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SPECTROSCOPIC PARAMETERS OF INTERACTING SYSTEMS I. AB INITIO STUDY OF VIBRATIONAL INTENSITY CHANGES DUE TO ION-MOLECULE INTERACTION. $H_2O...Li^+$*

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A series of systematic studies of the ion-molecule and molecule-molecule interaction effects on the molecular spectroscopic parameters is undertaken. In the present paper the vibrational intensity changes due to $H_2O...Li^+$ interaction are studied for both the IR and the Raman bands of symmetric modes of the water molecule. The relevant dipole moment and polarizability derivatives with respect to the corresponding normal coordinates are obtained from ab initio calculations employing the so-called electric-field-variant (EFV) GTO's. The computed intensity ratios indicate a very large enhancement of the intensity of the OH stretching band in the IR spectrum. The IR band due to HOH bending vibration is affected to a lesser extent. In the Raman spectrum the $H_2O...Li^+$ interaction leads to the intensity decrease for both bands. The results calculated for the model $H_2O...Li^+$ system are exploited for the discussion of several interpretations of the IR and Raman spectra of aqueous electrolyte solutions. Some of these interpretations are questioned as either too simplified or based on wrong assumptions.

1. *Introduction*

In recent years a considerable progress has been made in the experimental and theoretical investigations of the solvent-solute interactions in liquids. A particular attention has obviously been given to the aqueous solutions of electrolytes [1–3]. The spectroscopic methods proved to be extremely useful in the experimental investigation of these systems.

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The ion-molecule interactions introduce substantial changes in the measured spectra and among a variety of spectroscopic techniques the IR, Raman and NMR spectroscopies [2] are probably the most important ones. The electrolyte solution spectra, when interpreted in terms of the appropriate models, provide a deeper insight into the nature of the ion-water interactions. On the other hand, the majority of the pertinent theoretical studies was concerned primarily with the energetic aspects of these interactions [4]. The interaction energies were computed for several models of solvated ions in order to account for the thermodynamic properties of electrolyte solutions. The spectroscopic aspects of the ion-molecule interactions relevant for the IR, Raman or NMR spectroscopy of aqueous solutions of electrolytes were studied only occasionally and the corresponding theoretical data are rather scarce.

It follows from the energetically-oriented theoretical considerations of the ion-molecule interactions that even rather simple models of solvated ions may provide a useful information and may satisfactorily account for a number of qualitative features of extremely complicated liquid systems [4]. Also the spectroscopic solvation effects are quite frequently given a qualitative interpretation in terms of interactions within the so-called first solvation shell. This approach at least helps to understand several observed regularities. Moreover, the experimental data indicate that the cationic and the anionic effects can be, to some extent, treated separately [2]. These arguments could be used to justify the interest in the simplest possible models, i.e., the ion-molecule pair systems. Another, quite natural justification of such studies follows from quite obvious limitations of sophisticated theoretical approaches. Nevertheless, it is believed that at least in the case of strongly interacting species, the pair models can provide an interesting and meaningful information concerning the properties of solvent molecules in the electrolyte solutions.

The aim of the present series of theoretical studies is to investigate the spectroscopic effects of the ion-molecule and molecule-molecule interactions. The properties to be considered will refer to the ground electronic states of the interacting species and the changes of the solvent molecule spectroscopic parameters related to the IR, Raman and NMR spectra will be of primary concern. In the present paper the influence of the lithium cation on the IR and Raman spectroscopic parameters of the water molecule is investigated. The main attention was paid to the intensity changes in the corresponding spectra since they provide the most sensitive measure of the interaction effects.

The calculation of the intensities of spectral bands is usually more difficult than the calculation of interaction energies. In the case of the IR spectra one has to know the geometry dependence of the dipole moment of the system. Even more difficult appears the calculation of the intensity of the Raman bands which requires the knowledge of the polarizability derivatives with respect to the normal coordinates of molecular vibrations [5]. According to the perturbation theory classification the IR intensity corresponds to the second-order perturbed energies and the Raman intensity is the third-order quantity [6]. Their relatively accurate calculation represents a formidable task even for small systems. Thus, the majority of theoretical results is based on the use of semiempirical methods [7–11] and except for H_2^+ and H_2 there are only a few ab initio calculations of the pertinent intensities.

The calculations reported in this paper correspond to the SCF level of accuracy. They obviously suffer from the neglect of the correlation effects as well as from the incompleteness of the employed basis sets. The technique used for the calculation of the dipole moment and polarizability derivatives follows that described by Segal and Klein [7], i.e., the derivatives are computed numerically from a set of the dipole moment and polarizability values computed at different geometries. Thus the main attention is shifted towards the problem of a reliable calculation of molecular dipole moments and polarizabilities at a given geometry[1]. The methods used for this purpose are described in the next section. A subsequent section deals with the computational details of our study. The numerical results for H_2O and $H_2O\ldots Li^+$ and their mutual comparison are presented in Section 4. In the last section the theoretical results obtained for a simple model of the ion-solvent interaction are discussed from the point of view of some observed features of the IR and Raman spectra of aqueous solutions of electrolytes.

2. Relatively accurate molecular dipole moments and polarizabilities from small basis set SCF calculations. Description of the method

The natural limitations of the size of computers lead to the preference of rather small basis sets. Such sets, usually of the so-called double-dzeta quality, have been found quite satisfactory in the calculation of molecular energies [13, 14]. However, they evidently cannot account for the effects of the external electric field perturbation, and thus, the predicted molecular electric properties are substantially different from the expected near--Hartree-Fock values [13, 15]. Already in the case of dipole moments one has to augment the basis sets with the so-called polarization functions [13]. Computing near-Hartree-Fock values of electric dipole polarizabilities requires more polarization functions [16]; the polarizability results from the double-dzeta quality bases are completely unreliable [17]. In order to save the useful features of the small basis set calculations and simultaneously improve the quality of the computed molecular electric properties a new approach was recently proposed [17].

It is well known [18–20] that the quality of several molecular properties can be substantially improved by the property directed adjustment of the basis set. This is the idea behind the so-called floating (perturbation dependent) basis sets, which have been successfully used in the calculations of molecular force constants [21–24] and magnetic properties [25, 26]. The usefulness of such approaches follows from the fact that the perturbation dependence of the basis functions is a priori given in the analytic form [24, 25, 27]. The first attempt to make the basis set explicitly dependent on the external electric field strengths was by Moccia [28]. However, his proposal did not prove to be numerically efficient [28,29]. The method proposed by one of the present authors [17] exploits some features of the Gaus-

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[1] The neglect of the correlation effects leads to a wrong asymptotic behaviour of dipole moments and polarizabilities for large internuclear distances [12]. However, for molecules with relatively high dissociation energies this improper geometry dependence of these quantities is of a rather minor importance for geometries close to the observed or theoretical equilibrium.

sian functions, which by no means are currently the most popular basis functions in quantum-chemical calculations.

The method in question was originally devised for the molecular polarizability calculations [17]. The polarization of primitive Gaussian orbitals upon the influence of the external field **F** follows immediately from the harmonic oscillator theory. The electric field directed along the μ-th axis of the coordinate system induces a field-dependent shift of the orbital origin. In order to account for the differences between a set of harmonic oscillators and a set of Gaussians in an atom or molecule, the additional scale factor λ_μ was introduced. Thus in the presence of the external electric field the origin of each primittive Gaussian was assumed to be shifted by

$$r_\nu \to r_\nu + \Delta_\nu(F_\mu, \lambda_\mu), \tag{1}$$

where [17]

$$\Delta_\nu(F_\mu, \lambda_\mu) = \delta_{\mu\nu}\frac{\lambda_\mu F_\mu}{\alpha^2} \tag{2}$$

and α denotes the Gaussian orbital exponent.

The numerical value of the scale factor should be in principle independent of the direction of the external electric field. However, for finite incomplete bases it may exhibit some directional properties [30]. In spite of the physical picture leading to Eq. (1), the scale factor λ_μ should be in general considered as an additional variation parameter.

The components of the electric dipole polarizability tensor are proportional to the external electric field induced second-order perturbed energy [31]. Within the SCF HF approximation the external perturbation leads to the so-called coupled Hartree–Fock (CHF) scheme [32–34]. The explicit perturbation dependence of the basis set results in additional terms [6, 35, 36] in the ordinary CHF equations. It was also shown that in the present case the second-order CHF energy is a parabolic function of the scale factor [36]. Thus, the optimal value of λ_μ can be determined from the minimum condition of the diagonal components of the second-order energy tensor [17, 36] or equivalently from the maximum condition for the diagonal components of the polarizability tensor.

The method of calculation employed in this study is exactly the same as used previously [15, 30]. The polarizability components were first computed for some preselected values of λ_μ [15, 17] by using the finite field SCF perturbation method, which is virtually equivalent to the CHF scheme [37, 38]. Then the best values of λ_μ were determined numerically from the corresponding parabolic fits for the diagonal components of the polarizability tensor $\alpha_{\mu\mu}$. This procedure was repeated for several geometries of the considered systems.

The molecular dipole moment is proportional to the first-order perturbed energy [31]. However, using the variable basis set leads to the violation of the Hellmann–Feynman theorem and the dipole moment expression will contain some extra terms linear in λ_μ [36, 39]. Since no bound is provided by the first-order energy functional [40], the value of λ_μ determined from the polarizability calculations was also used for the evaluation of the dipole moment components [15, 30].

The method outlined in this section proved to be quite successful in practical applications [15, 17, 30, 36]. Even in the case of relatively small Gaussian bases, the computed molecular electric properties can compete with the results of rather extensive CHF calculations employing fixed, field independent basis functions [15, 17]. It was also shown that slightly larger bases can provide near-HF accuracy of the computed dipole moments and polarizabilities [30]. It is worth attention that according to our results the use of the so-called polarization functions in the electric-field-dependent Gaussian bases does not appear to be necessary.

For a given size of the Gaussian basis set the perturbation calculations utilizing its dependence on the external electric field strength will be naturally more time consuming than the ordinary CHF calculations with fixed basis set. However, in general rather small variable bases lead to quite acceptable results. The λ-optimization of the second-order energies ensures that a given original Gaussian basis set will be uniformly adapted to the electric field perturbation for a number of similar molecular geometries. Thus, although the absolute values of the computed dipole moments and polarizabilities can be still different from the corresponding HF limits, one can expect relatively accurate description of their geometry dependence. Thus the electric-field-variant Gaussian-type orbitals (EFV GTO's), constructed according to Eqs (1) and (2) are likely to represent a suitable basis set for the present purposes. More computational details pertinent to the material reported in this paper is presented in the next section.

3. Some computational details of the EFV GTO calculations for H_2O and $H_2O...Li^+$

It was previously found that at the experimental geometry the so-called 4–31G basis set of Ditchfield et al. [41] with explicit electric field dependence introduced according to the EFV GTO scheme, leads to a reasonable value of the water molecule polarizability [17]. The results of the EFV 4–31G calculations compared favourably with other CHF values computed using much larger bases [23, 42]. Moreover, since the 4–31G sets are sufficiently small to allow for a complete λ-optimization for a series of molecular geometries in a reasonable time, they were selected for the present study. However, for Li^+ the corresponding 4–31G basis set has not been determined and therefore a similar quality set of Clementi and Popkie [43] was employed. This basis set consists of 7 primitive *s*-type GTO's contracted to 3 CGTO's, i.e., (7/5, 1, 1).

The experimental geometry of H_2O [44] was chosen as a reference. Four other geometries, corresponding to the symmetric vibrations, were constructed according to the data of Table I. As regards the molecular geometry of the $H_2O...Li^+$ system, the $O...Li^+$ distance was kept constant at 3.57 a.u. with lithium cation on the C_2 symmetry axis. Similarly to our previous calculations using the fixed basis set approach [45] also the experimental geometry of H_2O in the interacting system was assumed as a reference. All these assumptions follow from the calculations of the potential energy hypersurface of $H_2O...Li^+$ by Diercksen and Kraemer [46]. Since only the symmetric OH stretching and the HOH bending vibrations are considered in the present study, the relevant variable molecular geometry parameters for $H_2O...Li^+$ are the same as for the isolated water molecule (see Table I).

As can be seen from the SCF energy values given in Table I, the theoretical equilibrium geometry for H_2O and $H_2O...Li^+$ is not significantly different from the available experimental data as far as the OH bond length is concerned. However, much larger deviation is observed for the HOH angle. The assumption of the experimental geometry of H_2O taken as a reference for the calculation of the first-order derivatives of molecular electric properties can be justified only if the corresponding properties vary almost linearly with the molecular geometry. This was in fact observed in similar calculations using much larger field-independent basis sets [45].

TABLE I

Geometries and computed SCF energies of the isolated H_2O molecule and $H_2O...Li^+$ system ($R_{O...Li^+} = 3.57$ a.u.)

Geometry set	Δr_{OH} [a] (a. u.)	$\Delta\alpha_{HOH}$	Total SCF energy (a.u.)	
			H_2O	$H_2O...Li^+$
I[b]	.0	.0	−75.907394	—83.213331
II	−0.025	.0	−75.907155	−83.212960
III	0.025	.0	−75.906941	−83.212995
IV	.0	−4.0°[c]	−75.905422	−83.211492
V	.0	+4.0°	−75.908392	−83.214115

[a] Symmetric stretch, $\Delta r_{OH} = \Delta r_{OH_1} = \Delta r_{OH_2}$. [b] Experimental geometry, $r_{OH} = 1.80887$ a.u., $\alpha_{HOH} = 104.52°$ [43].

For each of molecular geometries of H_2O and $H_2O...Li^+$ listed in Table I a set of finite field SCF calculations has been performed using both the field independent and the EFV GTO basis set. In the case of the EFV GTO SCF calculations the scale factors λ_μ were separately optimized for each geometry and for each direction of the external electric field. In general, the dipole moment components μ_μ and the diagonal components of the polarizability tensor $\alpha_{\mu\mu}$ were obtained as the first- and the second-order derivatives of the field-dependent molecular energy, respectively[2]. Some problems related to the numerical stability and accuracy of this procedure have already been discussed [15] and will not be repeated here.

The calculation of the dipole moment for $H_2O...Li^+$ brings a question of the choice of the coordinate origin, since for charged species the dipole moment will be origin-dependent. In our calculations the coordinate origin was always assumed at the oxygen atom. Fortunately enough as far as the derivatives of the dipole moment of $H_2O...Li^+$ are concerned, they are origin independent.

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[2] It should be pointed out that for the perturbation-dependent basis set the dipole moment expectation value is not in general equal to the average of the dipole moment operator [15, 39].

The derivatives of μ_μ and $\alpha_{\mu\mu}$ with respect to the internal coordinates Δr and $\Delta\alpha$, representing the symmetric OH stretching and the HOH bending, respectively, were computed by using the finite difference method. For the interpretation of the IR and Raman intensity data they have to be converted into the corresponding derivatives with respect to the normal vibration coordinates. These, in principle can be obtained from the calculated SCF potential energy hypersurfaces. However, the SCF force fields are usually rather inaccurate [23] and thus the transformation matrix $\boldsymbol{L}$ has been computed from the available experimental force fields [45]. Moreover, since the force field of the water molecule in $H_2O\ldots Li^+$ does not significantly change in comparison with that of the isolated H_2O, the $\boldsymbol{L}$ matrix was assumed to be the same in both cases.

For each electric property, say A, its derivatives with respect to the approximate normal coordinates Q_i ($i = 1$-symmetric OH stretching mode, $i = 2$-HOH bending mode) were obtained as [47, 48]

$$\frac{\partial A}{\partial Q_i} = \sum_j L_{ji} \frac{\partial A}{\partial S_j}, \tag{3}$$

where

$$S_1 = \frac{1}{\sqrt{2}}(\Delta r_{\mathrm{OH_1}} + \Delta r_{\mathrm{OH_2}}), \qquad S_2 = \Delta\alpha_{\mathrm{HOH}}$$

denote the internal symmetry coordinates. Finally, the derivatives (3) were used for the estimation of the relative IR and Raman intensities of the corresponding vibration bands.

The IR intensity of a given band of frequency ν_i can be expressed as [47]

$$I^{\mathrm{IR}}(\nu_i) = f(\nu_i)\left|\frac{\partial \boldsymbol{\mu}}{\partial Q_i}\right|^2 \tag{4}$$

and since the water molecule force field does not change very much due to $H_2O\ldots Li^+$ interaction, the frequency dependent factor can be assumed to be the same for both H_2O and $H_2O\ldots Li^+$ [45, 46]. The same assumption was utilized in the case of the Raman line intensities, which can be written as [49]

$$I^{\mathrm{R}}(\nu_i) = g(\nu_i)\,(3a_i^2 + \tfrac{2}{3}\,b_i^2), \tag{5}$$

where

$$a_i = \tfrac{1}{3}\left(\frac{\partial\alpha_{xx}}{\partial Q_i} + \frac{\partial\alpha_{yy}}{\partial Q_i} + \frac{\partial\alpha_{zz}}{\partial Q_i}\right) \tag{6}$$

$$b_i^2 = \tfrac{1}{2}\left[\left(\frac{\partial\alpha_{xx}}{\partial Q_i} - \frac{\partial\alpha_{yy}}{\partial Q_i}\right)^2 + \left(\frac{\partial\alpha_{yy}}{\partial Q_i} - \frac{\partial\alpha_{zz}}{\partial Q_i}\right)^2 + \left(\frac{\partial\alpha_{zz}}{\partial Q_i} - \frac{\partial\alpha_{xx}}{\partial Q_i}\right)^2\right]. \tag{7}$$

Thus, the relative IR and Raman band intensities can be written down solely in terms of the computed derivatives of the dipole moment and polarizability of both systems. Moreover, the knowledge of a_i and b_i allows also for the calculation of the depolarization ratios [49] of a given Raman band for linearly ($\varrho_{\perp,i}$) polarized and non-polarized (ϱ_i) exciting light.

The numerical values of the computed electric properties of H_2O and $H_2O...Li^+$ as well as the corresponding derivatives and the estimated relative IR and Raman intensities of the OH stretching and HOH bending mode are reported in the next section.

4. *Numerical results*

The results of the finite field perturbation calculations using the field independent basis set are collected in Table II. A comparison with rather accurate SCF perturbation calculations and with the available experimental data clearly shows how bad is the field independent 4–31G basis set from the point of view of molecular electric properties. This conclusion appears to be rather obvious and the main reason for the field independent calculations was to estimate the accuracy of the finite field perturbation procedure [15].

TABLE II

Results of the field independent 4–31G basis set calculations of the dipole moment and polarizability tensor of H_2O and $H_2O...Li^+$. All entries in a.u.

Molecule	Geometry set [a]	μ_x [b]	α_{xx}	α_{yy}	α_{zz}	α
H_2O	I	1.02596	4.295	1.314	6.576	4.062
	II	1.02389	4.159	1.340	6.284	3.927
	III	1.02785	4.437	1.295	6.887	4.206
	IV	1.05189	4.578	1.315	6.462	4.119
	V	0.99852	4.019	1.320	6.684	4.008
Reference results						
	I [c]	0.782	8.47	7.99	9.04	8.50
	I [d]	0.868	6.11	4.95	7.54	6.20
	Exptl. [e]	0.724				9.82
$H_2O...Li^+$	I	−2.30728	3.795	1.247	5.381	3.474
	II	−2.31964	3.686	1.266	5.161	3.371
	III	−2.29788	3.906	1.227	5.610	3.581
	IV	−2.26818	4.016	1.244	5.264	3.508
	V	−2.34773	3.580	1.250	5.489	3.440
Reference results						
	I [f]	−1.845	6.449	4.891	6.930	6.090

[a] See Table I.

[b] Molecule in *xz* plane, $x-C_2$ symmetry axis. The origin of the coordinate system at the oxygen atom.

[c] Very accurate finite perturbation SCF results of Werner and Meyer [20]. Presumably correspond to the HF accuracy.

[d] CHF results obtained using medium size polarized basis set [23, 42]. The same result was repeated within the finite field perturbation approach [45, 50].

[e] Taken from Ref. [20].

[f] CHF and finite field perturbation results obtained using medium size polarized basis set [45, 50].

For the field independent basis set both the dipole moment and the components of the polarizability tensor can be easily obtained either from the unperturbed calculations or from the ordinary CHF approach [34].

According to the results of the field independent basis set calculations there is a substantial decrease of the average polarizability of H_2O due to ion-molecule interaction. This result can be easily understood in terms of simple physical considerations. A similar effect, though much smaller was also observed in the calculations using large, polarized basis set [45, 50].

The results of the EFV GTO finite perturbation calculations are shown in Table III. As can be seen from a comparison with the data of Table II, the EFV GTO procedure leads to a substantial improvement for both the dipole moment and the polarizability tensor. The EFV GTO dipole moment becomes reasonably close to the experimental value for the water molecule and favourably compares with the results of fairly accurate SCF calculations. As regards the polarizability tensor, the present results are poorer than the expected HF limits. However, there are several reasons to believe that the variation of the polarizability tensor components due to changes of the molecular geometry is predicted with much higher accuracy. It should be pointed out that for each molecular geometry the λ_μ parameters were separately optimized and this procedure partly accounts for a different degree of completeness of a given basis set for different geometries. It is also worth attention that only minute changes of the optimized λ_μ values for a given system were observed. Also on passing from H_2O to $H_2O...Li^+$ the scale factors do not change considerably. This confirms already noticed stability of the optimized scale factors [12, 15, 30] and shows that some preselected values of λ_μ can be used for less accurate calculations.

TABLE III

Results of the EFV GTO finite perturbation SCF calculations of the dipole moment and polarizability tensor of H_2O and $H_2O...Li^+$. All entries in a.u. Values in parentheses are the optimized scale factors λ_μ.

Molecule	Geometry set[a]	μ_x[b]	$\alpha_{xx}(\lambda_x)$	$\alpha_{yy}(\lambda_y)$	$\alpha_{zz}(\lambda_z)$	α
H_2O	I	0.71716	7.268 (0.127)	5.963 (0.134)	8.413 (0.118)	7.215
	II	0.71525	7.124 (0.127)	5.913 (0.134)	8.144 (0.119)	7.060
	III	0.72015	7.415 (0.126)	6.013 (0.134)	8.691 (0.117)	7.373
	IV	0.74290	7.384 (0.125)	5.962 (0.134)	8.346 (0.118)	7.231
	V	0.69158	7.157 (0.128)	5.964 (0.135)	8.477 (0.119)	7.199
$H_2O...Li^+$	I	−2.41769	7.008 (0.135)	5.617 (0.129)	7.660 (0.123)	6.762
	II	−2.42702	6.882 (0.135)	5.573 (0.129)	7.445 (0.123)	6.633
	III	−2.40814	7.135 (0.134)	5.661 (0.130)	7.874 (0.122)	6.890
	IV	−2.38763	7.109 (0.132)	5.615 (0.129)	7.855 (0.122)	6.770
	V	−2.44633	6.908 (0.135)	5.620 (0.130)	7.724 (0.124)	6.751

[a] See Table I. [b] See footnote to Table II.

The dipole moment and polarizability tensor derivatives with respect to the internal symmetry coordinates have been computed directly from the data of Table II and Table III. Then, they were transformed into the corresponding derivatives with respect to the approximate [45] normal coordinates of both systems. The final computed values are shown in Table IV. Although the absolute values of the calculated derivatives for the field independent basis set are quite different from those obtained using the EFV GTO approach, their qualitative behaviour appears to be similar. Both sets of the derivatives calculated in the present paper resemble also the data following from our previous calculations [45] with much larger but fixed basis sets.

TABLE IV

Dipole moment and polarizability derivatives with respect to normal coordinates Q_1 (symmetric OH stretch) and Q_2 (HOH bending). All entries in a.u.

Basis set	Molecule	i	$\frac{\partial\mu_x}{\partial Q_i}$	$\frac{\partial\alpha_{xx}}{\partial Q_i}$	$\frac{\partial\alpha_{yy}}{\partial Q_i}$	$\frac{\partial\alpha_{zz}}{\partial Q_i}$
Field independent	H_2O	1	0.013	0.933	−0.151	2.033
		2	−0.073	−0.820	0.016	0.168
	$H_2O...Li^+$	1	0.063	0.726	−0.131	1.515
		2	−0.112	−0.640	0.018	0.206
λ-optimized EFV GTO	H_2O	1	0.016	0.978	0.335	1.844
		2	−0.071	−0.373	−0.020	0.057
	$H_2O...Li^+$	1	0.063	0.850	0.295	1.447
		2	−0.084	−0.329	−0.013	0.094

The relative IR and Raman intensities computed from the data of Table IV according to the formulae presented in the previous section are reported in Table V. Both sets of

TABLE V

Relative values of the IR and Raman intensities for H_2O and $H_2O...Li^+$

	Field independent basis		EFV GTO	
	ν_1	ν_2	ν_1	ν_2
$\frac{I^{IR}(\nu_i;\, H_2O...Li^+)}{I^{IR}(\nu_i;\, H_2O)}$	24.8 (6.2) [a]	2.3 (2.5)	15.7	1.4
$\frac{I^{R}(\nu_i;\, H_2O...Li^+)}{I^{R}(\nu_i;\, H_2O)}$	0.54 (0.68)	0.64 (0.49)	0.65	0.82

[a] Values in parentheses are the numbers obtained in the previous study [45] using medium size polarized basis set without field dependence.

calculations predict a very large IR intensity increase for the Q_1 mode. For both the field independent 4–31G and the corresponding EFV GTO basis set the calculated intensity increase is much higher than estimated in our previous calculations [45]. This apparently large intensity enhancement of the ν_1 band for $H_2O...Li^+$ seems to be understandable. For a sizable charged system like $H_2O...Li^+$ the OH stretches may easily introduce quite substantial changes of the total dipole moment because of enhanced polarity of the OH bond. As expected from the same model much lesser IR intensity changes are calculated for the Q_2 bending mode.

In contrast to the intensity of the IR bands, the Raman intensities are predicted to decrease for both Q_1 and Q_2 vibration. This result is again in agreement with simple model considerations, i.e., an increase of the polarity makes the system less polarizable and therefore leads to a decrease of the Raman intensities. Obviously, this empirical rule has no general character but it should be applicable in the case of well marked changes in polarity and polarizability of a given molecule.

According to the data of Table V one can conclude that as far as the isolated $H_2O...Li^+$ system is compared with the isolated water molecule both the IR and the Raman intensities of Q_1 and Q_2 modes should be markedly affected by the cation-molecule interaction. On the other hand, it follows from several other calculations that the corresponding frequencies only slightly depend on this interaction [45, 46]. The accuracy of the present calculations appears to be high enough at least for the validity of our conclusions concerning the qualitative features of the intensity data. Thus, it seems that our results can be rather safely used for a qualitative discussion of the cation effect in the IR and Raman spectra of aqueous solutions of electrolytes [2, 51].

5. *$H_2O...Li^+$ interaction and the vibrational spectra of aqueous solutions of electrolytes*

It is rather obvious that the calculated results for the model system $H_2O...Li^+$ cannot be directly compared with the experimental data. However, this and similar models proved to be very useful in the interpretation of several, mainly thermodynamic, features of the electrolyte solutions [4]. The intensity data provide much more sensitive probe of interactions and therefore the consideration of suitable models may reveal several interesting features of fairly complicated systems.

Being completely aware of a tremendous complexity of such liquid systems as the electrolyte solutions we also want to stress that the interpretation of the spectroscopic data in terms of separable cationic and anionic effects is a rather customary procedure adopted by experimentalists [52, 53]. Thus, the present model study directly refers to such interpretations and can be utilized for the asessment of their validity.

First of all let us point out that no cationic effect is observed in the IR and Raman spectra of aqueous solutions of electrolytes [51–58]. It is clear, therefore, that a simple model of the cation-molecule interaction [52] is not appropriate. On the other hand, the absence of the cation effect, especially in the case of vibrational intensities, is rather puzzling. As far as the pair interaction model is concerned, this effect should be large enough to be measurable. The present results clearly show that the model commonly invoked for the interpretation of the experimental data for aqueous solutions of electrolytes is definitely too simplified and cannot account for the diversity of interactions which influence the vibrational intensities.

The lack of the cationic effect in the IR and Raman spectra of aqueous solutions of electrolytes was interpreted by Weston [57] by a hypothesis of mutual compensation of opposite effects due to hydrogen bonding and ion-water interaction. However, the present data and the estimates of the IR intensity changes due to the hydrogen bonding [59,60] apparently contradict this hypothesis. In both cases the IR intensity of the ν_1 band changes in the same direction and by a similar amount. This observation would rather favour the interpretation proposed by Waldron [61], who anticipated that there is no considerable difference between the H-bonded and cation-bonded H_2O molecules. To confirm this alternative interpretation would require rather extensive studies of more sophisticated models.

It should be also pointed out that the separability of the cationic and anionic effects on the H_2O vibrational spectra is quite questionable. It may happen that the net effect of cations and anions interacting with hydrogen-bonded water molecules is relatively small, though each ion acting separately has a rather significant effect on the vibrational spectrum. Several more complicated models, taking into account both the anionic effects and the hydrogen bonding are currently under consideration.

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