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

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The effects of the cation-molecule interaction on the infrared and Raman intensity of the CN stretching band in hydrogen cyanide are investigated by a comparison of the pertinent theoretical results for HCN and HCN...Li^+ system. The dipole moment and polarizability tensor derivatives with respect to the CN stretching internal coordinate are calculated from the dipole moment and polarizability values computed for a series of different molecular geometries. The dipole moment and polarizability calculations are performed by using the finite field SCF perturbation method and the so-called electric-field-variant Gaussian-type orbital (EFV GTO) basis set. Employing these orbitals leads to highly accurate polarizability values for relatively small original basis set. Some instability of the method observed for the parallel component of the HCN molecule polarizability is also discussed. It follows from the calculated data that the cation-molecule interaction increases about 10 times the infra-red intensity of the CN stretching band, while the corresponding Raman intensity is slightly decreased.

1. Introduction

The vibrational spectroscopy of non-aqueous solutions of electrolytes undoubtedly represents one of the most important tools for the study of fundamental ion-molecule interactions [1–3]. The understanding of the observed spectroscopic effects is, however,

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intimately related to the construction of relatively simple models of interacting species. A careful theoretical study of such models provides the only way of justification and/or verification of naive and highly simplified pictures of tremendously complex structure of real systems.

As already discussed in Part I [4], the present series of theroetical studies is aimed at the investigation of spectroscopic effects due to ion-molecule interaction. The model systems chosen for this purpose either reflect some commonly accepted concepts concerning the structural units in solutions or follow from a detailed analysis of the spectroscopic data. Moreover, the selected model systems should be small enough for fairly accurate calculation of their properties. For this reason the model systems investigated in this series are chosen to reflect the most fundamental features of more realistic and unavoidably more complex structures.

The present model, HCN...Li^+, is expected to represent the basic aspects of the influence of the cation-molecule interaction on the vibrational properties of the triple CN bond. The analysis of the experimental data for the acetonitrile solutions of electrolytes [3] indicates that this very simple model should properly account for the perturbation of the CN bond region by the ion-molecule interaction. Since there is no detectable anionic effect on the spectroscopic properties related to the CN bond region [5, 6], the negative counter-ion was simply excluded from our considerations.

The present paper is rather theoretically oriented and the main attention is paid to the method of calculations and the reliability of the computed data. A more detailed discussion of the spectroscopic aspects of the present study and their relation to the regularities observed in the infra-red and Raman spectra of acetonitrile solutions of electrolytes [3] will be given elsewhere [7].

2. *Methods of calculations. Dipole moment and polarizability evaluation using the EFV GTO basis sets*

Similarly as in Part I of this series [4] all the calculations are performed at the ab initio level and are restricted to the SCF HF approximation [8]. The correlation effects are not taken into account and they are believed to be rather unimportant for the present purposes. The final results are interpreted only in terms of their relative values and these are not significantly influenced by the neglect of the correlation corrections.

As already pointed out, the calculation of the infra-red and Raman intensities can be reduced to the calculation of the dipole moment and polarizability tensor components at several molecular geometries. In order to determine the band intensity in the infra-red spectrum (I_i^{IR}) one needs in fact the dipole moment derivative with respect to the corresponding normal coordinate Q_i, i.e. [9]

$$I_i^{\mathrm{IR}} = f(\nu_i) \left| \frac{\partial \mu}{\partial Q_i} \right|^2, \tag{1}$$

where μ denotes the dipole moment vector of a given system and $f(\nu_i)$ is a general function [9] of the i-th band frequency ν_i. Similarly, the i-th band Raman intensity is defined by[1] [10]

$$I_i^{\mathrm{R}} = g(\nu_i)\,[45a_i^2+7b_i^2], \tag{2}$$

where $g(\nu_i)$ denotes some function of the band frequency and a_i and b_i are expressed in terms of the polarizability tensor ($\alpha_{\mu\nu}$) derivatives with respect to the i-th normal coordinate

$$a_i = \tfrac{1}{3}\sum_{\mu}\frac{\partial\alpha_{\mu\mu}}{\partial Q_i}, \tag{3}$$

$$\begin{aligned} b_i^2 = \tfrac{1}{2}\Bigg\{&\left(\frac{\partial\alpha_{xx}}{\partial Q_i}-\frac{\partial\alpha_{yy}}{\partial Q_i}\right)^2+\left(\frac{\partial\alpha_{yy}}{\partial Q_i}-\frac{\partial\alpha_{zz}}{\partial Q_i}\right)^2+\left(\frac{\partial\alpha_{xx}}{\partial Q_i}-\frac{\partial\alpha_{yy}}{\partial Q_i}\right)^2 \\ &+6\left[\left(\frac{\partial\alpha_{xy}}{\partial Q_i}\right)^2+\left(\frac{\partial\alpha_{yz}}{\partial Q_i}\right)^2+\left(\frac{\partial\alpha_{xz}}{\partial Q_i}\right)^2\right]\Bigg\}. \end{aligned} \tag{4}$$

In principle all these derivatives should be calculated at the equilibrium geometry of a given system.

In the case of fairly characteristic vibration mode the derivatives with respect to the normal coordinate Q_i can be replaced by the derivatives with respect to the relevant internal coordinate. The CN stretching vibration in HCN is well separated from the CH stretching mode, and therefore, one can safely use the dipole moment and polarizability tensor derivatives with respect to the CN bond length, R_{CN}, as substitutes of the quantities entering Eqs. (1)—(4) [13]. The lithium cation in the HCN...Li$^+$ system does not significantly affect the potential energy surface of the HCN molecule [14], and thus the above assumption applies as well. It is therefore enough for the present study to compute the dipole moment and polarizability of both HCN and HCN...Li$^+$ for a series of different values of R_{CN} with all the other geometry parameters kept constant.

The calculation of accurate, near-HF values of dipole moments and polarizabilities usually represents a formidable task and needs very large basis sets [15]. On the other hand, using basis sets of the appropriate size would obviously diminish the size of molecules which can be studied with the aid of conventional perturbation methods [16, 17]. However, recently a new approach to the calculation of second-order molecular electric properties was proposed [18] and appears to open the possibility of fairly accurate computation of molecular polarizabilities with relatively small basis sets [18–20]. The same method was also shown to improve the dipole moment values calculated within the standard schemes [19, 20].

The main idea of the method used for the calculation of molecular electric polarizabilities was to make the basis set following the external electric field perturbation. Utilizing some analogies with the harmonic oscillator theory [18] the primitive Gaussian orbitals of a given basis set were allowed to vary with the external electric field strength $\boldsymbol{F}$. In the

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[1] There are several different definitions of the Raman intensity depending on the conditions of the scattering experiment [10, 11]. The present definition refers to the so-called standard intensity of Bernstein and Allen [12].

presence of the external electric field directed along the μ-th coordinate axis each GTO with orbital exponent α_i is assumed to have its origin shifted by the amount $\Delta \boldsymbol{r}$,

$$\Delta r_\nu = -\delta_{\mu\nu} \frac{\lambda_\mu F_\mu}{\alpha_i^2} = -\delta_{\mu\nu} \frac{d_\mu}{\alpha_i^2}, \tag{5}$$

where λ_μ is the variation parameter common for all GTO's and determined via the optimization of the second-order perturbed energy. More details concerning the justification of this approach can be found elsewhere [18–21].

The second-order perturbed energy $E^{(2)}_{\mu\mu}$ for the electric field perturbation along the μ-th axis of the coordinate system is directly related to the corresponding component of the electric dipole polarizability tensor

$$\alpha_{\mu\mu} = -2E^{(2)}_{\mu\mu} \tag{6}$$

and within the EFV GTO perturbation approach becomes the parabolic function of the parameter λ_μ [21, 22]

$$E^{(2)}_{\mu\mu} = E^{(2)}_{\mu\mu}(\lambda_\mu) = E^{(2)}_{\mu\mu}(0) + \lambda_\mu B^\beta + \tfrac{1}{2}\lambda_\mu^2 A^{\beta\beta}, \tag{7}$$

where $E^{(2)}_{\mu\mu}(0)$ denotes the standard coupled Hartree-Fock (CHF) result obtained within the fixed basis set approximation. It was recently shown [23] that the coefficients B^β and $A^{\beta\beta}$ are simply the total energy derivatives with respect to d_μ and F_μ treated as independent variables, i.e.,

$$B^\beta = \left(\frac{\partial^2 E(d_\mu, F_\mu)}{\partial d_\mu \partial F_\mu}\right)_{\substack{d_\mu=0\\F_\mu=0}} \tag{8}$$

and

$$A^{\beta\beta} = \left(\frac{\partial^2 E(d_\mu, 0)}{\partial d_\mu^2}\right)_{d_\mu=0} \tag{9}$$

where $E(d_\mu, F_\mu)$ is the total field-dependent energy of a given system calculated with the EFV GTO's as defined by Eq. (1). In the present case $E(d_\mu, F_\mu)$ is the SCF energy. One should notice that the product $\lambda_\mu F_\mu = d_\mu$ can be treated as the additional parameter entering the wave function and energy also in the absence of the external perturbation [23] and that the unperturbed energy $E(d_\mu, 0)$ is not necessary in minimum for $d_\mu = 0$.

If the field-independent energy is not optimized with respect to d_μ, then both B^β and $A^{\beta\beta}$ can be of either sign and Eq. (7) may not represent an upper bound to the second-order energy leading to the failure of the EFV GTO approach. Fortunately enough the negative values of $A^{\beta\beta}$ occur quite rarely and for relatively large (for a given direction of perturbation [21]) bases, i.e., when the polarizability improvement due to the EFV GTO approach is not expected to be significant. It was therefore suggested [23], that in such cases either the total energy $E(d_\mu, 0)$ should be first reoptimized with respect to d_μ or the standard fixed basis set results can be accepted as the best ones. The total energy reoptimization with resepct to d_μ is computationally rather expensive and thus the second choice, guided by the estimated accuracy of $E^{(2)}_{\mu\mu}(0)$, is rather recommended [23].

The components of the dipole moment vector $\boldsymbol{\mu}$ are defined by the corresponding components of the first-order perturbed energy $E_{\mu}^{(1)}$. This can be shown to be a linear function of λ_μ [22, 23], i.e.,

$$E_{\mu}^{(1)} = E_{\mu}^{(1)}(0)+\lambda_\mu C^\beta \tag{10}$$

where

$$C^\beta = \left(\frac{\partial E(d_\mu, 0)}{\partial d_\mu}\right)_{d_\mu=0} \tag{11}$$

and $E_{\mu}^{(1)}(0)$ denotes the fixed basis set result calculated according to the Hellmann-Feynman theorem [24, 25]. If the EFV GTO scheme fails to improve the second-order perturbed energy, then using $E_{\mu}^{(1)}(0)$ as the best result is consequently recommended [23]. For the regular behaviour of the EFV GTO scheme, i.e., when the r.h.s. of Eq. (7) represents an upper bound to $E_{\mu\mu}^{(2)}$, using the value of λ_μ following from the minimization of Eq. (7) was suggested [19, 20]. This choice of the numerical value of λ_μ was found to give a considerable improvement upon the Hellmann-Feynman values of the dipole moment [19, 20].

It follows from the formulae given in this Section that in order to complete the calculations of molecular electric properties required in the vibrational intensity studies one has to compute for each geometry and for each direction of the external electric field ($\mu = x, y, z$) the following five quantities: $E_{\mu}^{(1)}(0)$, $E_{\mu\mu}^{(2)}(0)$, $A^{\beta\beta}$, B^β, and C^β. Moreover, the calculation of the non-diagonal components of the polarizability tensor requires the knowledge of $E_{\mu\nu}^{(2)}(0)$, $A^{\beta\beta}$, and B^β for each distinct pair ($\mu \neq \nu$). The number of unique non-zero terms is considerably reduced if a given system possesses some symmetry.

All of the mentioned quantities can be computed by using the explicit formulae of the analytic variable basis set perturbation theory [22]. However, the corresponding formulae require a direct use of the first- and second-order derivatives of molecular integrals and for this reason are computationally rather incovenient for larger bases. Computationally more feasible [24, 27, 28] seems ot be purely numerical approach [15, 26, 27] based on the appropriate finite difference formulae. This method was employed throughout the present study. Some computational details of our calculations are presented in the next Section.

3. *Computational details*

The experimental equilibrium geometry of HCN ($R_{\mathrm{CH}} = 2.00913$ a.u., $R_{\mathrm{CN}} = 2.18332$ a.u. [29]) was chosen as a reference geometry for both the isolated molecule and its complex. According to the recent data of Schuster et al. [30] the HCN...Li$^+$ complex is linear and the N...Li$^+$ distance is close to 3.7 a.u. The latter value was also adopted in the present calculations. No attempt was made to reoptimize the assumed molecular geometries. The origin of the coordinate system was chosen at the carbon atom and both molecules are assumed to lie on the z axis pointing towards nitrogen. Thus, the dipole moment and its derivative with respect to R_{CN} have only one non-vanishing (z) component. For the polarizability tensor and the corresponding derivatives with respect to R_{CN} there are only two unique non-zero components — $xx = yy$ and zz.

According to our previous calculations [20] the standard medium-size basis sets without polarization functions are already quite sufficient for highly accurate near-HF calculation of the dipole moment and polarizability tensor components within the EFV GTO approaches. In this respect the GTO expansions optimized by Huzinaga [31] with the contraction coefficients determined by Salez and Veillard [32, 33] appear to be quite efficient [20]. Thus, for carbon and nitrogen we used (11*s*7*p*) sets [31, 32] contracted to (5*s*3*p*). For hydrogen the (6*s*) set was contracted to (2*s*) [31, 32] and for Li^+ the (11*s*) set of Huzinaga [31, 32] was contracted to (5*s*) [32, 33]. Altogether this leads to 30 contracted GTO's for HCN and 35 basis functions for HCN...Li^+.

When using the numerical approach to the calculation of the pertubed energies one has to decide about the most appropriate values of the field strength. By a comparison of the finite field numerical perturbation results with the analytic ones obtained within the fixed basis set approximation the value of the external field strength was fixed at 0.005 a.u. and then used in the EFV GTO calculations. A series of numerical experiments was performed in order to select the appropriate numerical value of the parameter d_μ. It follows from the EFV GTO calculations performed at the assumed equilibrium geometry of HCN that $d_\mu = 0.0005$ a.u. leads to completely satisfactory accuracy of the $A^{\beta\beta}$, B^β and C^β term calculated from the corresponding SCF energies $E(d_\mu, 0)$ and $E(d_\mu, F_\mu)$.

In order to compute the dipole moment and polarizability derivatives the calculations of μ and $\alpha_{\mu\nu}$ have been repeated for the R_{CN} values increased or shortened by 0.025 a.u. in comparison with the assumed equilibrium bond length. All the other geometry parameters were kept constant. Finally, the required first-order derivatives of μ_z, α_{xx} and α_{zz} for HCN and HCN...Li^+ have been computed from the parabolic approximations of the R_{CN}-dependence of these properties.

One should mention that, for instance, the polarizability tensor derivatives with respect to the bond length represent the so-called third-order properties, i.e., they are proportional to the corresponding third-order perturbed energies. Within the present EFV GTO numerical approach the calculation of these derivatives is equivalent to the use of a variable basis set for both the external electric field perturbation and the perturbation due to the geometry change [34, 35]. In such a case the analytic SCF perturbation method [22, 34, 35] would evidently require an enormous computational effort. The numerical finite perturbation approach, though perhaps less elegant, is definitely more convenient. During the calculations one uses practically the same set of routines as in ordinary SCF programs. Although these calculations have to be repeated several times and performed with rather high accuracy, the numerical approach appears to be computationally much easier than the computations according to the analytic perturbation schemes.

4. *Results and discussion*

The results of the present dipole moment and polarizability tensor calculations for HCN and HCN...Li^+ obtained for the experimental equilibrium geometry of HCN [29] and $R_{N...Li^+} = 3.7$ a.u. [30] are collected in Table I. Both the standard field-independend basis set and the EFV GTO data are reported and compared with the results of other

TABLE I

Total SCF energy (E_{SCF}), dipole moment (μ_z) and non-zero components of the polarizability tensor ($\alpha_{xx} = \alpha_{yy}, \alpha_{zz}$)[a] for HCN and HCN...Li$^+$. Comparison of the field-independent basis set and EFV GTO results of the present paper with other theoretical and available experimental data. All entries in a.u.

Molecule	Method[b]	E_{SCF}	μ_z	$\alpha_{xx} = \alpha_{yy}$	α_{zz}	Ref.
HCN	A	−92.84900	1.313	8.398	22.256	This work
	B[c]	−92.84900	1.313	13.174	22.256	This work
	A	−92.73119	1.276	6.239	20.156	[39][d]
	A	−92.81330	1.282	9.322	21.344	[36, 46][e]
	A	−92.81450	1.282	13.024	21.335	[36, 46][f]
	A	−92.81768	1.284	13.125	21.233	[46][g]
	A	−92.89903	1.282	8.269	20.993	[46][h]
	B	−92.73119	1.276	11.489	20.156	[39][d]
	Exptl.		1.175	12.95	26.43	[47, 48]
HCN...Li$^+$	A	−100.14709	−1.585	7.488	21.576	This work
	B[i]	−100.14709	−1.585	12.152	21.576	This work
	A	−100.10900	—	—	—	[46][j]

[a] Molecular geometries as described in Section 3. For the HCN...Li$^+$ system the dipole moment was computed with the origin at nitrogen.

[b] A denotes the standard SCF perturbation procedure with fixed basis set, B corresponds to the EFV GTO SCF perturbation results.

[c] The dipole moment value and α_{zz} correspond to the field-independent basis set calculations as explained in the text. The optimized value of α_{xx} was calculated for $\lambda_x = 0.0954$.

[d] Molecular geometry as in the present study .4$-$31G basis set [38]. The values of μ_z and α_{zz} have not been optimized within the EFV GTO approach. The optimized value of α_{xx} corresponds to $\lambda_x = 0.1141$.

[e] $R_{CH} = 2.0075$ a.u., $R_{CN} = 2.13$ a.u. Basis set: C,N (8.4.1/5.3.1), H (3.1/2.1).

[f] Molecular geometry as in Footnote e. Basis set: C,N (8.4.2/5.3.2), H (3.1/2.1).

[g] Molecular geometry as in Footnote e. Basis set: C,N (8.4.2/5.3.2), H (5.2/3.2).

[h] $R_{CH} = 2.014$ a.u., $R_{CN} = 2.129$ a.u. Basis set: C,N (9.5.1/5.3.1), H (4.1/3.1).

[i] The EFV GTO results for $\lambda_x = 0.0951$, $\lambda_z = 0.1339$.

[j] No data for the dipole moment and polarizability of this system are available.

authors. The relative quality of the theoretical results can be to some extent asserted by a comparison of the corresponding SCF energies which are also presented in Table I. However, the results of different authors usually refer to slightly different molecular geometries.

The total molecular SCF energies calculated within the present study indicate that the CGTO basis set employed in these calculations is of relatively good quality. Also the calculated dipole moment and the parallel component of the polarizability tensor obtained within the standard approach (field-independent basis set) are close to the best available SCF data. On the other hand, the perpendicular component of the polarizability tensor (α_{xx}) computed within the fixed basis set approximation is much smaller than the best SCF values obtained with large polarized bases. In fact we could expect a rather poor result for α_{xx} in the fixed basis set approximation, since our basis set for HCN and

HCN...Li$^+$ cannot properly account for the effects of the external electric field perturbation perpendicular to the molecular axis. As already noticed by other authors [15, 36] the standard CHF approach with fixed basis sets requires a careful selection of the appropriate basis functions. This deficiency of the fixed basis set approximation is expected to be remedied within the EFV GTO approach.

It is worth attention that the electric properties of HCN for the parallel electric field perturbation are of very good quality already in the case of the field-independent basis set CHF calculations. This shows that the CGTO basis set employed in the present calculations properly accounts for the perturbation along the molecular axis. In other words, this basis set is in this case less incomplete than for the perturbation operator corresponding to the perpendicular external electric field [37]. From the quality of the fixed basis set results for μ_z and α_{zz} one can also expect that the EFV GTO approach may result eventually in a rather minute improvement of these quantities. In fact, when performing the EFV GTO perturbation calculations for the parallel direction of the external electric field a rather peculiar behaviour of the computed electric properties was observed.

In the case of the HCN molecule it was found that the $A^{\beta\beta}$ coefficient of Eq. (7) is relatively small and negative. Thus, according to the discussion presented in Section 2, the r.h.s. of Eq. (7) does not represent an upper bound to the second-order energy. Since the reoptimization of d_μ was found to be too time consuming, the fixed basis set results for μ_z and α_{zz} have been accepted as the best ones, i.e. they refer to optimal $\lambda_z = 0$. Moreover, it should be pointed out that $A^{\beta\beta}$ is small and negative for all molecular geometries of HCN considered in this paper, and consequently we set $\lambda_z = 0$ in each case.

It is interesting to notice that also for a smaller $4-31G$ basis set [38] the same behaviour of the EFV GTO approach for the parallel electric field perturbation is observed [39]. In this case, however, the basis set is much smaller and we have attempted the reoptimization of d_z. The unperturbed total SCF energy minimum was found to be close to $d_z = -0.015$ a.u.[2] and the EFV GTO perturbation calculations performed with this initial value of d_z resulted in a positive value of $A^{\beta\beta}$. However, the lowering of the second-order perturbed energy $E^{(2)}_{zz}(\lambda_z)$ due to its optimization with respect to λ_z is almost negligible [23]. It is also likely that for the basis set employed in the present calculations the effect of the reoptimization of d_z will be similar.

In the case of the EFV GTO perturbations for HCN...Li$^+$ the value of $A^{\beta\beta}$ for the parallel electric field turns out to be large and positive for all the geometries considered in this paper. Nevertheless, as shown by the data of Table I, the optimization of λ_z has a relatively small effect on the final value of α_{zz}.

In contrast to the RFV GTO data for the parallel electric field perturbation, there is an enormous improvement of the perpendicular polarizability component. In this case for both HCN and HCN...Li$^+$ the EFV GTO approach remedies the deficiency of the

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[2] The geometry of the HCN molecule and the coordinate system are the same as defined in Section 3. The negative value of d_z shows that the total SCF energy is lowered when the GTO origins are shifted in the negative direction of the z-axis of the coordinate system, i. e. from nitrogen towards hydrogen.

original field-independent basis set and indirectly introduces the so-called polarization functions. The EFV GTO value of the perpendicular component of the polarizability tensor for HCN compares favourably with the best results of other authors.

The dipole moment and polarizability tensor derivatives with respect to R_{CN} calculated for both HCN and HCN...Li$^+$ are shown in Table II. The present result for the dipole moment derivative for the HCN molecule is very close to the corresponding experimental value. This is unfortunately the only experimental result which can be directly compared with the calculated value. The data for HCN...Li$^+$ when compared with those for HCN seem to follow some simple rules. The interaction with the positive charge makes the dipole moment of HCN...Li$^+$ more sensitive to the bond length changes, and thus, the corresponding derivative increases in comparison with its value for the isolated molecule. Due to the interaction with the positive charge the π-electrons become more tightly bound within the system and thus the derivative of α_{xx} with respect to R_{CN} is smaller than in the isolated HCN molecule. The EFV GTO approach predicts a small increase of the pertinent derivative of α_{zz} while its value is slightly decreasing according to the fixed basis set calculations. Both changes of the derivative of α_{zz} with respect to R_{CN} seem to be relatively unimportant.

TABLE II

Components of the dipole moment and polarizability tensor derivatives with respect to the CN bond length for HCN and HCN...Li$^+$. All entries in a.u.

Molecule [a]	Method [b]	$\frac{\partial \mu_z}{\partial R_{CN}}$	$\frac{\partial \alpha_{xx}}{\partial R_{CN}}$	$\frac{\partial \alpha_{zz}}{\partial R_{CN}}$	Ref.
HCN	A	0.123	3.98	15.15	This work
	B [c]	0.123	7.05	15.15	This work
	A [d]	0.171	—	—	[49]
	Exptl	0.138	—	—	[50]
HCN...Li$^+$	A	-0.384	3.04	14.96	This work
	B	-0.376	5.82	15.33	This work

[a] Molecular reference geometries for the present results as described in Section 3.

[b] See Footnote b to Table I.

[c] The derivatives of μ_z and α_{zz} calculated with fixed basis set. See text for explanation.

[d] Results of Curtiss and Pople [49] calculated with field-independent 4-31G basis set [38] at optimized molecular geometry.

It follows from the SCF energy calculations for the unperturbed system that the minimum with respect to R_{CN} is in fact a little shifted towards shorter than assumed CN bond distances. For the HCN molecule the estimated shift amounts -0.028 a.u., while for HCN...Li$^+$ the corresponding estimate is -0.035 a.u. These results agree with our previous semiempirical CNDO data [40] calculated for a model system representing the CH_3CN molecule and its interaction with a positive charge. The SCF energy data of the present paper allow also for estimating the changes of the CN bond force constant in the

HCN molecule due to its interaction with the Li^+ ion. The CN bond force constant for HCN following from our calculations equals 1.303 a.u., while a slightly higher value od 1.306 a.u. was obtained for the Li^+ complex. These data as well as the estimated CN bond length changes do not correspond to a full molecular geometry optimization, and therefore, they can be considered solely in a qualitative way. Nonetheless, in both cases they follow the pattern obtained previously within the semiempirical CNDO method [40]. They are also in a general qualitative agreement with fairly accurate and complete calculations of the potential energy hypersurface of HCN and $HCN...Li^+$ performed by Schuster and his coworkers [41]. Moreover, it follows also from the normal coordinate analysis performed for CH_3CN and $CH_3CN...Li^+$ and based on the experimental frequency data, that the CN bond force constant should slightly increase due to cation-molecule interaction [42].

The data of Table II can be used for the estimation of the infra-red and Raman intensity changes of the CN band due to cation-molecule interaction. Since the CN stretching frequency changes are quite small, one can legitimately assume that the functions $f(\nu_{CN})$ and $g(\nu_{CN})$ entering Eqs. (1) and (2) are the same for both HCN and $HCN...Li^+$. Then, using the data of Table II one finds the following intensity ratios

$$\frac{I^{IR}_{CN}(HCN\cdots Li^+)}{I^{IR}_{CN}(HCN)} = \begin{cases} 9.78 \text{ (fixed basis set result)} \\ 9.42 \text{ (EFV GTO result)}, \end{cases}$$

$$\frac{I^{R}_{CN}(HCN\cdots Li^+)}{I^{R}_{CN}(HCN)} = \begin{cases} 0.91 \text{ (fixed basis set result)} \\ 0.90 \text{ (EFV GTO result)}. \end{cases}$$

It is interesting to notice that the relative intensities of the CN stretching band are independent of the approach used for the calculation of the dipole moment and polarizability derivatives. However, the absolute intensities, at least in the case of the Raman spectrum are much more sensitive to the method employed for their calculation. For instance, the factors $(45a^2+7b^2)$ which enter Eq. (2) are ca. 50 per cent higher when computed using the EFV GTO data. Thus, the fixed basis set method will lead to much lower than observed absolute intensities in the Raman spectra. This would also influence the relative intensities of different bands in the same molecule [43, 44]. The absolute IR intensities appear to be considerably less influenced in this respect [43, 44].

Finally, we want to mention the possibilities of the utilization of the present theoretical data for HCN and $HCN...Li^+$ for the interpretation of the observed spectroscopic regularities in the infra-red and Raman spectra of acetonitrile solutions of electrolytes. According to the experimental data [3, 6, 45] the intensity of the CN stretching band of CH_3CN increases upon the cation-molecule interaction in both the infra-red and Raman spectrum. For the infra-red spectrum this has already been given some interpretation based on the results of semiempirical calculations [40]. The present calculations seem to predict much much higher than observed increase of the intensity of the CN stretching band in the infra--red spectrum [45]. The lowering of the Raman intensity resulting from our calculations does not seem to be the effect of the simplified model we use. It is rather the structure of liquid acetonitrile which is broken by the ion-molecule interactions and leads to the spectroscopic effects opposite to or smaller than those following from the simplified model. However, a careful compilation of the available experimental and theoretical data is shown to result in a consistent interpretation of the observed spectroscopic effects. This analysis, which makes use of the intensity data computed in this paper, is a subject of a separate publication [7].

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