Theoretical Studies of Protonation and Lithiation of First- and Second-row Aldehydes

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We investigate the effects of protonation and lithiation upon the atomic and molecular properties of formaldehyde and thioformaldehyde. At the HF/6-311++G** level, protonation is much more exothermic than lithiation in both systems; protonation of the thioformaldehyde is favoured over formaldehyde, while lithiation of the aldehyde is favoured over the thioaldehyde. Lithiation results in a much larger dipole polarization and quadrupole depolarization of the $H_2CX|$ fragment than does protonation. On the atomic level, protonation is favoured by the large transfer of charge to the proton and its subsequent stabilization, while lithiation is driven by the inter-atomic stabilization afforded X by the proximity of Li^+. Lithiation of either aldehyde is well approximated by an electrostatic model, but protonation is not.

We are interested in the effects of direct interaction between solute and solvent molecules as a guide to more accurate models for the representation of direct solvation within large simulations. As proton transfer is one of the most facile processes in solution, we have investigated the difference in consequence of protonation between aldehydes and thioaldehydes, not only as a first step towards solvation, but also as an investigation of the difference in behaviour between first- and second-row systems. As a further characterization of solvent–solute interaction, we have included studies of lithiation of formaldehyde and thioformaldehyde as a comparison with the protonation studies. We are interested in the differences between the two complexation processes, the change each process causes in the aldehydes, and the properties necessary for accurate representation in simulations. Interestingly, it has been noted that lithiation is generally much less exothermic than is protonation despite what might at first seem to be a similar process.[1]

We note here that the protonation and lithiation of first- and second-row molecules has been studied extensively in the past, mainly with regard to issues of basicity (*vide infra*). In determining the origin of the energetics of protonation and lithiation, previous workers have often relied upon energy decomposition schemes as those of Morokuma[2] and Pullman.[3] These decompose the interaction between species into electrostatic, charge transfer, polarization and exchange contributions. However, as Morokuma himself stated unequivocally,[2] these energy decomposition schemes are not uniquely defined and are rather chosen for their ability to provide simple interpretation of quantum mechanical results along the lines of classical models. We wish to be precise in our investigations of interaction as greater insights into these processes will allow for the development of more sophisticated, and thus perhaps simpler, models. Hence we have performed a rigorous analysis of the consequences of protonation and lithiation utilizing not only molecular energetics, but also the atomic energetics afforded by subsystem quantum mechanics as developed within the theory of atoms in molecules.[4] The theory generalizes quantum mechanics to a subsystem of a total system, *i.e.*, an atom or group of atoms, and allows us to partition observable properties into atomic contributions, which are quantitatively additive, to yield the properties of the total system. The subsystems, be they atoms or functional groups, are transferrable between similar systems to within chemical accuracy.[5] Therefore the results obtained for these model compounds can be used to assess the driving forces for molecular interaction and changes within larger systems in a precise manner. Slee and Bader have previously investigated the protonation of a series of substituted carbonyl systems utilizing the theory of atoms in molecules,[6] in which they correlated the preferred orientation of the proton of the adduct to the substituent with the positions of the maxima in the valence shell charge concentrations of the neutral carbonyl compound. The analysis that we present here complements and extends their work by a more detailed investigation of the perturbation produced by protonation, and lithiation, of the system.

We relate the energy changes, at both the molecular and atomic levels, to physically meaningful changes of the properties of the systems. The total energy (and its change) is related to the attractive and repulsive potential energies (and their changes) *via* the virial theorem [eqns. (1) and (2)].[7] Since the various

$$E = -\tfrac{1}{2}V = -\tfrac{1}{2}(V_{NE} + V_{EE} + V_{NN}) \quad (1)$$

$$\Delta E = -\tfrac{1}{2}\Delta V = -\tfrac{1}{2}(\Delta V_{NE} + \Delta V_{EE} + \Delta V_{NN}) \quad (2)$$

contributions to the potential energy are well defined within the Hamiltonian and are related to the distribution of nuclear and electronic charges and their Coulumbic interactions, we can discuss the changes in the total energy of a process in terms of the changes in the nuclear and electronic distributions and the resulting changes in the interactions between them. This procedure provides a clear physical and fundamental picture of the changes within the system and has been successfully used in a number of studies to discuss the physical underpinnings of the energetic changes within systems.[8] We have applied this at both the molecular and atomic levels here to the study of protonation and lithiation energies within the first- and second-row systems.

We are interested not only in the energetic changes, but also the changes in molecular geometries, changes in vibrational frequencies, changes in the properties of the charge density, and changes in the atomic properties. For example, molecular interactions are routinely modelled *via* the multipole expansion of each of the individual molecular charge distributions,[9] so we are particularly interested in changes in the molecular and atomic moments resulting from complexation. The molecular moments can be rigorously partitioned into contributions from the spatially defined atoms of subsystem quantum mechanics, each of which is based upon the form of the charge distribution within that atom.[10] The multipole moments of the aldehydes within the complex and their polarizations can thus be

Table 1 Molecular energetics of the neutral, protonated and lithiated structures of formaldehyde and thioformaldehyde[a,b]

	H_2CO	H_2COH^+	Δ_1	Li^+	H_2COLi^+	Δ_2
E_{tot}	−113.9030	−114.1961	−0.2931	−7.2358	−121.2023	−0.0635
V_{NE}	−332.3518	−338.8002	−6.4484	−16.1230	−367.1335	−18.6584
V_{EE}	72.6589	72.7675	+0.1086	1.6514	81.9803	+7.6700
V_{NN}	31.9970	37.6405	+5.6435	0.0000	42.7486	+10.8616
V	−227.6959	−228.3922	−0.6963	−14.4716	−242.4046	−0.1270
ΔE	0.0		−183.923			−39.847
E_{zp}	18.015	27.260	+9.245		19.598	+1.583
Overall			−174.678			−38.264
Experiment			−177			−36
	H_2CS	H_2CSH^+	Δ_1	Li^+	H_2CSLi^+	Δ_2
E_{tot}	−436.5433	−436.8489	−0.3056	−7.2358	−443.8227	−0.0436
V_{NE}	−1127.9838	−1136.7927	−8.8089	−16.1230	−1167.7397	−23.6329
V_{EE}	209.7162	210.1423	+0.4261	1.6514	220.9456	+9.5780
V_{NN}	45.1809	52.9528	+7.7719	0.000	59.1487	+13.9678
V	−873.0867	−873.6976	−0.6109	−14.4716	−887.6465	−0.0872
ΔE	0.0		−191.767			−27.359
E_{zp}	16.568	23.449	+6.881		17.977	+1.409
Overall			−184.886			−25.950
Experiment			−185			

[a] The total and contributing energies are given in hartree (E_h) (1 hartree = 627.51 kcal mol^{-1}) and have been corrected for the virial defect. The energy differences and zero-point energies are in units of kcal mol^{-1} and given relative to the neutral molecule. [b] $\Delta_1 \equiv H_2XH^+ - H_2X$. $\Delta_2 \equiv H_2XLi^+ - H_2X$.

calculated and assessed in a meaningful way. For example, the molecular dipole of a system is expressed as a sum of inter-atom charge transfer terms, *plus* the resulting atomic polarization terms which are not accounted for in a simple spherical atom approach. The surprisingly low dipole moment of carbon monoxide, for example, is a consequence of a large induced polarization of the carbon atom in opposition to its charge transfer to oxygen, the two contributions effectively cancelling each other.[11] A robust model, such as those needed for dynamic simulations,[12] should attempt to address as many physical observable characteristics as possible, thus investigation of these atomic and molecular properties and their changes will provide a broader base of data from which to draw model characteristics.

Methodology

We have considered the neutral, protonated, and lithiated structures of formaldehyde and thioformaldehyde. All the atomic and molecular properties were determined from the triple-zeta, polarized, diffuse and balanced HF/6-311++G** wavefunctions determined at conformations optimized using the same level of theory.[13] The structures were characterized, *via* the determination of the analytical second derivatives, were each found to be a minimum, and the frequencies were used to provide for zero-point energy corrections to the total energies. The molecular calculations were performed using GAMESS.[14] The HF/6-311++G** wavefunction was used to determine the properties of the charge distribution and the atomic properties, using the theory of atoms in molecules as implemented within the AIMPAC suite of programs.[15] The appropriate weighted density distribution is integrated over the atomic basin, the volume of real space which is associated with a given atom, yielding the average value of that atomic property.

Results

We predict protonation to be exothermic for both aldehydes, H_2CO by 174.7 and H_2CS by 184.9 kcal mol^{-1},† after zero-point correction (see Table 1), and in excellent agreement with experiment for both systems.[16] Looking at the contributions to the total energy, one finds the driving force for complexation, on the molecular level, is the increase in attractive energies between the proton and the aldehyde which overcomes the associated increase in repulsive energies. Protonation results in an increase in the C–X bond length, the change being three times greater in H_2CO (see Table 2). The X–H bond is 0.96 Å and 1.34 Å and the C–X–H^5 angle is 117.1° and 99.3° in H_2COH^+ and H_2CSH^+, respectively. The C–H bonds shorten in both cases and the H–C–H bond angles increase.

Lithiation also stabilizes both aldehydes, but to a lesser extent: H_2CO by 38.3 and H_2CS by 26.0 kcal mol^{-1}. Again, this is in good agreement with the experimental value for formaldehyde.[17] Here also, the energetic stabilization is due to large gains in attractive energies overcoming large destabilizations from increased repulsion. The bond lengths and angles also change in a similar fashion to protonation, but by smaller amounts. The X–Li bond is longer in the thioaldehyde (1.79 Å and 2.40 Å in H_2COLi^+ and H_2CSLi^+, respectively). An interesting difference between the two systems is the directionality of the interaction, with the C–X–Li^5 angle equal to 180.0° for H_2COLi^+ (a C_{2v} structure) and 112.2° for H_2CSLi^+ (a C_s symmetric structure).

Another set of physical observables which provides insight into the change within the systems are the molecular moments and they are listed for the neutral and complexed molecules in Table 3. While only the first non-zero moment is origin-independent, we will discuss the general trends of the moments by choosing the centre of mass as the common origin. Protonation produces only small molecular dipole polarizations in both aldehyde complexes, but the quadrupole moment polarizes strongly out of the molecular plane in both systems. Lithiation produces sizable molecular dipole polarizations, but, as will be shown below, this mostly due to the presence of the lithium cation. The quadrupole moment also polarizes strongly out of the aldehyde plane after lithiation.

The interaction between atoms can be quantitatively characterized by the properties of the total charge distribution at the bond critical points (Table 4).[18] The magnitude of charge at the C=O bond critical point in formaldehyde decreases and the carbon bonded radius, the distance from carbon to the

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† 1 cal = 4.184 J.

Table 2 The geometric parameters within neutral, protonated and lithiated formaldehyde and thioformaldehyde[a,b]

	C^1-X^2	C^1-H^3	C^1-H^4	X^2-Y^5	H^3-C^1-H^4	H^3-C^1-X^2	C^1-X^2-Y^5
H_2CO	1.179	1.094	1.094	—	116.02	121.99	—
H_2COH^+	1.228	1.082	1.080	0.959	121.75	121.76	117.13
H_2COLi^+	1.199	1.087	1.087	1.786	118.12	120.94	180.00
H_2CS	1.597	1.080	1.080	—	115.82	122.09	—
H_2CSH^+	1.614	1.078	1.079	1.339	118.88	123.22	99.33
H_2CSLi^+	1.610	1.078	1.078	2.402	116.45	124.07	112.21

[a] All bond lengths are given in Å and all bond angles in deg. [b] The atoms are labelled as in the diagram below.

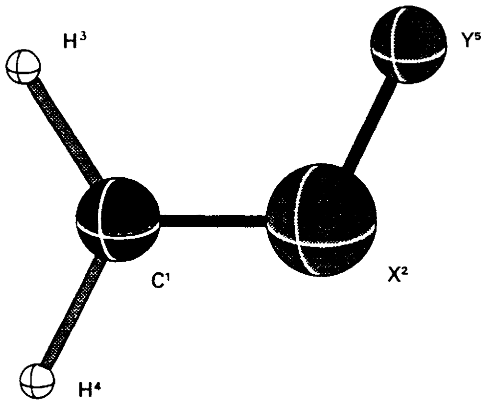

Table 3 Molecular moments of the neutral, protonated and lithiated structures of formaldehyde and thioformaldehyde[a,b]

	H_2CO	H_2COH^+	Δ_1	H_2COLi^+	Δ_2
μ	1.103	1.174	+0.071	1.654	0.551
θ_{zz}	0.041	−2.975	−3.016	−8.336	−8.377
	H_2CS	H_2CSH^+	Δ_1	H_2CSLi^+	Δ_2
μ	0.864	0.985	+0.121	2.954	+2.090
θ_{zz}	−0.979	−4.569	−3.590	−11.464	−10.485

[a] The moments are given in au; for the dipole, 1 au = 2.542 Debye (= 8.479 × 10^{-30} C m) and for the quadrupole, 1 au = 1.345 Buckingham (1 Buckingham = 1.602 × 10^{-23} C m^2). All moments are determined with the origin at the centre of mass and *zz* is the out-of-plane component of the quadrupole. [b] $\Delta_1 \equiv H_2CXH^+ - H_2CS$. $\Delta_2 \equiv H_2CXLi^+ - H_2CX$.

carbon–oxygen bond critical point, increases after both protonation and lithiation, with the former a much greater effect. This signals a lessening of the dominance of O in the interaction between C and O, with the critical point shifting away from C as a consequence of charge flowing to carbon. There is a significant increase in the ellipticity of this interaction with protonation of oxygen, a reflection of the quadrupole polarization observed upon protonation (*vide supra*). The O–H interaction is rather strong, with a large amount of charge and a large negative value of the Laplacian at the bond critical point. The O clearly dominates as seen by the small bonded radius to H. On the other hand, the O–Li interaction is a closed-shell affair, with a small amount of charge at the critical point and large bonded radii to both atoms. The differences between the two types of interaction can be clearly seen in Fig. 1, which shows the Laplacian of the charge density in the plane of the neutral, protonated and lithiated aldehydes. H_2COH^+ shows a classical picture of covalent binding of the proton to a carbonyl lone pair with a contiguous valence shell enveloping both atoms, whereas the closed-shell interaction between the O atom and Li^+ of H_2COLi^+ shows distinct, atom-like valence shells for each.

With H_2CS, protonation leads to a small increase in the charge at the C–S bond critical point, an increase in the C-bonded radius, and a smaller positive Laplacian. This is accompanied by a large increase in the ellipticity of the C–S interaction, again mirroring the quadrupole polarization. Lithiation of H_2CS produces only a small change in the C=S bond critical point properties, with a modest increase in the ellipticity. On examination of Fig. 1, the difference between the H_2CO and H_2CS can be clearly seen in that the maxima in the valence-shell charge concentrations are considerably more diffuse in the sulfur system, and the lithium binds to a site in thioformaldehyde which can be associated with a classical lone pair.

The changes in vibrational frequencies provide further insights into the consequences of complexation (see Table 5). In agreement with the characterization of the interactions above, protonation decreases the C=X stretching frequency in both aldehydes and thus signals a decrease in the magnitude of the interaction between C and X. The decrease in the C=O stretching frequency is around 200 cm^{-1}, while for C=S the decrease is only an eighth of that, both changes are in line with expectations based upon changes in the properties at the bond critical points. Lithiation is a much weaker interaction and consequently has a much smaller effect on the stretching force constants.

The atomic properties and energetics are listed in Table 6. In discussing the atomic energetic changes, it is useful to define two atomic quantities: $V_{NEO}(\Omega)$, the intra-atomic attraction energy between the nucleus and charge within its own space and $V_{NET}(\Omega) - V_{NEO}(\Omega)$, the inter-atomic attraction energy between the charge within an atom and the other nuclei for the system. In discussing the interplay of these two quantities (both of which can be readily calculated using the theory of atoms in molecules), we are determining how much a particular atom in a molecule relies upon the stabilization from within its own volume and how much it depends upon stabilization from outside.[8b] Protonation of formaldehyde is dominated by the transfer of charge to the added proton, 0.272 e, stabilizing the proton by 172.6 kcal mol^{-1}. Overall, charge is transferred from the formyl protons to the carbon and the added proton, with the charge on oxygen increasing slightly. These effects are mirrored in the energetics: the formyl protons are destabilized by the transfer of charge from them, losing both in terms of self-stabilization and inter-atom stabilization. The carbon is intra-atomically stabilized by its gain of charge, and the oxygen is stabilized by the inter-atom attraction to the added proton. In the thioaldehyde, there is considerably more charge transfer on protonation. The proton withdraws 0.924 e from the system, with the sulfur atom giving up the vast majority of charge. This stabilizes the proton by 350.5 kcal mol^{-1}, but the withdrawal of charge from the formyl hydrogens balances this in part, as in the case of formaldehyde. However in this system the sulfur atom is destabilized by the reorganization of electronic charge within its basin, which is only partially balanced by the gain in inter-basin interaction with the proton and the carbonyl carbon.

Lithiation does not result in such large charge transfer. The lithium cation gains only 0.031 e in lithiated formaldehyde, and while the oxygen and carbon atoms withdraw charge from the hydrogen atoms, the effects are now diminished compared with protonation. The stabilization of formaldehyde is due to the gain in inter-basin attraction between lithium and oxygen, with the intra-atomic energies relatively unchanged. Similarly, the lithiated thioaldehyde has only 0.044 e transferred to lithium and it is sulfur which gains 0.155 e of charge at the expense of the rest of the molecule. It is the gain in inter-basic interaction between sulfur and lithium that produces the overall stabilization of this system. Although the energetic consequences of this charge gain are highly favourable to the sulfur, they are almost balanced out by the concomitant increase in repulsion from the heavier lithium nucleus.

Table 4 Bond critical point properties in neutral, protonated and lithiated formaldehyde and thioformaldehyde[a]

Molecule	$\rho(r)$	$\nabla^2\rho(r)$	ε	r_a	r_b
H_2CO					
C–O	0.436	0.503	0.059	0.740	1.489
C–H	0.292	−1.105	0.009	1.327	0.742
C–H	0.292	−1.105	0.009	1.327	0.742
H_2COH^+					
C–O	0.381	0.417	0.171	0.758	1.563
C–H[b]	0.310	−1.302	0.003	1.405	0.635
C–H	0.308	−1.269	0.009	1.398	0.647
O–H[c]	0.361	−2.875	0.005	1.517	0.295
H_2COLi^+					
C–O	0.407	0.499	0.060	0.749	1.516
C–H[b]	0.303	−1.193	0.001	1.362	0.692
C–H	0.303	−1.193	0.001	1.362	0.692
O–Li	0.037	0.342	0.078	2.081	1.295
H_2CS					
C–S	0.244	0.405	0.125	1.879	1.138
C–H	0.296	−1.119	0.013	1.324	0.716
C–H	0.296	−1.119	0.013	1.324	0.716
H_2CSH^+					
C–S	0.251	0.208	0.745	1.907	1.143
C–H[b]	0.300	−1.197	0.028	1.383	0.654
C–H	0.301	−1.204	0.027	1.387	0.652
S–H[c]	0.235	−0.813	0.046	1.663	0.867
H_2CSLi^+					
C–S	0.242	0.312	0.275	1.897	1.145
C–H[b]	0.300	−1.160	0.023	1.344	0.693
C–H	0.301	−1.172	0.019	1.360	0.678
S–Li	0.238	0.104	0.034	3.078	1.468

[a] All values are in au. [$\rho(r)$ = e/a_0^3 = 1.081 × 10^{12} C m^{-3}; $\nabla^2\rho(r)$ = e/a_0^5 = 3.8611 × 10^{32} C m^{-5}; r_a, r_b are units of a_0 (Bohr radius) = 5.292 × 10^{-11} m; ellipticity is dimensionless.] The properties are determined at the (3, −1) critical point between the atoms: $\rho(r)$, the total charge density; $\nabla^2\rho(r)$, the Laplacian of the charge density; ε, the ellipticity, and r_a and r_b the bonded radii. [b] The proton *syn* to the adduct. [c] The added proton.

One can partition molecular moments into the atomic contributions in a straightforward manner in order to associate the changes in molecular properties with changes in the atomic properties (see Table 7).[10] The $H_2CO|$ fragment in both protonated and lithiated formaldehyde is quite dipole polarized with respect to the neutral molecule. Protonation produces polarization in the O and H atoms, but the charge transfer to C decreases its atomic polarization. Lithiation, in contrast, produces large polarizations within each atom, and in this case the smaller transfer of charge to C doesn't depolarize it as much. Both protonation and lithiation produce a quadrupole polarization out of the plane of the molecule. Protonation produces this polarization primarily in the H atoms while the O and C are quadrupole polarized towards the added proton. Lithiation has little effect on O, but the quadrupole polarization of the C and H atoms are sizable and it is this sum of contributions which produces the overall change.

For the $H_2CS|$ fragment, protonation depolarizes the first moment by both the large transfer of charge to the added proton combined with a depolarization of the S atom. As with $H_2CO|$, protonation increases the polarization of the H atoms and decreases that in C. Lithiation increases the fragment first moment primarily by a polarization of the S atom. Protonation produces a very large quadrupole polarization within the $H_2CS|$ fragment, mostly within the S atom, but with contributions from each atom. Lithiation decreases the quadrupole polarization away from the molecular plane due mostly to a depolarization of S.

Discussion

The atomic properties bring out the underlying driving forces in the energetic patterns. Protonation produces a substantial charge transfer to the added proton, as can be clearly seen in the Laplacian diagrams in Fig. 1. This withdraws charge from the rest of the system, primarily the formyl hydrogens, to the CXH| fragment. The intra-atom stabilization of the added proton drives the overall process with the inter-atom stabilization between the proton and X being the second largest stabilization. This inter-atomic stabilization by the proton makes the X atom more effectively electronegative as X can now use the proton nucleus to allow it to stabilize even more charge. This stabilization of charge using another nucleus requires that the

Table 5 Vibrational frequencies for neutral, protonated and lithiated formaldehyde and thioformaldehyde in units of cm^{-1} [a]

	H_2CO	H_2COH^+	H_2COLi^+	H_2CS	H_2CSH^+	H_2CSLi^+
	1336.3	1048.3	148.2	1079.3	908.1	177.0
	1362.3	1183.9	209.9	1147.1	913.8	358.0
	1650.3	1377.0	565.6	1170.1	1083.9	394.0
	1992.5 ν_1	1481.8	1354.8	1624.4 ν_1	1187.9	1072.3
	3094.6	1582.3	1378.1	3239.4	1218.9	1124.0
	3165.5	1805.7 ν_1	1644.4	3328.9	1593.8 ν_1	1178.3
		3253.0	1924.6 ν_1		2820.7	1625.8 ν_1
		3396.8	3185.1		3277.0	3269.8
		3939.9	3298.3		3399.0	3375.9
E_{zp} (cm^{-1} molecule)	6300.7	9534.2	6854.4	5794.6	8201.5	6287.5

[a] The C–X stretching mode is labelled ν_1.

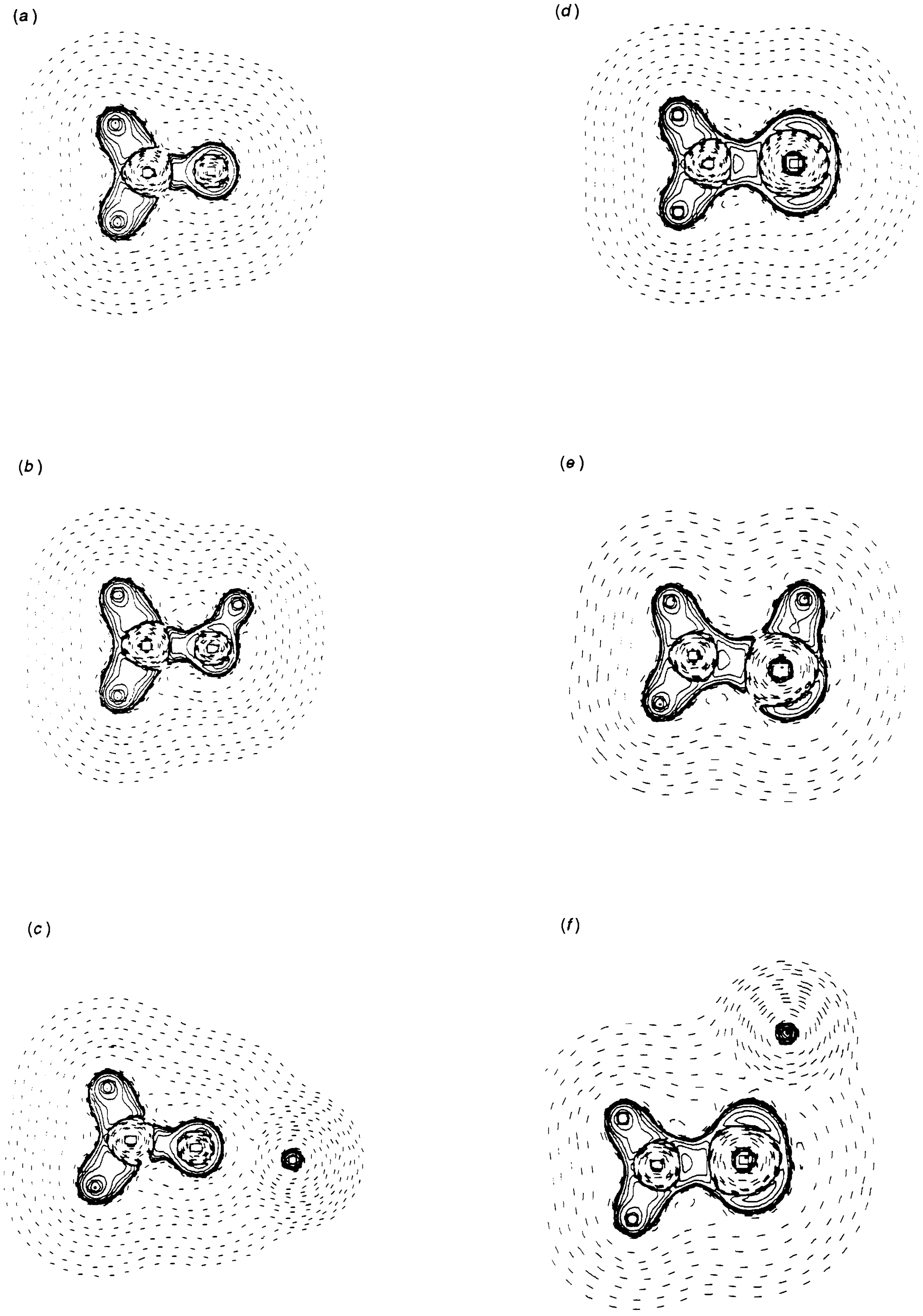

Fig. 1 Laplacian maps in the plane of the atoms of (*a*) formaldehyde, (*b*) protonated and (*c*) lithiated formaldehyde, (*d*) thioformaldehyde, (*e*) protonated and (*f*) lithiated thioformaldehyde

atom polarize its distribution so as to bring its charge closer to that nucleus and this is indeed what happens with both oxygen and sulfur. Protonation decreases the strength of the C–X bond, decreasing the bond stretching frequency, but increases the strength of the interaction between C and H. Therefore the difference between the two aldehydes is the strength with which

Table 6 Atomic properties of neutral, protonated and lithiated formaldehyde and thioformaldehyde[a]

	C^1	O^2 (S^2)	H^3	H^4	Y^5	Sum
Formaldehyde						
H_2CO						
$N(\Omega)$	4.747	9.245	1.004	1.004		16.000
$E(\Omega)$	−37.027	−75.622	−0.627	−0.627		−113.903
$V_{NEO}(\Omega)$	−84.549	−185.030	−1.291	−1.291		
$V_{NET}(\Omega)$	−104.500	−215.302	−6.274	−6.274		
$V_{REP}(\Omega)$	30.446	64.057	5.019	5.019		
$M(\Omega)$	0.918	0.598	0.123	0.123		
H_2COH^+						
$N(\Omega)$	4.943	9.238	0.761	0.785	0.282	15.999
$E(\Omega)$	−37.157	−75.708	−0.523	−0.533	−0.275	−114.196
$V_{NEO}(\Omega)$	−85.291	−185.481	−1.077	−1.099	−0.517	
$V_{NET}(\Omega)$	−106.888	−219.692	−5.023	−5.164	−2.033	
$V_{REP}(\Omega)$	32.572	68.274	3.976	4.098	1.484	
$M(\Omega)$	0.998	0.534	0.105	0.105	0.106	
H_2COLi^+						
$N(\Omega)$	4.813	9.371	0.893	0.893	2.031	18.001
$E(\Omega)$	−37.075	−75.676	−0.583	−0.583	−7.285	−121.202
$V_{NEO}(\Omega)$	−84.803	−185.734	−1.199	−1.199	−16.226	
$V_{NET}(\Omega)$	−107.308	−223.995	−6.023	−6.023	−23.784	
$V_{REP}(\Omega)$	33.156	72.639	4.856	4.856	9.213	
$M(\Omega)$	0.964	0.424	0.111	0.111	0.002	
Thioformaldehyde						
H_2CS						
$N(\Omega)$	6.633	(15.470)	0.949	0.949		24.001
$E(\Omega)$	−38.101	(−397.236)	−0.603	−0.603		−436.543
$V_{NEO}(\Omega)$	−91.364	(−943.066)	−1.243	−1.243		
$V_{NET}(\Omega)$	−134.323	(−979.000)	−7.331	−7.331		
$V_{REP}(\Omega)$	58.121	(184.527)	6.124	6.124		
$M(\Omega)$	1.027	(1.497)	0.128	0.128		
H_2CSH^+						
$N(\Omega)$	6.605	14.903	0.786	0.782	0.924	24.000
$E(\Omega)$	−38.141	−397.096	−0.528	−0.526	−0.558	−436.849
$V_{NEO}(\Omega)$	−91.389	−939.931	−1.092	−1.089	−1.163	
$V_{NET}(\Omega)$	−135.429	−980.420	−6.271	−6.266	−8.404	
$V_{REP}(\Omega)$	59.147	186.228	5.215	5.214	7.288	
$M(\Omega)$	0.875	1.236	0.109	0.110	0.037	
H_2CSLi^+						
$N(\Omega)$	6.586	15.625	0.892	0.853	2.044	26.000
$E(\Omega)$	−38.093	−397.300	−0.580	−0.562	−7.288	−443.823
$V_{NEO}(\Omega)$	−91.252	−944.200	−1.194	−1.158	−16.248	
$V_{NET}(\Omega)$	−136.789	−990.723	−7.304	−6.959	−25.964	
$V_{REP}(\Omega)$	60.603	196.122	6.144	5.836	11.388	
$M(\Omega)$	0.937	1.625	0.117	0.116	0.018	

[a] The sums of atomic energetics are given in hartree and have been corrected for the virial defect. $N(\Omega)$ is the population within the atomic basin, $E(\Omega)$ is the atomic contribution to the molecular energy, $V_{NEO}(\Omega)$ is the attractive energy from the charge within its own basin, $V_{NET}(\Omega)$ is the total atomic contribution to the molecular attractive energy, $V_{REP}(\Omega)$ is the atomic contribution to the molecular repulsion energy, and $M(\Omega)$ is the magnitude of the first moment within the basin.

the X atom binds its charge. The tightly held charge of oxygen transfers less charge to the proton and polarizes less than does the more loosely bound charge of sulfur. The substantial charge transfer in the latter case, 0.924 e, produces a large stabilization of the added proton and hence a stabilization of the whole system. The more tightly bound charge of oxygen is not as readily transferred nor is it as readily polarized, leading to a smaller stabilization of the added proton and thus a smaller stabilization of the entire system.

Lithiation results in a different process in that there is no significant transfer of charge to Li in either aldehyde. The interaction between lithium and X is closed-shell and electrostatic, as can be seen in the Laplacian diagrams in Fig. 1. It is the inter-atomic stabilization between X and Li that drives the formation of this complex. As in the case of protonation, the increased stabilization of X allows it to stabilize its charge with Li, allowing the interaction with C to decrease and polarizing the X atom, especially quadrupole polarization out of the plane of the molecule. Lithiation essentially perturbs the system less than does protonation: it does not decrease the C–X interaction as much as does protonation and the decrease in bond stretching frequency is not nearly as great. Hence, the difference in lithiation between the first- and second-row aldehydes is the size of the X atom and the form of charge concentrations within its valence shell. As can be seen from the Laplacian distributions, the charge concentrations in the valence shell of the oxygen are much more concentrated than those in sulfur. In fact, the compact valence shell of oxygen allows the Li^+ to nestle in between the two 'lone pairs' of the X atom. Sulfur has a much larger valence shell and the Li^+ atom can only interact

Table 7 Atomic contributions to molecular moments in neutral, protonated and lithiated formaldehyde and thioformaldehyde[a]

H_2CO	O^1	C^2	H^3	H^4	Sum		
$q(\Omega)$	−1.245	1.253	−0.004	−0.004	0.000		
μ^{Ω}_{x}	−0.789	−0.479	0.083	0.083	−1.103		
θ^{Ω}_{zz}	−0.053	−0.295	0.190	0.190	0.033		
H_2COH^+	O^1	C^2	H^3	H^4	H^5	Sum	$H^2CO|$
$q(\Omega)$	−1.239	1.057	0.239	0.215	0.728	1.000	+0.282
μ^{Ω}_{x}	−0.993	−0.236	−0.470	−0.411	1.464	−0.646	−2.110
θ^{Ω}_{zz}	0.137	0.449	−0.740	−0.698	−2.114	−2.966	−0.851
H_2COLi^+	O^1	C^2	H^3	H^4	Li^5	Sum	$H_2CO|$
$q(\Omega)$	−1.371	1.187	0.107	0.107	0.970	1.000	+0.031
μ^{Ω}_{x}	0.921	1.263	0.267	0.242	−3.613	−1.640	2.694
θ^{Ω}_{zz}	0.009	−0.522	−0.425	−0.427	−6.843	−8.208	−1.365
H_2CS	S^1	C^2	H^3	H^4	Sum		
$q(\Omega)$	0.530	−0.633	0.051	0.051	0.000		
μ^{Ω}_{x}	−0.985	0.270	−0.075	−0.075	−0.864		
θ^{Ω}_{zz}	0.827	−1.713	−0.047	−0.047	−0.979		
H_2CSH^+	S^1	C^2	H^3	H^4	H^5	Sum	$H_2CS|$
$q(\Omega)$	1.097	−0.605	0.214	0.218	0.076	1.000	+0.924
μ^{Ω}_{x}	−0.546	−0.062	0.456	0.538	−0.173	0.213	0.386
θ^{Ω}_{zz}	−1.457	−0.694	−0.870	−0.844	−0.412	−4.278	−3.865
H_2CSLi^+	S^1	C^2	H^3	H^4	Li^5	Sum	$H_2CS|$
$q(\Omega)$	0.375	−0.587	0.108	0.147	0.956	1.000	+0.046
μ^{Ω}_{x}	0.957	0.027	0.227	0.297	−2.842	−1.335	1.507
θ^{Ω}_{zz}	1.342	−1.223	−0.337	−0.497	−13.471	−14.186	−0.715

[a] All values are given in units of au and are given with respect to the centre of mass of the $H_2CX|$ fragment within the complexes. The x axis is along the C=X bond and the zz component of the quadrupole is the out-of-plane component.

with one at a time, thus producing a smaller energy of complexation.

The conclusions that we have reached on the basis of both the molecular and atomic properties can now be compared with previous studies. Pullman and Schuster[19] analysed the potential surface for the lithiation of formaldehyde with a minimal basis set and no geometry optimization using the decomposition scheme of Dreyfus and Pullman,[3] and found very little charge transfer. Kollman and Rothenberg[20] examined the protonation and lithiation of a series of first- and second-row systems, including formaldehyde, using a 4-31G basis with partial geometry optimization in order to assess the origin of relative basicity effects. Using a Morukama analysis[2] they reported that protonation involved significant charge transfer. Subsequent work using higher levels of theory established this to be a general trend for first- and second-row systems.[21] Therefore the results obtained using less precisely defined molecular energetic decomposition schemes agree well with the rigorous spatial partitioning approach employed here, although they do not uncover the atomic basis of the complexation energetics, nor the atomic polarizations.

The insights gleaned from this study have interesting implications for models and simulations designed to incorporate these processes. Lithiation would be well represented by an electrostatic interaction between cation and adduct. A molecular moment representation of the complex should produce the large quadrupole polarization of the system as this term could readily change important interaction terms with the rest of the dynamical system. A simple monopole representation of the cation in the complex would not correctly describe the higher-order terms of the complex nor would it generate the quadrupole polarization.

Protonation of the aldehyde results in a covalent, shared interaction and produces large changes in the interaction between C and X. A model which correctly represented the facile proton transfer must take into account the large changes associated with protonation upon carbonyl (and thiocarbonyl) systems: changes in the charges, restoring force constants, and dipole and quadrupole moment terms within the adduct. Simulations which attempt to incorporate solvation and proton transfer, such as those with low pH, acidic molecules, *etc.*, will have to incorporate the significant change in the carbonyl moiety in order correctly to represent the properties of these systems.

Conclusions

We have presented a detailed study of the changes in atomic and molecular properties of formaldehyde and thioformaldehyde resulting from protonation and lithiation as first steps towards models for direct solvation and solvent–solute interaction. Protonation energetics are dominated by the large transfer of charge from the $H_2CX|$ fragment to the H^+, while lithiation is primarily an electrostatic interaction driven by the inter-atomic stabilization between X and Li^+. The difference in protonation energy is the larger transfer of charge from S in H_2CSH^+ producing a larger stabilization than in H_2COH^+. In lithiation, the compact valence shell of O allows for a more effective complexation in H_2COLi^+ than in the sulfur analogue. Lithiation can be readily represented by electrostatic models between the cation and carbonyl system, while protonation causes large changes to the adduct and requires changes to the representation of the carbonyl interaction.

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