



## Structure of the doubly charged $C_5O_2^{2-}$ anion

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### ABSTRACT

The dianion  $C_5O_2^{2-}$  was recently observed mass spectrometrically as a half-integer peak at Arizona State University. Here the structure of this small gas-phase dianion is studied. Six  $C_5O_2^{2-}$  isomers are investigated with regard to their stability in the gas phase. Only one isomer is found to be stable with respect to electron autodetachment, yet, three other isomers are close to electronic stability, and examination of the repulsive Coulomb barriers shows that long ( $\gg 10^{-5}$  s) autodetachment lifetimes can be expected. Implications for larger doubly charged clusters are briefly discussed.

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### 1. Introduction

All doubly charged negative ions discussed in freshman chemistry, such as  $CO_3^{2-}$ ,  $SO_3^{2-}$ , or  $SO_4^{2-}$ , cannot be observed in a mass spectrometer. While these dianions are perfectly stable within solids or polar liquids, in the gas phase they are unstable with respect to electron autodetachment, and show autodetachment lifetimes orders of magnitude shorter than the  $\approx 10 \mu\text{s}$  required for mass spectrometric detection [1–3]. Nonetheless, many small dianions have been observed mass spectrometrically (see [1,4–8] for review articles and e.g., [9–12] for some recent work). These small gas-phase dianions are in turn more often than not unknown in solution chemistry, and show unusual structures optimized for accommodating two excess electrons in a very small volume (see e.g., [11,13,14]). A second unusual property of gas-phase dianions is that even metastable species can exhibit very substantial lifetimes due to the repulsive Coulomb barriers [15–17] in both typical decay channels, dissociation into two monoanions [14,15,18] and dissociation into a monoanion and an electron [2,6,16,17,19]. Thus, living very much on the edge, small dianions offer a unique perspective on molecular properties and test bonding concepts established for less extreme cases.

The current study focuses on  $C_5O_2^{2-}$ . As briefly mentioned in footnote 21c of Ref. [10] this dianion was detected by Klaus Franzreb and Peter Williams at Arizona State University, and we are very grateful for permission to show their experimental data in Fig. 1. The half-integer mass-over-charge peak at 48.5 amu/au has been

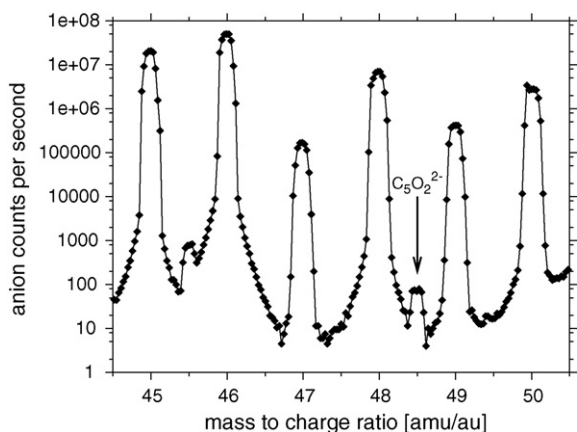
assigned to  $^{13}C_5^{16}O_2^{2-}$ , and clearly demonstrates that the  $C_5O_2^{2-}$  dianion has a lifetime in excess of  $\approx 10 \mu\text{s}$ . Here we are concerned with finding the geometrical structure of  $C_5O_2^{2-}$ . Experience from earlier studies on the closely related systems  $C_n^{2-}$  [13,20–22] and  $OC_n^{2-}$  [23] shows that the structures of these small, covalently bound dianions do not follow simple patterns, but that each species needs to be considered individually. Thus, more than 15 possible isomers of  $C_5O_2^{2-}$  have been examined, most of which are however highly unstable with respect to electron autodetachment. In the main body of the paper the six most promising isomers are described in detail with particular emphasis on the vertical detachment energies. One isomer is predicted to be stable with respect to electron autodetachment, and three isomers are predicted to be unstable yet long-lived.

### 2. Computational details

All  $C_5O_2^{2-}$  isomers considered here have closed-shell electronic ground states. As a first step each isomer was optimized using the Hartree Fock self-consistent field (SCF) method and Pople's 6-31+G\* split valence basis set [24] followed by computing harmonic frequencies to identify the stationary points as minima. At this stage the isomers clearly unstable to electron autodetachment at the level of Koopmans's Theorem (KT), i.e., those isomers whose highest occupied molecular orbital (HOMO) did show large positive energies, were discarded. The other isomers were re-optimized using second-order Møller-Plesset perturbation theory (MP2) and Dunning's polarized valence triple- $\zeta$  basis [25,26] augmented with diffuse s and p-type functions (the exponents of the diffuse functions were chosen by dividing the corresponding smallest exponents in the valence basis set by 3.5). This basis set

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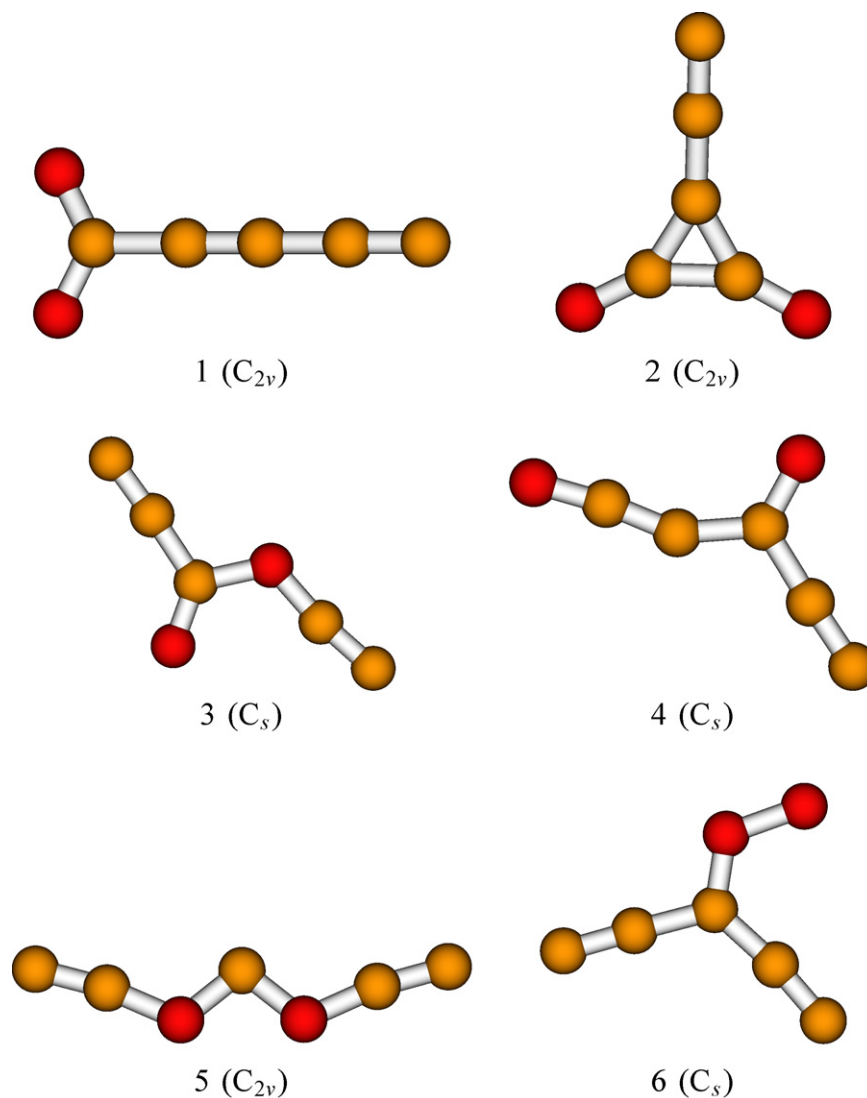


**Fig. 1.** Experimental data provided from courtesy of Klaus Franzreb and Peter Williams (Arizona State University, 2006, c.f. footnote 21c of [10]). Shown is the negative ion mass spectrum resulting from  $\text{Cs}^+$  bombardment of  $^{13}\text{C}$ -enriched ( $\approx 96\%$ ) graphite powder under oxygen flooding. Dianions observed as half integer mass peaks are  $^{13}\text{C}_7^{2-}$  at  $m/z = 45.5$ , and  $^{16}\text{O}_2^{13}\text{C}_5^{2-}$  at  $m/z = 48.5$ .

will be denoted TZVPD. At the MP2 geometries the vertical electron detachment energy (VDE) was computed using two *direct* methods, the outer-valence Green's function (OVGF) method [27] and the equation-of-motion coupled-cluster with single and double substitution (EOM-CCSD) method [28], as well as indirect, so-called  $\Delta$ -methods where the energy is computed as the difference between the total energies of the dianion and monoanion. For the  $\Delta$ -calculations, the SCF, MP2, CCSD, and CCSD with non-iterative triple substitutions (CCSD(T)) methods were employed. (Core electrons were not frozen in any of the calculations.) Geometry optimization and OVGF calculations were performed with the GAMESS-UK program [29], and for all coupled-cluster calculations the Mainz-Austin-Budapest version of the Aces II program [30] was used.

### 3. *Ab initio* results

It is well known that carbon cluster dianions as well as carbon–oxygen cluster dianions show a wide range of structural motifs [13,20–23]. Earlier work (see [13] for a comprehensive discussion of the structural motifs of carbon cluster dianions) established a number of guidelines for the search of stable structures of



**Fig. 2.** Structures and symmetries of the six  $\text{C}_5\text{O}_2^{2-}$  isomers considered in the text.

**Table 1**  
Relative energies (in eV) of the six  $C_5O_2^{2-}$  isomers shown in Fig. 2

Isomer	SCF	MP2	CCSD	CCSD(T)
1	0	0	0	0
2	1.14	1.10	1.13	1.12
3	2.49	2.68	2.47	2.48
4	0.92	0.81	0.87	0.82
5	5.37	5.89	5.37	5.41
6	5.86	6.05	5.68	5.56

All computations were performed using the TZVPD basis set and the MP2/TZVPD optimized geometries.

dianions: first, for these covalently bound species, decay into two monoanions can be ignored. Second, for electronic stability any small dianion needs at least two substructures with a large local electron affinity. With carbon and oxygen atoms available promising subgroups are a terminal O atom (EA of  $CH_3O$  is 1.570 eV), a terminal  $C_2$  group (EA of HCC is 2.969 eV), and a carboxyl group (EA of HCOO is 3.498 eV) [31]. Finally, these substructures need to be connected by a scaffold such that a closed-shell electronic structure results for the whole dianion. For  $C_5O_2^{2-}$ , we considered initially 15 different  $C_5O_2^{2-}$  isomers, however, here we report only results for the six most promising isomers which are shown in Fig. 2.

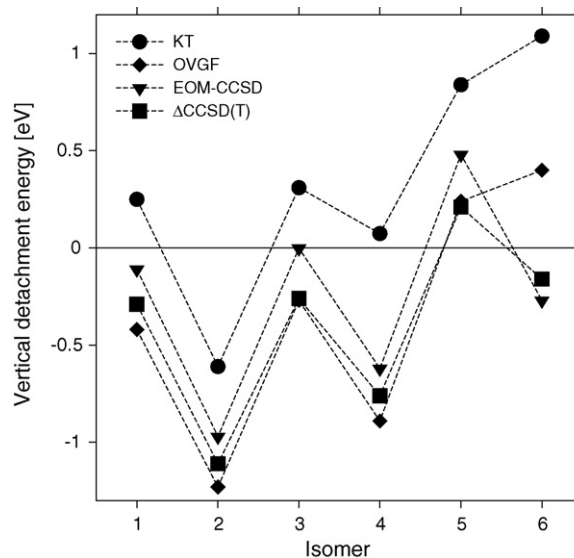
All six  $C_5O_2^{2-}$  isomers have closed-shell electronic ground states and show either  $C_{2v}$  or  $C_s$  symmetry. Isomer 1 can be understood as the dianion of 2,4-pentadiynoic acid, and from a total energy point of view, it is by far the most stable structure. Relative energies of the other isomers computed using SCF, MP2, and coupled-cluster methods are collected in Table 1. The results depend somewhat on the theoretical level, however, the energy differences between the individual isomers are much larger than the differences between the results obtained using different theoretical methods. Particularly high in total energy are the carbene 5 and the peroxide 6 (Table 1).

Yet, the most critical property for the stability of a covalently bound dianion in the gas phase is not its total energy but its VDE. Unfortunately, simple electrostatic considerations, which work well for highly ionic compounds [15], strongly overestimate the electronic stability of these covalently bound systems [32], and consequently, the VDEs of all isomers have been computed using a variety of *ab initio* methods (Table 2). Results obtained using the computationally least expensive method, KT, and the most accurate methods, OVGf, EOM-CCSD, and  $\Delta$ CCSD(T), are displayed in Fig. 3. Regarding the different methods, in the first place, KT clearly overestimates the VDE of all isomers by several tenths of an eV (Fig. 3), and KT can therefore be used as a screening tool to identify promising isomers. In the second place, for isomers 1–5 the three presumably most accurate methods, OVGf, EOM-CCSD, and  $\Delta$ CCSD(T), agree well with each other (Fig. 3), and suggest that (1) isomers 2 and 4 are clearly unstable with respect to electron loss, (2) isomers 1 and 3 are unstable, but so close to electronic stability that a substantial lifetime is probable (see below), and (3) isomer 5 is

**Table 2**  
Vertical detachment energy (in eV) of the six  $C_5O_2^{2-}$  isomers shown in Fig. 2

Isomer	$\Delta$ SCF	$\Delta$ MP2	$\Delta$ CCSD(T)	$\Delta$ CCSD	KT	EOM-CCSD	OVGF
1	-1.21	0.71	-0.30	-0.29	0.25	-0.11	-0.42
2	-1.92	-0.59	-1.17	-1.11	-0.61	-0.97	-1.23
3	-1.36	0.083	-0.35	-0.26	0.31	-0.0016	-0.27
4	-1.54	-0.13	-0.78	-0.76	0.074	-0.62	-0.89
5	-0.17	0.43	0.29	0.21	0.84	0.48	0.24
6	-0.63	1.40	0.37	-0.16	1.09	-0.27	0.40

A negative detachment energy implies that the dianion is unstable with respect to electron loss. All computations were performed using the TZVPD basis set and the MP2/TZVPD optimized geometries.

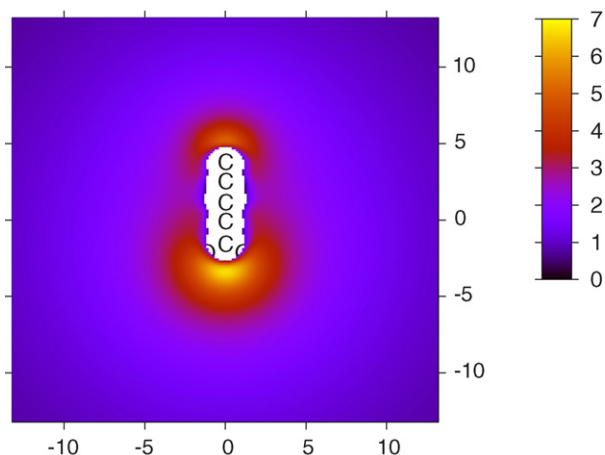


**Fig. 3.** Vertical detachment energies of the six  $C_5O_2^{2-}$  isomers shown in Fig. 2. Displayed are results obtained using Koopman's theorem (circles), the outer-valence Green's function method (diamonds), the equation-of-motion coupled-cluster method (triangles), and the single-double substitutions coupled cluster with perturbative triples method (squares), with the latter method being presumably most accurate.

stable to autodetachment. For isomer 6 the case is not so clearcut, since the OVGf value of the VDE deviates from the EOM-CC and  $\Delta$ CCSD(T) results (Fig. 3). Based on the coupled-cluster values, we group isomer 6 with the almost stable isomers 1 and 3.

While a positive VDE suggests at least metastability, in principle, electron detachment can still be fast if the potential energy surface of the monoanion crosses the surface of the dianion close to the Franck-Condon region. For closed-shell covalently bound system this type of dynamic electron loss is improbable since the excess electrons typically occupy orbitals whose occupation has a relatively small influence on the equilibrium geometry which implies that the surface of the anion cannot have a large gradient at the geometry of the dianion. For isomer 1 we examined the possibility of dynamic electron loss by computing the adiabatic electron affinity, and found indeed that the geometry of the anion is very similar to that of the dianion, and that the adiabatic electron affinity is only slight (0.1 eV) more negative than the VDE (anion energy computed at the CCSD(T) level after EOM-CCSD geometry optimization). Thus, the VDE of these covalently bound dianions is expected to be sufficient to judge the overall stability with respect to electron detachment.

Considering both stability criteria, relative energy and VDE, it is obvious that the VDE of an isomer does not correlate with its relative stability. Isomer 1 has by far the lowest total energy, whereas the electronically most stable isomer 5 is more than 5 eV above 1. In this situation a rough idea of the autodetachment lifetime of dianion 1 is needed. To this end a local approximation of the repulsive Coulomb barrier was computed by using the frozen orbitals of the dianion to represent the charge distribution of the monoanion. This method is described in detail in Ref. [16], and is referred to as dianion frozen orbital static approximation (DFOSA). Fig. 4 shows the DFOSA Coulomb barrier in the molecular plane. The height of the barrier is between 4 and 7 eV at the ends of the molecule, but only about 2.5 eV at the middle of the carbon chain (Fig. 4). A very conservative estimate for the tunneling lifetime through this three-dimensional barrier was obtained by considering only a single tunneling path through the barrier at the position where the height is minimal and so is consequently its width. For this



**Fig. 4.** Repulsive Coulomb barrier of  $C_5O_2^{2-}$  isomer **1**. Displayed is the DFOSA potential of **1** within the molecular plane. The distance unit is Ångström and the unit for the potential (color coded) is eV.

one-dimensional path the tunneling time can be computed using the well-known semiclassical approximation

$$\tau = \frac{1}{P_T \times \nu} \quad (3.1)$$

where  $P_T$  is the tunneling probability for a one-dimensional barrier, and  $\nu$  is the frequency with which the electron impinges on the barrier. The tunneling probability was computed by integrating the DFOSA barrier along the tunneling path described above. In this way the average height of the three-dimensional barrier is strongly underestimated, and the tunneling probability will be far overestimated. The resulting  $P_T$  is of course strongly energy dependent: at an energy of 0.3 eV above the anion, as suggested by the coupled-cluster methods (see Table 2),  $P_T$  is  $2 \times 10^{-14}$ , while at 0.2 eV it is  $10^{-19}$ , and at 0.4 eV it is close to  $10^{-11}$ . When then the impinging frequency  $\nu$  is taken as  $0.2 \text{ fs}^{-1}$  (estimated from an electron with a kinetic energy of 10 eV crossing the molecular system), the resulting tunneling lifetime  $\tau$  is  $10^{-3} \text{ s}$  at 0.3 eV, 100 s at 0.2 eV, and  $10^{-5} \text{ s}$  at 0.4 eV above the anion.

#### 4. Conclusions

The *ab initio* results for six  $C_5O_2^{2-}$  isomers show that four of these isomers may contribute to the 48.5 amu/au peak in the observed mass spectra. Only one isomer (**5**) is stable with respect to vertical electron autodetachment, but there are three other isomers **1**, **3**, and **6**, that are sufficiently close to electronic stability to suggest substantial lifetimes on the mass spectrometric timescale. For isomer **1** a highly conservative estimate of the electron autodetachment lifetime yielded  $10^{-3} \text{ s}$ , and it is likely that similar calculations for isomers **3** and **6** would yield lifetimes in the same order of magnitude. In view of these long lifetimes, we predict that the observed peak corresponds to a mixture of **1**, **3**, **5**, and **6**, and that **1** dominates the population owing to its low total energy. This prediction can be tested experimentally by trapping enough dianions for photo-detachment spectroscopy. An alternative is to prepare the dianions selectively in solution and to use electro-spray ionization to study each species separately. In particular **1**, **3**, and **4** can be prepared by deprotonating fairly standard organic compounds.

Finally, let us mention that the dianion  $C_7O_2^{2-}$  that also has been detected by Franzreb and Williams [33] can be explained in terms

of the same type of structures. As for  $C_5O_2^{2-}$ , there will be several electronically stable isomers that can be derived from isomers **1** to **6** by inserting  $C_2$  groups into the structures. For example adding another  $C_2$  group to the chain of **1** yields the dianion associated with 2,4,6-heptatriynoic acid ( $^-C_2-C_2-C_2-COO^-$ ) which on the basis of our results for  $C_5O_2^{2-}$  is predicted to be the most stable  $C_7O_2^{2-}$  isomer. A EOM-CCSD calculation for this species predicts a VDE 0.75 eV, i.e., a stabilization of more than 1 eV relative to **1** making this dianion a strong candidate for dominating the observed  $C_7O_2^{2-}$  population.

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We are grateful for permission to show Klaus Franzreb's and Peter Williams's experimental data in Fig. 1. Valuable discussions with Debra Dolliver and her students are gratefully acknowledged.

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