Study of the structure of molecular complexes. X. Dipole moment surface for the lithium–fluoride–water complex

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The dipole moment for 252 configurations of the Li–F–H_2O complex has been computed using Hartree–Fock wavefunctions. The computed values are fitted with an analytical expression. The results clearly indicate that the water dipole moment, having the expected form of point charge-induced dipole moment, acts only as a relatively small perturbance on the dipole moment of the LiF ion pair.

In a previous computation,[1] we have analyzed the Hartree–Fock energy and wavefunction for the Li–F–H_2O complex in 252 different geometrical configuration conformations. In this work, we discuss the surface one can obtain by computing the dipole moment for such conformations; the values of dipole moments computed for each of the 252 geometries have been fitted with an analytical expression. The analytical expression has the following form, in atomic units:

$$\mu = \mu_{H2O} + X_{LiF}[A + B\exp(-R_{LiF})] + X_{Li}[\mathbf{C} + \mathbf{D}\exp(-R_{Li})]R_{Li}^{-3} + X_F[\mathbf{E} + \mathbf{F}\exp(-R_F)]R_F^{-3}.$$

The oxygen atom is taken as the origin of the Cartesian coordinates system; the two hydrogen atoms of H_2O are in the XY plane symmetrically placed in the third and fourth quadrant (the water molecule has been constrained[1] at the experimental geometry, with C_{2v} symmetry), X_{Li} and X_F are the coordinate vectors for the Li and F nuclei, respectively, and X_{LiF} is the vector pointing from F^- to Li^+; μ_{H2O} is a vector with x, y, and z components equal to -0.8925 a.u., 0.0 a.u., 0.0 a.u., respectively. A and B are two scalar constants of value 0.9957 and -2.5878, respectively. The quantities **C**, **D**, **E** and **F** are matrices, defined below:

$$\mathbf{C} = \begin{pmatrix} -6.6780 & 0.0 & 0.0 \\ 0.0 & -7.2066 & 0.0 \\ 0.0 & 0.0 & -5.6153 \end{pmatrix},$$

$$\mathbf{D} = \begin{pmatrix} 40.185 & 0.0 & 0.0 \\ 0.0 & 39.511 & 0.0 \\ 0.0 & 0.0 & 33.056 \end{pmatrix},$$

$$\mathbf{E} = \begin{pmatrix} 6.3566 & 0.0 & 0.0 \\ 0.0 & 14.1288 & 0.0 \\ 0.0 & 0.0 & 6.6300 \end{pmatrix},$$

$$\mathbf{F} = \begin{pmatrix} -10.723 & 0.0 & 0.0 \\ 0.0 & -62.715 & 0.0 \\ 0.0 & 0.0 & -42.962 \end{pmatrix}.$$

The physical interpretation of this fitting expression (and let us stress that our main interest is to obtain a reliable fitting expression of the computed dipole moments) is that contributions to the dipole moment of the

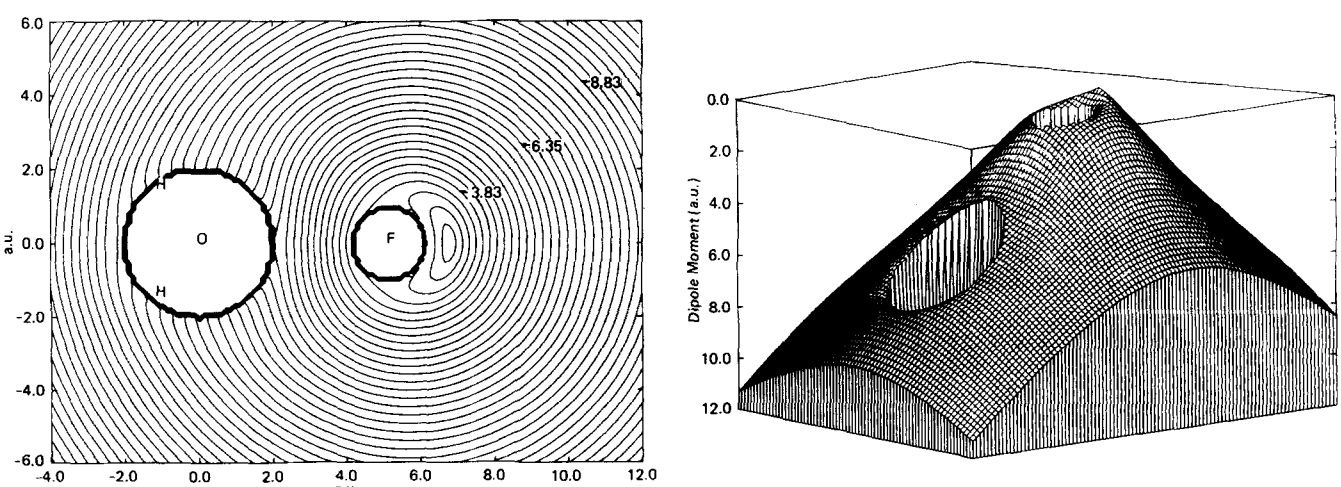

FIG. 1. Contours for dipole moment and three-dimensional representation. To the left, the contours are given with 0.25 a.u. intervals. The regions around F and H_2O enclosed by a heavy circle define the area where the fitting expression is no longer valid. The three-dimensional surface (right) has been rotated in such a way as to clearly show the area around the water. The fluorine ion is at 5.15 a.u. from the oxygen of H_2O. The lithium ion can assume any position in the plane defined by the H_2O molecule.

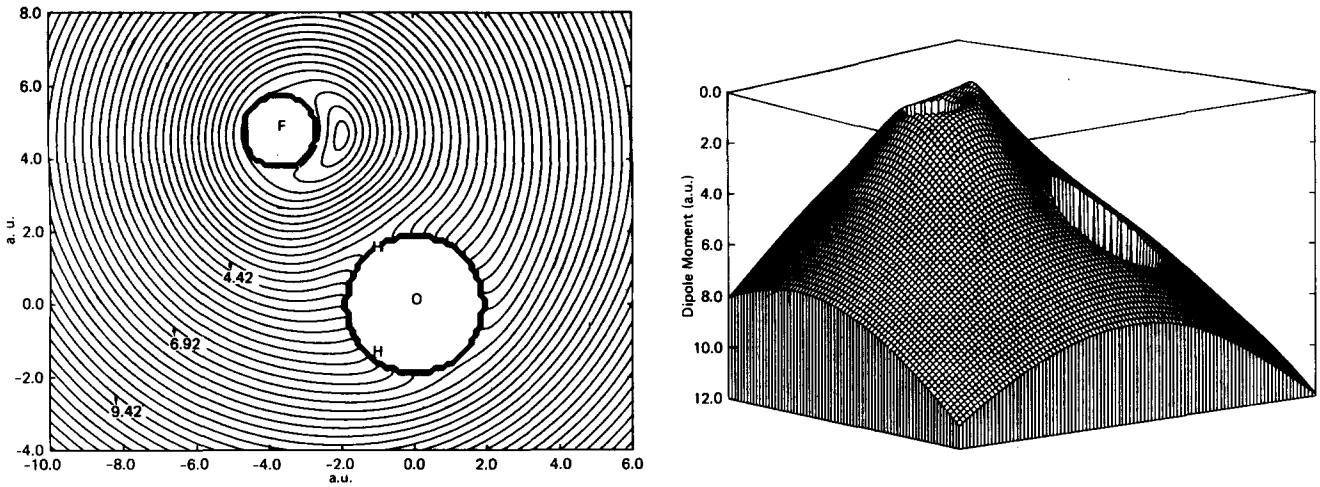

FIG. 2. Contours for dipole moment and three-dimensional representation. To the left, the contours are given with 0.25 a.u. intervals. The fluorine atom is hydrogen bonded to the water molecule (the oxygen is at the origin); the position of fluorine is $x = -3.66$ a.u., $y = 4.76$ a.u., and $z = 0.0$ a.u. The three-dimensional representation is at the right. The Li^+ assumes any position in the plane defined by H_2O.

complex are (a) the dipole moment of the two ions F^- and Li^+, (b) a constant dipole moment from H_2O, (c) an induced dipole moment on H_2O due to the field of the positive ion, and (d) an induced dipole moment on H_2O due to the field of the negative ion. Let us note, in addition, that the induced dipole moment has an $1/R^2$ dependency, R being the distance between the point charge and the origin of the dipole vector; this dependency is correct only for relative large distances between the induced dipole moment (on water) and the point charges (on the ions); for smaller distances a correction term must be introduced.

In the above fitting expression, the first term represents the permanent water dipole moment in the $LiFH_2O$ complex; the second term is a simple analytical representation for the dipole moment of two point charges (the expression is valid for $R(Li-F) > 1.0$ a.u., namely is not valid in the region of little physical interest); the third and the fourth terms are the induced dipole moments that depend on the direction cosines of the positional vectors of Li^+ or F^- (note that the oxygen is at the origin of the coordinate system, not far from the water dipole vector). Each of the last two terms contains two matrices (**C** and **D** or **E** and **F**, respectively), the second one being a correction to the first one for the case of small dipole–point charge distances. Each matrix is diagonal; when the diagonal matrix elements are not too different in a given matrix, we might assume that this suggests a nearly isotropic polarizability. However, let us stress that all the constants in the four matrices are simply fitting parameters.

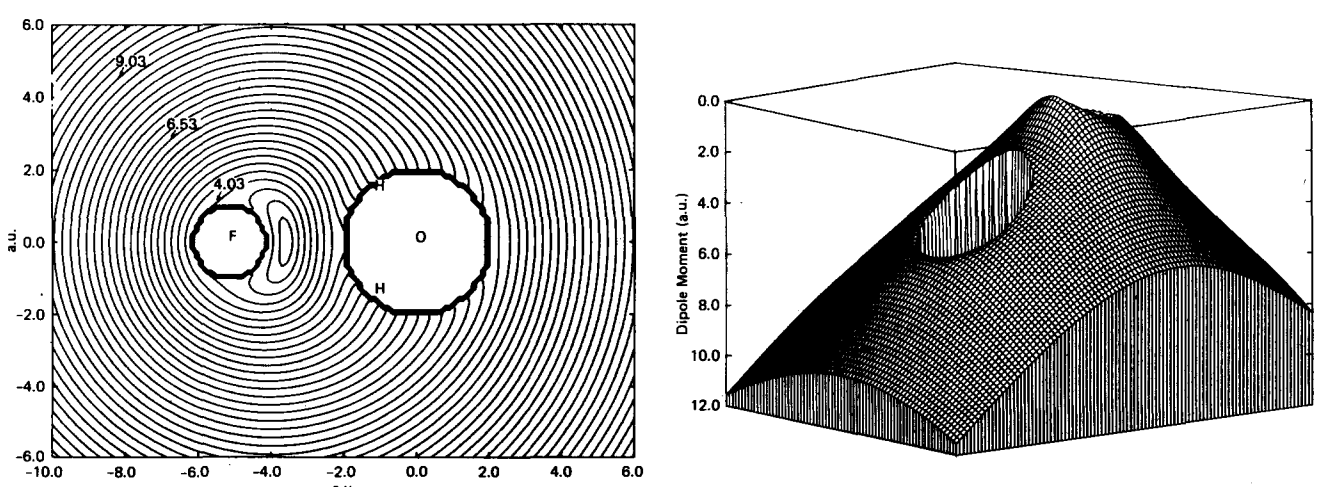

FIG. 3. Contours for dipole moment and three dimensional representation. To the left the contours are given with 0.25 a.u. intervals. As in Fig. 1, the H_2O and F^- atoms have C_{2v} symmetry, however; the representation here chosen is not the energetically most favorable. The fluorine coordinates are $x = -5.15$ a.u., $y = 0.0$ a.u., and $z = 0.0$ a.u. The Li^+ assumes any position in the plane defined by H_2O.

The 252 conformations studied contain 515 nonzero x-, y-, and z components of the dipole moment. The analytical expression reproduces all the zero components and gives an average error of 1.87% for the nonzero ones, with an average absolute error of 0.17 D (or 0.067 a.u.).

The conclusion of this analysis is that the water introduces only a relatively small perturbation on the dipole moment of the Li^+ and F^- system. This is clearly seen by analyzing Figs. 1, 2, and 3. In these figures we have considered three sets of conformations for the $Li-F-H_2O$ complex. In one, the first set (Fig. 1), the fluorine ion is complexed to H_2O yielding $F^- - H_2O$ (see a previous work[2] for additional details on the $F^- - H_2O$ complex) in the most stable C_{2v} conformation; the lithium ion is free to move in any position of the $F^- - H_2O$ plane. In the second set of conformations (see Fig. 2), the fluorine ion is hydrogen bonded to the water and the lithium ion is again free to assume any position in the $F^- - H_2O$ plane.

In the third set of conformations (see Fig. 3), the fluorine ion is placed in a C_{2v} symmetry position that is energetically unfavorable, and the lithium ion assumes any position in the $F^- - H_2O$ plane. For all these cases, the H_2O geometry is the experimental one and the fluorine to oxygen distance is 5.15 a.u. As noted, the analytical expression is not valid for small Li–F or small $Li-H_2O$ distances: therefore, in all the figures we have left blank the regions of nonvalidity (that correspond to highly repulsive conformations).

The three sets of computed dipole moments for the conformations are presented twice in each figure, once with contour diagrams, in order to exhibit quantitative features, and then in a three-dimensional form, that yields immediately the main physical picture, as previously pointed out.

The computed values for the dipole moment for each configuration are not reported in this paper (for space limitations), but are made available to the interested reader.[3] Finally, we wish to point out that the study here reported is a needed first step in attempting to obtain dielectric constants in ionic solutions; for this reason, we have considered the system Li^+, F^-, and H_2O. Additional steps in this direction, such as a study of the structure of the Li, F ion pair in small[4] and large clusters[5] of water molecules, are published elsewhere.

On account of the above analyses, we note that, although the fitted equation is obtained only from the configurations where the F^- ion is constrained to the H_2O plane, similar accuracy can be expected from the equation for any configuration of the $Li-F-H_2O$ complex.

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[1]J. W. Kress, E. Clementi, J. J. Kozak, and M. E. Schwartz "Study of the Molecular Complexes. IX The Hartree–Fock Energy Surface of the $H_2O-Li-F$ Complex" (submitted to J. Chem. Phys.).

[2]H. Kistenmacher, H. Popkie, and E. Clementi, J. Chem. Phys. 58, 5627 (1973).

[3]Such data have been deposited with the National Auxiliary Publication Service of the American Society for Information Sciences. See NAPS Document Number No. 02508 for 11 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, 440 Park Avenue South, New York, NY 10016. Remit in advance for each NAPS accession number $1.50 for Microfiche and $5.00 for photocopies up to 30 pages, 15¢ for each additional page. Make checks payable to Microfiche Publications. Outside of the United States and Canada, postage is $2.00 for a photocopy or $0.50 for a fiche.

[4]R. O. Watts, E. Clementi, and J. Fromm, J. Chem. Phys. 61, 2550 (1974).

[5]J. Fromm, E. Clementi, and R. O. Watts, "Coordination Numbers for the Li^+, F^- Ion Pair in Water" (submitted to J. Chem. Phys.).