

Ab initio STUDY OF THE Li-CO VAN DER WAALS COMPLEXVladimír LUKES^{a1}, Viliam LAURINC^{a2,*}, Michal ILČIN^{a3} and Stanislav BISKUPIC^{z,b}^a Department of Chemical Physics, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovak Republic; e-mail: ¹ lukes@chelin.chtf.stuba.sk,² laurinc@cvt.stuba.sk, ³ ilcin@chelin.chtf.stuba.sk^b Department of Physical Chemistry, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovak Republic; e-mail: biskupic@cvt.stuba.sk

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Dedicated to Professors Petr Čársky, Ivan Hubač and Miroslav Urban on the occasion of their 60th birthdays.

The adiabatic potential energy surface (PES) of the Li-CO complex in the van der Waals region, described by Jacobi coordinates ($r = 1.15 \text{ \AA}$, R , Θ), was investigated using the supermolecular coupled-clusters CCSD(T) method. Our calculations indicate minima for bent arrangements. The first minimum was found on the carbon side of CO molecule at $R = 5.27 \text{ \AA}$ ($\Theta = 50.7^\circ$) with a well depth of $D_e = -167.2 \mu E_h$. The second minimum is indicated at $R = 5.35 \text{ \AA}$ ($\Theta = 148.7^\circ$) with a well depth of $D_e = -121.9 \mu E_h$. The saddle point is localised at $\theta = 111.5^\circ$ and $R = 5.35 \text{ \AA}$. The physical origin of the weak interaction studied was analysed by the intermolecular perturbation theory based on the single determinant UHF wave function. The separation of the interaction energies shows that the locations of the predicted stable bent structures are primarily determined by the anisotropy of the repulsive Heitler-London exchange penetration and attractive dispersion and induction energy components.

Keywords: Interaction energy; Potential energy surface; Lithium; van der Waals complex; Carbon monoxides; Intermolecular perturbation theory; Ab initio calculations.

Intermolecular systems involving carbon monoxide are actually of interest not only from the point of view of the basic research but also from the point of view of its technological applications¹⁻⁵. In particular, the co-adsorption of CO molecules with alkali atoms is still strongly investigated due to its catalytic importance^{6,7}. Alkali metal-carbonyl binding is responsible for the modification of catalytic properties of transition metal surfaces⁸.

The LiCO molecule has been characterised experimentally in noble-gas matrices^{9,10} by a red shift of the CO stretching mode and a Li-CO vibration in the region of $610\text{--}620 \text{ cm}^{-1}$ indicating a relatively strong Li-C bonding.

Although the results are not easily interpretable due to the complications of the solid-noble gas matrices and to the difficulty of controlling the relative subsystem concentrations, it is clear that the interaction between these systems is relatively strong. Surprisingly, the behaviour of Li differs from Na or K¹.

LiCO molecule has been studied theoretically by *ab initio* HF, post-HF and DFT methods. Conflicting results of *ab initio* calculations published by Silvi *et al.*¹¹ and density functional results of Pullumbi *et al.*¹² stimulated the *ab initio* CISD (with Davidson corrections) calculations of Kalemos *et al.*² on isovalent species LiCO and LiCS. They found the Li-CO and Li-OC ²Π states bound with respect to Li ²P and all LiCO ²Σ⁺ states to be repulsive. At the distances typical of complexes of the van der Waals type, their potential energy curves do not reveal any minima. In their study no bent geometries were examined.

The *ab initio* determination of the stationary points on the potential energy surface (PES) can simplify the interpretation of experimental results, mainly dissociation dynamics. Furthermore, the separation of the interaction energy into fundamental parts can be also helpful for deeper understanding the dynamic processes. Although several theoretical studies are devoted to the structural characteristics of isovalent species LiCO, very little has been known about the van der Waals (vdW) stationary points on the PES. These weak vdW systems might be prereactive complexes formed in the entrance valleys of PES. Furthermore, the presence of unpaired electron might induce a new type of electronic anisotropy.

With respect to previous theoretical works, the main goal of this paper is threefold: (i) to provide the detailed and improved BSSE (basis set superposition error) corrected^{13,14} characterisation of the PES of the Li-CO complex at the supermolecular coupled-clusters theoretical level, (ii) to present the fitted functional form of the obtained *ab initio* results and (iii) to analyse the origin of the anisotropy and stability of PES minima by the intermolecular perturbation theory.

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Methodology and Definitions

In order to investigate the weak interaction within the radical vdW system, we will use the standard *ab initio* supermolecular approach¹⁵⁻¹⁸. At a given level of perturbation or CCSD(T) theory, the interaction energy is calculated from the expression:

$$\Delta E_{\text{int}}^{(n)} = E_{\text{AB}}^{(n)} - E_{\text{A}}^{(n)} - E_{\text{B}}^{(n)} \quad n = \text{HF}, 2, 3, 4, \dots \text{ or CCSD(T)}, \quad (1)$$

where E_{AB} is the energy of the supersystem AB, and E_{A} (E_{B}) stands for the energy of the non-interacting monomer A (B). The level of theory is indicated by the superscript index “ n ”, e.g. $\Delta E_{\text{int}}^{(2)}$ denotes the MP2 interaction energy.

To analyse the supermolecular results, the interpretation tools based on the intermolecular perturbation theory (I-PT) are applied at the SCF as well as at post-HF theoretical levels^{19–22}. In the case of the open-shell systems, the interaction energy contributions can be calculated in the framework of single-determinant RHF and/or UHF approaches^{23–29}. In spite of some advantages, their application is associated with certain problems. In general, the Hamiltonian matrix elements provided by the RHF solutions for radical monomers are not invariant to the arbitrary orthogonalisation procedure. On the other hand, the use of UHF wave function is associated with difficulties resulting from its spin contamination. If this contamination is not serious, I-PT based on the UHF determinant is conceptually more straightforward than that based on the RHF determinant because of the presence of an additional one-particle operator^{25,26}.

The UHF-SCF interaction energy can be decomposed as follows

$$\Delta E^{\text{UHF}} = \Delta E^{\text{HL}} + \Delta E_{\text{def}}^{\text{UHF}}, \quad (2)$$

where ΔE^{HL} is the Heitler–London (HL) energy^{30,31} and $\Delta E_{\text{def}}^{\text{UHF}}$ represents the UHF deformation contribution. According to the I-PT defined in orthogonalised basis sets^{21,22,31}, the unrestricted orbitals may be conveniently orthogonalised in any order. ΔE^{HL} may be further divided into the first-order Hartree–Fock electrostatic $E_{\text{els}}^{(100)}$ (for the perturbation terms notation, see, e.g., ref.¹⁷) and HL exchange-penetration $\Delta E_{\text{exch}}^{\text{HL}}$ components

$$\Delta E^{\text{HL}} = \Delta E_{\text{exch}}^{\text{HL}} + \Delta E_{\text{els}}^{(100)}. \quad (3)$$

The UHF deformation energy defined by Eq. (2) originates from mutual electric polarisation effects and exchange effects due to the Pauli principle. An important and the simplest exchangeless approximation to $\Delta E_{\text{def}}^{\text{UHF}}$ is the

second-order UHF Coulomb induction energy¹⁷⁻¹⁹. It may be viewed as the classic induction effect between the permanent and induced multipole moments resulting from the polarization of monomer A by the permanent multipole moments of monomer B and *vice versa*.

Similarly to the closed-shell cases, the second-order UMP2 correlation interaction energy can be partitioned as

$$\Delta E_{\text{int}}^{(2)} = \Delta E_{\text{disp}}^{(200)} + \Delta E_{\text{els}}^{(12)} + \Delta E_{\text{other}}^{(2)}. \quad (4)$$

$\Delta E_{\text{disp}}^{(200)}$ represents the second-order Hartree–Fock dispersion³² and it results from interactions of induced instantaneous electric moments. $\Delta E_{\text{els}}^{(12)}$ denotes the second-order electrostatic correlation energy (containing $\Delta E_{\text{els}}^{(102)}$ and $\Delta E_{\text{els}}^{(120)}$ energies). It describes electrostatic interactions of the correlated multipole moments of monomer A with uncorrelated moments of monomer B and *vice versa*. The remaining term $\Delta E_{\text{other}}^{(2)}$ encompasses the exchange and deformation correlation corrections as well as the response effects¹⁷⁻²⁰.

Using the diagrammatic techniques, it is possible to distinguish the third-order interaction energy contributions like the dispersion-correlation ($\Delta E_{\text{disp}}^{(210)}$, $\Delta E_{\text{disp}}^{(201)}$) and Hartree–Fock third-order dispersion ($\Delta E_{\text{disp}}^{(300)}$) energies^{19,27}. However, complete physical interpretation of higher than second-order contributions of interaction electron-correlation energies is not straightforward.

Calculation Details

All I-PT calculations were performed using our own program codes interfaced to the Gaussian 94 program package³³. The supermolecular BSSE was determined via the counterpoise method of Boys and Bernardi¹³. The presented UHF interaction energy terms were developed using dimer-centered basis sets of the constituent monomers¹⁴. The HL energy was obtained using the standard Gram–Schmidt orthogonalization procedure. All electrons were correlated in the presented calculations.

The standard polarized basis set POL reported by Sadlej and Urban^{34,35} has been used for the atoms studied. It represents the near triple- ζ quality basis set augmented by the polarization functions optimized to reproduce molecular electric properties, in particular polarisabilities. In order to improve the effects of the basis set on the quality of the interaction energy calculations, we have also used the modified set of the midbond functions

[3s3p2d] of Tao and Pan (with the exponents sp: 1.8, 0.6, 0.2 and d: 1.2, 0.4)³⁶. These bond functions are fixed at the center of the axis defined by the Li and CO centers of mass. The corresponding extended basis set is denoted as POL+bf.

A system of Jacobi coordinates (r , R , Θ) was used in all our calculations. The coordinates r , R and Θ represent the intramolecular C-O distance, the distance from Li atom to the centre of mass of CO molecule, and the Jacobi angle, respectively. If this convention is used, $\Theta = 0^\circ$ denotes the linear orientation Li-CO, while $\Theta = 180^\circ$ designates the linear orientation Li-OC. In this work, the r distance was kept at the value of 1.15 Å which represents the equilibrium bond distance of the carbon monoxide molecule optimised at the CCSD(T) level of theory in the standard polarized basis set POL³⁴.

RESULTS AND DISCUSSION

Features of the PES

The investigation of the PES within the POL+bf basis sets was carried out for the distances in the range of R from 3.5 to 10.0 Å and for angles Θ ranging from 0 to 180° (the data and the Fortran routine generating the potential are available on the request). The calculated potential energy points were fitted to the following general functional form

$$\Delta E_{\text{int}}^{\text{CCSD(T)}} = \sum_{L=0}^7 P_L^0(\cos \Theta) \sum_{k=0}^4 a_k^L [\exp(-b_1(R-b_2))]^k, \quad (5)$$

where the energies are given in μE_h and $P_L^0(\cos \Theta)$ denote associated Legendre polynomials up to the order $L = 7$. The rigorous least-square fitting procedure based on the singular value decomposition was used to determine all 42 variational parameters (see Table I). Prior to the least-square calculation, the original grid of 399 potential energy points has been expanded by the bicubic spline interpolation procedure³⁷ to 2063 points (the points above the energy 100 μE_h were excluded from the calculation). The RMS error of the fit was smaller than 0.6 μE_h . It should be noted that the function used for the fit which offers good results for the calculated PES range, does not contain long-range terms and therefore is not fully acceptable for larger distances.

The evaluated PES reveals three stationary points (see Fig. 1). The potential energy minimum corresponds to a bent geometry $\theta = 50.7^\circ$ (carbon side of the CO system) at $R = 5.25 \text{ \AA}$, and its interaction energy amounts to $-167.2 \mu E_h$ (see Table II). A secondary LiOC vdW minimum was localised for the bent geometry $\theta = 148.7^\circ$ at $R = 5.48 \text{ \AA}$ and the interaction energy equals $-121.9 \mu E_h$. The fitted supermolecular CCSD(T) results reveal that the saddle point is localised at $\theta = 111.5^\circ$ and $R = 5.35 \text{ \AA}$.

TABLE I
Parameters of the analytical potential (Eq. (5))^a

L	a_0^L	a_1^L	a_2^L	a_3^L	a_4^L
0	-1.26110	-52.25021	-137.20617	89.29314	-9.20321
1	0.42901	-16.77285	-39.20027	37.58628	-7.48926
2	0.07101	-11.73353	-43.88511	50.12303	-10.59447
3	0.00262	0.17499	-8.35782	20.73016	-4.75762
4	-0.46941	4.49286	-13.59833	19.89272	-3.97767
5	-0.69403	6.95000	-16.28809	13.15928	-2.71875
6	-0.36914	3.60579	-8.54580	6.94360	-1.53116
7	0.89557	-8.94615	19.79131	-13.88290	2.88284

^a The values of a parameters are in $10^{-6} E_h$ ($b_1 = 0.6535554 \text{ \AA}^{-1}$, $b_2 = 5.9152135 \text{ \AA}$).

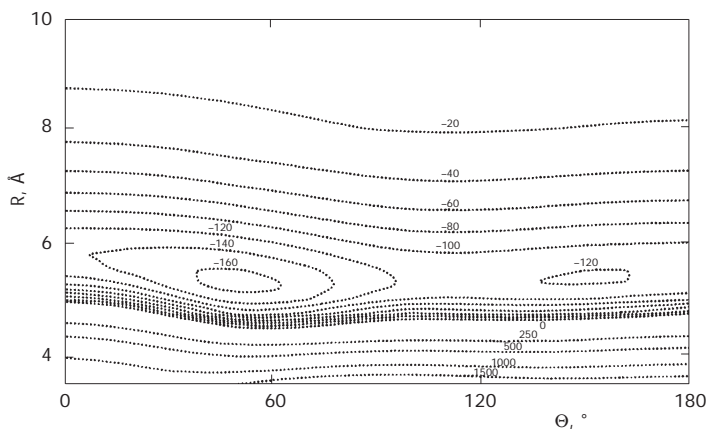


FIG. 1
Contour plot of the PES calculated at the CCSD(T)/POL+bf level of theory. All energies are in μE_h

Within the supermolecular calculations, the truncation effect of the correlation treatment on the values of interaction energies is important. Its role is illustrated in Table II. The major repulsive contribution originates from the UHF interaction energy (ΔE^{UHF}). A dominant part of the interaction correlation energy naturally originates from the values computed at the UMP2 level of theory. Despite of the fact that the contributions of $\Delta E^{(3)}$ ($\Delta E_{\text{int}}^{(3)} - \Delta E_{\text{int}}^{(2)}$) and of $\Delta E^{(4)}$ ($\Delta E_{\text{int}}^{(4)} - \Delta E_{\text{int}}^{(3)}$) are smaller (ca 5–25% with respect to the $\Delta E^{(2)}$ value), they significantly affect the value of the interaction en-

TABLE II
Interaction energies of the Li-CO complex. All energies are in μE_{h}

Interaction energy	$R = 5.27 \text{ \AA}, \Theta = 50.7^\circ$		$R = 5.35 \text{ \AA}, \Theta = 148.7^\circ$		$R = 5.33 \text{ \AA}, \Theta = 111.5^\circ$	
	POL	POL+bf	POL	POL+bf	POL	POL+bf
ΔE^{UHF}	274.3	274.8	114.0	122.6	129.2	129.3
$\Delta E^{(2)}$	-333.0	-365.5	-158.8	-179.2	-168.8	-189.0
$\Delta E_{\text{int}}^{(2)}$	-58.7	-90.7	-44.8	-56.7	-39.6	-59.8
$\Delta E^{(2+3)}$	-342.3	-376.6	-169.9	-188.2	-181.7	-201.2
$\Delta E_{\text{int}}^{(3)}$	-68.0	-101.8	-55.9	-65.6	-52.5	-71.9
$\Delta E^{(2+3+4)}$	-408.8	-446.9	-210.5	-231.9	-213.5	-235.7
$\Delta E_{\text{int}}^{(4)}$	-134.4	-172.1	-96.5	-109.4	-84.3	-106.5
$\Delta E^{\text{CCSD(T)}}$	-403.9	-442.0	-222.6	-244.5	-221.9	-244.3
$\Delta E_{\text{int}}^{\text{CCSD(T)}}$	-129.6	-167.2	-108.6	-121.9	-92.7	-115.1
ΔE^{HL}	391.6	394.3	182.2	192.2	161.3	162.0
$E_{\text{els}}^{(100)}$	-254.9	-261.7	-185.0	-181.8	-138.2	-141.1
$E_{\text{exch}}^{\text{HL}}$	646.5	656.0	367.2	374.0	299.5	303.1
$\Delta E_{\text{def}}^{\text{UHF}}$	-117.3	-119.5	-68.2	-69.6	-32.1	-32.7
$E_{\text{ind}}^{(200)}$	-471.8	-479.4	-351.6	-356.7	-294.4	-298.5
$E_{\text{els}}^{(12)}$	-16.1	-11.3	3.9	-2.7	1.5	-1.8
$E_{\text{disp}}^{(200)}$	-410.4	-453.3	-298.8	-318.1	-255.6	-275.6
$\Delta E_{\text{other}}^{(2)}$	93.4	99.1	136.1	141.6	85.3	88.4
$E_{\text{disp}}^{(210)} + E_{\text{disp}}^{(201)}$	-97.8	-107.3	-62.4	-66.6	-54.2	-58.8
$E_{\text{disp}}^{(300)}$	9.1	19.3	1.4	4.2	2.2	5.1
SCF+DISP ^a	-127.0	-159.2	-183.4	-191.3	-124.2	-141.2

^a $\Delta E^{\text{UHF}} + E_{\text{disp}}^{(200)} + E_{\text{disp}}^{(300)}$.

ergies. The interaction energies calculated using CCSD(T) method for the basis sets used appear to be slightly deeper around the localised minima when compared with the UMP4 values. All these data clearly indicate weak bonding for the investigated complex in its electronic ground state. In all cases, the spin contamination was negligible because the $\langle S^2 \rangle = 0.750$ corresponds to the exact value in radical monomer as well as dimer.

Partitioning of Interaction Energies

Further goal of this work is to study the physical origin of the stability of indicated vdW structures. Using the decomposition of the supermolecular UMP interaction energy, we can analyse and estimate how the fundamental components determine its anisotropy in the region at 5.3 Å. These dependences are shown in Fig. 2.

The UHF interaction energies (ΔE^{UHF}) display a striking angular dependence. In the linear arrangement ($\Theta = 0^\circ$), the total UHF interaction energy curves show a maximum, while the second linear one ($\Theta = 180^\circ$) corresponds to a minimum of ΔE^{UHF} (see also Table II). The decomposition of the ΔE^{UHF} energy leads to the repulsive HL and attractive $\Delta E_{\text{def}}^{\text{UHF}}$ terms. The angular dependence of the above-mentioned terms shows three extreme points in the investigated range. Consecutive separation of the HL energy according to Eq. (3) reveals that the positive value of this term comes out only from the repulsive character of the HL exchange-penetration energy contributions ($\Delta E_{\text{exch}}^{\text{HL}}$). The attractive character of the Coulomb forces represented by $E_{\text{els}}^{(100)}$ energy evidently appears at the carbon side of CO molecule (see Fig. 2a). This might be explained by stronger nuclear and mainly electron repulsion between the lithium atom and oxygen side of the CO system. The maximisation of these repulsion contributions appears around the perpendicular arrangement. The flattening of $\Delta E_{\text{exch}}^{\text{HL}}$ and $E_{\text{els}}^{(100)}$ angular dependence close to the oxygen atom might indicate the flattening of the diffuse part of the electron density.

The UHF deformation term ($\Delta E_{\text{def}}^{\text{UHF}}$) has a reciprocal character to the dependence of HL energy and has a minimal effect on the total UHF interaction energy around the perpendicular configuration. The origin of the largest value of the $\Delta E_{\text{def}}^{\text{UHF}}$ energy (especially around $\Theta = 0^\circ$) is also interesting. An important part of this energy is the UHF induction term ($E_{\text{ind}}^{(200)}$) which describes the classic charge-induction. As can be seen from Fig. 2a, the induction interaction between the neutral lithium atom and CO molecule in the linear arrangement ($\Theta = 0^\circ$) is about twice higher than for $\Theta =$

90°. The large differences between $E_{\text{ind}}^{(200)}$ and $\Delta E_{\text{def}}^{\text{UHF}}$ energies indicate that the repulsive exchange-induction energies play a non-negligible role in the UHF deformation energy^{17,18}.

The correlation components are plotted in Fig. 2b. As expected, $\Delta E^{(2)}$ is important in forming the shape of the total UMP2 interaction energy

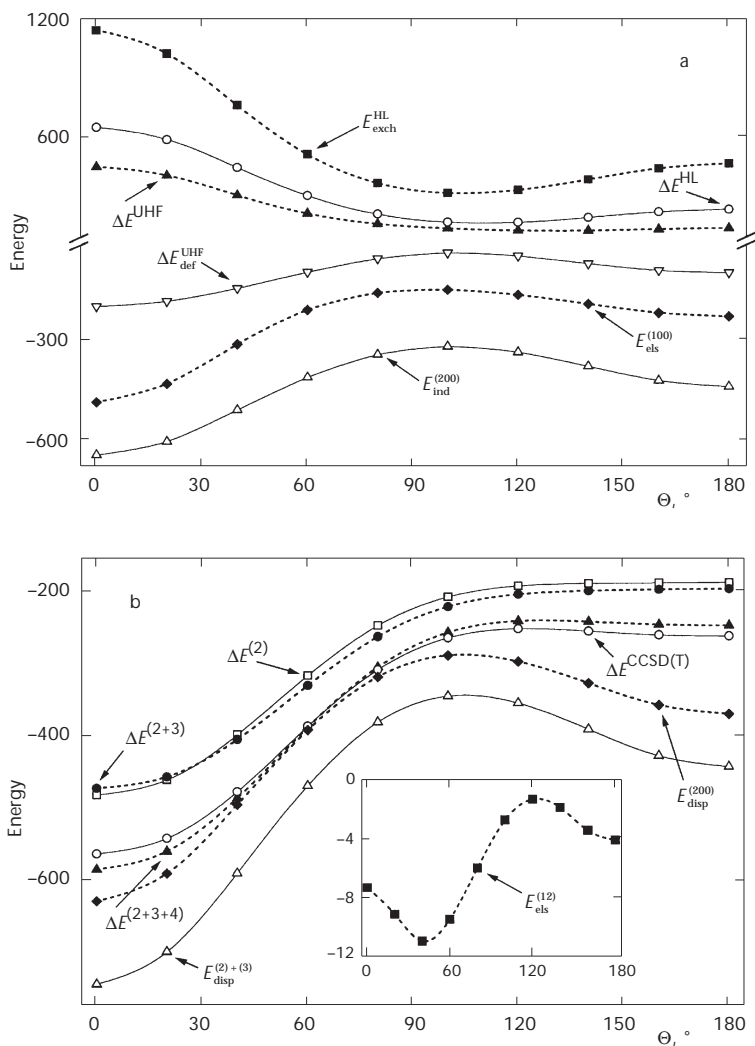


FIG. 2

Angular dependence of the HF and interaction correlation UMP-n as well as CCSD(T) energies and their components at $R = 5.3 \text{ \AA}$ (calculated in the POL+bf basis set). All energies are in μE_h

curves. The $E_{\text{disp}}^{(200)}$ makes the dominant attractive contribution within the interaction correlation energy (see Table II). Obviously, the dispersion component favours linear arrangements. A comparison of the interaction energy components calculated within the POL and POL+bf basis sets shows that extension of basis set affects primarily the dispersion energies. The remaining calculated coulombic terms represent the electrostatic correlation energy ($E_{\text{els}}^{(12)}$). Interestingly, it has maxima at 0 and 120° and minima at 50 and 180°. It seems that the reshaping of the electron density due to the second-order correlation effects occurs mainly at the side of the carbon atom. The repulsive contributions collected in $E_{\text{other}}^{(2)}$ energy importantly affect the angular dependence of the second-order interaction correlation energy $\Delta E^{(2)}$. Contrary to the $\Delta E_{\text{exch}}^{\text{HL}}$ energy, it has the maximal values at the side of the oxygen atom (see also Table II).

The higher-order dispersion corrections ($E_{\text{disp}}^{(210)}$, $E_{\text{disp}}^{(201)}$ and $E_{\text{disp}}^{(300)}$) that appear in the third-order interaction correlation energy ($\Delta E^{(3)}$) are presented in Fig. 2b and Table II (see $E_{\text{disp}} = E_{\text{disp}}^{(200)} + E_{\text{disp}}^{(300)} + E_{\text{disp}}^{(210)} + E_{\text{disp}}^{(201)}$). The negative sum of the higher-order dispersion corrections does not approximate (in both basis sets used) the third-order contribution of the interaction correlation energy and the sum of the remaining relevant energies (*i.e.* third-order electrostatic correlation, exchange-penetration and deformation contributions) seems to be non-negligible (*e.g.* 76.9 μE_{h} for POL+bf at $\Theta = 50.7^\circ$). For simple modelling of LiCO aggregates, it is of primary importance to examine another approach which is often used in such studies, namely SCF+DISP¹⁷. The SCF+DISP model approximately twice overestimates the interaction energy in comparison with UMP3 results. The depicted angular dependences of the interaction correlation energies reveal that the energies calculated up to the fourth-order of PT ($\Delta E^{(2+3+4)}$) correspond very well with the CCSD(T) approach.

CONCLUSIONS

The *ab initio* potential energy surface for the Li-CO interaction was evaluated in detail at the supermolecular CCSD(T) level. The minima occur for bent geometries and the transition state for the nearly perpendicular orientation. The angular dependence of the interaction energy at $R = 5.3 \text{ \AA}$ was analysed using the I-PT. The interaction energies were separated into four fundamental components – electrostatic, exchange-penetration, induction and dispersion – which have a similar physical interpretation as those arising among the closed-shell species (see, *e.g.*, refs^{19,27}). The analysis of these components reveals that the UHF interaction energies calculated for the

perpendicular arrangements are practically determined by the repulsive HL energy.

In both investigated geometries, the attractive $E_{\text{disp}}^{(200)}$ energy dominates $\Delta E^{(2)}$ and the dispersion interactions plays the leading role in the $\Delta E^{(3)}$. However, the stabilisation effect of $E_{\text{disp}}^{(200)}$ is compensated due to the relatively large repulsive contributions included in the $E_{\text{other}}^{(2)}$ energy.

In order to understand the role of alkali atoms in the aggregation processes with the CO molecule, theoretical studies of this type for NaCO and KCO vdW systems are desirable. The obtained pair potentials can be used later as inputs for the modelling of the dynamic processes on monolayer surfaces, useful from the technological point of view.

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