Applicability of the SQM Force Field Method to the Vibrational Spectra of Sodium Acetate

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The applicability of the scaled quantum mechanical force field (SQM FF) method to the prediction of the vibrational spectra of a charged molecule has been studied by the example of the acetate ion ($CH_3CO_2^-$) in sodium acetate for which an efficient empirical valence force field (SVFF) based on observed IR spectra of six isotopomers of sodium acetate is available in the literature. Standard SQM FF calculations done on a free acetate ion at the B3LYP/6-31G* level failed to give an acceptable estimation of even the most characteristic features of the observed spectra, which can be exemplified by the gross overestimation of the frequency separation of the $\nu_a CO_2^-$ and $\nu_s CO_2^-$ vibrations. In search for a better description, SQM calculations were done for three simple structural models of sodium acetate, testing different QM methods. The results indicate that in addition to taking into account the dielectric field effect of the surrounding medium, incorporation of a Na^+ counterion is necessary to achieve a realistic simulation of the IR and Raman spectra. Satisfactory results were obtained with a bidentate Na−acetate complex by the SQM method coupled with a continuum model at the B3LYP/6-31+G** level, whereas the use of the Onsager-type spherical cavity model and the polarizable continuum model (PCM) were found preferable over SCI−PCM.

Introduction

In recent years, the application of ab initio and density functional theory (DFT) quantum chemical calculations to the analysis of vibrational spectra gained exceptional popularity. This is due to the success of these methods in the prediction of vibrational frequencies and associated infrared and Raman intensities even for relatively large organic molecules (up to 30−40 atoms). This means that practically all fundamental transitions observed in the vibrational spectra of these molecules can be successfully analyzed and reliably interpreted, e.g., on the basis of density functional theory (DFT) calculations of the force field followed by normal coordinate calculations performed according to the so-called scaled quantum mechanical force field (SQM FF) approach.[1,2] Using suitable transferable scale factors[3,4] in conjunction with a standard DFT method (e.g., B3LYP/6-31G*), the average error in calculated frequencies can be kept close to or even below 10 cm^{-1} (or less than 1%), which is usually sufficient for unequivocal assignment of all observed bands. Since these calculations are generally done on single, isolated molecules, difficulties may occur with condensed phase spectra of molecular systems having strong intermolecular interactions. Our experience has been very positive with the application of the SQM FF method to condensed phase spectra of weakly interacting molecules, whereas the calculations allowed interpreting fine secondary structural effects as well, e.g., cis−trans isomerism and conformational changes due to hindered internal rotation.[5−7]

Although these methods proved to be quite successful in the case of the most neutral organic molecules, little is known about their applicability to ionic species (charged molecules). Characteristically, the best vibrational analysis published for the acetate anion, $CH_3CO_2^-$, has been done by Kakihana et al.[8] with the use of an empirical simplified valence force field (SVFF) consisting of 27 independent parameters (harmonic force constants) refined to reproduce a set of 82 observed frequencies of 6 isotopomers of sodium acetate with a root-mean-squares deviation of 3.3 cm^{-1}. The acetate ion has been subjected to ab initio molecular orbital studies as well, but we have not found in the available literature a complete vibrational analysis based on a QM force field. Anyway, such a high level of agreement with experiment as mentioned above cannot be expected from an ab initio type full harmonic force field. What is more, our first DFT calculations on the free acetate ion suggested that the situation was much worse than expected: with an unscaled force field, the average error in frequencies was above 75 cm^{-1}, and even selective scaling of the force field was unable to reduce it below 50 cm^{-1}. Notably, huge deviations of opposite sign were obtained for the pair of antisymmetric and symmetric CO_2^- stretching frequencies, so that their calculated frequency separation ($\Delta\nu_{a-s} = 380$ cm^{-1}) was overestimated compared to that of the measured ones (around 160 cm^{-1}) by more than 200 cm^{-1}! This clearly indicated that there was something intrinsically wrong with the raw computed force field, since this kind of error could not be compensated even by selective scaling within the framework of the accepted Pulay-type scaling scheme[1,2] where the two CO stretching force constants and their interaction term were multiplied by the same factor.

Actually, the $\Delta\nu_{a-s}CO_2$ frequency separation has been the subject of a computational study by Nara et al.,[9] who have demonstrated that $\Delta\nu_{a-s}$ strongly depends on the type of coordination of the carboxylate group to metal cations and water molecules. This dependence was shown to be related to changes in the CO bond lengths and OCO bond angle. Nara et al. have reported only the calculated $\nu_a CO_2^-$ and $\nu_s CO_2^-$ frequencies for CD_3COO^- ions interacting with a metal ion (Na^+, Mg^{2+}, and Ca^+) in different interaction models optimized at HF

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(SCRF) level and found reasonable agreement with the single $\Delta\nu_{a-s}$ value observed in aqueous solution for sodium acetate-d_3, where it was 140 cm^{-1}. Ragazzi and Ferro[10] have done ab initio computations to model the molecular mechanics (MM2) type force field of ionic sugars, whereas their model compounds included acetic acid and the acetate ion as well. However, they did not treat their vibrational behavior. In a more recent attempt to develop MM3(2000) molecular mechanics force field parameters that would more correctly model the geometries and energetics of charged and zwitterionic species, Kirschner et al.[11] have included the acetate ion in their carboxylate training set. They have performed vibrational analysis of the free acetate ion by MM3, scaled quantum mechanical (at MP2/6-31+G** level) and density functional (B3LYP/6-31+G**) force fields as well, whereas the MM3 force constants were adjusted to fit the SQM calculated spectra, not the experimental ones. The overall frequency agreement of these calculations, especially those of the $\nu_aCO_2^-$ and $\nu_sCO_2^-$ modes, with the experimental values are rather poor, producing the same gross overestimation of the $\Delta\nu_{a-s}$ frequency separation as in our first DFT calculation mentioned above.

Initially, the aim of this work has been to compare the highly successful 27-parameter simplified valence force field of Kakihana et al.[8] to a full quadratic DFT force field of the acetate ion generated by the scaled quantum mechanical (SQM) method.[1-4] Before the start, we had assumed that the standard B3LYP/6-31G* calculation on a free acetate ion would prove satisfactory for prediction of the vibrational spectra of sodium acetate ($CH_3CO_2^-$ Na^+). However, when it turned out that the usual methodology well proven for neutral molecules failed to deliver acceptable results, we extended the scope of our study to the examination of various computational methods and interaction models in search for the best solution in the framework of the SQM approach.

Experimental Data

The IR and Raman spectra of sodium acetate trihydrate (99% purity, a product of Reanal, Hungary) have been recorded in this work only for illustration purposes, for visual comparison to the computed spectra in this paper. The measurements were done at room temperature, with Nicolet Magna 750 FT-IR and Nicolet 950 FT-Raman spectrometers, respectively, at 2 cm^{-1} resolution. A KBr pellet was used for the IR measurement, with a 0.4 mg sample dispersed in 250 mg of KBr (128 scans accumulated). The Raman scattering from a finely ground, pure polycrystalline sample was excited with a Nd:YAG laser (1064 nm, 100 mW at sample) and collected at backscattering geometry (256 scans accumulated).

Sodium acetate is available commercially in two crystalline modifications: anhydrous, and as a trihydrate. Anhydrous sodium acetate was reported to exist in two related crystalline forms.[12] When exposed to air, it adsorbs water and its IR spectrum may occasionally show even higher water content than the trihydrate. Differences in water contents lead to changes in positions and intensities of the IR and Raman bands of the acetate ion as well, so one can observe a variety of the Na-acetate spectra showing slight differences.[8,13-15]

The trihydrate, $CH_3CO_2Na\cdot 3H_2O$, whose crystal structure is well established,[16] is stable up to 331 K at which temperature it decomposes. It has a monoclinic lattice, belongs to space group $C2/c$ (no. 15, factor group C_{2h}) with $Z = 8$, corresponding to 4 formula units per Bravais cell ($Z_B = 4$), where the acetate ions occupy general positions (C_1 sites). Thus, as a result of intermolecular vibrational coupling, all acetate vibrations may split into four close-lying components, two of which may become IR active and the other two Raman active, with alternative exclusion, i.e. non-coincidence of frequencies in IR and Raman. In practice, the expected splittings are observed neither in IR absorption nor in Raman scattering alone, but clear differences can be observed in some IR and Raman band positions, which is the consequence of correlation splitting in the centrosymmetric lattice. (Note that the spectra of the anhydrous material found in some spectral collections exhibit extra bands and splittings in both IR and Raman due to a larger, non-centrosymmetric unit cell.) The observed differences between the IR and Raman band positions, if any, are always less than 20 cm^{-1}. Although they are not quite negligible, we have ignored the Raman data in this computational study, and have accepted the measured IR frequencies reported by Kakihana et al.,[8] because no other experimental data are available for all six isotopomers.

Computational Methods

The quantum chemical calculations (geometry optimizations, force field and vibrational frequency calculations in harmonic approximation) were done with the Gaussian 98[17] and Gaussian 03[18] program packages on PC-cluster and mainframe computers, respectively. In addition to calculations done with different QM methods on the isolated ("free") acetate ion, self-consistent reaction field (SCRF) calculations were carried out in conjunction with DFT calculations at the B3LYP/6-31+G** level in order to take into account the effect of surrounding dielectric medium (which was assumed to be water). Three SCRF models have been tested in the form as implemented in Gaussian 03: (i) the Onsager model (which places the molecule in a spherical cavity within the solvent reaction field);[19,20] (ii) the polarizable continuum model (PCM, in which the cavity is formed by a series of overlapping spheres);[21,22] and (iii) the self-consistent isodensity polarizable continuum model (SCI−PCM).[23]

Follow-up normal coordinate calculations were performed in order to scale the force fields and obtain the vibrational energy distributions (PEDs or TEDs) among internal or symmetry coordinates. These calculations were done with the *Molvib* program (version V7.0) written by Sundius.[24] For this, the QM force field matrix and the dipole and polarizability derivatives (expressed in Cartesian coordinates) were transferred from the archive part of the Gaussian output to *Molvib* and transformed to the appropriate set of internal coordinates. Scaling of the force field was done according to the selective scaling method[1,2] using the recommended values[3,4] of transferable scale factors first, with subsequent least-squares fitting of the frequencies through refinement of the scale factors. To ensure that the refinement process is well conditioned, only 8 scale factors were applied. During least-squares fitting of the force field (in the SVFF) and the scale factors (in the SQM calculation), the same set of 82 observed IR frequencies belonging to the six isotopomers were used as in the work by Nara et al.[9] Then, the frequencies, normal modes, PEDs, and IR and Raman intensities were updated with the use of the final scaled force field. For visual comparison of the calculated spectra to the observed ones, the calculated Raman "activities" (more correctly: Raman scattering cross sections) were converted to Raman intensities by taking into account the actual excitation frequency and the ν^4-law of Raman scattering.[25] For the spectral simulations, Lorentzian line shapes were used with 10 cm^{-1} bandwidths (fwhh).

Note that refinement of the scale factor values was needed to achieve an acceptable level of reproduction of experimental frequencies in this case. The procedure was justified by several

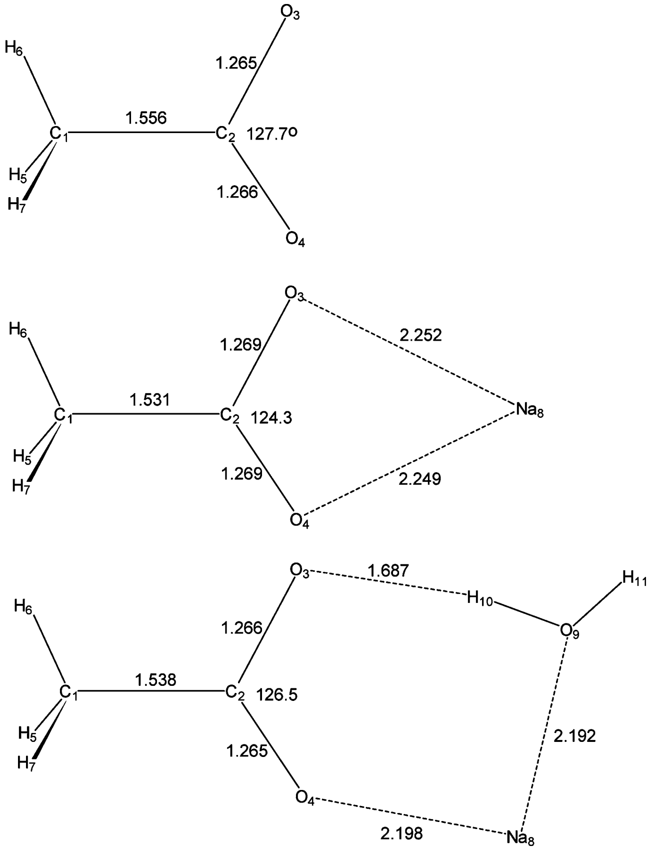

Figure 1. Optimized structures of the free acetate ion (**1**), a bidentate complex of sodium acetate (**2**), and a pseudo-bridging Na-acetate hydrate complex (**3**) calculated according to the solvated Onsager model at the B3LYP/6-31+G** level.

reasons: (i) The set of widely accepted, transferable scale factors had been developed for isolated (gas phase) molecules, whereas the IR and Raman spectra of ionic compounds such as sodium acetate are measurable only in condensed phases. Thus, the refined scale factors will include some effects from the environment; that is, they can be considered as correcting factors leading to an effective force field in the solid phase. (ii) The starting set of recommended scale factors[3,4] is compatible with the standard B3LYP/6-31G* method/basis set combination, whereas in our final calculations we used the 6-31+G** basis set (augmented with polarization and diffuse functions) that was known to perform better for charged molecular species; (iii) A further deviation from the standard conditions was the use of continuum (SCRF) models in order to take into account the effect of surrounding dielectric field effects on the force field. Any of these factors alone would already justify adjustments in the particular set of scale factors.

Results and Discussion

Structural Models and Vibrational Coordinates. Ab initio and DFT calculations have been performed for the three types of structures depicted in Figure 1. Retaining the terminology of Nara et al.[9] we call them a free acetate ion (**1**), an acetate ion forming a bidentate complex with a sodium cation (**2**), and a pseudobridging complex (**3**) in which one acetate oxygen is engaged in hydrogen bonding to a water molecule while the Na^+ cation is coordinated to the other acetate oxygen and to the oxygen atom of the water molecule as well. At the outset all these structures were defined as having C_s symmetry, with an eclipsed conformation of the methyl group (with the plane of symmetry passing through all the heavy atoms). At later stages, to get a convergence during structure optimization for some continuum models, the symmetry restriction had to be removed, which led to slightly asymmetric structures with the methyl group rotated to assume a conformation closer to the staggered form.

To ensure comparability of the resulting SQM force fields with the published empirical SVFF of Kakihana et al.,[8] first we reproduced their normal coordinate calculations. For this, some uncertainties regarding the relative signs of some interacting coordinates had to be resolved and a sign error discovered in the definition of the in-plane CO_2 rocking coordinate in the reference work had to be corrected, before the overlay calculation of the 6 isotopomers led to an RMS error of 3.46 cm^{-1}, very nearly the same as in the original SVFF work.[8] With this, the defined internal and symmetry coordinates, together with the set of 82 observed IR frequencies of the sodium acetate isotopomers were accepted for use in the SQM force field calculations.

Structure and Carboxylate Stretching Vibrations of the "Free Acetate Ion" Models. The essence of the problem with the ab initio and DFT force fields of free acetate ion is represented by selected frequency data compared to the experimental values in the upper half of Table 1. The calculated frequencies shown here correspond to the "raw" QM frequency calculations done without scaling of the force field. These frequencies are expected to be overestimated by all of the applied QM methods but, surprisingly, the actual overestimation of the antisymmetric CO_2 stretching frequency ($\nu_a CO_2^-$) wildly exceeds the usual level, whereas the symmetric CO_2 stretch ($\nu_s CO_2^-$) is underestimated. Thus, the frequency separation of the two modes ($\Delta\nu_{a-s} CO_2^-$) is calculated more than twice as large as the observed one, the error being about 220 cm^{-1}! In addition, $\nu_s CO_2^-$ becomes lower than the frequency of the antisymmetric methyl deformation mode, which can lead to altered mixing of vibrational modes and uncertain band assignments. In this respect, MP2 or the DFT methods do not perform any better than the Hartree−Fock approximation.

The $\Delta\nu_{a-s} CO_2^-$ frequency separation has been correlated to the O−C−O bond angle and to the difference between the two C−O bond lengths by Nara et al.[9] The results of our calculations support the correlation with the O−C−O bond angle. In Table 1, we have collected all relevant observed and calculated data concerning the $\Delta\nu_{a-s}$ frequency separation. It seems that while the CO stretching frequencies (and C−O bond lengths) calculated with the same basis set strongly depend on the QM method, the $\Delta\nu_{a-s}$ frequency differences remain fairly similar. However, switching from 6-31G* to the 6-31+G** basis set decreases the $\Delta\nu_{a-s}$ values by 70−100 cm^{-1}, which is still insufficient to approach the observed value. Note that at the same time the O−C−O bond angles become ∼1° smaller, which appears to be consistent.

It may be of interest also to compare the full IR and Raman spectra calculated for the free acetate ion at the standard B3LYP/6-31G* level (force field scaled by the widely accepted scale factors of Rauhut and Pulay[3]) to the measured ones. In this calculation, the RMS error (including all 6 isotopomers) was as large as 54.6 cm^{-1}. A quick look at the measured and simulated spectra shown in Figure 2 (compare curves a and b for IR, and d and e for Raman) is enough to reject the free acetate model. In addition to the problem with the $\Delta\nu_{a-s}$ frequency separation, there are other striking differences in the region below 1000 cm^{-1}, especially in the Raman spectrum: notably, false prediction of the CC stretching mode at 596 cm^{-1}

TABLE 1: Observed Antisymmetric and Symmetric Carboxylate Stretching Frequencies and Their Separations ($\Delta\nu_{a-s}CO_2^-$) Compared to Those Calculated for the Free and Solvated Acetate Ion and Sodium Acetate Complexes by Different QM Methods for Various SCRF Models

method	$\nu_a CO_2^-$ (cm^{-1})	$\nu_s CO_2^-$ (cm^{-1})	$\Delta\nu_{a-s} CO_2^-$ (cm^{-1})	r(C−O) (Å)	∠O−C−O (degree)
Measured IR, solid	1584^a/1579	1424^a/1426	160^a/153	1.253, 1.257^e	123.7^e
aqueous solution^b	1551	1416	135		
Measured Raman, solid	1562^c/1567	1424^c/1418	138^c/149	1.253, 1.257^e	123.7^e
aqueous solution^d	1556	1420	136		
Calculated, empirical SVFF^a	1584	1428	156	1.253, 1.257^e	123.7^e
Free acetate ion					
HF/6-31G*	1900	1551	349	1.2333, 1.2354	129.5
BHandH/6-31G*	1889	1498	391	1.2364, 1.2379	129.6
BHandHLYP/6-31G*	1842	1469	373	1.2424, 1.2439	129.6
MP2/6-31G*	1780	1404	376	1.2634, 1.2645	129.7
B3LYP/6-31G*	1757	1377	380	1.2565, 1.2577	129.8
HF/6-31+G**	1817	1535	282	1.2373, 1.2388	128.8
BHandHLYP/6-31+G**	1752	1452	300	1.2469, 1.2480	128.7
MP2/6-31+G**	1662	1383	279	1.2704, 1.2709	128.8
B3LYP/6-31+G**	1661	1358	303	1.2617, 1.2625	128.7
Solvated acetate ion^f					
HF/6-31G*/Onsager model	1864	1555	309	1.2364, 1.2383	128.5
HF/6-31+G**/Onsager	1808	1536	271	1.2380, 1.2395	128.5
B3LYP/6-31+G**/Onsager	1622	1367	255	1.2649, 1.2657	127.7
Bidentate Na−acetate complex^f					
B3LYP/6-31G*/Onsager	1666	1420	246	1.2656, 1.2670	125.2
B3LYP/6-31+G**/Onsager	1607	1422	185	1.2695, 1.2685	124.3
B3LYP/6-31+G**/PCM	1547	1424	123	1.2712, 1.2714	123.5
B3LYP/6-31+G**/SCI−PCM	1606	1421	185	1.2695, 1.2702	124.1

[a] IR solid-phase data from Kakihana et al.[8] [b] IR solution data from Cabannis et al.[13] [c] Raman data from Frost and Kloprogge.[14] [d] Raman solution data from Bickley et al.[15] [e] X-ray data determined for Na−acetate trihydrate.[16] [f] Self-consistent reaction field (SCRF) calculations where water was selected as a dielectric medium.

that should, instead, give rise to the strongest Raman band around 930 cm^{-1}).

It is to be mentioned that, depending on the QM approximation, the assumed eclipsed conformation of the methyl group may not always correspond to the global minimum of energy. However, calculations done on both the eclipsed and staggered conformations indicate that the energy difference is very small, and the change in conformation affects the methyl torsional frequency the most (it may occasionally become imaginary) and alters the CO_2 wagging and bending frequencies only slightly (the shift is not more than 20 cm^{-1}), whereas the frequencies of all other normal modes do not change.

Returning to the problem of $\Delta\nu_{a-s}$ frequency separation, scaling of the force field would correct for overestimation of frequencies in general, but since both CO stretching vibrations are similarly affected by scaling, the frequency separation in question remains too high to be acceptable. If the key to lowering the value of frequency separation is to decrease the O−C−O bond angle (to get closer to the experimental value of 123.7° found by X-ray diffraction),[16] then it seems to be reasonable to explore the effect of the surrounding dielectric medium and consider also the effect of interaction with a sodium counterion on both the geometry and the vibrations of the acetate ion.

Solvation Models: Effect of Surrounding Dielectric Medium. The effect of surrounding dielectric medium (water) on the optimized structural parameters and on calculated carboxylate stretching frequencies is presented in the lower half of Table 1. According to the self-consistent reaction field (SCRF) calculation on a single acetate ion by the Onsager model, the O−C−O angle becomes slightly smaller than in the free state, and together with a 40 cm^{-1} lowering of the $\nu_a CO_2^-$ frequency, the $\Delta\nu_{a-s}$ frequency separation also decreases by about the same amount. Nevertheless, even in the case of the B3LYP/6-31+G** calculation, the $\Delta\nu_{a-s}$ frequency separation is still 255 cm^{-1}, roughly a 100 cm^{-1} greater than the target value.

Effect of Interaction with a Sodium Counterion: A Bidentate Complex. Interaction of the carboxylate group with a Na$^+$ cation present in a bidentate complex (Figure 1b) significantly decreases the O−C−O bond angle which approaches the experimental value. Concomitantly, the frequency of the CO_2^- symmetric stretching vibration increases, whereas its antisymmetric counterpart slightly decreases. At the B3LYP/6-31+G** level, the separation between them becomes 185 cm^{-1}, not much higher than the observed value. Considering that this may further decrease on scaling of the force field, this interaction model seems quite satisfactory.

Two other solvation models have been considered at the same level of theory. When solvation is taken into account according to the polarizable continuum model (PCM), there is a further substantial decrease in the $\nu_a CO_2^-$ frequency. This time the $\Delta\nu_{a-s}$ value becomes 123 cm^{-1}, somewhat overshooting the target (as to the solid) but getting quite close to the value observed in aqueous solution (135 cm^{-1}). Finally, the SCI−PCM solvation model, although computationally more demanding, leads to practically the same results as the spherical-cavity Onsager model.

Pseudobridging Complex Containing Water. In structural model **3** depicted in Figure 1, in addition to surrounding water considered as a dielectric medium, a single water molecule was incorporated in the complex and considered explicitly in the vibrational analysis. For lack of space, we are not going to present the corresponding numerical results here, we only mention that both the O−C−O angle and the $\Delta\nu_{a-s}$ frequency separation became larger again than in the bidentate complex, so it did not bring us closer to an acceptable solution. (Details of this calculation are given in the Supporting Information.)

Simulation of Full IR and Raman Spectra with SQM Force Fields. Based on the previous results obtained without scaling of the QM force fields, we have chosen the DFT method and the B3LYP/6-31+G** level to explore the performance of the selected continuum (or SCRF) models in full normal

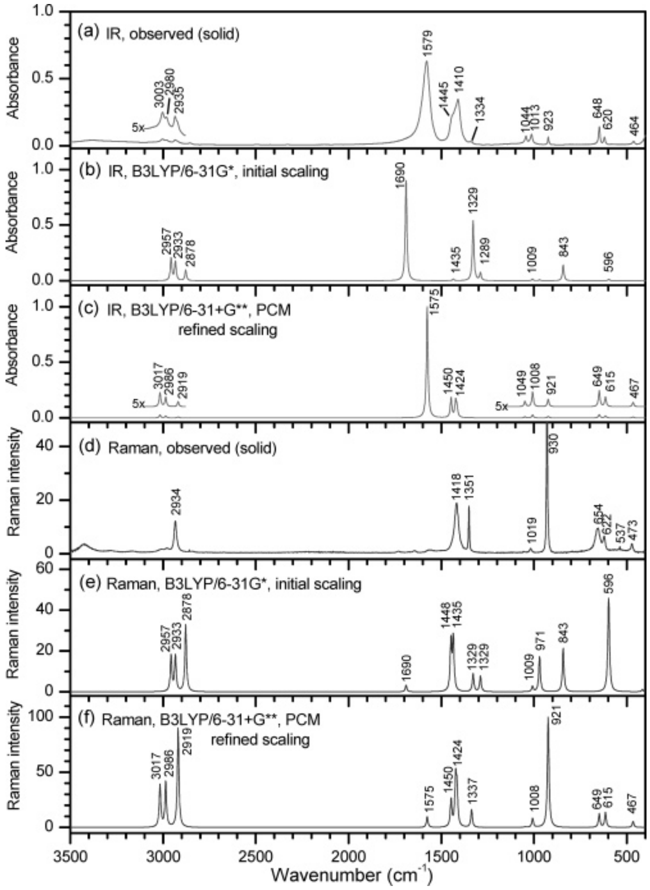

Figure 2. Illustration of the goodness of spectral simulations of the IR and Raman spectra of solid sodium acetate by SQM force field methods: (a) Measured IR spectrum (KBr pellet); (b) Simulated IR spectrum obtained in calculation A for a "free" acetate ion at the B3LYP/6-31G* level using the basic set of transferable scale factors; (c) IR spectrum obtained in calculation C for the bidentate Na-acetate complex at the B3LYP/6-31+G** level according to the polarizable continuum model (PCM) with refined scale factors; (d) Measured Raman spectrum solid sodium acetate trihydrate (powder); (e) Simulated Raman spectrum obtained in calculation A; (f) Simulated Raman spectrum obtained in calculation C.

coordinate calculations with scaled force fields. Representative results restricted to the fundamental frequencies of the main acetate isotope ($^{12}CH_3{}^{12}CO_2$) alone, taken from three different calculations, are compared in Table 2. Calculation A deals with a "free" acetate ion enclosed in a spherical cavity in a dielectric medium (Onsager model); calculation B refers to a bidentate sodium acetate complex in a similar Onsager-type spherical cavity; and calculation C refers to the bidentate complex in a dielectric medium described by the polarizable continuum model (PCM). The calculated frequencies reported here were obtained with selective scaling of the DFT force fields after least-squares refinement of the scale factors. The RMS errors (ϵ) calculated for the whole set of six isotopomers are also given in the lower part of the table, in the columns of frequency deviations ($\Delta\nu$). This can be considered as the main measure of goodness of the given model, method, and force field. When assigning the calculated frequencies to the observed ones during the least-squares refinement, the assignment-preserving feature of Molvib[24] was switched on in an effort to preserve the assignment of vibrational modes that was made by Kakihana et al.[8] However, the restrictions imposed by the raw DFT force fields caused mutual changes in assignment of the three close-lying bands in the 1450−1400 cm^{-1} region where the CO_2 symmetric stretching ($\nu_s CO_2$) and the two CH_3 asymmetric bending ($\beta_{as}CH_3$ and $\beta_{op}CH_3$) modes appear in extensive coupling with each other and with some other internal coordinates. (Note that the latter two vibrations have not been resolved in any room-temperature spectra.)

It is clear that application of the Onsager-type continuum model (calculation A in Table 2) substantially improved the situation compared to the free acetate ion calculations. Even so, calculation A neglecting the effect of the counterion proved to be the least successful of the three calculations as indicated by the overall root-mean-squares frequency error ($\epsilon = 20.3$ cm^{-1}).

The superiority of the bidentate structure is evident if judged by the RMS errors. By this criterion, calculations B and C corresponding to the Onsager and PCM solvation models proved to be the best, with sufficiently low 9.4 and 8.2 cm^{-1} average errors, respectively, in the whole set of 82 frequencies. The refined scale factors obtained in these calculations are listed in Table 3. Force constants associated with torsional coordinates and with coordinates involving the Na^+ displacements have not been scaled. Note that some of the scale factors are greater than unity, which is rarely the case in isolated, neutral molecules, but they are all within a ±10% margin around unity, which is considered tolerable.

A similar calculation was also done for the pseudobridging structure (not included in the tables), but the frequency fit was unacceptably poor in the region below 1000 cm^{-1} and even some unacceptably high scale factor values were obtained (e.g., a value greater than 1.3 for OCO bending), thus we have discarded this model. (Details of this calculation called calculation D are given in the Supporting Information.)

Contrary to our expectation, scaling affected the $\Delta\nu_{a-s}CO_2$ frequency separation differently in different models, as it is shown in the last but one row of Table 2 (the values obtained without scaling are also given there in parentheses): it decreased noticeably in calculation A (by 35 cm^{-1}) and remained almost unchanged in calculations B and C. Since the two CO stretching force constants and their interaction terms have been corrected with the same scale factors within a given model, the changes in $\Delta\nu_{a-s}CO_2$ during selective scaling must be due to different extent of mixing of CO stretches with other internal coordinates in different models, i.e., to differences in the actual normal modes assigned to $\nu_s CO_2$ vibration. Thus, calculation B (Onsager model) led to the assignment of the CO_2 symmetric stretching vibration in the main isotopomer to the lowest frequency band of the 1450−1400 cm^{-1} region (1404 cm^{-1}), whereas in calculation C (PCM model), it got attributed predominantly to the highest frequency band (1450 cm^{-1}). Note that both of these assignments differ from the "empirical" assignment of Kakihana et al.[8] that could not be reproduced in our SQM FF calculations. Together with the remaining uncertainty, we regard both calculations B and C equally acceptable approximations.

The other pair of normal modes whose frequency separation is affected by the choice of the theoretical model is the split pair of methyl in-plane and out-of-plane asymmetric bending modes. The values of measured and computed splittings, $\Delta\delta_{as}CH_3$, are compared in the last row of Table 2. Note that the calculated splittings are always substantially smaller than the reported experimental value of 40 cm^{-1} (based on a low-temperature measurement[8]), which again raises the question of correctness of the assignment in this critical spectral region by Kakihana et al.[8] As a feasible alternative, we present in Table 2 the assignment according to the PED values obtained in our calculation C.

TABLE 2: Vibrational Frequencies (cm^{-1}) of Acetate Ion and Its Sodium Complex Calculated with Scaled B3LYP/6-31+G Force Fields (Harmonic Approximation) Using Different Continuum Models, with Scale Factors Refined to Fit 82 Observed IR Frequencies of Six Na−Acetate Isotopomers**

mode no.	symm. species (C_s)	experimental		preliminary assignment[a]	solvated acetate ion		bidentate Na−acetate complex in dielectric field (water)				assignment by PED (%) in sym. coords.[b]
					calculation A		calculation B		calculation C		
		IR[a]	Raman		Onsager model		Onsager model		polarizable continuum model (PCM)		
		ν_{obs}	ν_{obs}		ν_{calc}	$\Delta\nu$	ν_{calc}	$\Delta\nu$	ν_{calc}	$\Delta\nu$	
1	A′	3002.8	3008	CH_3 as ip stretch	3010	8	3014	11	3017	14	$\nu_{op}CH_3$ (99)
2	A″	2974.4	2980	CH_3 as oop stretch	2986	11	2986	12	2986	12	$\nu_{as}CH_3$ (94), ν_sCH_3 (6)
3	A′	2930.1	2934	CH_3 sym stretch	2926	−4	2922	−8	2919	−11	ν_sCH_3 (93), $\nu_{as}CH_3$ (6)
4	A′	***1583.7***	1567	CO_2 asym stretch	***1598***	14	***1587***	3	***1575***	−9	$\nu_{as}CO_2$ (83), ρCO_2 (9), ρCH_3 (6)
5	A″	1447.3		CH_3 oop bend	1438	−9	1438	−9	***1450***	3	ν_sCO_2 (45), $\beta_{as}CH_3$ (21), νCC (16), βCO_2 (11)
6	A′	***1423.7***	1418	CO_2 sym stretch	1424	0	1429	5	1424	0	$\beta_{as}CH_3$ (59), ν_sCO_2 (23), νCC (6), βCO_2 (5)
7	A′	1407.3		CH_3 as ip bend	***1378***	−29	***1404***	−3	1415	8	$\beta_{op}CH_3$ (89)
8	A′	1332.5	1351	CH_3 sym bend	1325	−7	1328	−5	1337	4	β_sCH_3 (90), ν_sCO_2 (6)
9	A″	1044.4	1055	CH_3 oop rock	1052	8	1053	9	1049	5	$\rho_{op}CH_3$ (62), ωCO_2 (29), $\beta_{as}CH_3$ (8)
10	A′	1011.8	1019	CH_3 ip rock	1020	8	1014	2	1008	−4	ρCH_3 (82), $\nu_{as}CO_2$ (7), $\beta_{op}CH_3$ (6)
11	A′	923.6	930	CC stretch	944	20	932	8	921	−3	νCC (54), βCO_2 (27), ν_sCO_2 (18)
12	A′	650.3	654	CO_2 bend	661	11	659	9	649	−1	βCO_2 (49), ωCO_2 (21), νCC (18), $\rho_{op}CH_3$ (8)
13	A″	622.1	622	CO_2 wag	623	1	618	−4	615	−7	ωCO_2 (53), $\rho_{op}CH_3$ (26), βCO_2 (12), νCC (6)
14	A′	462.4	473	CO_2 rock	458	−4	460	−2	467	5	ρCO_2 (79), ρCH_3 (17)
15	A′		(260)	NaO_2 sym stretch			279		201		ν_sNaO (98)
16	A′		(188)	NaO_2 asym stretch			191		123		τCH_3 (54), $\nu_{as}NaO$ (39)
17	A″		(162)	$Na(O_2)$ wag			107		113		τCH_3 (44), $\nu_{as}NaO$ (39), ρCO_2 (8)
18	A″	?	?	CH_3 torsion	22 i		19 i		60		ωNa (91), ωCO_2 (7)
RMS error, ϵ[c]						20.3		9.4		8.2	
$\Delta\nu_{a-s}CO_2$[d]		160	149		220 (255)		183 (185)		125 (123)		
$\Delta\delta_{as}CH_3$		40			14		9		9		

[a] Following Kakihana et al.[8] Notation: asym, as, antisymmetric; sym, symmetric; ip, in-plane; oop, out-of-plane; [b] Abbreviation used in PED: ν, stretching; b, bending; ρ, rocking; ω, wagging; τ, torsion; s, sym; as, asym; op, out-of-plane. [c] RMS error calculated for 82 observed frequencies of 6 isotopomers; [d] The values of $\Delta\nu_{a-s}CO_2$ corresponding to the raw force fields (no scaling) are given in parentheses. Normal modes with the frequencies in bold italic have the greatest contribution from the CO_2 antisymmetric and symmetric stretching modes.

TABLE 3: Scale Factors Used with the B3LYP/6-31+G Force Fields of Solvated Bidentate Na−Acetate Complex in Calculations B (Onsager Model) and C (PMC)**

type of internal coordinate	calculation B		calculation C	
	final value of scale factor	error	final value of scale factor	error
CH stretch	0.9258	0.0016	0.9214	0.0013
CO stretch	0.9666	0.0065	1.0463	0.0048
CC stretch	1.0692	0.0309	0.9904	0.0292
HCC bend	0.9829	0.0082	0.9613	0.0072
HCH bend	0.9338	0.0051	0.9363	0.0047
CCO bend	1.0810	0.0254	1.0455	0.0218
OCO bend	0.9515	0.0463	0.9572	0.0698
CO_2 wag	0.9963	0.0175	1.0357	0.0164

To judge about the quality of the SQM calculation C on the basis of prediction of IR and Raman intensities as well, the calculated spectra are compared to the experimental ones for the main isotopomer in Figure 2 (see the simulated IR and Raman spectral curves in panes c and f, respectively). The substantial improvement as compared to the situation presented for the "free" acetate ion is undisputable. Thus, all considered, the bidentate structure treated according to the polarizable continuum model (PCM) in calculation C proved to be a viable extension of the SQM method as a theoretical approximation to model the vibrational spectra of a charged molecule measured in solid state. (Full results of this calculation including all six isotopomers can be found in the Supporting Information.)

Comparison of Empirical and SQM Force Fields Obtained for Sodium Acetate. One of the aims of this work has been to compare the old empirical valence force field developed by Kakihana et al.[8] (to describe the solid-state spectra of sodium acetate) to a reliable SQM force field of this substance. For a molecule whose vibrations are described by n internal coordinates, there are generally $n(n + 1)/2$ force constants in harmonic approximation. Only for very small molecules is it possible to determine all of the force constants on empirical grounds, so usually many of the cross terms are set to zero, or some of them are considered equal. This is also the case for Kakihana's 27-parameter simplified valence force field, SVFF (based on 16 internal coordinates), where there are 136 force constants in all, but 93 of the 120 off-diagonal elements are assumed to be zero. The SQM force field of the acetate ion, on the other hand, is derived from a quantum mechanical calculation where all of the 136 force constants can be determined and appear to be

TABLE 4: Comparison of Selected Force Constants (mdyn/Å) of the SVFF Force Field with Those Obtained in SQM Force Field Calculations A and C

matrix element (coordinate or interaction)	SVFF[a] free acetate ion	A acetate ion, Onsager model	C-1[b] bidentate complex, PCM	C-2[c] bidentate complex, PCM
C_2-O_3 stretch	9.358	9.079	6.160	9.403
C_2-O_4 stretch	9.282	9.054	6.148	9.387
CO,CO stretch−stretch	2.015	1.512	0.137	1.959
CCO bending	2.432	2.273	2.156	1.077
OCO bending	2.125	2.094	1.026	0.972
CO,OCO stretch−bend	0.450	0.330	−1.112	0.314
O−Na stretching	-	-	0.365	0.195
C−O−Na bending	-	-	0.535	-
O−Na−O bending	-	-	1.366	-
CO,ONa stretch−stretch	-	-	1.190	0.064
CO,ONaO stretch−bend	-	-	2.037	-

[a] From Kakihana et al.[8] [b] Scaled force field expressed in a redundant set of internal coordinates including all possible bond angles in the four-membered ring formed with the Na^+ ion. [c] Scaled force field expressed in a minimal set of internal coordinates ignoring in-plane bond angles involving the Na^+ ion.

different from zero (but they have to be scaled in order to correct for approximations in the theory).

It seems reasonable to restrict our discussion to some salient features of the scaled force field obtained in calculations A and C, i.e., with a “free” acetate ion and a bidentate sodium acetate complex in a dielectric field, at the B3LYP/6-31+G** level. The actual comparison of the SVFF and SQM force constant values shows few close numerical coincidences, even among the corresponding diagonal elements, which is understandable if we consider that the effect of neglected off-diagonal elements should be made up by the rest of the force field. For instance, the CCH and HCH bending force constants are 15−20% lower in the SQM force field, which is compensated by significant interaction terms (of the order of 0.1 mdyn/Å) that have been ignored in the SVFF.

The carboxylate CO stretching and bending force constants and some of their interaction terms are compared in Table 4 for the SVFF and for the SQM force fields obtained in calculations A and C. Addition of the sodium atom in case of the bidentate sodium acetate complex (calculations B and C) introduces 3 new normal modes. For description of the extra vibrations of the four-membered $CO_2^-Na^+$ ring, six additional internal coordinates can be defined (two O- -Na stretches, an O- -Na- -O, and two C−O- -Na bendings, and a ring puckering or Na wagging), including three redundant bending coordinates. Several important matrix elements of the computed DFT force field transformed to these coordinates (and scaled in a least squares procedure) differ very substantially from their counterparts in both the empirical SVFF and from the scaled DFT force field of the free acetate ion, as can be seen in Table 4 (see the column headed C-1).

It is interesting to see that, although the key force constant values obtained for the acetate anion in calculation A are quite similar to the corresponding SVFF values, calculation A proved unable to produce acceptable CO_2 stretching frequencies. On the other hand, the substantially different force field obtained in calculation C-1 for the bidentate complex gave a very good overall frequency fit. In the latter case, the surprisingly low C−O force constants were compensated by new force field terms: the force constants of the O- -Na bonds and very large interaction constants of C−O stretching coordinates with O- -Na stretches and with angle deformations in the CO_2- -Na tetragon. (Notably, the other end of the acetate complex including the C−C bond and the methyl group had force constants very close to those in the SVFF of the isolated acetate ion.)

Alternatively, if the three redundant bending coordinates involving the Na atom are omitted from the system of internal coordinates (on the pretext that they are not formed by covalent bonds) and the computed DFT force field is transformed to this nonredundant (minimal) set of coordinates, we obtain another representation of the force field (see the column headed C-2 in Table 4) in which the values of the CO stretching force constants get closer again to those in the SVFF of the acetate ion. Note that substantially different F-matrices obtained in the calculations C-1 and C-2 lead to the same calculated frequencies and IR and Raman intensities, so it is fair to state that they are equally effective alternative representations of the same force field of sodium acetate.

Conclusions

SQM force field calculations based on an isolated acetate ion cannot lead to satisfactory description of the fundamental vibrations observed in the IR and Raman spectra of sodium acetate. The DFT-based force field and normal coordinate calculations presented here indicate that explicit consideration of the effect of the Na^+ counterion on the molecular geometry and on the force field and of the influence of the dielectric medium (by the SCRF approach) are required to achieve acceptable descriptions of the vibrational behavior of the negatively charged carboxylate group in the acetate ion, as observed in condensed phase. At the same time, the $\Delta\nu_{a-s}CO_2$ frequency separation is very sensitive to the actual continuum model used. This study indicates that the Onsager and PCM models lead to somewhat different but similarly acceptable results, with the Onsager model not quite reaching and PCM slightly overreaching the target, whereas the more complicated SCI−PCM model gives practically the same results as the Onsager-type spherical cavity approximation. The reliability of these calculations has been checked and confirmed by an excellent frequency fit of all IR spectral features of six isotopomers of sodium acetate observed above 400 cm^{-1}.

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Supporting Information Available: Details of Molvib output corresponding to the PCM model for two variants of calculation C (C-1 and C-2) of the bidentate Na−acetate complex, and for the pseudo-bridging model (calculation D). This material is available free of charge via the Internet at http://pubs.acs.org.

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