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Ab initio study of the interaction of dimethylsulfoxide with the ions Li^+ and I^-

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This paper is dedicated to the memory of Werner Lindinger.

Abstract

We report analytical expressions for the dimethylsulfoxide (DMSO)–Li^+ and DMSO–I^- potential energy hypersurfaces. Quantum chemically calculated energies were fitted to polynomial functions of different number of parameters. These calculations are augmented by calculations of the electrostatic potential in the vicinity of DMSO. Global geometry optimizations and calculations of ion-induced frequency shifts have been performed. We find that at its global energy minima, Li^+ in the DMSO–Li^+ complex is bound to the oxygen atom with an energy of about 2.6 eV while I^- in the vicinity is bound between the two methyl groups in a shallow energy minimum with about 0.6 eV. (Int J Mass Spectrom 223–224 (2003) 263–270)
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1. Introduction

DMSO (cf. Fig. 1) is a theoretically interesting and technologically extremely important molecule. Besides applications in organic synthesis it serves as an important solvent [1] because it is a small aprotic but highly polar molecule. It has the highest dipole moment (4.3 Debye) and highest dielectric constant (48 at 20 °C) of the common dipolar aprotic solvents. Theoretical interest comes from a long-standing controversy of how to correctly describe the sulfur–oxygen bond which is responsible for the molecule's high dipole moment [2] and because it is the only pyramidal molecule among similar widely used organic compounds like dimethylformamide ($HCON(CH_3)_2$), acetonitrile ($N{\equiv}CCH_3$) or acetone ($O{=}C(CH_3)_2$).

Despite the fact that there exist a few X-ray [3,4] and neutron diffraction (ND) studies [5] involving liquid DMSO, we know only of one study where intermolecular DMSO-ion potential functions were devised. In [6] the authors calculated the potential of mean force of an Na^+Cl^- ion pair in DMSO. They described the interactions by a Lennard–Jones potential whose coefficients were obtained by combination rules and they described the methyl groups as united atoms. It is, however, always unclear how accurate the use of transferable potential functions is. For the potential of mean force mentioned above, no experimental

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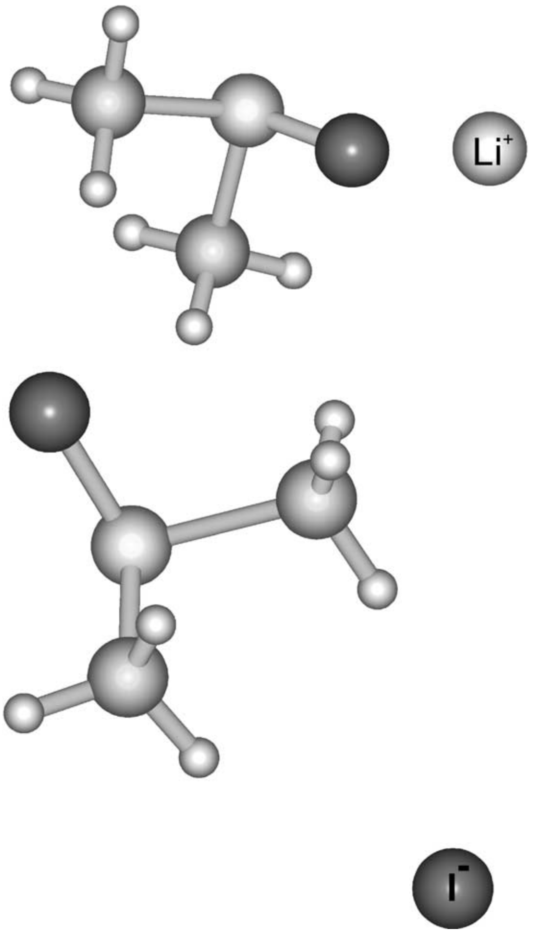


Fig. 1. Structure of the DMSO–Li^+ (upper part) and DMSO–I^- (lower part) complexes in their optimized geometries. The geometry of the free DMSO molecule is nearly unchanged upon complexation.

data exist, but the agreement between ND and simulation results with similar transferable potentials for the DMSO−DMSO interaction (no ions present) in [5] was only modest. In the case of molecules that exhibit special features like the S–O bond and the pyramidal structure of DMSO there are good reasons why a dedicated potential energy function developed via quantum chemical calculations is to be preferred.

2. The DMSO molecule

In principle, DMSO possesses two potential coordination sites at its S and O atoms. Since carbon atoms of methyl groups normally carry only small partial charges, it can be assumed that the dipole moment vector of DMSO is more or less parallel to the S–O bond. Table 1 lists the angle between the dipole moment vector (defined as going from negative to positive charge) of the molecule and the S → O bond vector as a result of various quantum chemical methods and basis sets. The value of the total dipole moment as calculated by those various methods deviates by about ±10% from the experimental value (4.3 Debye). However (with exception of the smallest basis set (cc-pvdz [7]), both the density functional (B3LYP [8]) and the wave-function based (MP2 [9]) methods with all basis sets give the same results with respect to the dipole orientation. The dipole moment vector deviates from the S–O axis by an angle of about 25.5° in the direction of the methyl groups.

Table 1

Dipole moment of DMSO (in Debye) and the angle between it and the S–O bond vector as calculated by various methods

Method	Basis set	Dipole moment vector			Total dipole moment	Vector S → O			Angle (°)
		x	*y*	*z*		*x*	*y*	*z*	
B3LYP	SDD	0.0001	5.1637	0.8665	5.2359	0.0000	1.4032	0.9303	25.68
	aug-cc-pvdz	0.0001	4.2730	0.6138	4.3169	0.0000	1.2869	0.8466	25.16
	aug-cc-pvtz	0.0005	4.0862	0.5640	4.1250	0.0002	1.2545	0.8311	25.66
	cc-pvdz	0.0001	3.7561	0.7433	3.8289	0.0000	1.2698	0.8530	22.70
MP2	SDD	−0.0009	5.8261	0.8335	5.8855	0.0002	1.3931	0.9328	25.66
	aug-cc-pvdz	−0.0008	4.8605	0.6965	4.9102	0.0002	1.2888	0.8513	25.30
	aug-cc-pvtz	−0.0027	4.6316	0.6504	4.6771	0.0008	1.2524	0.8348	25.69
	cc-pvdz	−0.0006	4.5445	0.8969	4.6321	0.0002	1.2644	0.8516	22.79

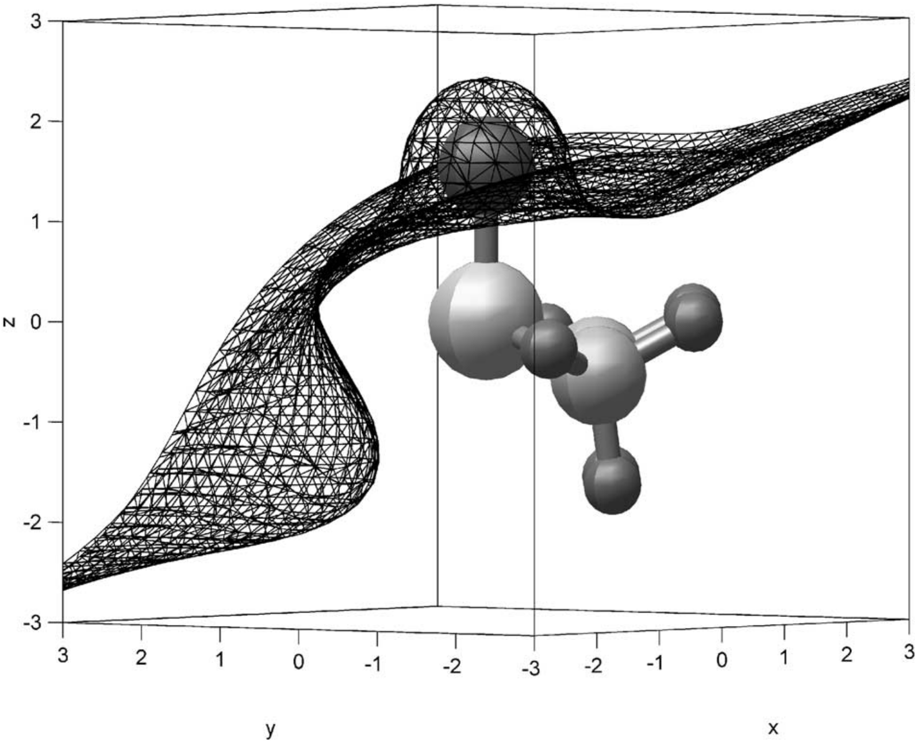


Fig. 2. Surface of zero EP of the DMSO molecule.

For the same reasons as described above, the electrostatic potential (EP) of DMSO is also an interesting quantity. We have calculated the EP in a cubical grid around the molecule. A marching-cube algorithm [10] was used to extract isosurfaces with constant EP. In Fig. 2 the dividing surface defined by EP equal to 0 is shown in a mesh representation. The DMSO molecule is oriented such that one methyl group nearly eclipses the one behind. All nuclei are located in the lower halfspace defined by EP > 0. The upper (EP < 0) halfspace comes close to the oxygen atom which carries a negative partial charge while the CH_3 groups are deep inside the positive region.

3. The DMSO–Li^+ complex

Geometry optimizations starting from different initial configurations showed that, regardless of its initial position, Li^+ always coordinates to the oxygen atom of DMSO. This and the rather simple and not bifurcated structure of the EP make in likely that no other local minima on the DMSO–Li^+ energy hypersurface exist. Table 2 shows the binding energies ΔE as calculated by the B3LYP density functional and MP2 methods and with small to large basis sets. Depending

Table 2
Binding energy of Li^+ ion to DMSO as calculated by various methods and basis sets (values in parentheses: kcal/mol)

Method	Basis set	ΔE (eV)
B3LYP	SDD	3.09 (71.3)
	cc-pvdz	2.91 (67.2)
	aug-cc-pvdz	2.56 (59.1)
	aug-cc-pvtz	2.53 (58.4)
MP2	SDD	3.20 (73.8)
	cc-pvdz	2.80 (64.5)
	aug-cc-pvdz	2.41 (55.6)

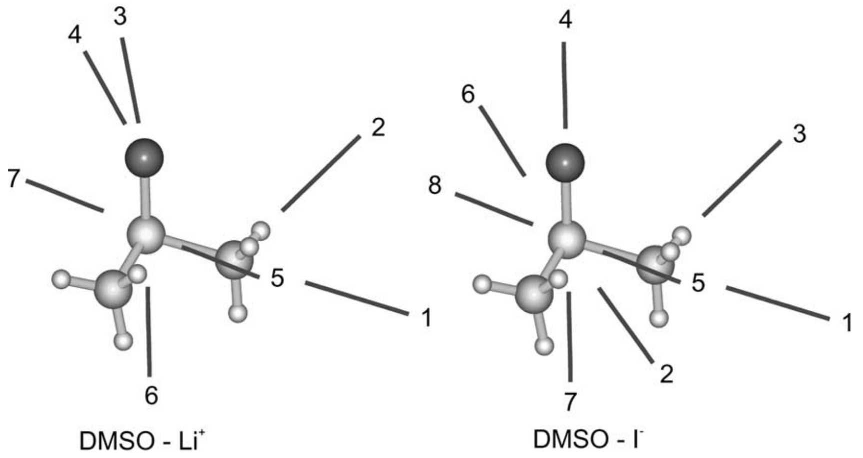
on the calculation, binding energies between 2.4 eV (55 kcal/mol) and 3.2 eV (70 kcal/mol) result. Most of the differences arise from the basis sets and not from the method. The smallest (SDD [11]) basis set probably overestimates the DMSO–Li$^+$ attraction although its calculation times are about 25 times less than for the aug-cc-pvdz [7] basis set. On the basis of these results we decided to perform subsequent calculations of the potential energy surface with the B3LYP density functional and the aug-cc-pvdz basis set. The dipole moment from this basis set is also closest to the experimental one (Table 1). Fig. 1 (upper picture) shows a picture of the optimized DMSO–Li$^+$ complex.

The binding of Li$^+$ (Li–O distance 1.710 Å) causes changes in geometry and in the vibrational frequencies of the DMSO molecule. The O–S bond becomes elongated by 0.037 Å and the vibrational frequency of the O–S stretching mode shows a slight downshift from 1027 to 1021 cm^{-1}.

4. Analytical potential energy function for DMSO–Li$^+$ complex

A set of energies was calculated by placing the Li$^+$ ion at various positions in the vicinity of the DMSO molecule. In order to be able to view them conveniently as one-dimensional curves, these energies were calculated at points positioned on straight lines as defined below (cf. Fig. 3). The energies at the B3LYP/aug-cc-pvdz level were then fitted to analytical expressions. We chose to take atom–atom distances as the independent parameters and to use a sum of simple polynomials of these distances as the energy expression. Polynomials were fitted to the energy/distance data. We have written a computer code that allows optimization of the polynomial powers via simple linear regression. It uses the algorithm described in [12] in order to restrict the sign or value of the coefficients. We fitted both one simpler (Eq. (2)) and one more extended (Eq. (1)) potential energy function to our data. The 1/r–dependent terms of the potential energy function were not fitted but were taken from a natural population analysis [13] of the wave-function of the isolated DMSO molecule. Not refining the charges at the fitting stage ensures that all 1/r terms are consistent and realistic and that the total charge of DMSO and Li$^+$ is exactly maintained. The partial charges of the atoms in DMSO were obtained as −0.700, +0.199, −1.040 and +1.250 for C, H, O and S, respectively. An expression with four fitted parameters for each type of interaction

$$V_{\text{fit}}^{\text{DMSO–Li}^+} = \sum_{n=1}^{10} \left[\frac{q_k q_i}{r_{ki}} + \frac{A_{ki}}{r_{ki}^2} + \frac{B_{ki}}{r_{ki}^3} + \frac{C_{ki}}{r_{ki}^4} + \frac{D_{ki}}{r_{ki}^5} \right] \tag{1}$$



DMSO - Li$^+$ DMSO - I$^-$

Fig. 3. Placement of Li$^+$ (left side) and I$^-$ (right side) ions for the calculation of the quantum chemical interaction energies. See text for details.

(k = C, H, O or S and i = Li; the sum goes over the 10 different atom–atom distances) provided good agreement with the quantum chemically calculated energies. We fitted also a more compact two-parameter expression, which still provides a fair description of the data

$$V_{\text{fit}}^{\text{DMSO–Li}^+} = \sum_{n=1}^{10} \left[\frac{q_k q_i}{r_{ki}} + \frac{A'_{ki}}{r_{ki}^3} + \frac{B'_{ki}}{r_{ki}^5} \right] \quad (2)$$

The coefficients A to D and A' to B' are given in Table 3. Fig. 4 shows the calculated energies and the ones fitted according to Eq. (1). The different curves in Fig. 4 were constructed by moving Li^+ in directions defined by (cf. Fig. 3):

1. the S → C vector;
2. the C → H vector;
3. the C_s symmetry plane of DMSO and an the S–O–Li angle of 168.0°;
4. like in 3, above but the S–O–Li angle is 146.5°;
5. a vector S → X where X is the center of the C–C–O triangle;
6. the O → S vector;
7. the same as in 5, above but Li^+ moves on the S side.

Table 3
Coefficients of the polynomials in Eqs. (1) and (2)

	k			
	C	H	O	S
A	2046.5	−498.8384	804.215	−1547.6
B	−4956.2	1143.9	−1710.0	1874.5
C	3690.2	−969.67	1441.2	−366.13
D	0	329.74	0	616.34
A'	59.3919	2.9797	392.7667	−1286.1
B'	−465.4938	39.7882	13.4738	2661.1

If the distances are given in units of Ångström, energies are obtained as kilocalories per mole.

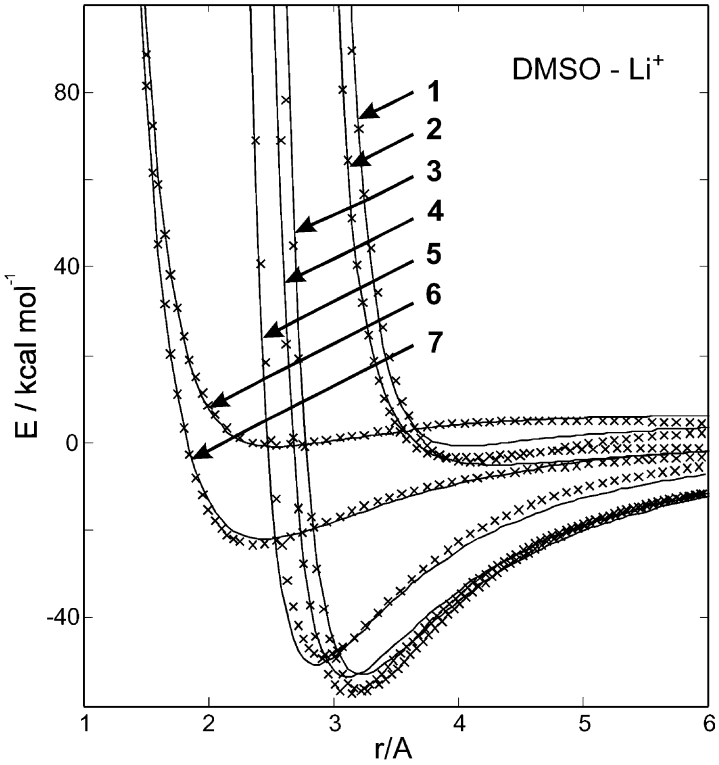


Fig. 4. Quantum chemical (crosses) and fitted (full lines) interaction energies for DMSO–Li^+. See text for the definition of curves 1–7.

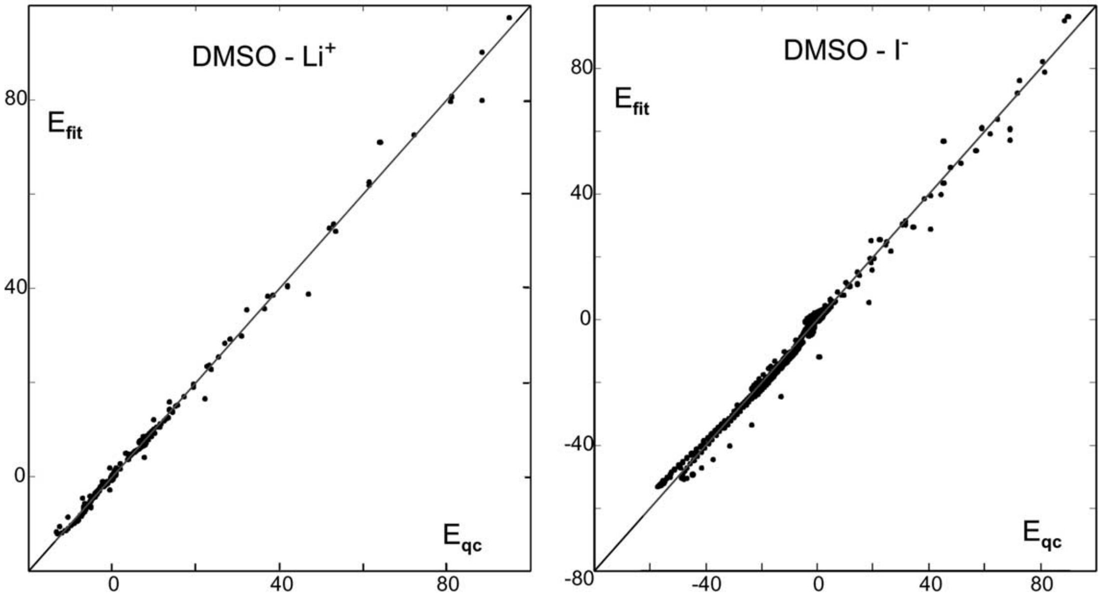


Fig. 5. Agreement between calculated (x axis) and fitted (y axis) energies for DMSO–Li$^+$ (left) and DMSO–I$^-$ (right). Energies in kilocalories per mole.

From Fig. 4 and the overall agreement between the ab initio and fitted energies (Fig. 5, left) it can be seen that the energy expression (1) indeed reproduces the quantum chemical results over a wide range of energies. The highest polynomial power in Eqs. (1) and (2) is 5. We observed nearly no change in quality of the fit if this power is replaced by a value of 6 or 7 (with re-optimized coefficients) but even higher values lead to a lower quality of the fit if the total number of parameters is kept constant. We attribute this to the fact that the repulsive part of the quantum chemical atom–atom interactions is considerably less steep than, for example, the r^{-12} term from a Lennard–Jones expression. The relatively smooth repulsion at small distances (resembling more a Morse-type than a Lennard–Jones potential) is a realistic feature of the calculations.

5. The DMSO–I$^-$ complex

The same investigations as outlined above for the DMSO–Li$^+$ complex were performed for the complexation of I$^-$ to DMSO. Due to the high nuclear charge of iodine, quantum chemical calculations are more demanding and we used the SDD basis set since in contrast the all electron basis sets it incorporates relativistic effects. Geometry optimizations of the DMSO–I$^-$ complex with the B3LYP density functional (as well as test calculations with other methods and basis sets) resulted in a geometrical arrangement (lower part of Fig. 1) where I$^-$ is located between the two methyl groups (approximately incididing with the continuation of the O–S bond). Despite the fact that iodide also is a singly charged ion, the more diffuse distribution of regions with positive EP (compared to the negative regions), and the much smaller charge/radius ratio of iodine results in a binding energy of only 0.60 eV (13.87 kcal/mol), about four times lower than for Li$^+$. An analytical potential function was constructed from the B3LYP/SDD calculations analogous to DMSO–Li$^+$ complex. Here, a three-parameter formula already provides a good agreement to the quantum chemical energies

$$V_{\text{fit}}^{\text{DMSO–I}^-} = \sum_{n=1}^{10}\left[\frac{q_k q_i}{r_{ki}} + \frac{A_{ki}}{r_{ki}^2} + \frac{B_{ki}}{r_{ki}^3} + \frac{C_{ki}}{r_{ki}^6}\right] \quad (3)$$

Table 4
Coefficients of the polynomial in Eq. (3)

	k			
	C	H	O	S
A	564.9065	−227.1393	−765.2684	1290.9
B	−1427.4	366.7548	864.4071	−2462.7
C	15504.0	691.4628	2325.0	25942.0

If the distances are given in units of Ångström, energies are obtained as kilocalories per mole.

The coefficients *A* to *C* are given in Table 4. Fig. 6 shows the calculated energies and those fitted according to Eq. (3). In Fig. 6, the curves 1–8 were constructed by moving the iodide anion in directions defined by (cf. Fig. 3):

1. the S → C vector away from C;
2. the bisector of the C–S–C angle on side of the methyl groups;
3. the C → H vector away from H;
4. the S → O vector away from O;
5. a vector S → X where X is the center of the C–C–O triangle;
6. a vector X → S where X is the midpoint of both C atoms;
7. the O → S vector away from S;
8. the negative vector defined in 5 (pointing away from the S atom).

From Fig. 6 and the overall agreement (Fig. 5, right) it can be seen that here too the quantum chemical energies are well reproduced.

6. Summary

We have developed analytical expressions for the interaction between DMSO and Li^+ and I^- ions. We find that formulae with a three- or four-term polynomial for each atom–ion interaction can be fitted to agree well with the quantum chemically derived energies. These potential functions can be used in geometry optimizations or molecular dynamics

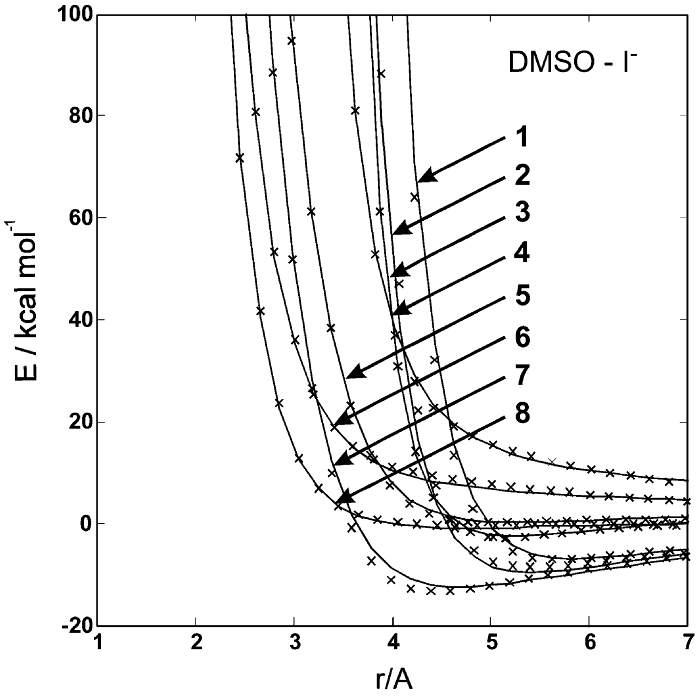


Fig. 6. Quantum chemical (crosses) and fitted (full lines) energies for DMSO–I^-. See text for the definition of curves 1–8.

simulations of $(\mathrm{DMSO})_n$–$(\mathrm{ion})_m$ systems. We find that at the energy minimum, Li^+ in the DMSO–Li^+ complex binds to the oxygen atom with about −2.6 eV while in the DMSO–I^- complex, the I^- anion is bound between the two methyl groups by about 0.6 eV.

Acknowledgements

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