Theor Chim Acta (1986) 70: 297-302

Theoretica Chimica Acta

Covalent-ionic nature of the potential energy surface of the Li–CO_2 complex

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(Received April 3, 1985, revised and accepted May 17, 1986)

Unrestricted Hartree-Fock calculations with large basis sets, including *d*-functions, and the estimation of the correlation energy, show that the potential energy surface for the Li-CO_2 complex is built from the crossing of two states, each of them corresponding to a different electron arrangement. One has a strong ionic character and the other is of van der Waals type. Each portion of the energy surface presents a minimum, which is stable in respect to the dissociation limit.

Key words: Li-CO_2 complex — UHF plus correlation calculations — Potential energy surfaces

1. Introduction

The Li-CO_2 system has been studied by *ab initio* methods [1-3]. Two completely different descriptions of the interaction responsible for the complex formation are obtained, depending on the CO_2 geometry adopted before the global optimization of the Li-CO_2 complex. If one takes the structure corresponding to the CO_2 ground state as a starting point, the optimization description leads to a weakly bounded complex with an interaction description of van der Waals type [1]. On the other hand, if one takes the ground state of the CO_2 ion as a starting point, a more stable minimum is obtained at the end of the optimization, having a strong ionic character [2, 3].

These results suggest the coexistence of two different descriptions for the electronic ground state of the complex, each one associated to a different region of the potential energy hypersurface, in contradiction with the work of Margrave et al. [4] who have found only two geometrical isomers of $LiCO_2$ (C_{2v} and C_s forms), both corresponding to the ionic description. In order to clarify this question, we have carried out a study of selected potential energy sections (PES), by means of *ab initio* UHF calculations and a subsequent refinement of the most significant points through the evaluation of the correlation energy (CE).

2. Calculations and results

The SCF calculations were made within the UHF approximation, which provides good wave functions for this system [1-3]. To scan the PES, a GTO 3-21G basis set [5] was used, which has shown to give satisfactory results [2]. All the calculations were made with the GAUSSIAN80 [6] and GAUSSIAN80-USCF [7] programs. All optimizations were carried out by analytic calculations of the energy gradient.

One of the surface's cuts selected corresponds to C_{2v} symmetry, in which the C and Li atoms are placed on the C_2 axis, showing a rhombic structure. Each point of this PES is defined by R and θ in Fig.1a. For every point of this C_{2v} surface, the C-O distance has been optimized. In Fig. 2 the SCF energies for this C_{2v} cut are represented. The PES obtained by a cubic-spline interpolation method, from an original grid of 60 *ab initio* points. It appears as two valleys separated by the dotted line in Fig. 2b. An analysis of the wave function shows that they correspond to two very different descriptions of the interaction between the Li atom and the CO_2 molecule. The upper valley, along which Li does initiate the approach to CO_2 (in a C_{2v} restricted symmetry), describes a van der Waals interaction [1]; the lower valley corresponds to the Li-CO_2 description given in [2, 3]. Therefore, the C_{2v} PES for the Li-CO_2 ground state is built from a crossing (avoided in the adiabatic approximation) of two electronic states of the molecule.

Local minima are known to exist in the PES, corresponding to C_s and $C_{\infty v}$ symmetry point groups. One (C_s), obtained in [2, 3] is of ionic type, and the

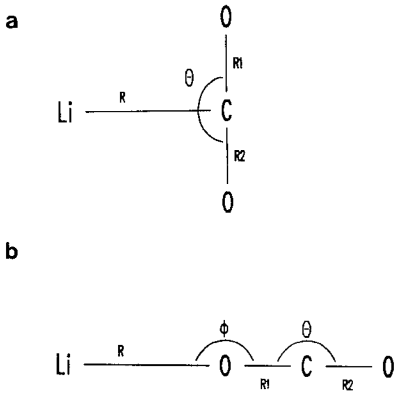

Fig. 1. Geometric configurations studied in this paper

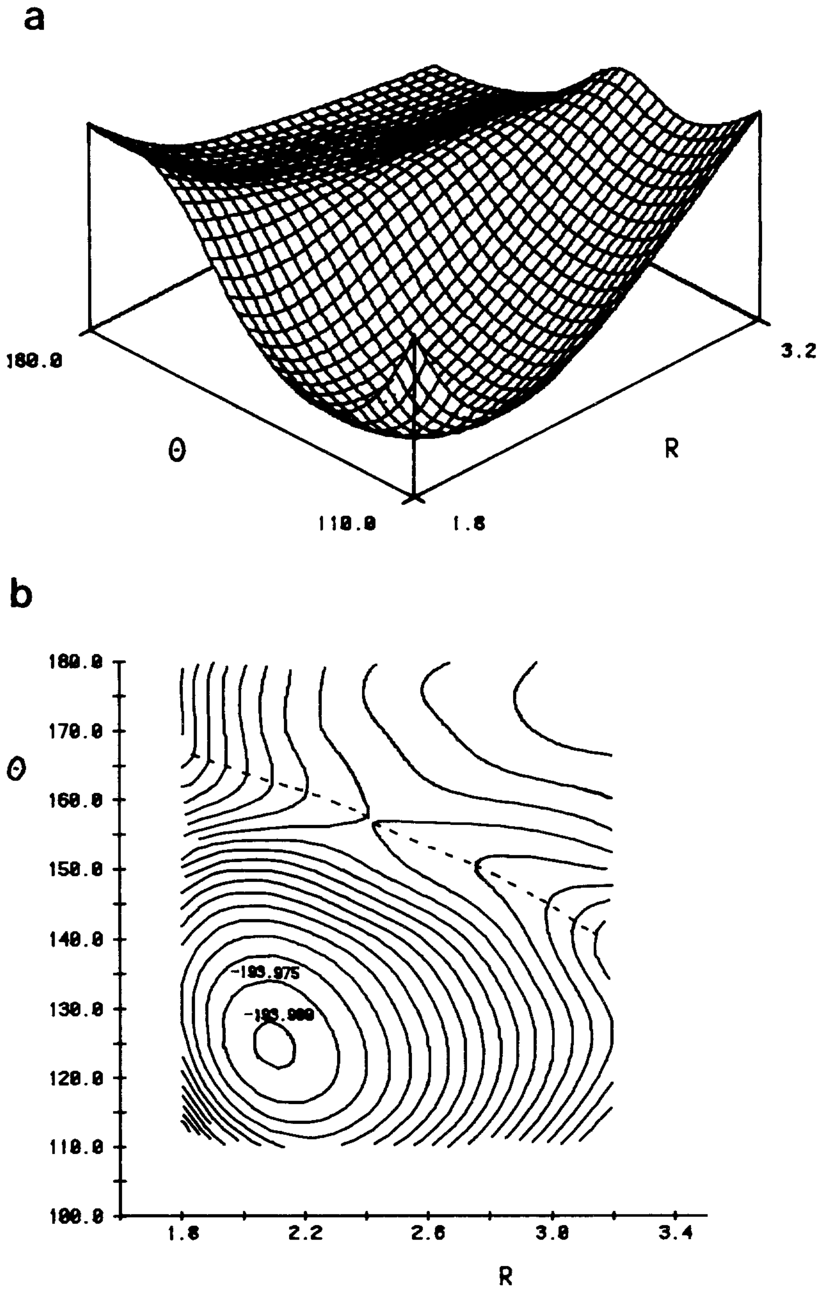

Fig. 2. Potential energy surface for Li-CO_2 calculated with 3-21G basis set. R in Å, θ in degrees and energy in a.u.

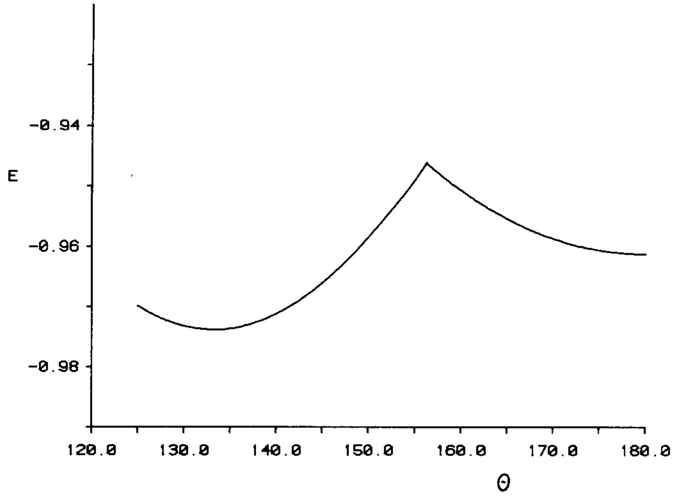

Fig. 3. Potential energy curve for C_s Li-CO_2, versus θ. 3-21G basis set. Energy in a.u. and θ in degrees

other ($C_{\infty v}$), [1], is of van der Waals type. According to our C_{2v} results it is expected both minima to be separated by a potential energy barrier.

From the equilibrium geometry obtained in [1] ($C_{\infty v}$ symmetry) a scan of the θ angle was made, optimizing all the geometry parameters in Fig. 1b. The minimum energy curve is plotted in Fig. 3, in which it is seen that the minima and the C_s barrier are below the dissociation limit (The value obtained for the barrier is probably overestimated, since it belongs to crossing of two states of the same symmetry and its adiabatic value should be inferior). In Table 1 the results

Table 1. Li-CO2 complex parameters. 3-21G basis set. In a.u. and degrees

Parameter[a]	C_{2v}	A[b]	C_s	$C_{\infty v}$
E (UHF)	−193.9809	−193.9326	−193.9738	−193.9612
μ	1.9440	0.9174	3.5226	1.9513
TCF (Li)	0.0119	0.1638	0.0062	0.1167
TCF (01)	0.1256	0.0342	0.1751	0.0634
TCF (C)	0.4053	0.0029	0.3835	0.0021
TCF (02)	0.1256	0.0342	0.1005	−0.0035
Q (Li)	0.5903	−0.0491	0.6425	−0.1055
Q (01)	−0.6883	−0.5149	−0.8112	−0.6157
Q (C)	0.7862	1.0789	0.7705	1.1969
Q (02)	−0.6883	−0.5149	−0.6017	−0.4757
R	3.9796	5.2912	3.0267	3.4979
R1	2.3754	2.1921	2.4273	2.2034
R2	2.3754	2.1921	2.2675	2.1600
θ	124.94	170.00	133.10	180.00
ϕ	—	—	181.20	180.00

[a] The UHF energy for the quasi-dissociated system is −193.9428
[b] At the upper valley in Fig. 2b

Table 2. Li-CO2 complex energies. 3-21G basis set. In a.u.

Energy	C_{2v}	C_s	$C_{\infty v}$	Dissociated[a]
UHF	−193.9809	−193.9738	−193.9612	−193.9428
UHF+MP2	−194.3072	−194.2973	−194.3060	−194.2872
UHF+MP3	−194.2873	−194.2786	−194.2759	−194.2563
UHF+CID	−194.2713	−194.2626	−194.2605	−194.2410
UHF+CID (size)	−194.3040	−194.2851	−194.2840	−194.2643

[a] R(Li-O) = 8 Å

obtained for the minima and a point of the upper valley from Fig. 2b are shown. The dipole moment, the Fermi contact term and the atom charges clearly show what kind of interaction characterizes each point.

The small energy differences between the minima suggest that the effect of the correlation energy should be considered in order to establish their relative stability. We have carried out CI including double-excitations [8] and perturbational calculations at second and third order Møller-Plesset (MP2 and MP3) theory [9]. The four occupied molecular orbitals corresponding to 1s electrons were kept frozen in both types of calculations. In Table 2 the total energy at the C_{2v}, C_s and $C_{\infty v}$ minima and for the quasi-dissociated Li-CO_2 system [10] are presented. The inclusion of the correlation energy does not modify the relative order of the three minima obtained at UHF level, though the differences are reduced.

Table 3. Li-CO_2 complex parameters. 6-31G* basis set. In a.u. and degrees

Parameter[a]	C_{2v}	C_s	$C_{\infty}v$
E (UHF)	−195.0794	−195.0578	−195.0669
E (UHF+MP2)	−195.5487	−195.5266	−195.5369
μ	1.9698	3.7678	1.6936
TCF (Li)	0.0153	0.0082	0.1717
TCF (01)	0.1455	0.1954	0.0707
TCF (C)	0.4787	0.4456	−0.0006
TCF (02)	0.1455	0.1246	0.0105
Q (Li)	0.6390	0.7090	−0.0505
Q (01)	−0.6681	−0.7449	−0.4891
Q (C)	0.6971	0.5634	0.9392
Q (02)	−0.6681	−0.5275	−0.3996
R	3.9136	3.1313	3.9117
R1	2.3263	2.3886	2.1751
R2	2.3263	2.2374	2.1430
θ	126.70	132.80	180.00
ϕ	—	182.30	180.00

[a] The UHF and UHF+MP2 energies for the quasi-dissociated system are −195.0655 and −195.5336, respectively

At these points, we have carried out calculations using a 6-31G* basis set which includes *d*-orbitals [11]. For the C_{2v} and C_s minima we have taken those optimized geometries from [3], and for the $C_{\infty v}$ and quasi-dissociated points those optimized by us. Correlation energy has been estimated at MP2 level. In Table 3 we present the results obtained, the most significant of which being the destabilization, at the two, UHF and MP2, levels, of the C_s minimum, which is stable with the 3-21G basis set. The stability order between the absolute C_{2v} minimum and the $C_{\infty v}$ does not vary, with an energy difference of 0.3 eV.

3. Conclusions

UHF calculations reveal the existence of a potential energy surface of Li-CO_2 formed by intersection of two states with very different electron distributions. All calculations place the absolute minimum in the PES region described by an ionic charge distribution, coincident with the description in [2, 3]. The $C_{\infty v}$ minimum, whose existence is discussed in [1], is situated in van der Waals region of PES.

Both minima are below the dissociation limit. This fact, and the change in the nature of interaction when going from any entrance channel to the zone of maximum stability of the system, must be considered to interpret correctly the reaction between the lithium atom and the CO_2 molecule.

Acknowledgment. This work is part of project No. 160/81 supported by Comisión Asesora de Investigación Cientifica y Técnica.

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