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International Journal of Mass Spectrometry 228 (2003) 341–348

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Electron affinity versus Coulomb repulsion—when dialkoxides become stable gas phase species

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Received 2 October 2002; accepted 18 March 2003

Abstract

The possible existence of α,ω-dialkoxide species (deprotonated terminal diols) in the gas phase is investigated by density functional and ab initio quantum methods. The calculations reveal that terminal aliphatic dialkoxides $^{-}O–(CH_2)_n–O^{-}$ are unstable with respect to electron loss up to a very high chain length ($n > 22$). Contrary to what one expects from a classical Coulomb distribution of point charges, charge conjugation through an alkene or alkyne chain stabilizes the two negative charges and $^{-}O–(C_2H_2)_m–O^{-}$ ($m \geq 10$) and $^{-}O–(C{\equiv}C)_k–O^{-}$ ($k \geq 6$) are predicted to be stable with respect to electron loss in the gas phase.

Keywords: Electron affinity; Coulomb repulsion; Dianions

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1. Introduction

It is now well established that atomic dianions (A^{2-}) do not exist. Even the system ($A^{-} + e^{-}$) can only exist in resonance states with lifetimes in the femto-second range [1] and the existence in intensive laser fields is being suspected [2]. Textbook examples like O^{2-} or S^{2-} represent a formal oxidation state only, but these species are not stable in the gas phase [3]. Also, diatomic dianions AB^{2-} remain elusive up to this date. Compounds like $C_2{}^{2-}$ or BN^{2-} are again only resonance states [4,5]. Even larger and well known inorganic species like $CO_3{}^{2-}$ or $PO_4{}^{3-}$ are unstable with respect to electron detachment [6–8]. In a more recent study, Sommerfeld showed that dianions of cyclooctatetraene and cyclobutadiene, which should have aromatic character, are unstable with respect to electron loss [9]. In contrast, the repulsive Coulomb barrier between the charged fragments $A^{q+} + B^{(n-q)+}$ can be overcome for the multiply charged diatomic cations AB^{n+} [10–13]. Recent examples are UF^{3+} [14], YHe^{3+} [15] or MHe^{2+} [16] (M = first row transition element). The first experimental evidence for a long-lived, doubly charged rare gas dimer, $HeAr^{2+}$, has been reported recently [17]. The smallest stable theoretically predicted dianions are $MX_3{}^{2-}$ with M = Li or Na, and X = F or Cl [18]. The smallest observed dianions are $MX_4{}^{2-}$ (M = Be, Mg or Ca, and X = F or Cl), as identified by mass spectroscopy [19], in line with earlier predictions by Cederbaum and co-workers [20,21]. The subject of dianions has very recently been reviewed by Dreuw and Cederbaum [22].

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1387-3806/$ – see front matter © 2003 Published by Elsevier Science B.V.
doi:10.1016/S1387-3806(03)00128-3

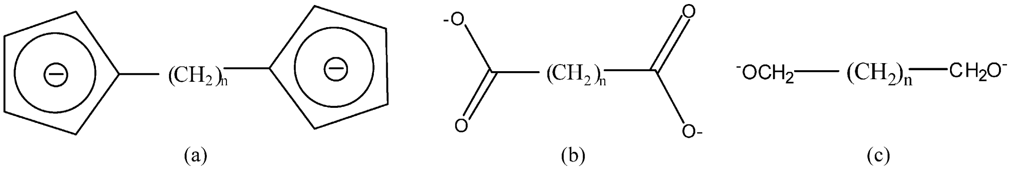

Fig. 1. Possible dianionic organic compounds in the gas phase.

A number of multiply charged anionic species of larger molecules have been reported previously [23–27]. In recent years, particular attention has been paid to the question if two-fold deprotonation of organic compounds can yield dianions which are stable with respect to electron loss or fragmentation [28,29].

Potential candidates are unbranched chainlike molecules with terminal functionalities and three examples are shown in Fig. 1. These molecules contain functional groups with a sizable electron affinity E_A. For C_5H_5, we have $E_A = 1.79\,eV$ [30]; for HCO_2, $E_A = 3.50\,eV$ [31]; and for CH_3O, $E_A = 1.57\,eV$ ([32], The electron affinity for a variety of molecules has been reviewed recently in [33]). Biscyclopentadienyl derivatives are used extensively in organometallic chemistry as chelating or bridging ligands [34], but the isolated dianion has not yet been observed in the gas phase. In line with that observation, ab initio and density functional calculations on fulvalenediyl^{2-}, $(C_5H_4)_2{}^{2-}$, carried out in our group [35] showed no bound states with respect to electron loss for this species not even for the perfluorinated derivative $(C_5F_4)_2{}^{2-}$. For the second example (Fig. 1b), aliphatic dicarboxylates, dianions up to a carbon chain of 10 atoms were observed experimentally by photoelectron spectroscopy [36]. Dialkoxides (Fig. 1c) also remain elusive up to now.

In a classical electrostatic model, a stable dianion can only exist if the Coulomb repulsion between the two isolated charges at a distance R is lower than the electron affinity of the monoanion. Using the electron affinity of the two isolated functional groups as an approximation one obtains (in a.u.)

$$E_A > R^{-1} \tag{1}$$

$R_c^{-1} = E_A$ is roughly the distance where the two potential curves, for $O^- + O$ and $O^- + O^-$, cross and autoionization can take place. According to this simple model, in the case of aliphatic dialkoxides (Fig. 1) the electron affinity of oxygen, $E_A = 1.461\,eV$ [37], would be sufficient to stabilize a dianion at a distance of $R(O–O) > 10\,Å$. This roughly corresponds to a chain length of $n = 7$ in $^-O–(CH_2)_n–O^-$. Early calculations by Nakatsuji and Nakai also suggest that the curve crossing between $O^- + O$ and $O^- + O^-$ occurs well beyond 5 Å [38]. In reality, however, the repulsive Coulomb interaction between the two negative charges is larger than predicted by classical electrostatics. In the case of the linear dianions $C_n{}^{2-}$, for example, the onset of stability occurs at $n = 8$ for even carbon chains which is equivalent to a distance of 9 Å between the terminal carbon atoms. However, a distance of only ca. 4.8 Å is predicted by Eq. (1), using the electron affinity of 2.97 eV for HCC [39] as reference.

In this paper, we try to establish the minimum aliphatic chain length necessary to stabilize terminal dialkoxides in the gas phase by using quantum theoretical methods. Furthermore, we investigate the influence of charge conjugation in unsaturated carbon chains. Therefore, we also included the fully unsaturated polycarbon chains $^-O–(C{\equiv}C)_n–O^-$, which resemble $(C{\equiv}C)_n{}^-$, and the polyacetylene derivates $^-O–(C_2H_2)_n–O^-$. It has been demonstrated before that charge conjugation over two carboxylate groups in $^-O_2C–(CH_2)_n–CO_2{}^-$ decreases the classical Coulomb repulsion substantially [40].

2. Computational details

Density functional (B3LYP) [41,42] calculations were performed for the fully extended conformations of unbranched $^-O–(CH_2)_n–O^-$, $^-O–(C_2H_2)_n–O^-$

Table 1
Vertical and adiabatic ionization potentials (in eV) for the negatively charged alkoxides, i.e., the deprotonated forms of ethanole, ethenole and ethynole

Molecule	Method	IP(vertical)	IP(adiabatic)	Experimental
$C_2H_5O^-$	DHDZ/B3LYP	1.07	0.84	1.71
	DHDZ/MP2	0.87	0.66	
	aug-ccPVDZ/B3LYP	1.82	1.65	
	aug-ccPVDZ/MP2	2.05	1.86	
$C_2H_3O^-$	DHDZ/B3LYP	1.55	1.44	1.82
	DHDZ/MP2	1.73	1.55	
	aug-ccPVDZ/B3LYP	1.94	1.83	
	aug-ccPVDZ/MP2	2.40	2.09	
C_2HO^-	DHDZ/B3LYP	2.20	2.13	2.35
	DHDZ/MP2	2.69	2.38	
	aug-ccPVDZ/B3LYP	2.38	2.30	
	aug-ccPVDZ/MP2	2.82	2.55	

Experimental values are from [45–47].

and $^-O–(C{\equiv}C)_n–O^-$ (n denotes the number of carbon atoms in the following) [43]. Initial geometry optimizations on the doubly negatively charged species were carried out at the B3LYP pseudopotential level using the Dunning–Huzinaga double-zeta basis sets (DHDZ) [44]. Even though these basis sets were not designed for negatively charged species, lacking additional diffuse *p*-functions for both the carbon and the oxygen atoms, the onset of stability for the doubly charged anions is already approximately correctly described at this level of theory. More importantly, the orbital coefficients of the few highest occupied molecular orbitals (HOMO) show no anomalously large values for the doubly charged species. To further test the performance of the chosen basis sets and method, we calculated the electron affinities for CH_3CH_2O, CH_2CHO and HC_2O in comparison to larger aug-ccPVDZ all-electron basis sets and MP2 calculations. The results are shown in Table 1 together with experimental reference values [45–47]. The relatively small DHDZ basis sets underestimate most electron affinities except for ethynole. With the larger aug-ccPVDZ all-electron basis sets B3LYP yields satisfying results compared to experiment, while MP2 overestimates the electron affinities.

Once the approximate carbon chain length for $^-O–(C{\equiv}C)_n–O^-$ was established, more accurate optimizations at the B3LYP and, if possible, MP2 level of theory were performed. Therefore, we used correlation consistent basis sets of Dunning (cc-pVDZ) with an additional diffuse (sp) function set for C and O, equivalent to aug-cc-pVDZ without the most diffuse *d*-function [48]. Additional more diffuse functions brought little change to the total electronic energy. The B3LYP functional has previously proven to give quite reliable results for doubly charged anionic species [26]. Due to the high symmetry of the fully unsaturated species $^-O–(C{\equiv}C)_n–O^-$ and their relatively small size we could calculate additional single point energies at the CCSD(T) level of theory [49]. For $^-O–(CH_2)_n–O^-$ and $^-O–(C_2H_2)_n–O^-$, however, calculations beyond the B3LYP(MP2) level using DHDZ basis sets became prohibitively computer time consuming. For $^-O–(C_2H_2)_n–O^-$ and $^-O–(C{\equiv}C)_n–O^-$, we also performed additional geometry optimizations for the corresponding singly charged open-shell system to obtain the adiabatic ionization potential of the doubly charged species. For the unsaturated radical $[O–(CH_2)_n–O]^-$, the SCF calculations became increasingly difficult to converge with increasing chain length n. A typical result of the unrestricted open-shell calculation was localization of the negative charge on one of the oxygen atoms. Hence, more accurate calculations would require a multi-reference treatment.

3. Results and discussion

Geometry optimization for the polycarbon dialkoxides gives a perfectly linear arrangement, and thus, a $^1\Sigma_g{}^+$ ground state for $^-$O–(C≡C)$_n$–O$^-$. Detachment of an electron from this linear chain yielding the corresponding singly charged radical occurs either from a π_u orbital in $^-$O–(C≡C)$_{2k+1}$–O$^-$ leading to a $^2\Pi_u$ electronic state, or from a π_g orbital in $^-$O–(C≡C)$_{2k}$–O$^-$ leading to a $^2\Pi_g$ state. This situation is closely related to the electron detachment of polycarbon chains [50]. However, the two Π-states are close in energy, e.g., for the O–(C≡C)$_5$–O$^-$ radical the $^2\Pi_u$ state is only 0.15 eV above the $^2\Pi_g$ state. Using the vertical ionization potentials as calculated at the DHDZ/B3LYP level of theory, we obtain the onset of a stable dianion for $^-$O–(C≡C)$_6$–O$^-$ (IP(vertical) $= 0.20$ eV) at an oxygen–oxygen distance of $r_{\mathrm{O-O}} = 16.80$ Å. The adiabatic ionization potential of 0.06 eV at the same theoretical level also predicts a stable dianion and changes only marginally to 0.07 eV when using the all-electron aug-ccPVDZ basis set. For the next higher species $^-$O–(C≡C)$_7$–O$^-$, we obtain an adiabatic IP of 0.50 eV with the aug-ccPVDZ basis set. For comparison, we also carried out MP2 calculations which give adiabatic ionization potentials of 0.34 eV for 10, 1.28 eV for 12, and 1.78 eV for 14 carbon atoms. Thus, at the MP2 level even $^-$O–(C≡C)$_5$–O$^-$ is stable with respect to electron detachment. However, single point coupled cluster calculations (CCSD(T)) at the MP2 optimized geometry give -0.29 eV for a chain of 10 and 0.31 eV for a chain of 12 carbon atoms. Obviously, the MP2 method overestimates the ionization energies for the dianions just like found in our test calculations (Table 1). In contrast, B3LYP appears to underestimate these values. For the polyacetylene species, the smallest stable dianion occurs at $^-$O–(C$_2$H$_2$)$_{10}$–O$^-$ and $r_{\mathrm{O-O}} = 26.15$ Å with a vertical IP of 0.14 eV. By optimizing the singly charged radical at the B3LYP level of theory, we obtain an adiabatic ionization potential of -0.01 eV, corresponding to an unstable dianion. Similarly, for $^-$O–(C$_2$H$_2$)$_{11}$–O$^-$, the vertical IP is slightly higher than the adiabatic value, i.e., 0.33 eV as compared to 0.18 eV. Hence, stability is achieved at 22 carbon atoms, but this result might change if better basis sets and more sophisticated ab initio methods were applied.

In line with the reduced charge and the reduced Coulomb repulsion, the distance between the oxygen atoms decreases when going from the doubly to the singly charged molecule. Interestingly, this effect is about constant for both unsaturated ions with $\Delta r_{\mathrm{O-O}}$ between 0.12 and 0.15 Å and $\Delta r_{\mathrm{O-O}}$ decreasing with increasing chain length as one expects. For example, for $^-$O–C≡C–O$^-$, we have $\Delta r_{\mathrm{O-O}} = 0.15$ Å and for $^-$O–(C≡C)$_6$–O$^-$, $\Delta r_{\mathrm{O-O}} = 0.13$ Å at the B3LYP level of theory. For $^-$O–(C≡C)$_6$–O about 40–50% of this reduction in the chain length is localized in the C–O bond distance, as one would expect. It is interesting, however, that while the C–C single bonds shrink by as much as 0.03 Å, the C≡C triple bonds expand by about 0.01 Å on removing an electron from the doubly charged species. A similar situation is found for the polyacetylene species. Addition of a negative charge weakens the single bond and strengthens multiple C–C bonds. This was also recently observed by Schaefer and co-workers for neutral and anionic polyacetylene chains [50]. In summary, we can conclude that stable dianions of the type $^-$O–(C$_2$H$_2$)$_n$–O$^-$ exist for $n \approx 11$, and of the type $^-$O–(C≡C)$_n$–O$^-$ for $n \approx 6$. The exact number varies slightly with the theoretical method and the basis set applied.

In distinct contrast, for the saturated aliphatic chains $^-$O–(CH$_2$)$_n$–O$^-$, the second negative charge would be unstable even at a chain length of 22 carbon atoms and a distance $r_{\mathrm{O-O}} = 29.57$ Å. Fig. 2 shows the vertical ionization energy of the dianions as a function of chain length, calculated from the energy differences between the singly and doubly charged species. Even though positive values of ΔE have to be taken with great care,[1] the qualitative difference between the alkane chains and the unsaturated species is quite obvious. While the IPs of the latter drop sharply to

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[1] A complete basis set would lead to values of $\Delta E = 0$ in our calculations, and the observed repulsive Coulomb barrier between an electron and a negatively charged molecule is only described correctly by scattering theory.

intersect with the zero line, where the onset of stability for the dianion occurs, only a very slow, almost asymptotic convergence can be seen for the saturated species. This suggests that for an alkane chain the two negatively charged oxygen atoms have to be separated by far more than 30 Å in order to prevent loss of an electron. Already for 22 carbon atoms, the calculations were rather computer time consuming and the SCF convergence for the radical anion became very slow with increasing chain length. Addition of more diffuse *p*-functions for oxygen only lowered the ΔE value to 0.013 a.u. for $n = 22$, but still would not stabilize the dianion. Hence, we did not consider larger chain lengths.

How can we explain that a charge separation of 30 Å is not sufficient to overcome the Coulomb repulsion? Fig. 3 shows the structures of the stable species $^{-}O–(C{\equiv}C)_6–O^{-}$ and $^{-}O–(C_2H_2)_{10}–O^{-}$ compared to the unstable $^{-}O–(CH_2)_{22}–O^{-}$ together with their Mulliken atomic charges for the carbon and oxygen atoms. Due to charge conjugation the negative charge

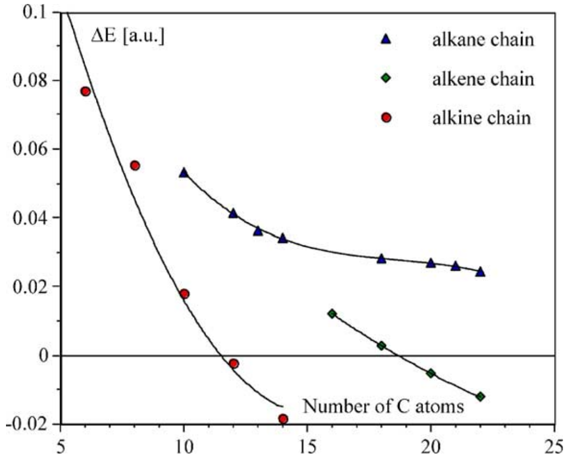
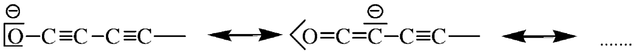


Fig. 2. Differences in energies between the doubly and singly charged species at the DHDZ/B3LYP level of theory (calculated at the optimized geometry of the dianion for the alkene and alkane species). A positive value indicates instability of the dianion with respect to electron loss.

on the oxygen atoms is significantly reduced in the unsaturated species as compared to the alkane dialkoxide. In addition, the carbon atoms of the alkane chain bear nearly equally negative charges. In contrast, in the alkene and alkyne species the carbon charges alternate with every second carbon atom carrying a larger charge. For the alkyne species the terminal carbon atoms even have a slightly positive charge. This charge alternation can be explained by charge conjugation using mesomeric structures, e.g., for the alkyne species



$$\overset{\ominus}{\underline{|O}}-C\equiv C-C\equiv C- \longleftrightarrow \langle O=C=\overset{\ominus}{\overline{C}}-C\equiv C- \longleftrightarrow \ldots\ldots$$

Fig. 4 shows orbital plots for the HOMO of each of the dialkoxides. Evidently, the negative charges are localized at the oxygen atoms in the alkane compound and more delocalized for the unsaturated species. Our results indicate that distributing the charge over the chain of carbon atoms reduces the Coulomb repulsion between the two negative charges and leads to their stabilization. In contrast, Wang and co-workers suggested that charge delocalization can *increase* Coulomb repulsion between terminal $–CO_2^{-}$ units. So, it came as a surprise that $^{-}O_2C–C{\equiv}C–CO_2^{-}$ could be observed by photoelectron spectroscopy in contrast to $^{-}O_2C–CH_2–CH_2–CO_2^{-}$ [36].

The question arises whether charge delocalization increases or decreases the Coulomb barrier. If we consider equidistant point charges distributed over a certain length R such that the total charge Z is conserved (see Fig. 5), the classical Coulomb repulsion dependent on the number of point charges n can be expressed by the formula (in a.u.),

$$V^{(n)}_{\text{linear}}(R)=\frac{Z^2}{R}f_n=\frac{Z^2}{R}\,\frac{n-1}{n^2}\sum_{k=1}^{n-1}\frac{n-k}{k} \qquad (2)$$

Eq. (2) follows a sum over $1/k$ behavior and we obtain $\lim_{n\to\infty}V^{(n)}_{\text{linear}}(R)=\infty$, that is if the charge is completely delocalized. The factor f_n, for up to $n = 250$, is depicted in Fig. 5 and shows that simply distributing charges over different centers should increase the Coulomb repulsion. This might explain

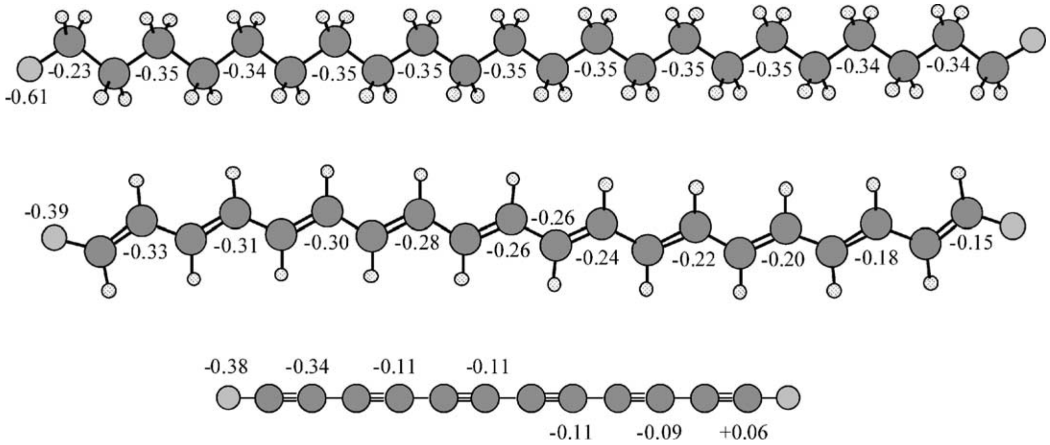


Fig. 3. Optimized structures and corresponding Mulliken charges for $^{-}$O–(CH$_2$)$_{22}$–O^{-}, $^{-}$O–(HC=CH)$_{10}$–O^{-} and $^{-}$O–(C≡C)$_6$–O^{-}.

why $^{-}$O–(CH$_2$)$_n$–O^{-} species are unstable with respect to electron loss up to a very high chain number. The larger negative charges at each carbon atom in the alkane chain contribute more to the Coulomb repulsion than the alternating charges in the unsaturated chains. In addition, each atomic or molecular subunit in the chain can be ascribed an electron affinity. This electron affinity counteracts the Coulomb repulsion and it is larger for sp-hybridized carbon atoms (–C≡C–) than for to sp^3-hybridized carbons in the alkane chains. Both effects increase the stability of the dianions leading to shorter O–O bond lengths for the onset of stability in the corresponding doubly negatively charged alkene and alkyne species. The same arguments can be used to explain that the deprotonated species of acetylene dicarboxylic acid, $^{-}$O$_2$C–C≡C–CO$_2$$^{-}$, is a

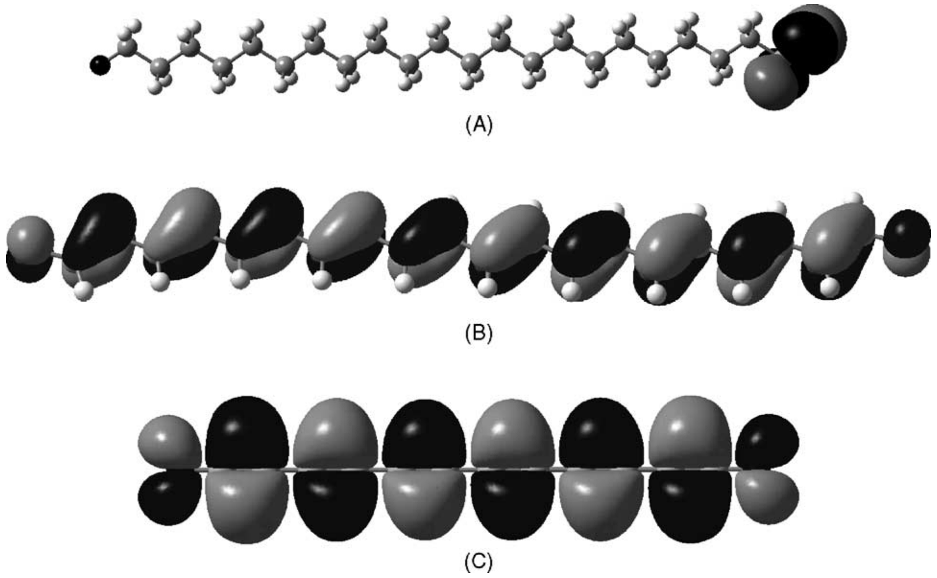


Fig. 4. Highest occupied molecular orbitals (HOMO) for (A) $^{-}$O–(CH$_2$)$_{22}$–O^{-}, (B) $^{-}$O–(HC=CH)$_{10}$–O^{-} and (C) $^{-}$O–(C≡C)$_6$–O^{-}.

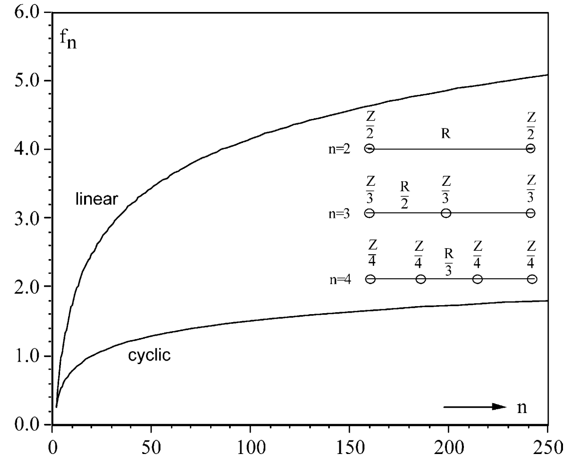


Fig. 5. Coefficient f_n for the classical Coulomb interaction of charges arranged equidistantly on a line (linear or cyclic) of length R (see Eqs. (2) and (3)). A schematic representation of the point charges on a one-dimensional line is also shown.

stable gas phase species (which is confirmed by our MP2 aug-ccPVDZ calculations). Moreover, in this species the charge is also conjugated over the carboxyl groups perpendicular to the axis going through the four carbon atoms, leading to a two-dimensional charge distribution. In a similar way as above, we can distribute the charges in two dimensions, for example on a circle of diameter R (in a.u.),

$$V^{(n)}_{\text{circle}}(R) = \frac{Z^2}{R} f_n = \frac{Z^2}{R}\frac{1}{n^2}\sum_{k=1}^{n-1}\frac{n-k}{\sin(k\pi/n)} \qquad (3)$$

This diameter was chosen because the same Coulomb repulsion is obtained for both equations in the case of $n = 2$. The factor f_n, for up to $n = 250$, for both the linear and cyclic case is depicted in Fig. 5. This demonstrates that charge distribution over more than one dimension helps to decrease the Coulomb repulsion. Charge distribution over three-dimensional space will further reduce the Coulomb repulsion as nicely demonstrated by Weikert and Cederbaum for BeF_4^{2-} or MgF_4^{2-} [21]. However, as mentioned at the beginning, the dianions of both cyclobutadiene and cyclooctatetraene are unstable with respect to electron loss [9]. Here, the charges are localized in a relatively small space.

Acknowledgements

We are grateful to the Alexander von Humboldt Foundation for financial support. Two of the authors enjoyed extensive collaborations with Prof. Helmut Schwarz over many years and wish him a happy birthday.

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