

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/244134201>

Shape resonance of the ethylene anion stabilized in a molecular trap

ARTICLE *in* CHEMICAL PHYSICS LETTERS · MARCH 2003

Impact Factor: 1.9 · DOI: 10.1016/S0009-2614(03)00139-8

CITATION

1

READS

20

2 AUTHORS:



Iwona Wanda Anusiewicz

University of Gdansk

52 PUBLICATIONS 1,137 CITATIONS

SEE PROFILE



Piotr Skurski

University of Gdansk

141 PUBLICATIONS 3,383 CITATIONS

SEE PROFILE

Shape resonance of the ethylene anion stabilized in a molecular trap

Iwona Anusiewicz, Piotr Skurski *

Department of Chemistry, University of Gdańsk, Sobieskiego 18, Gdańsk 80-952, Poland

Department of Chemistry, University of Utah, Salt Lake City, UT 84112, USA

Received 29 November 2002; in final form 13 January 2003

Abstract

The possibility of stabilizing an electronically metastable anion in a molecular trap is studied using ab initio electronic structure methods. The ${}^2B_{2g}$ $C_2H_4^-$ d-wave shape resonance state is used as the metastable anion solute, and a pair of inwardly oriented LiCN molecules ($NCLi \cdots LiCN$) is used as a molecular trap. Although the global minimum of the $C_2H_4 + 2LiCN + e$ system is the $(LiCN)_2^-$ anion with a weakly (van der Waals) bound C_2H_4 molecule, it was found that for the $(NCLi \cdots LiCN)$ trap at its local minimum geometry, the ${}^2B_{2g}$ state becomes electronically stable and is the ground state of the system. It is also found that, in this model trap, three other (excited) anionic states are bound (2A_g , ${}^2B_{1u}$, and ${}^2B_{2u}$). Detailed numerical results are presented for the $(NCLi \cdots H_2C=CH_2 \cdots LiCN)^-$ species (i.e., the trapped ethylene anion) whose vertical electron detachment energy is 2.97 eV at the CCSD(T) level with the augcc-pVDZ basis sets.

© 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

It is known that isolated C_2H_4 (ethylene) anion is not electronically stable [1]. There are several experimental and theoretical reports available in the literature that describe the position and lifetime of the low-energy $(\pi)^2(\pi^*)^1({}^2B_{2g})$ shape resonance of ethylene anion [1–5]. In particular, the observation of the ${}^2B_{2g}$ state of $C_2H_4^-$ by electron transmission spectroscopy (by Burrow and Jordan [2]) show that this feature is centered near 1.8 eV with a width of approximately 0.7 eV, and the

electron energy loss measurements confirm these findings [3]. The results of theoretical calculations are in excellent agreement with the experimental measurements [4,5]. Specifically, Schneider et al. [4] performed complex Kohn variational calculation of the low-energy electron scattering from ethylene revealing a shape-resonance ${}^2B_{2g}$ state at 1.83 eV, while Donnelly [5] employed the second-order treatment utilizing the coordinate-rotated electron propagator that yielded similar energy and width of this state.

Since we consider this d-wave ${}^2B_{2g}$ shape resonance of ethylene as a widely studied species, we decided to undertake a model study in which this metastable state is rendered electronically stable when surrounded in a molecular trap. Having in

* Corresponding author.

E-mail address: piotr@chem.univ.gda.pl (P. Skurski).

mind that some well-known strategies of binding of atomic and molecular cations within macro-molecular cages (such as crown ethers) to separate such ions from complex solution mixtures have proven very useful, we believe that analogous techniques can also be employed for negatively charged species. In particular, such strategies can be used to trap, identify, and separate electronically stable anions. However, if one wants to trap the anion whose lowest energy electronic state is not electronically stable, additional complications arise when devising strategies for trapping and stabilizing such species. The idea of using an electrostatic potential to stabilize a temporary anion has been introduced in the past and it has been the basis of stabilization methods (as described in [6]). In particular, the electrostatic potential generated by the surrounding molecular trap must serve both to lower the electronic energy of the resonance state, thus rendering it electronically stable, and to bind the resulting anion to the molecular framework of the trap itself. A potential that is strong enough to so stabilize a resonance anionic state may also be strong enough to bind the extra electron on its own. As a result, two kinds of anionic states can be observed in such trap-stabilized anionic systems: (i) states arising from resonance states of the ‘solute’ anion and (ii) states arising as the trap’s electrostatic potential binds the excess electron (trap-bound states).

We have recently shown this procedure could be successfully used for stabilizing the $^2\Pi_g$ shape resonance state of N_2^- metastable anion. This species was stabilized in a molecular trap consisting of a pair of inwardly oriented LiCN molecules [7]. In the present work we employ a similar molecular trap to stabilize the d-wave $^2B_{2g}$ shape resonance of ethylene. It is our belief that the results of this prototype anion plus trap study suggest the kind of behavior that is to be expected when other anions and other (experimentally more accessible) traps are considered.

2. Methods

The equilibrium geometries of the neutral and anionic species have been optimized and their

harmonic vibrational frequencies calculated at the second-order Møller–Plesset (MP2) level of theory. In these calculations, the values of $\langle S^2 \rangle$ never exceeded 0.769 for the doublet anionic states, so we are confident that the spin contamination effects are not serious. The electronic stabilities of the anions were calculated using Møller–Plesset perturbation theory up to the fourth order as well as the coupled-cluster method with single, double, and noniterative triple excitations (CCSD(T)) [8]. For studying the bound excited electronic states of the anions, we used the CCSD(T) method, in which cases our investigations were limited to the vertical electron binding energies for those states (i.e., only single-point energy calculations were performed at the equilibrium geometry of the D_{2h} anionic ground state). The choice of the atomic orbital basis set used to describe the neutral molecule and the excess bound electron is very important for reproducing the correct value of the electron binding energy. In this contribution we employed the aug-cc-pVDZ basis set [9] whose usefulness for describing various molecular anions has been documented previously [10]. Moreover, we chose that particular basis set since it proved to be appropriate for studying the electron binding energies of the anions in which the LiCN units were used as building blocks [11].

All calculations were performed with the GAUSSIAN 98 program [12] on Intel Pentium IV and AMD Athlon computers and a Compaq Sierra numerical server. The three-dimensional plots of molecular orbitals were generated with the MOLDEN program [13].

3. Results

3.1. The $(NCLi \cdots LiCN)$ structure as a molecular ‘trap’

The system studied in this work consists of an ethylene ‘solute’ molecule and two LiCN molecules that play the role of ‘molecular trap’ when oriented in a head-to-head manner (see Fig. 1 where the relevant geometrical parameters are given). It should be noted, however, that there exist several other structures possessing the same stoichiome-

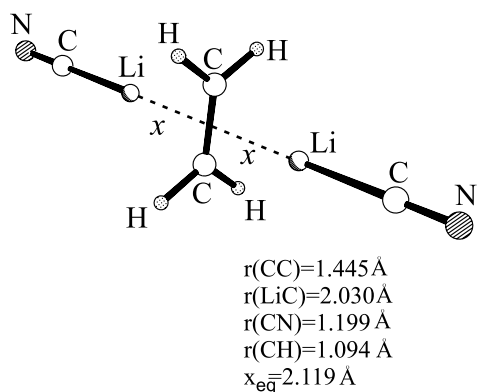


Fig. 1. The MP2 equilibrium D_{2h} geometry of the ground state of the $(\text{NCLi} \cdots \text{C}_2\text{H}_4 \cdots \text{LiCN})^-$ anion and the definition of the x parameter used in this work.

try, that are lower in energy than the structures studied here. We examined the relative stabilities of several alternative neutral and anionic geometries in order to determine the thermodynamic stability of the $D_{2h}(\text{NCLi} \cdots \text{C}_2\text{H}_4 \cdots \text{LiCN})^-$ anion considered here as a molecular trap with an imbedded anion. The results pertaining to the thermodynamic stabilities of various neutral and anion isomers are summarized (at the MP2 level) in Fig. 2. It is clear that the global minimum for the anion is the $(\text{LiCN})_2^-$ anion with a weakly (van der Waals) bound C_2H_4 molecule, and correspondingly, the global minimum for the neutral is the $(\text{LiCN})_2 \cdots \text{C}_2\text{H}_4$. This finding is not surprising since the neutral $(\text{LiCN})_2$ possesses a very

large dipole moment (21.2 D) and binds an excess electron by 1.433 eV at the MP2 level [11]. Moreover, in the $(\text{LiCN})_2$ geometry, the repulsive dipole-dipole potential present in the $(\text{NCLi} \cdots \text{LiCN})$ structure is absent.

As shown in Fig. 2, the D_{2h} -symmetry $(\text{NCLi} \cdots \text{C}_2\text{H}_4 \cdots \text{LiCN})^-$ anion which is the focus of this work, is thermodynamically less stable than $(\text{LiCN})_2^- \cdots \text{C}_2\text{H}_4$ by 0.232 eV. However, because the transformation leading from $(\text{NCLi} \cdots \text{C}_2\text{H}_4 \cdots \text{LiCN})^-$ to $(\text{LiCN})_2^- \cdots \text{C}_2\text{H}_4$ requires significant geometrical reorganization and must surmount a kinetic barrier, we conclude that the $(\text{NCLi} \cdots \text{C}_2\text{H}_4 \cdots \text{LiCN})^-$ anion is locally stable and may be sufficiently long-lived to be experimentally accessible if it can be formed at this geometry. With this assumption in mind we now move on to discuss our examination of the two kinds of anion states discussed in Section 1 at the geometry corresponding to that of the $(\text{NCLi} \cdots \text{LiCN})$ trap.

3.2. The ground $^2B_{2g}$ state of $(\text{NCLi} \cdots \text{C}_2\text{H}_4 \cdots \text{LiCN})^-$: the stabilized shape resonance of ethylene anion

The ground electronic state of the D_{2h} anion at the geometry where this structure has its local minimum is the $^2B_{2g}$ state and consists of the d-wave shape resonance state of C_2H_4^- that has been stabilized by the $(\text{NCLi} \cdots \text{LiCN})$ trap. The singly occupied molecular orbital (SOMO) of this state possesses b_{2g} symmetry and is localized on the ethylene molecule (see Fig. 3c) and has the characteristic d symmetry of the π antibonding orbital of C_2H_4 (which causes d-wave angular distribution of the electron ejected from the C_2H_4^- resonance anion).

The geometry of the $(\text{NCLi} \cdots \text{C}_2\text{H}_4 \cdots \text{LiCN})^-$ anion was optimized at the MP2 level and the resulting optimized geometrical parameters are gathered in Fig. 1. The vertical electron detachment energies for this anion were calculated at various levels of theory with the aug-cc-pVDZ basis sets. In the ground $^2B_{2g}$ state, the anion is strongly bound even at Koopmans' theorem (KT) level [14], and we observe relatively strong orbital relaxation that increases the electron binding

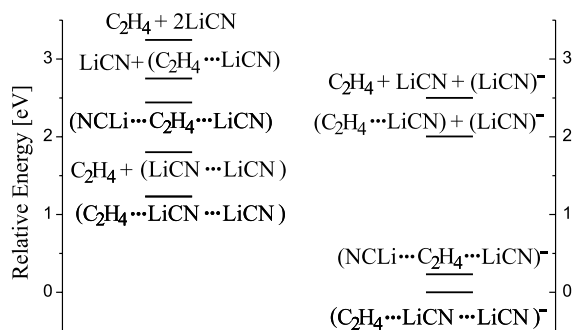


Fig. 2. Schematic diagram with relative energies of the stationary points (minima) located on the potential energy surface of the neutral supermolecule ($2\text{LiCN} + \text{C}_2\text{H}_4$) and its anionic daughter ($2\text{LiCN} + \text{C}_2\text{H}_4 + e$).

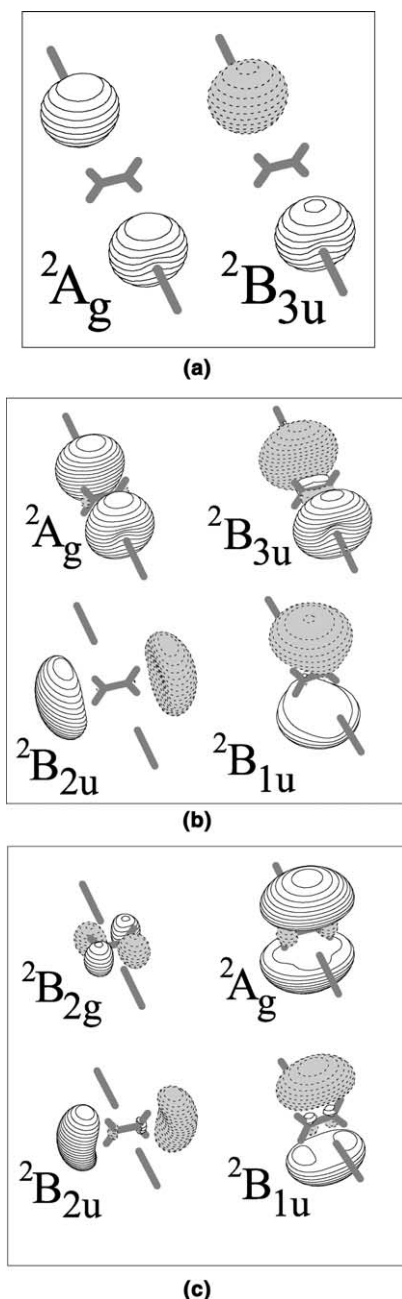


Fig. 3. The singly occupied molecular orbitals for various anionic states of $(\text{NCLi} \cdots \text{C}_2\text{H}_4 \cdots \text{LiCN})$ at the stretched D_{2h} ((a) and (b)) and at the equilibrium D_{2h} geometry (and its vicinity) (c) of the ground ${}^2B_{2g}$ state of the anion. The orbitals correspond to $x = 7 \text{ \AA}$ (a), $x = 4 \text{ \AA}$ (b), and $x = x_{\text{eq}} = 2.119 \text{ \AA}$ (c) (see Fig. 1 for the definition of the x parameter).

Table 1

The vertical electron binding energies D (in eV) for the ground ${}^2B_{2g}$ electronic and bound excited states of the $(\text{NCLi} \cdots \text{C}_2\text{H}_4 \cdots \text{LiCN})^-$ anion calculated with the aug-cc-pVDZ basis sets

	Ground-state ${}^2B_{2g}$	Bound-excited state 2A_g	Bound-excited state ${}^2B_{2u}$	Bound-excited state ${}^2B_{1u}$
D^{KT}	1.80	0.49	0.16	0.16
D^{SCF}	2.69	0.54	0.19	0.18
D^{MP2}	3.04	0.80	0.36	0.33
D^{MP3}	3.06	0.81	0.36	0.34
D^{MP4}	2.98	0.85	0.40	0.37
D^{CCSD}	2.99	0.83	0.40	0.37
$D^{\text{CCSD(T)}}$	2.97	0.86	0.42	0.39

energy (D) to 2.69 eV (see Table 1). The convergence of the MPn series is satisfactory and the MP4 result ($D^{\text{MP4}} = 2.98 \text{ eV}$) is close to our best estimate of D which is the value obtained at the CCSD(T) level (2.97 eV, see Table 1). Hence, the overall correlation contribution (calculated as the difference between $D^{\text{CCSD(T)}}$ and D^{SCF}) is stabilizing and responsible for 9% of the total value of D (see Table 1) so we conclude that correlation effects should be taken into account for reproducing accurate electron binding energy of the ${}^2B_{2g}$ anion.

3.3. Bound excited states of $(\text{NCLi} \cdots \text{C}_2\text{H}_4 \cdots \text{LiCN})^-$: the trap-bound and other stabilized resonance states

It is well-known that only a small percentage of molecular anions possess bound excited states with respect to electron detachment [1]. In the system described in this work, we studied the possibility of forming bound excited anionic states by calculating their energies at the CCSD(T) level for the D_{2h} structure defined in Fig. 1, and the resulting data are collected in Table 1 (where the results obtained at various levels of theory are also shown). According to our findings, there are four electronically stable states of the anion at this geometry. First, is the stabilized shape resonance ground anionic state ${}^2B_{2g}$ that has already been analyzed in Section 3.2 (and classified as the lowest shape resonance state of the ethylene anion stabilized by the molecular trap). The next three states (2A_g , ${}^2B_{2u}$, and ${}^2B_{1u}$) have vertical electron binding energies estimated at

the KT level of 0.49, 0.16, and 0.16 eV, respectively. For these states, the orbital relaxation effects are not that important as it was the case for the ground $^2B_{2g}$ anionic state (they are responsible for ca. 5–7% of the total value of D , see Table 1). The correlation contributions, however, are more important for reproducing the correct values of the electron binding energies for the 2A_g , $^2B_{2u}$, and $^2B_{1u}$ anionic states; they are responsible, respectively, for ca. 37%, 55%, and 54% of the net electron binding energy (see Table 1). Our final values of the electron binding energies for the 2A_g , $^2B_{2u}$, and $^2B_{1u}$ bound excited anionic states were calculated (at the CCSD(T) level) to be 0.86, 0.42, and 0.39 eV, respectively.

We decided to determine the physical origins of the 2A_g , $^2B_{2u}$, and $^2B_{1u}$ states by monitoring the evolution of their binding energies and orbital character as the distance x (see Fig. 1), and thus the stabilizing strength of the trap, is varied. Retaining D_{2h} symmetry, we varied the x parameter between 2.119 Å (which corresponds to x_{eq}) and 50 Å in a series of single-point SCF calculations. At each point, we calculated the energies of all electronically stable anionic states and the energy of the neutral system. The results are depicted in Fig. 4 (for which we limited the range for x to 20 Å because the data for $x = 20$ –50 Å did not provide any qualitatively new information). The corresponding SOMOs in the anionic systems are depicted in Fig. 3 for three selected ranges of x : part A (for $x > 6.5$ Å), part B (for $x = 4$ –6.5 Å), and part C (for $2.119 \text{ Å} \leq x < 4$ Å, where 2.119 Å corresponds to $x = x_{eq}$).

In region A, the trap plus solute system consists essentially of two separated LiCN molecules, each of which can bind an extra electron to form a dipole-bound state, with an ethylene molecule in the middle. As expected, at such geometries we find two anionic states 2A_g and $^2B_{3u}$, (see Figs. 3a and 4) whose energies are nearly degenerate and whose single occupied orbital lobes are localized on the LiCN units and not distorted by the presence of the ethylene molecule. Therefore, we can consider the 2A_g and $^2B_{3u}$ states as the trap-bound states (because these anions are bound to the molecular framework of the trap itself). It should also be noted that, at these geometries, the C_2H_4 molecule

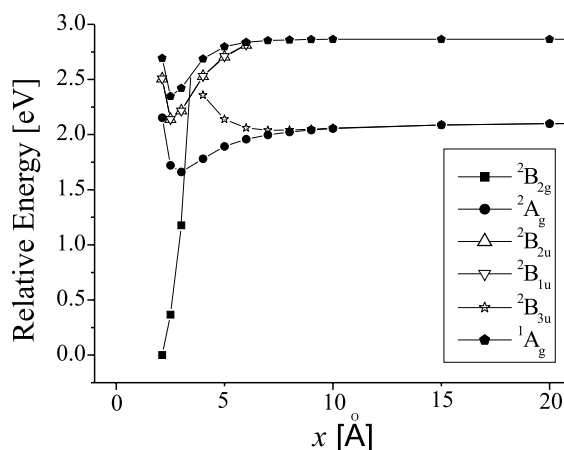


Fig. 4. Relative energies of various anionic states of $(NCLi \cdots C_2H_4 \cdots LiCN)$ at the stretched and equilibrium D_{2h} geometries compared to the energy of the neutral system (in its ground singlet 1A_g state). The x parameter measures the distance between a Li atom and the center of the $C=C$ bond in ethylene molecule and is identical for both sides of the system in order to preserve the D_{2h} symmetry of the anion (see also Fig. 1). The value x_{eq} corresponds to $x = 2.119 \text{ Å}$, which is the equilibrium distance for the optimized geometry of the ground $^2B_{2g}$ state of the anion.

can bind the excess electron to form the shape resonance state; however, this state is not bound with respect to the neutral system, and therefore its energy is not shown in Fig. 4. In addition, the doubly charged anion is also stable relatively to the singly charged anion in this region because each of the LiCN units can bind one extra electron when they are separated by distances that are large enough to overcome their mutual Coulomb $1/r$ repulsion. The stability of the dianion vanishes when x approaches 10 Å.

In region B, the two LiCN molecules are close enough to C_2H_4 and to each other to interact. As a consequence, the orbital lobes localized on the LiCN units are perturbed by the exclusion and orthogonality interactions with the C_2H_4 (see Fig. 3b). The energies of two 2A_g and $^2B_{3u}$ anionic states are split in this region due to their differential interactions with the C_2H_4 (the g state becomes more stable than the u , see Fig. 4). In addition, in region B we found two more electronically stable excited states as $^2B_{2u}$ and $^2B_{1u}$ also become stable. These two states can be classified as the next (i.e.,

higher in energy than the ${}^2B_{2g}$ ground anionic state) stabilized shape resonance states whose energy decrease as x approaches ca. 3–4 Å (see Figs. 3b and 4). As far as the ${}^2B_{2g}$ resonance state is considered, it is not yet stable in the region B although its energy drops as x decreases. However, this state is still not shown in Fig. 4 in region B (for $x = 4\text{--}6.5$ Å) since it is higher in energy than the neutral species.

Region C denotes the equilibrium geometry of the ${}^2B_{2g}$ anion ($x = x_{eq} = 2.119$ Å and its vicinity (for $x < 4$ Å). In this region, the energy of the ${}^2B_{2g}$ anion drops very rapidly and this state becomes electronically stable when x decreases to achieve approximately 3.5 Å (see Fig. 3c). Moreover, the ${}^2B_{2g}$ becomes the ground anionic state in the vicinity of $x = x_{eq}$. In this region, the two higher stabilized shape resonance states (i.e., ${}^2B_{2u}$ and ${}^2B_{1u}$) and the trap-bound 2A_g state are still stable but their energies increase as x approaches its equilibrium value (see Fig. 4). In contrast, the trap-bound ${}^2B_{3u}$ anionic state becomes unstable in this region as its energy increases to exceed the energy of the neutral species (for this reason the SOMO for this state is not plotted in Fig. 3c).

3.4. Testing an ability of a simple stabilization method to reproduce the position of the shape resonance of ethylene anion

It has been recently proposed by the Simons group that a simple stabilization model could be applied to estimate the position of metastable anionic states [15]. Therefore, we decided to test its ability to reproduce the energy of the isolated shape resonance of $C_2H_4^-$ even though the position of this well-known resonance anion has already been determined and reported in the literature. In order to do this, we carried out a series of $C_2H_4^- \rightarrow C_2H_4$ electron binding energy calculations at a variety of levels ranging from Koopmans' theorem to the CCSD(T) with the aug-cc-pVDZ basis sets, as described in [15]. Because $C_2H_4^-$ is not electronically stable with respect to electron loss to generate C_2H_4 , it is not rigorously appropriate to compute its electronic energy by simply performing an SCF, MPn or CCSD(T) calculation. Specifically, if a

much more flexible atomic orbital basis set were used, the SCF process (carried out in the UHF manner) would produce an energy for $C_2H_4^-$ equal to that of C_2H_4 and a wave function equal to the UHF function of C_2H_4 multiplied by a free-electron function having zero kinetic energy. That is, the UHF process would undergo variational collapse. Because the SCF orbitals and energies form the starting point for the MPn and CCSD(T) calculations, this problem also plagues the latter methods. It is for this reason we must use the stabilization method, which allows us to compute the energy of $C_2H_4^-$ as if it were electronically stable and to subsequently extrapolate such data into the range of interest where $C_2H_4^-$ is unstable.

While doing so, we follow the procedure proposed by Nestmann and Peyerimhoff [16], and, more recently, by Simons et al. [15], and we first calculate the electron binding energy of $C_2H_4^-$ but using +0.5 a.u. point charge ($\Delta q = 0.5$ a.u.) added to each carbon nucleus charge (Z). This makes each of the two carbon centers to possess $Z = 6.5$ nuclear charge, and our system to be electronically stable since the total charge of this species is equal to zero. As noted above, we computed the binding energy at a variety of levels ranging from the KT to CCSD(T). Next, we calculated the binding energy at both carbon nuclear charges of $Z = 6.45, 6.40, 6.35, 6.30$, and 6.25 . We stopped the procedure for $Z = 6.25$ because for $Z < 6.25$ the $C_2H_4^-$ species becomes electronically unstable so the variational description of such a system would be incorrect. A plot of the resultant electron binding energy (D) vs. Δq is shown in Fig. 5 (where Δq represents the artificial charge added to *each* carbon nuclear charge). To make the Fig. 5 simpler, we plotted only the SCF and CCSD(T) electron binding energies while in Table 2 the corresponding results found at the KT, MP2, MP3, and MP4 levels are also gathered. Note that the data are linear when plotted as D vs. Δq (the linear regression correlation coefficient is 0.9998 when the CCSD(T) data points are approximated with the first-order polynomial, see Table 2). To obtain our estimate of the energy of $C_2H_4^-$ relative to C_2H_4 , we extrapolated the plots of D vs. Δq down to $\Delta q = 0$ (which corresponds to $Z = 6.0$).

It should be noted, as shown in Table 2, that we obtain a significant range of values for the instability energy of $C_2H_4^-$ at various levels of theory. Our KT result is -3.87 eV and our best prediction is -2.82 eV (at the CCSD(T) level, see Fig. 5 and Table 2). Since the experimental estimate of this energy is less negative (-1.8 eV) [2,3] we conclude that, unlike for other species (see [15]) the simple stabilization model we tested on the ethylene resonance anion does not provide satisfactory results in this case. We also verified that supplementing our aug-cc-pVDZ basis set with additional sets of

s, p, and d diffuse functions does not improve the estimate of the resonance position. However, it should be noted that our estimate of the resonance position becomes less and less negative when the level of calculations increase (see Table 2) so one may expect this value to approach the experimental -1.8 eV energy [2,3] when the higher-level calculations are performed (such as CCSDT or CCSDTQ).

We are aware of the fact that employing a conventional application of the stabilization method (see [17–19]) would provide much more accurate results, however, our goal was to test that simple model we used rather than perform standard stabilization calculations.

4. Summary

Our results indicate that it is possible to stabilize the $^2B_{2g}$ d-wave shape resonance of $C_2H_4^-$ in a molecular trap consisting of two LiCN molecules with their dipoles directed inward. In such a trap, the former resonance state becomes electronically stable and is the ground state of the anion at some geometries. For the $(NCLi \cdots C_2H_4 \cdots LiCN)^-$ anion the vertical electron detachment energy (for the $^2B_{2g}$ state) was found to be 2.97 eV. Three excited anionic states of this system are also electronically bound. One of them is the trap-bound 2A_g state (whose vertical electron binding energy is 0.86 eV), the $^2B_{2u}$ and $^2B_{1u}$ states, however, are stabilized shape resonance states of $C_2H_4^-$ and

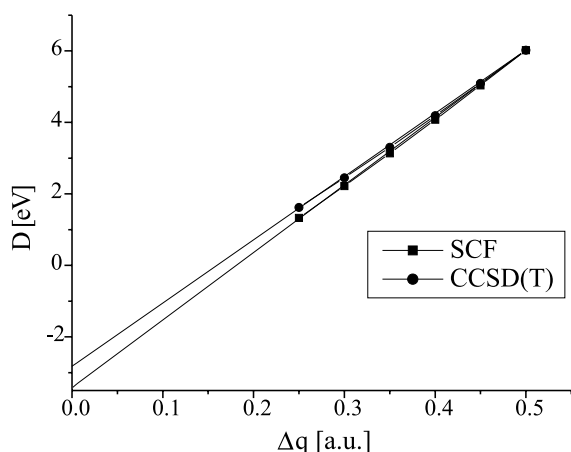


Fig. 5. Plot of the vertical electron detachment energy (D in eV) (computed at the SCF and CCSD(T) levels) for isolated ethylene anion vs. the magnitude of stabilizing point charges (Δq) added to each carbon nuclear charge. Linear fits to data are also shown and extrapolated.

Table 2

The vertical electron binding energies D (in eV) of the $C_2H_4^-$ anion calculated in the presence of the stabilizing point charges added to both carbon nuclear charges

	Stabilizing positive charge Δq (in a.u.) added to each carbon nuclear charge							Regression correlation coefficient (r)
	0.50	0.45	0.40	0.35	0.30	0.25	0.00 ^a (extrapolated value)	
D^{KT}	4.81	3.88	2.99	2.12	1.29	0.50	-3.87	0.99959
D^{SCF}	6.02	5.04	4.08	3.14	2.22	1.33	-3.41	0.99984
D^{MP2}	6.18	5.20	4.30	3.41	2.56	1.73	-2.76	0.99234
D^{MP3}	6.14	5.79	4.29	3.40	2.53	1.69	-3.08	0.99961
D^{MP4}	5.83	5.11	4.21	3.32	2.47	1.64	-2.62	0.99961
$D^{CCSD(T)}$	6.02	5.09	4.19	3.31	2.45	1.62	-2.82	0.99981

^a $\Delta q = 0.0$ a.u. means that there is no additional positive charge on carbon atoms thus it refers directly to the isolated ethylene molecule.

their vertical electron binding energies are 0.42 and 0.39 eV, respectively. We believe that the existence of the above two classes of bound anion states should be subjected to experimental (likely gas-phase spectroscopic) study.

Acknowledgements

This work was supported by the Polish State Committee for Scientific Research (KBN) Grant No. DS/8371-4-0137-2 to P. Skurski and the NSF Grant 9982420 to J. Simons. The computer time provided by the Academic Computer Center in Gdańsk (TASK) and the Center for High Performance Computing at the University of Utah is also gratefully acknowledged.

References

- [1] J. Simons, K.D. Jordan, *Chem. Rev.* 87 (1987) 535.
- [2] P.D. Burrow, K.D. Jordan, *Chem. Phys. Lett.* 36 (1975) 594.
- [3] I.C. Walker, A. Stamatovic, S.F. Wong, *J. Chem. Phys.* 69 (1978) 5532.
- [4] B.I. Schneider, T.N. Rescigno, B.H. Lengsfeld III, C.W. McCurdy, *Phys. Rev. Lett.* 66 (1991) 2728.
- [5] R.A. Donnelly, *J. Chem. Phys.* 84 (1986) 6200.
- [6] M.F. Falcetta, Y. Choi, K.D. Jordan, *J. Phys. Chem. A* 104 (2000) 9605.
- [7] P. Skurski, J. Simons, *J. Phys. Chem. A* 104 (2000) 712.
- [8] G.D. Purvis III, R.J. Bartlett, *J. Chem. Phys.* 76 (1982) 1910.
- [9] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, *J. Chem. Phys.* 96 (1992) 6796.
- [10] P. Skurski, M. Gutowski, J. Simons, *Int. J. Quantum Chem.* 80 (2000) 1024.
- [11] P. Skurski, M. Gutowski, J. Simons, *J. Chem. Phys.* 111 (1999) 9469.
- [12] M.J. Frisch et al., *GAUSSIAN 98*, Revision A.7, Gaussian, Inc., Pittsburgh, PA, 1998.
- [13] G. Schaftenaar, J.H. Noordik, *J. Comput. Aided Mol. Design* 14 (2000) 123.
- [14] T. Koopmans, *Physica (Utrecht)* 1 (1933) 104.
- [15] A. Whitehead, R. Barrios, J. Simons, *J. Chem. Phys.* 116 (2002) 2848.
- [16] B. Nestmann, S.D. Peyerimhoff, *J. Phys. B* 18 (1985) 615.
- [17] H.S. Taylor, *Adv. Chem. Phys.* 18 (1970) 91.
- [18] J. Simons, *J. Chem. Phys.* 75 (1981) 2465.
- [19] R.F. Frey, J. Simons, *J. Chem. Phys.* 84 (1986) 4462.