Solvated Succinate Dianion: Structures, Electron Binding Energies, and Dyson Orbitals

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Structures and isomerization energies for the succinate dianion, $O_2C(CH_2)_2CO_2^{2-}$, in coordination with one or two water molecules are obtained from ab initio calculations. For the monohydrated case, the most stable structure has two hydrogen bonds between the water and one of the carboxylate groups in a bifurcated arrangement, while the next most stable structure places the water in a bridge between the carboxylate groups. Electron detachment energies obtained from electron propagator calculations agree closely with anion photoelectron spectra. Corresponding Dyson orbitals are most concentrated on carboxylate oxygens that are not directly involved in hydrogen bonds. For the dihydrated complex, the most stable structure has a water molecule coordinated to each carboxylate in a bifurcated arrangement, but there is a closely lying alternative in which there is one bifurcated water molecule coordinated to a carboxylate and another water molecule that bridges between the carboxylates. Predicted electron detachment energies are close to estimates that are made by extrapolation from experimental data on related hydrated dianions. Carboxylate oxygens make the largest contributions to the Dyson orbitals for the lowest electron detachment energies. In the alternative dihydrated structure, carboxylate oxygen amplitudes are reduced by the presence of hydrogen bonding in the Dyson orbitals for the lowest electron detachment energy.

Introduction

Considerable advances have been made recently in the preparation and characterization of multiply charged anions in the gas phase.[1] Stable, dicarboxylate dianions, $O_2C(CH_2)_nCO_2^{2-}$, where $n = 3-10$, have been investigated by Wang and coworkers using electrospray ionization coupled with photoelectron spectroscopy.[2,3] Lewis structures of these dianions suggest that repulsions between two negative charges localized on the carboxylate groups may be separated by a saturated, carbon-chain backbone of variable length. For the dianion where $n = 2$ (succinate), only a weak signal is obtained in the mass spectrum, and it has been concluded that this species is metastable. Theoretical investigations on the succinate dianion have found it to have a vertical electron detachment energy that is positive, while the adiabatic electron detachment energy is negative.[4,5] Only a weak signal is found in the mass spectrum for the bare succinate dianion. However, the succinate dianion complexed with a single water molecule has been observed in gas phase[3] and its photoelectron spectrum has been recorded. Solvation plays a crucial role in stabilizing multiply charged anions in the gas phase.[6] A theoretical study of the effects of water molecules on the structure and electron binding energies of the succinate dianion is the subject of the present investigation. Dyson orbitals pertaining to electron detachment of the dianion provide a one-electron interpretation of photoelectron spectra.

Computational Details

Geometry optimizations were done using second-order Møller−Plesset perturbation theory (MP2)[7] with the 6-311++G** basis set[8−10] for the succinate dianion (SD). An earlier investigation of the succinate dianion showed a structure with C_2 symmetry to be the lowest in energy[5] among the several geometries it may assume, and this structure was considered for the solvation of the dianion in this study. Frequency calculations for even the monohydrated succinate dianion were not feasible with MP2/6-311++G** total energies because of the N^4 dependence of computer memory requirements on the number of basis functions. Therefore, to reduce the number of basis functions, the effect of diffuse functions on the optimized structures was deduced by selective inclusion or removal of diffuse functions on the succinate dianion bonded with a single water molecule. Comparison of geometry optimizations with different basis sets which included diffuse functions and those with the 6-311G** basis does not show significant differences in the hydrogen bonds which are of primary interest in this study. Hence, the 6-311G** basis was used for all optimizations to allow comparison of the energies for the succinate dianion mono- and dihydrates. Default convergence criteria (maximum component of force <0.00045 au, root-mean-square of forces <0.0003 au, maximum displacement for last step <0.0018 au, and root-mean-square of displacement for last step <0.0012 au) were used for all optimizations done using Gaussian 98.[11] Harmonic vibrational frequencies for all optimized structures were calculated to confirm that they were indeed minima.

Vertical electron detachment energies (VEDEs), defined as the difference between single point energies of the dianion and those of the monoanion at the dianion's geometry for the hydrated succinate dianions, were calculated using ΔMP2 and the P3 electron propagator method.[12−15] All calculations were performed using the Gaussian 98 program.[11]

Results and Discussion

Succinate Dianion Monohydrate (SDMH). A single water molecule can complex with the succinate dianion in four possible ways as depicted in Figure 1. A water molecule may associate with the succinate dianion through one hydrogen bond (Figure 1a, syn, and 1b, anti) via two hydrogen bonds forming

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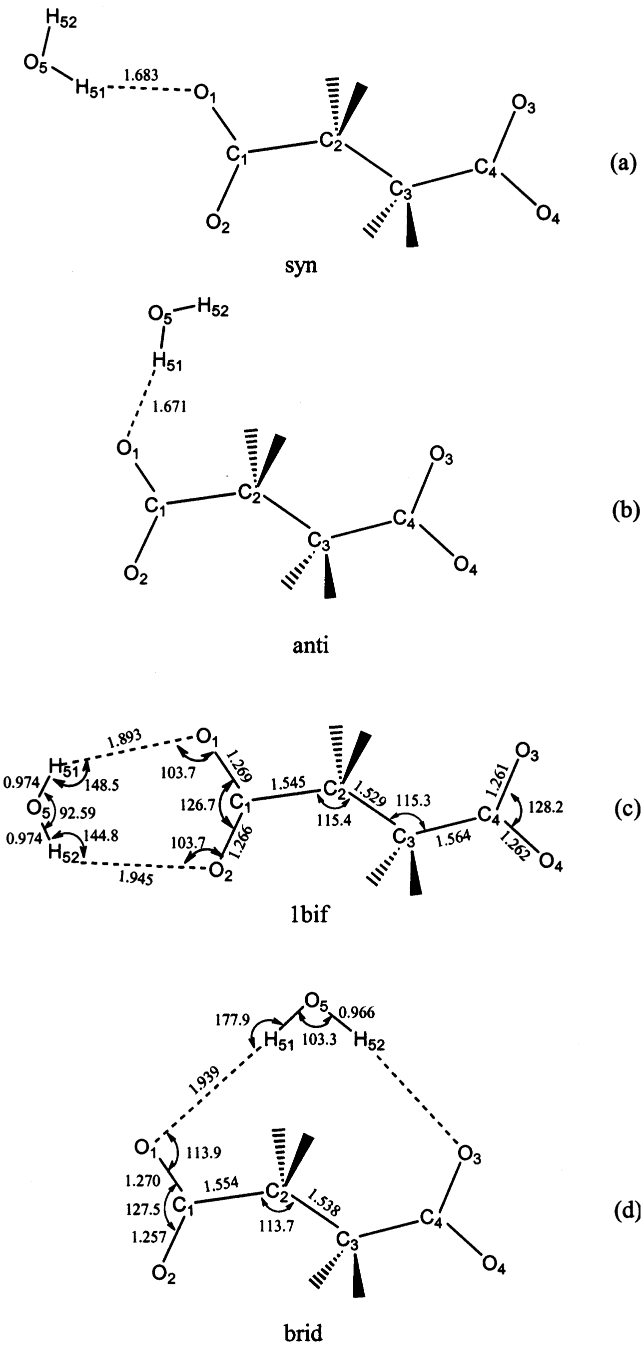

Figure 1. a. Succinate dianion monohydrate with a single hydrogen bond (syn). b. Succinate dianion monohydrate with a single hydrogen bond (anti). c. Succinate dianion monohydrate with two hydrogen bonds (1bif). d. Succinate dianion monohydrate with two hydrogen bonds (brid).

a bifurcated structure or through a bridge-type structure (Figure 1c, 1bif, and 1d, brid). Water molecules may be in-plane or out-of-plane with respect to the carboxylate group in structures 1a and 1b. As expected, structures 1a and 1b have a shorter hydrogen bond (1.683 Å for syn and 1.671 Å for anti) because of lesser constraint for bonding compared to the structure with two hydrogen bonds. O···H−O bond angles are 158.7° and 177.1°, respectively, for the syn and anti structures. Consistent with MP2/6-31G** calculations on acetate monohydrate,[16] optimization of the syn structure using 6-311G** and 6-311++G** bases gave the bifurcated structure, 1bif. Optimization initiated with an anti structure converges to the bridge structure, brid. The 1bif structure consists of two hydrogen bonds with bond lengths of 1.893 and 1.945 Å, and the bridge structure, having C_2 symmetry, has two hydrogen bonds of equal length at 1.939 Å for the 6-311G** basis. Hydrogen bond lengths for the 1bif structure are shorter compared to a similar structure obtained for acetate monohydrate[16] (1.998 and 2.005 Å) calculated with MP2/6-311++G** and adipate dianion monohydrate[17] (1.955 and 1.972 Å) calculated with B3LYP/6-31+G**. However, our results are comparable to the experimental values of 1.89, 1.937, 1.940, and 1.960 Å observed for water molecules hydrogen bonded to succinate dianion in sodium succinate hexahydrate.[18,19] Shorter bond lengths for the hydrogen bonds in the sodium succinate hexahydrate are observed, as oxygen atoms of water molecules also coordinate with sodium ions. The two hydrogen bond lengths in the 1bif structure of succinate dianion monohydrate are not the same because of the difference in the two C−O bonds in the carboxylate group which are not equal in length, as observed even in the succinate dianion[5] and also in the adipate dianion.[17] Binding of a water molecule to the dianion also decreases the $O_1-C_1-O_2$ bond angle to allow for formation of the two hydrogen bonds, while the $O_3-C_4-O_4$ angle increases for the 1bif structure. The smaller calculated $O_1-H_{51}-O_5$ and $O_2-H_{52}-O_5$ bond angles of 148.5° and 144.8° for 1bif are consequences of the constraint of binding both the hydrogen atoms of the water molecule to the oxygen atoms of the carboxylate group. C−O−H bond angles in the succinate monohydrate (1bif) structure at 103.7° are slightly smaller compared to those for the acetate monohydrate[16] complex. C−O and C−C bond distances and the O−C−O bond angles for the 1bif structure are similar to those reported for the adipate dianion monohydrate.[17] The $C_1-C_2-C_3$ bond angles are slightly smaller and hydrogen bond distances are longer in the adipate dianion monohydrate because of the 6-31+G* basis used in ref 17.

The binding energy of the water molecule to the succinate dianion calculated with MP2/6-311G** for the 1bif structure was 1.23 eV and is larger compared to that of 0.93 eV obtained for the acetate monohydrate[20] complex with MP2/6-31+G*. This difference may reflect neglect of diffuse functions in our calculations and the presence of an additional carboxylate group instead of the methyl group in acetate. Our value is closer to the water binding energy of 1.056 eV of adipate dianion monohydrate[17] calculated with B3LYP/6-31+G* for the bifurcated mode of binding. The binding energy for the water in the bridge structure was slightly smaller at 1.16 eV.

Succinate Dianion Monohydrate Electron Detachment Energies. VEDEs calculated with ΔMP2/6-311++G** at the geometry obtained with MP2/6-311++G** were 1.14 and 0.73 eV, respectively, for the 1bif and bridge structures (see Table 1). Adiabatic electron detachment energies (AEDEs) were 0.75 and 0.01 eV for the 1bif and bridge structures. Relaxation energy, $\Delta E_{\mathrm{relax}}$, defined as difference between the VEDE and AEDE for the succinate dianion monohydrate is therefore 0.39 eV for the 1bif structure and 0.72 eV for the bridge structure. Electron propagator calculations with the P3 approximation[12−14] estimate the VEDEs for the 1bif and bridge structures to be 1.10 and 1.02 eV, respectively, at the MP2/6-311++G** geometry. The best estimate of the AEDE from our calculations therefore is 0.71 eV for the 1bif structure and 0.30 eV for the bridge structure. Increasing the basis size to 6-311++G(2df,p) changed the P3 VEDE for 1bif by 0.11 eV and that for the bridge structure by 0.16 eV. For the succinate dianion, the VEDE calculated from P3/6-311++G** was 0.67 eV.[5] Changes in the VEDE produced by attachment of a single water molecule to the succinate dianion are 0.43 and 0.35 eV for the 1bif and the bridge structures, respectively. The experimentally deter-

TABLE 1: MP2 Total Energies, VEDEs, AEDEs, and Binding Energies of Succinate Dianion Monohydrate

system	total energy, au	VEDE, eV		AEDE, eV		BE, eV	isomerization energy,[a] eV
		ΔMP2	P3	MP2	P3/MP2		
1bif							
6-311G**	−530.979485					1.23	0
6-311++G**	−531.047948	1.14	1.10	0.75	0.71		
6-311++G(2 d,2p)			1.16		0.77		
6-311++G(2 df,p)			1.27		0.88		
brid							
6-311G**	−530.978279					1.16	0.07
6-311++G**	−531.047121	0.73	1.02	0.01	0.30		
6-311++G(2 d,2p)			1.06		0.34		
6-311++G(2 df,p)			1.18		0.46		

[a] Values reported are with respect to the 1bif structure.

mined AEDE[3] of 0.35 eV agrees more closely with the best calculation for the bridge structure, 0.46 eV, than with the corresponding calculation for the slightly more stable 1bif structure, 0.88 eV. Contributions from both isomers are likely to be present in the broad feature that begins near 0.35 eV and extends to 2.2 eV[3].

Succinate Dianion Dihydrate (SDDH). Two water molecules can bind to the same carboxylate group or to the two carboxylate groups of the succinate dianion individually. Four of the possible isomeric structures with water molecules binding to the same carboxylate group are depicted in Figure 2. The second water molecule may form a hydrogen bond with the oxygen of the water molecule bound to the carboxylate group in the 1bif structure (Figure 2a) or to the more negatively charged oxygen of the carboxylate group (Figure 2b). Optimization from the 2a initial structure converges to the 2d structure. 2c and 2d structures are similar to that obtained for acetate dihydrate[20] with HF/4-31-G except that the $O_1 \cdots H_{51}$ hydrogen bond for the acetate dihydrate structure is only 1.580 Å compared to 1.879 Å in the nbif-1 and nbif-2 structures. 2c and 2d structures are also similar to that obtained with B3LYP/6-31+G** for adipate dianion dihydrate.[17] The difference in total energies for the two structures calculated with MP2/6-311G** is 0.32 kcal/mol. However, frequency calculations showed that both forms have all positive frequencies and indeed correspond to two different minima.

In the water molecules binding to the two carboxylate groups individually, several possible isomers exist containing the 1bif, syn, and anti mode of binding, of which four possible minima were obtained. (See Figure 3b−3e.) An optimization starting from a 2syn structure shown in Figure 3a ends with the 2bif structure. Other possible isomers which contain the syn configuration for one of the binding water molecules invariably resulted in the 1bif binding mode as observed for the monohydrate. Four isomers displayed in Figure 4 which have water molecules binding to both the carboxylate groups may be obtained from addition of a water molecule to the bridge structure of the monohydrate in 1bif, syn, or anti modes of binding. Once again, the initial syn geometries converge upon optimization to structures with the 1bif mode of binding.

Isomerization energies given in Table 2 show that the 2bif (Figure 3b) and the brid−1bif (Figure 4b) structures are lowest in energy and are separated by only 0.114 eV. 2bif is the lowest-energy isomer among all the dihydrated succinate dianion structures studied, as also obtained for the adipate dianion dihydrates.[17] Structural parameters of the brid−1bif isomer (Figure 4b) are closer to those of the bridge structure of the succinate dianion monohydrate. The O_1-H_{61} bond is longer by 0.091 Å and the O_3-H_{62} bond is shorter by 0.043 Å compared to that in the bridge structure of the monohydrate. The $C_1-O_1-H_{61}$ and $C_4-O_3-H_{62}$ bond angles are smaller at 110.9 and 113.1° compared to the $C_1-O_1-H_{51}$ bond angle of the bridge structure of the monohydrate in which they are 113.9°.

The binding energy of the second water molecule with respect to the succinate dianion monohydrate (1bif) with MP2/6-311G**

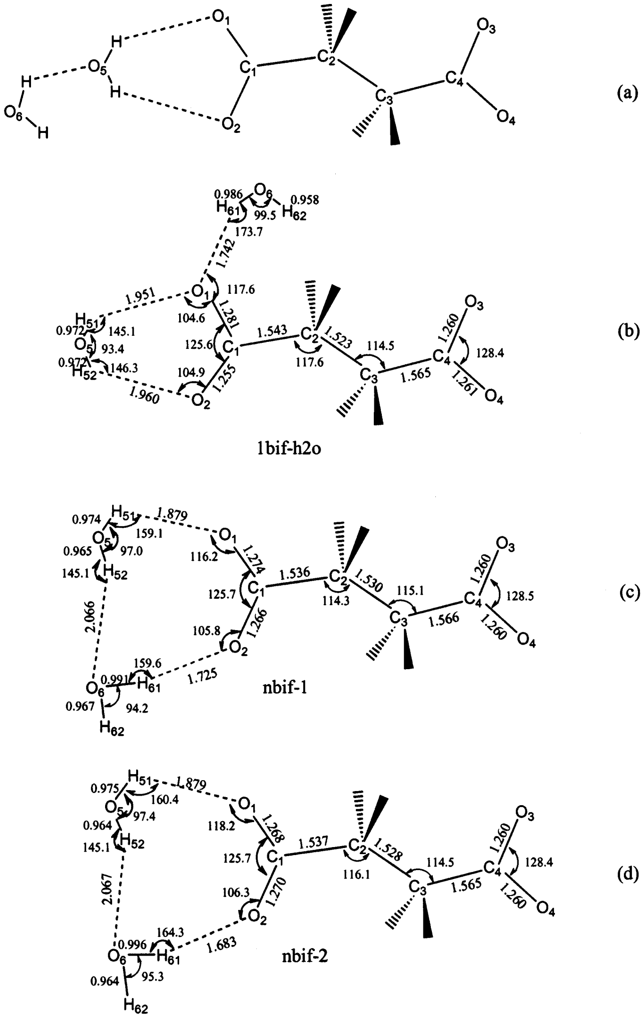

Figure 2. a. Succinate dianion dihydrate with one water molecule bound to a $-CO_2^-$ group in a bifurcated way and the second water molecule bound to the oxygen of the first water molecule through a hydrogen bond. b. Succinate dianion dihydrate with one water molecule bound to a $-CO_2^-$ group in a bifurcated way and the second water molecule bound to the more negatively charged oxygen of the carboxylate through a hydrogen bond (1bif−h2o). c. Succinate dianion dihydrate with two water molecules bound to a $-CO_2^-$ group (nbif-1). d Succinate dianion dihydrate with two water molecules bound to a $-CO_2^-$ group (nbif-2).

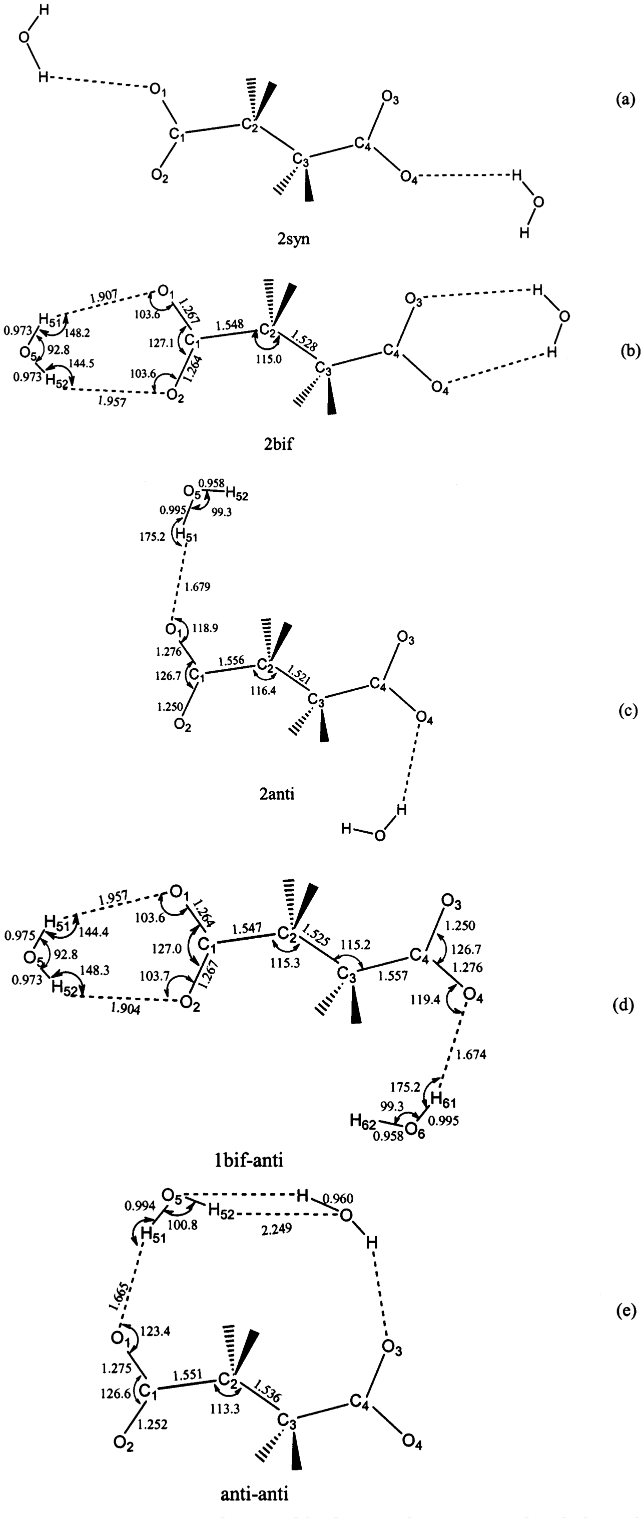

Figure 3. a. Succinate dianion dihydrate with a water molecule bound to each of the two $-CO_2^-$ groups in syn mode with C_2 symmetry (2syn). b. Succinate dianion dihydrate with a water molecule bound to each of the two $-CO_2^-$ groups in bifurcated mode with C_2 symmetry (2bif). c. Succinate dianion dihydrate with a water molecule bound to each of the two $-CO_2^-$ groups in anti mode with C_2 symmetry (2anti) and water molecules trans to each other. d. Succinate dianion dihydrate with two water molecules bound to the two $-CO_2^-$ groups in anti and bifurcated modes (1bif−anti). e. Succinate dianion dihydrate with two water molecules bound to the two $-CO_2^-$ groups in anti mode with C_2 symmetry (anti−anti) and water molecules cis to each other.

was calculated to be 1.17 eV for the 2bif structure. For the brid−1bif structure, a somewhat lower value, 1.06 eV, was obtained.

TABLE 2: Binding and Isomerization Energies of Succinate Dianion Dihydrates

system	BE,[a] eV	isomerization energy,[b] eV
2bif, Figure 4b	1.17	0
brid−1bif, Figure 5b	1.06	0.114
1bif−anti, Figure 4d	0.96	0.212
brid−cyc, Figure 5a	0.92	0.255
nbif-1, Figure 3c	0.92	0.257
nbif-2, Figure 3d	0.90	0.271
1bif−h2o, Figure 3b	0.87	0.309
brid−anti, Figure 5d	0.86	0.311
anti−anti, Figure 4e	0.77	0.407
2anti, Figure 4c	0.76	0.413
brid−h2o, Figure 5c	0.69	0.484

[a] Binding Energy (BE) with respect to that of monohydrate (1bif) for the dihydrate structures optimized at MP2/6-311G**. [b] Values reported are with respect to the 2bif structure.

TABLE 3: MP2 Total Energies, VEDE, AEDE of Succinate Dianion Dihydrate

system	total energy, au	VEDE, eV		AEDE, eV	
		ΔMP2	P3	MP2	P3/MP2
2bif					
6-311G**	−607.291055	0.79	1.28	0.13	0.62
6-311++G**	−607.361133	1.32	1.72	0.64	1.04
6-311++G(2d,2p)			1.77		1.09
brid−1bif					
6-311G**	−607.288057	1.03	0.99	0.54	0.50
6-311++G**	−607.359287	1.62	1.49		1.00
estimate			1.54		1.05

TABLE 4: VEDEs for the Succinate Dianion Monohydrate and Dihydrate Structures Calculated from P3 and the Corresponding Pole Strengths

system	basis	orbital	P3 eV	pole strength	KT[a] eV
1bif	6-311++G(2df,p)	36(A)	1.27	0.90	2.55
		34(A)	1.36	0.90	3.02
		35(A)	1.68	0.89	2.71
		32(A)	2.01	0.90	3.53
		31(A)	2.01	0.90	3.72
		33(A)	2.21	0.89	3.35
		30(A)	4.40	0.90	5.53
brid	6-311++G(2df,p)	36(A)	1.18	0.90	2.48
		33(A)	1.51	0.90	3.23
		32(B)	1.63	0.90	3.27
		35(B)	1.79	0.89	2.89
		34(A)	1.85	0.89	2.94
		31(B)	1.88	0.90	3.46
		30(B)	3.82	0.91	5.32
2bif	6-311++G(2d,2p)	41(A)	1.77	0.90	3.20
		37(A)	2.16	0.90	4.00
		38(B)	2.21	0.90	3.83
		40(B)	2.37	0.89	3.64
		36(B)	2.43	0.90	4.22
		39(A)	2.45	0.89	3.68
		35(B)	4.01	0.91	5.85
brid−1bif	6-311++G**	41(A)	1.49	0.90	3.01
		39(A)	1.70	0.90	3.62
		40(A)	1.96	0.89	3.27
		36(A)	2.29	0.90	4.26
		37(A)	2.33	0.90	4.07
		38(A)	2.47	0.89	3.86
		35(A)	3.99	0.91	5.68

[a] KT: Koopmans's theorem results.

Succinate Dianion Dihydrate Electron Detachment Energies. For the lowest energy structure (2bif) with C_2 symmetry obtained with MP2/6-311G** optimizations, the ΔMP2/6-311++G** VEDE was 1.32 eV (see Table 3). P3/6-311++G**

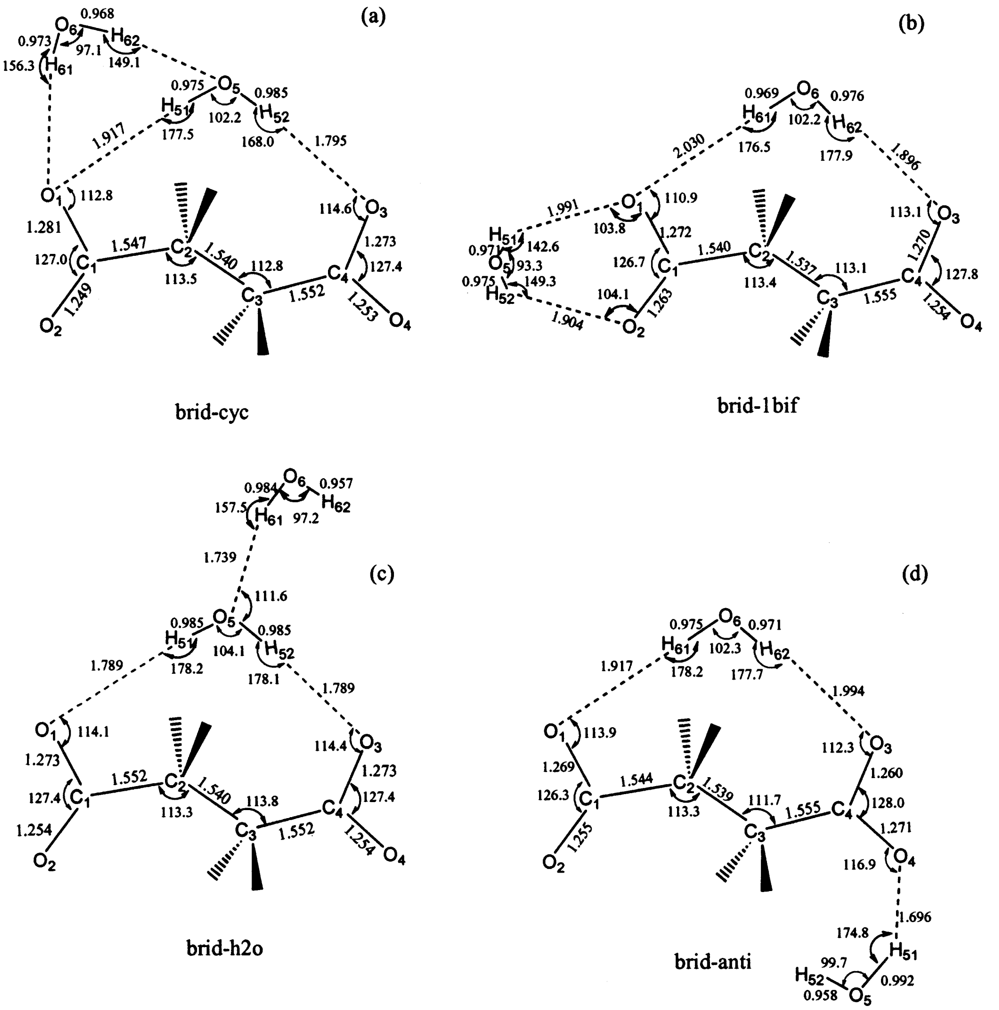

Figure 4. a. Succinate dianion dihydrate with water molecules bound in bridge and cyclic modes. (brid−cyc). b. Succinate dianion dihydrate with water molecules bound in bridge and bifurcated modes. (brid−1bif). c. Succinate dianion dihydrate with a water molecule bound in bridge mode and bound to a second water molecule (brid−h2o). d. Succinate dianion dihydrate with water molecules bound in bridge and anti modes. (brid−anti).

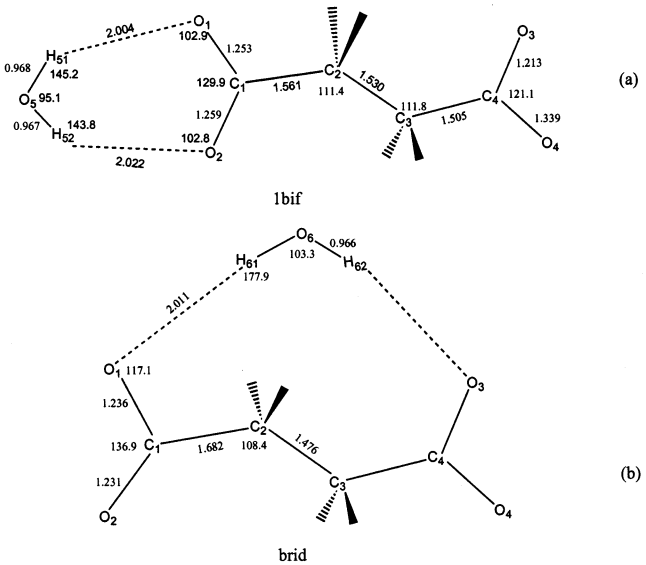

Figure 5. a. Structure of succinate monoanion monohydrate (1bif). b. Structure of succinate monoanion monohydrate (brid).

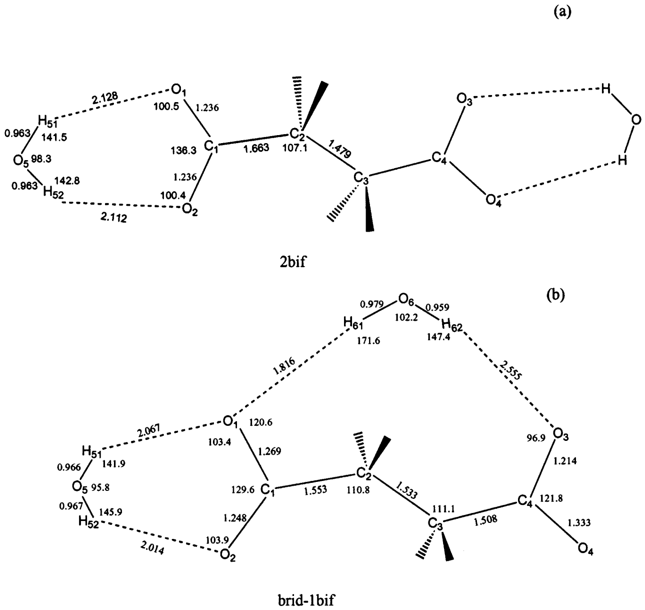

Figure 6. a. Structure of succinate monoanion dihydrate (2bif). b. Structure of succinate monoanion dihydrate (brid−1bif).

predicts the VEDE for this structure to be 1.72 eV. The AEDE for the 2bif structure with ΔMP2/6-311++G** was 0.64 eV. Using a relaxation energy of 0.68 eV (which is unlikely to change much with improvements to the MP2/6-311++G** model) and the P3 VEDE (1.77 eV) calculated with the best basis, 6-311++G(2d,2p), one may estimate the AEDE to be 1.09 eV.

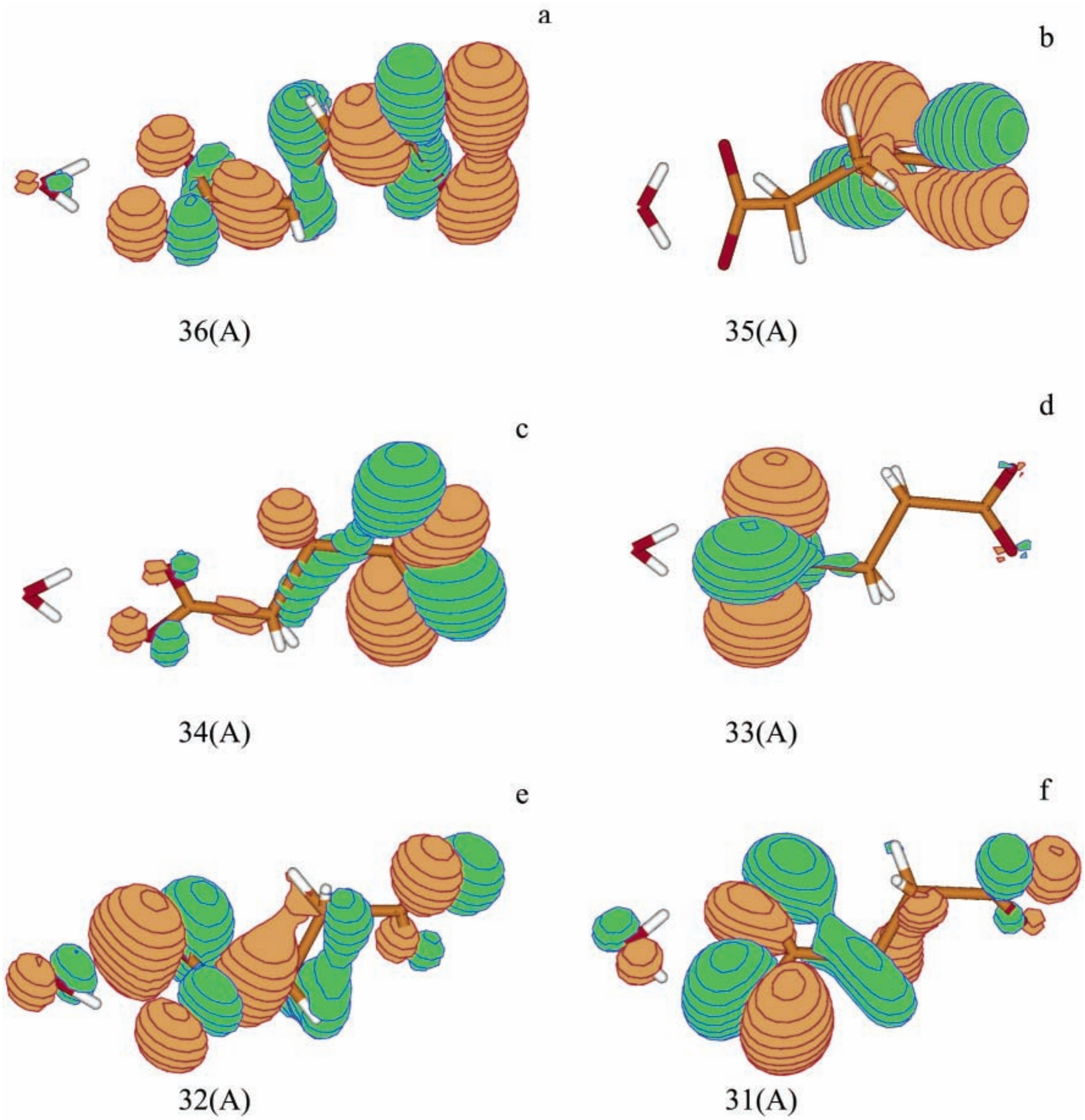

Figure 7. Dyson orbitals corresponding to VEDEs of succinate dianion monohydrate (1bif).

For the brid−1bif structure, the VEDE from ΔMP2/6-311++G** calculations was 1.62 eV with the MP2/6-311G** geometry, while the AEDE was 0.54 eV. An estimate of the AEDE from P3/MP2 calculations with the 6-311++G** basis is 1.00 eV for the brid−1bif structure. From the 2bif result, an additional estimate of the effect of additional polarization functions may be made: 0.05 eV. The best estimate of the AEDE is therefore 1.05 eV. No photoelectron spectrum was reported for succinate dihydrate, but extrapolation of results for related species[3] suggests an AEDE value near 1.0 eV. Both theoretical values for these nearly isoenergetic species, 1.09 and 1.05 eV, are in close agreement with this extrapolation.

Succinate Monoanion Monohydrate. The monoanion geometry corresponding to the succinate dianion monohydrate structure (1bif) was optimized with MP2/6-311G**. Results obtained for the monoanion (see Figure 5) are similar to those for the dianion. C_1-O_1 bond lengths for the monoanion are shorter than those for the dianion in both cases. The C_4-O_3 bond is shorter, at 1.213 Å, and the C_4-O_4 bond is longer, at 1.339 Å, compared to those in the succinate dianion monohydrate calculated with MP2/6-311G**. The $O_1-C_1-O_2$ bond angle increases (to 129.9°) and the $O_3-C_4-O_4$ bond angle decreases (to 121.1°) in comparison with those in the succinate dianion monohydrate. Electron detachment causes the C_3-C_4 bond distance to be shorter for the monoanion. As shown in Figure 5b, a comparatively large increase of the C_1-C_2 bond length and a decrease in the C_2-C_3 bond length are observed for the bridge structure compared to the monoanion of the 1bif structure.

Succinate Monoanion Dihydrate. Optimized geometries of the monoanions of the 2bif and the brid−1bif isomers of the succinate dianion dihydrate calculated with MP2/6-311G** are displayed in Figure 6. Changes in the bond distances and bond angles are similar to those observed for the monohydrate structure with a larger C_1-C_2 bond distance, a shorter C_2-C_3 bond distance, and a larger $O_1-C_1-O_2$ angle in the 2bif structure in comparison with the 1bif structure. The $C_1-C_2-C_3-C_4$ dihedral angle in the monoanion of the 2bif structure is 180° while the $O_1-C_1-C_2-C_3$ dihedral angle is 91.1°. Changes in the bond lengths and bond angles for the monoanion of the brid−1bif structure are similar to those observed in the monoanion of the 1bif structure for the monohydrate except for a large change in the hydrogen bond lengths for the water

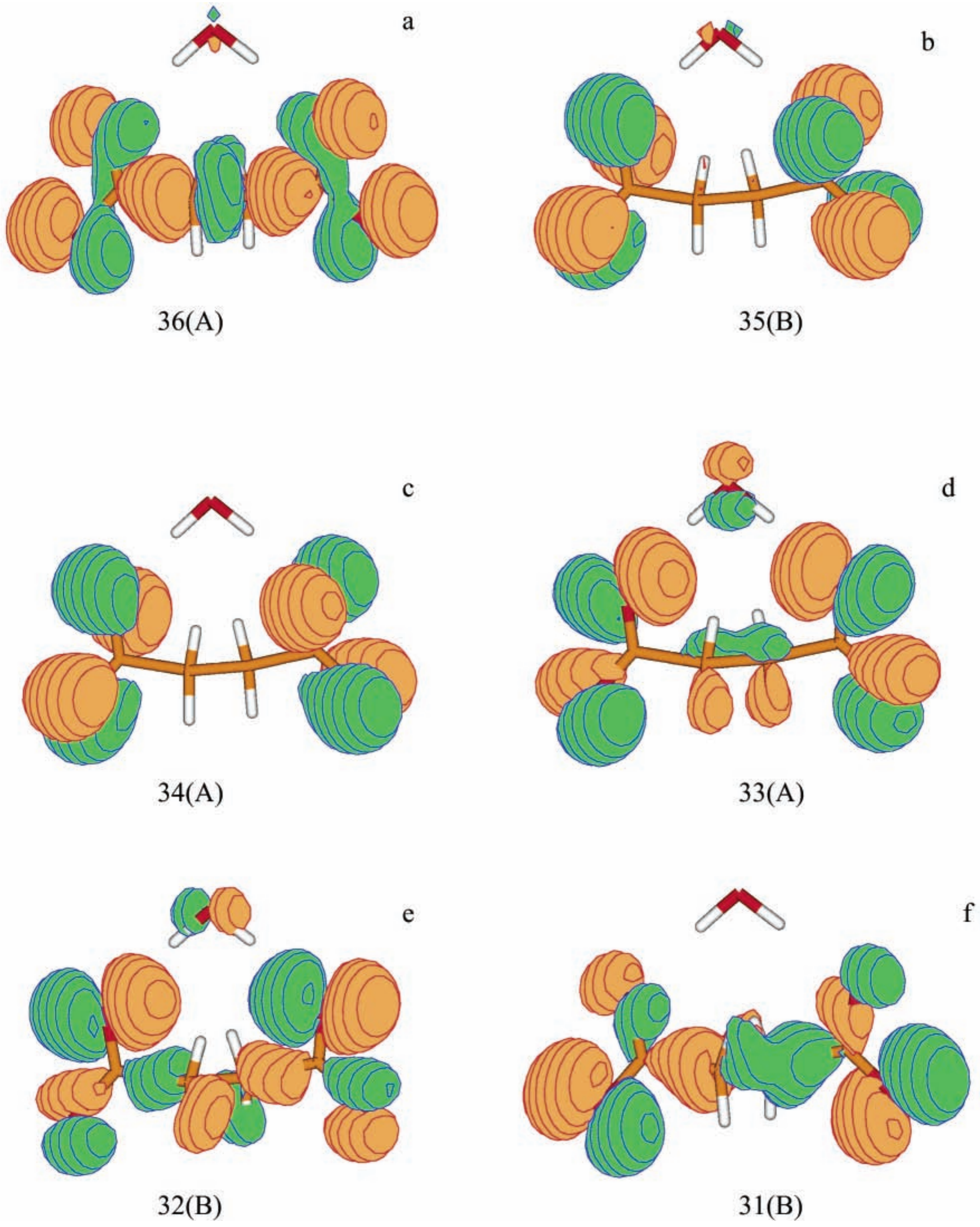

Figure 8. Dyson orbitals corresponding to VEDEs of succinate dianion monohydrate (brid).

molecule bound in bridge mode in comparison to the brid−1bif dianion structure.

Dyson Orbitals of Succinate Dianion Mono- and Dihydrates. To each electron detachment energy calculated with the P3 electron propagator method, there corresponds a Dyson orbital defined by

$$\Phi^{\mathrm{Dyson}}(x_1) = N^{1/2} \int \Psi^*{}_{\mathrm{anion}}(x_2, x_3, x_4, ..., x_N) \Psi_{\mathrm{dianion}}(x_1, x_2, x_3, ..., x_N)\, \mathrm{d}x_2\, \mathrm{d}x_3\, \mathrm{d}x_4 \ldots \mathrm{d}x_N$$

that describes the change in electronic structure between the dianion and the singly charged anion. When the normalization integral of the Dyson orbital, also known as the pole strength, is between 0.85 and unity, the perturbative description of relaxation and correlation corrections to Koopmans's theorem results provided by the P3 approximation is confirmed.[11−14] Plots of the Dyson orbitals in Figures 7−10 were generated with MOLDEN.[21] Contours of ±0.03 are displayed.

Table 4 displays P3 VEDEs for the most stable structures of the monohydrated and dihydrated dianions. All pole strengths are close to 0.9 and confirm the qualitative validity of the Koopmans description of the VEDEs. Nonetheless, correlation corrections from P3 calculations exceed 1 eV and sometimes change the order of the final states.

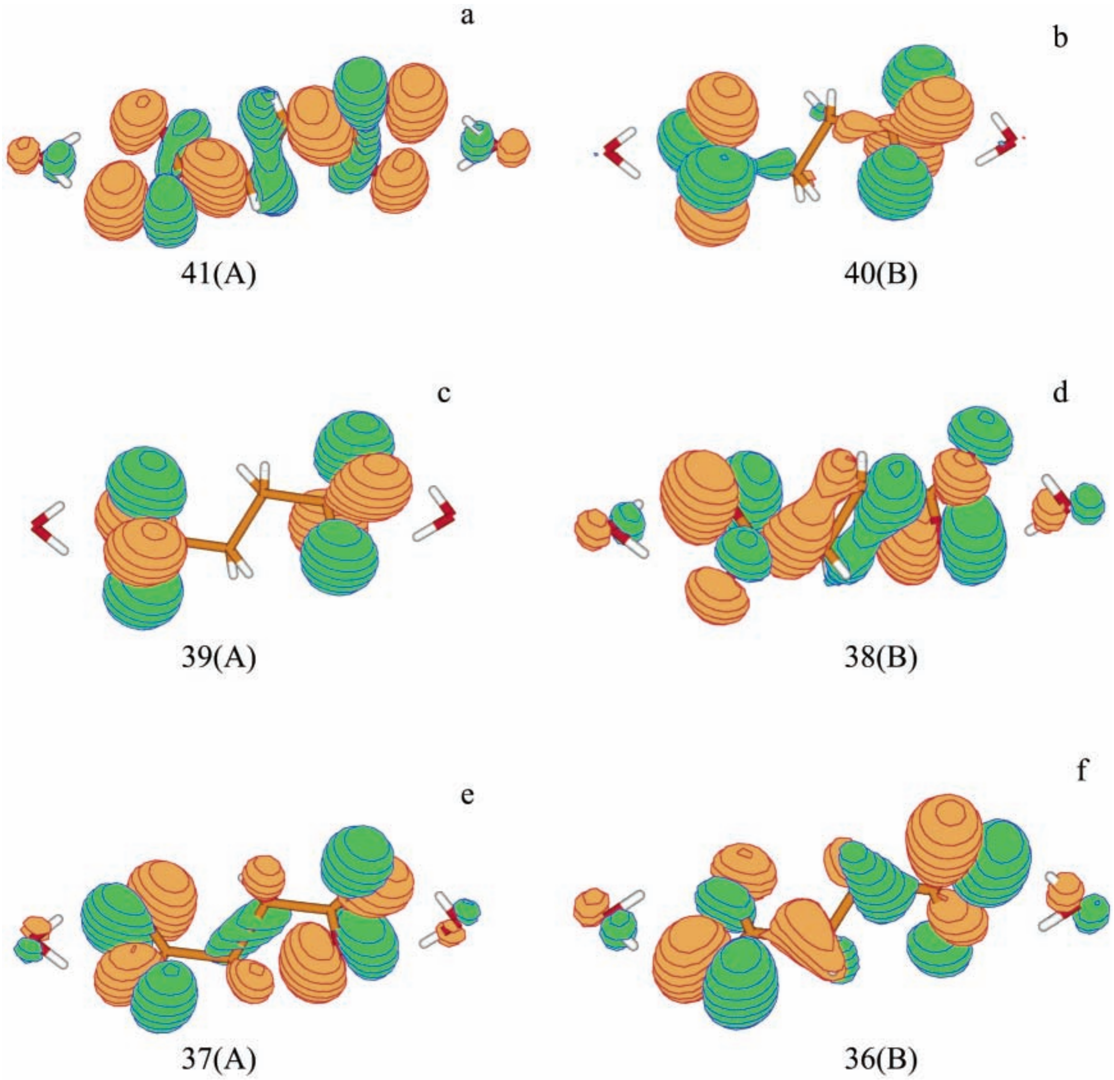

Figure 9. Dyson orbitals corresponding to VEDEs of succinate dianion dihydrate (2bif).

For the 1bif structure, the lowest VEDE corresponds to a Dyson orbital (36A) that is spread over the entire complex in Figure 7. Contributions from the uncoordinated carboxylate oxygens are larger than their hydrogen-bonded counterparts. In the Dyson orbitals of the first three VEDEs (34A, 35A, 36A), the same carboxylate's contributions are dominant. P3 VEDEs lie within 0.4 eV of each other. At higher VEDEs are three Dyson orbitals (31A, 32A, 33A) that are more concentrated on the carboxylate that is hydrogen-bonded to the water molecule. These three states are within 0.2 eV of each other.

In the bridged structure, C_2 point-group symmetry implies a or b classifications of the Dyson orbitals. For the lowest VEDE, the Dyson orbital (36A) in Figure 8 is spread chiefly over the four oxygens, but there are significant contributions from the methylene groups. Somewhat larger lobes are found on the uncoordinated oxygens. Unlike the previous structure, there is no energetic separation into two groups of three closely lying states. In this structure, the water molecule does not effect localization of the Dyson orbitals on one carboxylate or the other. In the photoelectron spectrum of ref 3, a complicated feature with many maxima and shoulders has its onset near 0.35 eV, a global maximum near 0.8 eV, and a tail near 2.2 eV. Given the numerous P3 VEDEs that lie in this range, it is likely that this feature has contributions from many final states from both isomers that exhibit significant vibronic mixing.

In the 2bif dihydrated complex, the lowest VEDE (41A) is well separated from the next five VEDEs (See Table 4.) The Dyson orbitals are dominated by carboxylate oxygen contributions. (See Figure 9.) Symmetry again enforces an equal distribution over the two carboxylate groups. Lobes on the four oxygens are of approximately equal size.

For the brid−1bif structure, two groups of three closing lying VEDEs are obtained. For the three lowest VEDEs, the Dyson orbitals of Figure 10 (41A, 40A, and 39A) are concentrated on the carboxylate that is linked only to the bridging water molecule. The oxygen that is most remote from hydrogen bonds makes the largest contribution to the Dyson orbital for the lowest VEDE. For the fourth, fifth, and sixth VEDEs, the Dyson orbitals (36A, 37A, 38A) are concentrated on the carboxylate that is linked by hydrogen bonds to both water molecules.

Conclusions

Electron detachment energies of succinate dianion are changed markedly by one or two water molecules. The succinate dianion monohydrate is indeed stable adiabatically with respect to electron detachment and the structure with a bifurcated hydrogen bond is slightly more stable than the structure having a water molecule bound to the dianion in a bridge type linkage. The calculated AEDE of the less stable form agrees closely with

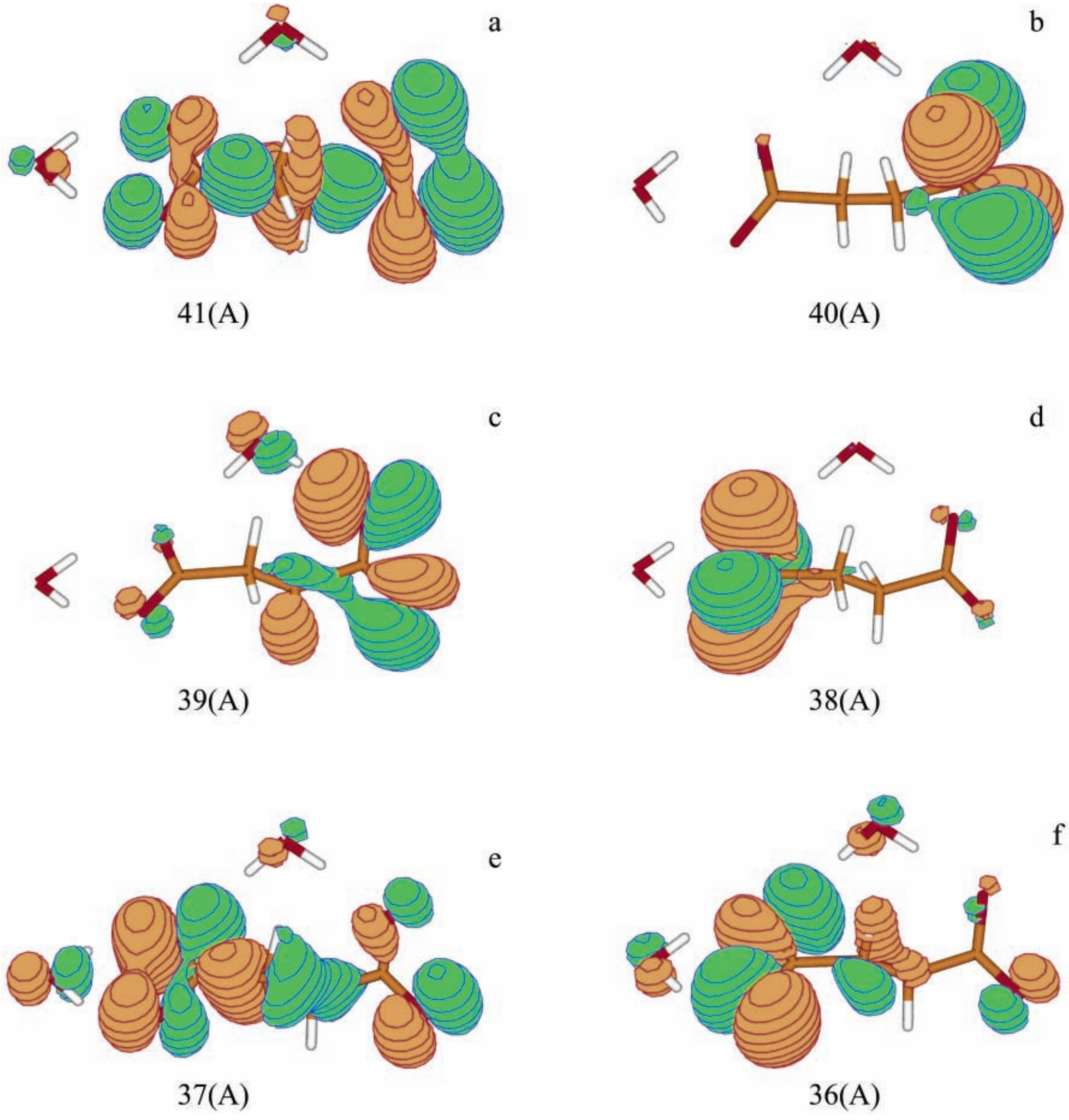

Figure 10. Dyson orbitals corresponding to VEDEs of succinate dianion dihydrate (brid−1bif).

the experimental threshold for photodetachment. Dyson orbitals for the lowest VEDEs are shifted toward the carboxylate oxygens that are most remote from hydrogen bonds.

The succinate dianion dihydrate has several isomeric structures with the water molecules bound to both carboxylate groups individually or to the same carboxylate group to give isomers close in energy. The structure with both water molecules bound in bifurcated hydrogen bonds is the most stable and has an AEDE of 1.1 eV. Another structure with water molecules bound in bifurcated as well as in a bridge linkage is only 0.114 eV higher in energy and has an AEDE that is lower by 0.04 eV. In the former structure, the Dyson orbital for the lowest VEDE is approximately evenly distributed over all four carboxylate oxygens. In contrast, for the bifurcated−bridge structure, the Dyson orbital for the lowest VEDE is shifted toward the carboxylate oxygens that are least involved in hydrogen bonding.

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