limited to the low energy region, important for a proper description of the low-frequency motions. The geometry of water is fixed at its equilibrium value. Secondly, in the calculations of the rotational energies all in-plane vibrations are assumed to be harmonic. This allows us to use a very economic "harmonic" nonrigid inverter theory, recently developed in one of our laboratories [10].

The analytical evaluation of the molecular gradient and Hessian makes it easier to determine and characterize the relevant stationary points. In addition, the potential energy surface may be modeled with fewer geometries than is necessary when only the energy is available. This is our first attempt to use gradient and Hessian information to map potential energy surfaces. It looks promising both with respect to computational efficiency (fewer points) and to a reliable determination of the structure of the surface.

## 2. The vibrational and nonrigid inverter Hamiltonians

To describe the rotation-vibration dynamics of the  $\text{H}_2\text{O}\cdot\text{Na}^+$  complex we use the following curvilinear symmetry coordinates (see fig. 1):

$$\mathcal{R}_1(A_1) = R - R_e,$$

$$\mathcal{R}_2(A_1) = (r_1 + r_2 - 2r_e)/\sqrt{2},$$

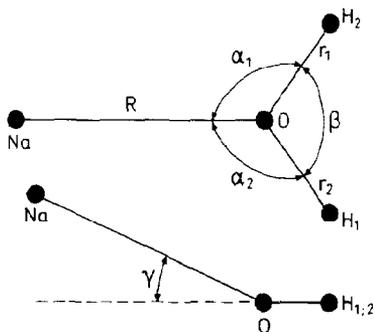


Fig. 1. Geometry parameters of  $\text{H}_2\text{O}\cdot\text{Na}^+$ .

$$\mathcal{R}_3(A_1) = \beta - \beta_e,$$

$$\mathcal{R}_4(B_1) = (r_2 - r_1)/\sqrt{2},$$

$$\mathcal{R}_5(B_1) = (\alpha_2 - \alpha_1)/\sqrt{2},$$

$$\mathcal{R}_6(B_2) = \gamma, \quad (1)$$

where  $R_e$ ,  $r_e$  and  $\beta_e$  characterize the reference (equilibrium) molecular configuration. If we neglect kinematic anharmonicity, vibrational angular momenta and the Watson pseudopotential term [11], the vibrational energies are the eigenvalues of the Hamiltonian

$$H_{\text{vib}} = \frac{1}{2} \sum_{i,j} \hat{P}_i G_{ij}^0 \hat{P}_j + V. \quad (2)$$

Here  $\hat{P}_k$  are the momenta conjugate to the  $\mathcal{R}_k$  for the pure vibrational part of the total Hamiltonian, and  $G_{ij}^0$  are the elements of Wilson's  $G$  matrix [12] at equilibrium. The potential energy function  $V$  is assumed to have the form

$$V = \sum_{i < j} F_{ij} S_i S_j + \sum_{i < j < k} F_{ijk} S_i S_j S_k \\ + \sum_{i < j < k < l} F_{ijkl} S_i S_j S_k S_l, \quad (3)$$

where  $S_i = 1 - \exp(-a_i \mathcal{R}_i)$ ,  $i = 1, 2$ , and  $S_j = \mathcal{R}_j$ ,  $j = 3, \dots, 6$ . The parameters  $a_1$  and  $a_2$  are constants to be determined in the fit of the *ab initio* data.

The rotational energies are evaluated using the following "harmonic" nonrigid inverter Hamiltonian [10,13]:

$$\mathcal{H}_{\text{vir}} = \frac{1}{2} \mu_{\rho\rho}^0 \hat{J}_\rho^2 + \frac{1}{2} (\hat{J}_\rho \mu_{\rho\rho}^0) \hat{J}_\rho \\ + \frac{1}{2} \sum_{\alpha, \beta = x, y, z} \mu_{\alpha\beta}^0 \hat{J}_\alpha \hat{J}_\beta \\ + \frac{1}{4} \sum_{\alpha, \beta, \gamma, \delta = x, y, z} \tau_{\alpha\beta\gamma\delta} \hat{J}_\alpha \hat{J}_\beta \hat{J}_\gamma \hat{J}_\delta \\ + \frac{1}{2} \sum_{\alpha = x, y, z} \left( \sum_k X_k^{\alpha\rho} Q_k \right) \hat{J}_\alpha \hat{J}_\rho \\ + \frac{1}{2} \sum_{\alpha = x, y, z} \left( \sum_k (\hat{J}_\rho X_k^{\alpha\rho} Q_k) \right) \hat{J}_\alpha \\ + \frac{1}{2} \sum_k X_k^{\rho\rho} Q_k \hat{J}_\rho^2 \\ + \frac{1}{2} \sum_k (\hat{J}_\rho X_k^{\rho\rho} Q_k) \hat{J}_\rho + V_{\text{eff}}(\rho).$$

Here  $\hat{J}_\alpha$  ( $\alpha = x, y, z$ ) are the components of the total

angular momentum operator and  $\hat{J}_\rho = i\hbar \partial/\partial\rho$ , where the out-of-plane bending angle  $\rho$  is made by the O–Na bond with the bisector of the HOH plane for  $R=R_e$ ,  $r_1=r_2=r_e$ , and  $\beta=\beta_e$ . The components of the inverse moment of the molecular inertia tensor are approximated as

$$\mu_{\alpha\beta} = \mu_{\alpha\beta}^0(\rho) + \sum_k X_k^{\alpha\beta}(\rho) Q_k(\rho),$$

where  $Q_k$  are in-plane normal coordinates. The effective potential energy function is

$$V_{\text{eff}}(\rho) = V_o(\rho) + \frac{1}{2} \sum_k \lambda_k(\rho) Q_k^2 + V_{\text{pseudo}}(\rho),$$

where  $V_o$  is the out-of-plane potential,  $\lambda_k = 4\pi^2 c^2 \omega_k^2$  ( $\omega_k$  being the harmonic wavenumber of the  $k$ th normal mode), and  $V_{\text{pseudo}}$  is a pseudopotential term arising due to the  $\rho$  dependence of the reduced mass. Finally,  $\tau_{\alpha\beta\gamma\delta}(\rho)$  ( $\alpha, \beta, \gamma, \delta = x, y, z$ ) are effective centrifugal distortion constants.

### 3. The ab initio calculations

The ab initio energies, gradients, and Hessians were calculated at selected geometries using the SIRIUS-ABACUS program system [14–16]. We used the basis sets designed by Clementi and coworkers [9,17] to describe the interaction between the alkali cations and water. The water basis was taken from ref. [17], except that the oxygen basis was slightly modified in order to get equivalent  $p_x$ ,  $p_y$ , and  $p_z$  orbitals. For orbitals 13, 16, and 29 in table II of ref. [17] we used contraction coefficients 0.32 and 0.30; for orbitals 14, 17, and 30 we used the coefficients 0.17, 0.062, 0.014, and 0.0019. The water basis consisted of (11s7p1d/6s1p) Gaussian orbitals contracted to [4s3p1d/2s1p]. The sodium basis was taken from ref. [9]. It consists of (13s8p1d) primitive Gaussians contracted to [7s4p1d], leading to a total of 54 contracted Gaussian basis functions for the  $\text{H}_2\text{O}\cdot\text{Na}^+$  complex. Compared to the work by Kistenmacher et al. [9], our treatment is improved in two respects: An MCSCF rather than SCF function is used and the water molecule is not kept rigid.

To determine an adequate correlation level we carried out MP2 natural orbital (NO) analyses [18] at four geometries: one close to the planar  $C_{2v}$  equilib-

rium structure, one with  $12^\circ$  in-plane bend, one with  $45^\circ$  out-of-plane distortion, and finally a planar structure of  $C_{2v}$  symmetry with the hydrogen atoms pointing towards sodium. It is known that a reasonable description of the equilibrium structure and harmonic frequencies of water requires a complete active space correlating the eight valence electrons of water in  $4a_1$ ,  $2b_1$ , and  $2b_2$  orbitals. This is reflected in the MP2 occupation numbers of the NOs localized on water. (We examined all NOs with occupation  $\geq 0.001$  and these are localized either on water or on sodium.)

The MP2 calculations indicate that correlation in  $\text{Na}^+$  is significant. The occupation of  $\text{Na}2p$  is 1.989, compared to 1.986 for  $\text{O}2s$  in water. However, the occupation numbers of sodium are almost independent of the geometry, differing by less than 0.0002 electrons. In the complex, the  $\text{Na}2p$  NO pointing towards water has an occupation of 1.9890 while the other  $2p$  orbitals have occupations of 1.9888. In the free cation, the occupation is 1.9889. (In contrast, the occupation numbers in water vary on the order of 0.003 electrons.) Therefore, the  $\text{Na}^+$  correlation is internal and not significant for the relative energies on the potential energy surface.

All calculations were therefore carried out with a complete active space of eight electrons in eight orbitals (CAS1), corresponding to the water correlation discussed above. As a precaution, we compared the CAS1 and MP2 energies at the last three geometries relative to the equilibrium geometry, as the relative energies are the important entities of the potential energy surface. We found the differences between CAS1 and MP2 relative energies to be less than 0.2 mhartree for the two middle geometries and 1.5 mhartree for the last geometry. The differences between the SCF and MP2 energies are less than 2.5 and 3.7 mhartree, respectively. This supports our assumption that the CAS1 space gives a good potential energy surface. The MP2 analysis is also in agreement with the conclusion by Kistenmacher et al. [9]: "The binding is mainly electrostatic in origin and is enhanced by the effect of the charge transfer within the water molecule...".

The actual ab initio calculations were performed at nine geometries. The resulting 9 energies, 30 symmetry independent gradient elements, and 108 Hessian elements were used to fit (practically quanti-

Table 1

Potential energy function parameters for  $\text{H}_2\text{O}\cdot\text{Na}^+$  obtained by fitting eq. (3) to ab initio calculated data

| Parameter          | MCSCF    | Parameter                | MCSCF              |
|--------------------|----------|--------------------------|--------------------|
| $F_{11}$ (mdyn Å)  | 0.10140  | $F_{155}$ (mdyn Å)       | -0.00964           |
| $F_{22}$ (mdyn Å)  | 7.86372  | $F_{166}$ (mdyn Å)       | -0.02632           |
| $F_{33}$ (mdyn Å)  | 0.38750  | $F_{266}$ (mdyn Å)       | -0.01926           |
| $F_{44}$ (mdyn Å)  | 4.15721  | $F_{666}$ (mdyn Å)       | 0.00387            |
| $F_{55}$ (mdyn Å)  | 0.04847  | $F_{556}$ (mdyn Å)       | 0.06333            |
| $F_{66}$ (mdyn Å)  | 0.03425  |                          |                    |
| $F_{12}$ (mdyn Å)  | 0.01048  | $R_e$ (Å)                | 2.26282            |
| $F_{13}$ (mdyn Å)  | -0.00826 | $r_e$ (Å)                | 0.97345            |
| $F_{23}$ (mdyn Å)  | 0.19657  | $\beta_e$ (deg)          | 104.284            |
| $F_{45}$ (mdyn Å)  | 0.01082  | $a_1$ (Å <sup>-1</sup> ) | 1.59 <sup>a)</sup> |
| $F_{113}$ (mdyn Å) | 0.01184  | $a_2$ (Å <sup>-1</sup> ) | 0.72 <sup>a)</sup> |

<sup>a)</sup> Held fixed after preliminary determination.

tatively) the most important force constants of eq. (3) (see table 1). The calculated  $\text{Na}^+$  binding energy is 24.6 kcal/mol.

#### 4. The vibration-rotation energies

The vibrational energy levels were obtained variationally by diagonalizing the Hamiltonian (2) as a matrix over basis functions expressed as products  $\prod_{i=1}^6 \Phi_i(v_i)$ . The functions  $\Phi_1(v_1)$  and  $\Phi_2(v_2)$  were obtained numerically by solving the corresponding uncoupled one-dimensional Schrödinger equations. For the remaining modes we used harmonic oscillator eigenfunctions. To keep the calculations manageable, the total basis set was constrained by imposing  $v_2, v_4 \leq 1$  (OH stretches). With this restriction, the required lowest eigenvalues (see table 2) are

Table 2

Calculated vibrational energies of  $\text{H}_2\text{O}\cdot\text{Na}^+$  and  $\text{D}_2\text{O}\cdot\text{Na}^+$  (in  $\text{cm}^{-1}$ )

| $v_1$ | $v_2$ | $v_3$ | $v_4$ | $v_5$ | $v_6$ | $\text{H}_2\text{O}\cdot\text{Na}^+$ | $\text{D}_2\text{O}\cdot\text{Na}^+$ |
|-------|-------|-------|-------|-------|-------|--------------------------------------|--------------------------------------|
| 0     | 0     | 0     | 0     | 0     | 0     | 0.0                                  | 0.0                                  |
| 1     | 0     | 0     | 0     | 0     | 0     | 286                                  | 278                                  |
| 0     | 0     | 0     | 0     | 1     | 0     | 462                                  | 345                                  |
| 0     | 0     | 0     | 0     | 0     | 1     | 467                                  | 353                                  |
| 2     | 0     | 0     | 0     | 0     | 0     | 572                                  | 562                                  |
| 1     | 0     | 0     | 0     | 1     | 0     | 752                                  | 631                                  |
| 1     | 0     | 0     | 0     | 0     | 1     | 757                                  | 638                                  |
| ZPE   |       |       |       |       |       | 5303                                 | 3917                                 |

completely converged using 160 basis set functions.

To assess the reliability of our calculations and to estimate solvation effects, we also evaluated the harmonic frequencies of the isolated water molecule at the same level of ab initio theory. The results are collected in table 3 and indicate that the employed MCSCF wavefunction is capable of reproducing the experimental vibrational constants within  $30 \text{ cm}^{-1}$ .

We evaluated the rotational energies of the vibrational ground and  $v_6=1$  states by diagonalizing the Hamiltonian (4) as a matrix over the basis functions expressed as the products  $S(\theta, \varphi, \chi) \Phi(v_6)$  ( $v_6=0, 1, \dots, 7$ ). The out-of-plane bending functions  $\Phi(v_6)$  were obtained numerically by solving the out-of-plane Schrödinger equation, and  $S(\theta, \varphi, \chi)$  are normalized symmetric top rotational wavefunctions. Both  $\text{H}_2\text{O}\cdot\text{Na}^+$  and  $\text{D}_2\text{O}\cdot\text{Na}^+$  are near symmetric top molecules and their rotational energies exhibit sizeable  $K$  splittings only for  $K=1$ . Consequently, the energies can be fitted quantitatively using the ex-

Table 3

Harmonic vibrational frequencies of  $\text{H}_2\text{O}\cdot\text{Na}^+$  and  $\text{H}_2\text{O}$  (in  $\text{cm}^{-1}$ )

| Frequency      | $\text{H}_2\text{O}\cdot\text{Na}^+$ |      | $\text{H}_2\text{O}$ |                    |
|----------------|--------------------------------------|------|----------------------|--------------------|
|                | MCSCF                                | SCF  | MCSCF                | exp. <sup>a)</sup> |
| A <sub>1</sub> | $\omega_1$                           | 292  | 302                  |                    |
|                | $\omega_2$                           | 3788 | 4091                 | 3832               |
|                | $\omega_3$                           | 1713 | 1788                 | 1654               |
| B <sub>1</sub> | $\omega_4$                           | 3885 | 4169                 | 3938               |
|                | $\omega_5$                           | 448  | 446                  | 3943               |
| B <sub>2</sub> | $\omega_6$                           | 437  | 470                  |                    |

<sup>a)</sup> Ref. [19].

Table 4  
Rotational and centrifugal distortion constants<sup>a)</sup> of H<sub>2</sub>O·Na<sup>+</sup> and D<sub>2</sub>O·Na<sup>+</sup> (in cm<sup>-1</sup>)

| Constant                              | H <sub>2</sub> O·Na <sup>+</sup> |           | D <sub>2</sub> O·Na <sup>+</sup> |           |
|---------------------------------------|----------------------------------|-----------|----------------------------------|-----------|
|                                       | $\nu_6=0$                        | $\nu_6=1$ | $\nu_6=0$                        | $\nu_6=1$ |
| <i>A</i>                              | 13.746                           | 13.005    | 6.945                            | 6.682     |
| <i>B</i>                              | 0.305                            | 0.306     | 0.273                            | 0.274     |
| <i>C</i>                              | 0.298                            | 0.300     | 0.263                            | 0.264     |
| 10 <sup>6</sup> <i>D<sub>J</sub></i>  | 0.78                             | 1.25      |                                  |           |
| 10 <sup>4</sup> <i>D<sub>JK</sub></i> | 0.30                             | 0.44      | 0.24                             | 0.27      |
| 10 <sup>3</sup> <i>D<sub>K</sub></i>  | 1.91                             | 1.32      | 0.45                             | 0.44      |

<sup>a)</sup>  $\nu_1 = \nu_2 = \nu_3 = \nu_4 = \nu_5 = 0$ .

PLICIT expressions derived by Winnewisser [20]. The corresponding spectroscopic constants are given in table 4.

## 5. Summary and conclusions

Molecular ab initio energies, gradients, and Hessians have been used to probe the potential energy surface of H<sub>2</sub>O·Na<sup>+</sup> in the electronic ground state. Altogether 9 energies (up to 2000 cm<sup>-1</sup> above equilibrium), 30 first derivatives and 108 second derivatives have been evaluated at 9 geometries selected so as to allow for a detailed description of the regions important for a proper description of the low-frequency (aggregation) vibrational and rotational motions. The remaining regions of the surface are assumed to be harmonic in the relevant vibrational coordinates. All ab initio energies and derivatives have been fitted quantitatively to a simple polynomial function strongly dominated by the harmonic terms. This finding has facilitated the variational evaluation of the vibrational and rotational energies of H<sub>2</sub>O·Na<sup>+</sup> and D<sub>2</sub>O·Na<sup>+</sup> by means of simple model vibrational and rotational Hamiltonians.

To assess the reliability of the calculated rovibrational energies, the harmonic frequencies of the isolated water molecule were evaluated at the same ab initio level. These frequencies are in close agreement with experiment. We believe the present results to be

of reasonable quality and useful for an unambiguous experimental identification of the H<sub>2</sub>O·Na<sup>+</sup> complex.

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