PERKIN 2

The unusual neutral OCOCO and possible charged analogues. A theoretical investigation

Suresh Dua, Salvatore Peppe and John H. Bowie

Department of Chemistry, The University of Adelaide, South Australia, 5005

Received (in Cambridge, UK) 17th September 2001, Accepted 12th October 2001
First published as an Advance Article on the web 9th November 2001

Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory indicate that singlet neutral OCOCO is unstable with respect to dissociation to CO_2 and CO. In contrast, triplet OCOCO is a stable species provided it can be formed with excess energy of less than 41 kJ mol^{-1} [the process ^{3}OCOCO ⟶ ^{1}CO + $^3CO_2$ is endothermic by only 9 kJ mol^{-1}, but the barrier for this process is 41 kJ mol^{-1}]. Triplet OCOCO is not accessible by one-electron oxidation from [OCOCO]$-^{\bullet}$ or one-electron reduction from [OCOCO]$^{+\bullet}$ because neither of these charged species is stable at the level of theory used for these calculations. A report by Cooper and Compton indicates that dissociative electron capture by maleic anhydride results in loss of the elements of C_2H_2 yielding an anion $C_2O_3^{-\bullet}$. Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory suggests that the ion radical $C_2O_3^{-\bullet}$ may be the stable species $[O_2C\text{–}CO]^{-\bullet}$ provided that the dissociating maleic anhydride radical anion has excess energy of at least 260 kJ mol^{-1}.

Introduction

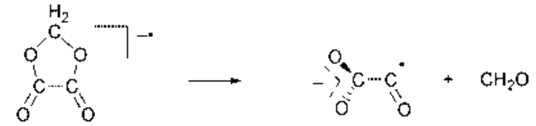
Carbon monoxide and carbon dioxide cluster ions are important in atmospheric chemistry. Carbon dioxide cluster neutrals and ions have been studied extensively in the gas phase: these studies include their photoelectron,[1–6] vibrational,[7–10] electron spin resonance,[11–13] and infrared[14,15] spectra. The van der Waals complex between carbon dioxide and carbon monoxide was first formed in a pulsed molecular beam using diode laser spectroscopy combined with Fourier-transform microwave spectroscopy.[16] This CO_2–CO complex has since been studied extensively both experimentally and theoretically.[17–21] The complex is proposed to have the T-shaped geometry shown in **1**,[22] but infrared spectroscopy suggests that there may be two stable conformers of the complex.[20,21]

We have calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory that there are six C_2O_3 neutral structures which occupy minima on the C_2O_3 potential surface.[23] Structures which contain O–O bonds have not been considered in either the earlier report[23] or this paper. The six stable structures are shown (with relative energies in kJ mol^{-1}) in Scheme 1.

Scheme 1

The singlet state of the van der Waals complex **1** is the structure most negative in energy, but it decomposes to CO_2 and CO when the excess energy is only 6 kJ mol^{-1}. The other structures are all covalently bound. Only bond connectivities are shown in Scheme 1, full geometric data have been reported previously.[23]

We have used neutralisation/reionisation of negative ions ($^-$NR$^+$)[24] in a mass spectrometer to investigate the formation and characterisation of short-lived neutrals in the gas phase. The anion radical corresponding to neutral **2** was synthesised by electron capture of 1,3-dioxolane-2,5-dione, followed by a retro cleavage as shown in eqn. (1). One-electron oxidation by



(1)

a Franck–Condon process of this anion radical should produce the triplet neutral **2**, but ionisation of the neutrals formed from $[O_2CCO]^{-\bullet}$ does not give a detectable parent cation $[O_2CCO]^{+\bullet}$, and we concluded that any transient triplet neutral O_2CCO, if formed during this experiment, must have a lifetime less than 10^{-6} s.[23] Another conclusion reached in this study was that none of the other neutrals shown in Scheme 1 were accessible following one-electron oxidation of the radical anion $[O_2CCO]^{-\bullet}$. This raises an interesting question. Could any of the other neutrals shown in Scheme 1 be synthesised in a mass spectrometer by way of a suitable neutralisation–ionisation experiment? Although the syntheses of charged precursors of neutral **4**† and **5** seem unlikely processes, the formation of a neutral corresponding to triplet OCOCO does, at first sight, appear to be worth consideration.

This paper investigates the triplet neutral system OCOCO and possible precursors, either positively or negatively charged.

Results and discussion

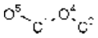
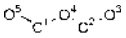
Data concerning the geometry of triplet OCOCO [calculated at the B3LYP/6-31+G(d) level of theory] and energy [at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level] are listed in Table 1. The end and central C–O bond lengths are 1.18 and 1.39 Å, respectively, with OCO and COC angles being 124.3

---

† Singlet **4** is only 'stable' using the definition of theoretical stability: *i.e.* the occupation of a potential minimum on the neutral potential surface. Increasing the bond length of either C–C or C–O bonds of the ring of **4** by only 0.1 Å results in immediate decomposition to CO_2 and CO in a process exothermic by 250 kJ mol^{-1} at the level of theory used in this study.

DOI: 10.1039/b108425a

Table 1

		 TS
State	$^3A'$	$^3A'$
Symmetry	C_s	C_s
Energy (Hartree)[a]	−301.08681	−301.07120
Rel. energy (kJ mol^{-1})	0.00	40.93
Adiabatic electron affinity/eV	0.00	0.42
Dipole moment/Debye [a]	0.65	2.11
Bond length/Å[b] or angle/°[b]		
C^1C^2	2.35	2.74
C^2O^3	1.18	1.14
C^1O^4	1.38	1.31
C^2O^4	1.38	1.95
C^1O^5	1.18	1.20
$C^1C^2O^3$	156.4	147.4
$C^2C^1O^4$	31.9	41.2
$C^2C^1O^5$	156.4	163.8
$O^4C^1O^5$	124.4	122.6
$O^3C^2C^1O4$	0.0	0.0
$O^3C^2C^1O^5$	0.0	0.0
Total atomic charges		
C^1	0.444	0.387
C^2	0.444	0.280
O^3	−0.300	−0.144
O^4	−0.289	−0.240
O^5	−0.300	−0.283
Sum of Mulliken charges	0.000	0.000

[a] CCSD(T)/aug-cc-pVDZ level of theory including zero point energy (calculated from vibrational frequencies at the B3LYP/6-31+G(*d*) level of theory and scaled by 0.9804.) [b] Geometries at B3LYP/6-31+G(d) level of theory.

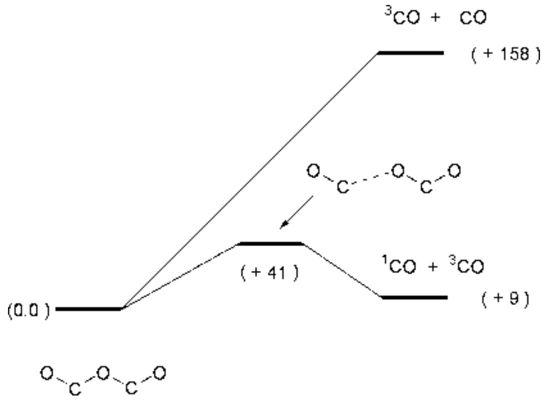


Fig. 1 Decompositions of triplet OCOCO. CCSD(T)/aug-cc-pVDZ// B3LYP/6-31+G(d) level of theory. Relative energies in kJ mol^{-1}. Geometries and energies of triplet OCOCO and transition state shown in this figure are listed in Table 1.

and 111.4°, respectively. This is consistent with the end CO bonds being double bonds and the two central bonds being single bonds. Thus the structure of triplet OCOCO may be represented as the classical valence bond structure O=C–O–C=O. The dipole moment of triplet OCOCO is calculated to be 1.35 D.

Of the possible decomposition pathways of triplet OCOCO, those forming CO_2 and CO are the most likely: these processes are depicted [energies determined using the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory] in Fig. 1. Decomposition to ^3CO plus $^1CO_2$ is endothermic by 158 kJ mol^{-1}. The alternative decomposition to ^1CO and $^3CO_2$ is endothermic by only 9 kJ mol^{-1}, but this dissociation process has a barrier of 41 kJ mol^{-1}. Details of the transition state for this process are given in Table 1. We conclude from these data that triplet OCOCO should, in principle, be accessible in a neutralisation–reionisation experiment from either a negative or positive ion precursor provided any excess energy of the neutral is less than 41 kJ mol^{-1}.

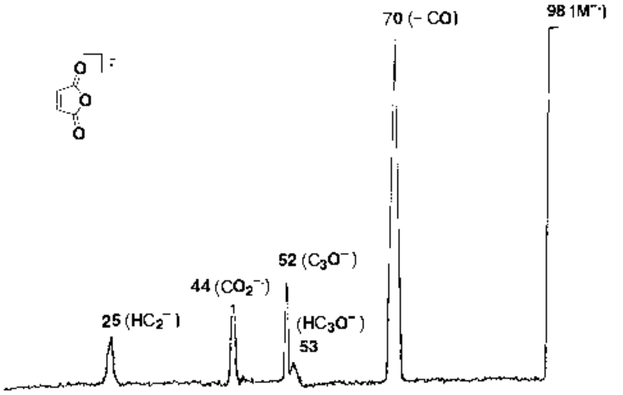


Fig. 2 The collision induced mass spectrum (MS/MS) of the molecular radical anion of maleic anhydride. Micromass VG ZAB 2HF mass spectrometer. For experimental details see the Experimental section.

In order to form OCOCO by a neutralisation–reionisation experiment, we must first synthesise either $[OCOCO]^{-\bullet}$ or $[OCOCO]^{+\bullet}$. There are no literature reports of a radical cation corresponding to this structure, but Cooper and Compton[25] have reported that maleic anhydride, which has an electron affinity of about 1.4 eV, captures a low-energy electron to form a molecular radical anion $C_4H_2O_3$, together with four fragment ions formed by dissociative electron attachment; these are $C_2H_2CO_2^-$, $C_2H_2CO^-$, $C_2O_3^{-\bullet}$ and $CO_2^{-\bullet}$. The C_2O_3 radical anion is formed at 0.1, 1.2, 2.2 and 2.7 eV, with the lifetime of the ion formed at 1.2 eV being 117 μs. The $C_2O_3^{-\bullet}$ ion was not observed in the negative ion spectra of any other anhydrides.[25] The authors do not propose a structure for $C_2O_3^{-\bullet}$ (*m*/*z* 72) formed from maleic anhydride, but, at least initially, it must correspond to a radical anion with bond connectivity OCOCO.

We next attempted to calculate the structures of both $[OCOCO]^{-\bullet}$ and the radical cation analogue $[OCOCO]^{+\bullet}$ at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory. We find that neither ion occupies a potential minimum on the appropriate potential surface. Each structure is unstable with respect to dissociation to form charged and/or neutral (as appropriate) CO_2 and CO. Since neither of the charged species corresponding to OCOCO is stable, we will not be able to use neutralisation–reionisation to effect the synthesis of the desired triplet neutral OCOCO.

Since the radical anion $[OCOCO]^{-\bullet}$ is an unstable species, what then is (are) the structure (structures) of the $C_2O_3^{-\bullet}$ species(s) formed on dissociative electron capture of maleic anhydride? We do not have the experimental facilities to allow us to repeat the experiment of Cooper and Compton, so we are unable to determine whether the peak at *m*/*z* 72 corresponds to $C_2O_3^{-\bullet}$ or to some source-formed impurity. We have, however, measured the collision induced spectrum of the maleic anhydride molecular anion: this is shown in Fig. 2.

The collision induced spectrum of the maleic anhydride radical anion shows fragment peaks corresponding to $C_3H_2O_2^{-\bullet}$, $C_3HO^{-\bullet}$, C_3O^-, $CO_2^{-\bullet}$ and C_2H^-. No peak at *m*/*z* 72 ($C_2O_3^{-\bullet}$) is noted in this spectrum. This observation by itself does not imply that *m*/*z* 72 formed in the experiment of Cooper and Compton is an impurity. It may be that a $C_2O_3^{-\bullet}$ species is formed on collisional activation of the molecular anion of maleic anhydride, but that it has sufficient excess energy to effect decomposition, and, as a consequence not be observable in Fig. 2. However, in this context, it needs to be noted that a peak corresponding to low-energy $CO_2^{-\bullet}$ ions is observed in Fig. 2. The $CO_2^{-\bullet}$ story is a complex one, but in summary, carbon dioxide has an electron affinity of −0.6 ± 0.2 eV (−59 ± 19 kJ mol^{-1}),[26,27] but there is a small barrier of *ca.* 15 kJ mol^{-1}

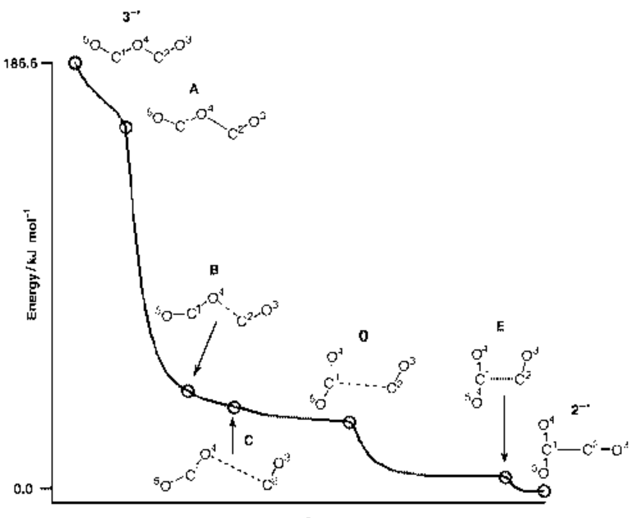


Fig. 3 MOLDEN projections of the reaction coordinate of the $[OCOCO]^{-\bullet}$ to $[O_2CCO]^{-\bullet}$ rearrangement. CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory. Internuclear lengths (Å): $\mathbf{3}^{-\bullet}$, C^1C^2 (2.29), C^2O^4 (1.40); **A**, C^1C^2 (2.35), C^2O^4 (1.85); **B**, C^1C^2 (3.38), C^2O^4 (2.97); **C**, C^1C^2 (4.07), C^2O^4 (4.02); **D**, C^1C^2 (2.44), C^2O^4 (3.16); **E**, C^1C^2 (1.79), C^2O^4 (2.52); $\mathbf{2}^{-\bullet}$, C^1C^2 (1.61), C^2O^4 (2.38).

to electron detachment which enables the detection of $CO_2^{-\bullet}$ provided that the ion does not have sufficient energy (≥15 kJ mol^{-1}) to surmount the barrier for electron detachment.[25]

If there is a species $[C_2O_3]^{-\bullet}$ formed from maleic anhydride following or accompanying dissociative electron capture, then it does not correspond to $[OCOCO]^{-\bullet}$ but to some rearranged structure. We have carried out calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory on this system and have used the MOLDEN program,[28] to track the reaction coordinate of any such rearrangement. The results of these computations are shown in Fig. 3. The data in Fig. 3 show that, on formation, unstable $[OCOCO]^{-\bullet}$ ($\mathbf{3}^{-\bullet}$) rearranges to the isomer $[O_2CCO]^{-\bullet}$ ($\mathbf{2}^{-\bullet}$). The only potential minimum shown in Fig. 3 is that of product $\mathbf{2}^{-\bullet}$; all other indicated structures are points on the reaction coordinate chosen to illustrate the mechanistic course of the rearrangement. The intimate details of the rearrangement are interesting. The radical anion begins to dissociate at a region corresponding to structure **A**. Instead of dissociating further at this point, the system, essentially now CO_2 and $CO^{-\bullet}$, rotates within the plane to form **D** which is held together by weak electrostatic interactions. Mulliken analysis indicates that the OCO and $CO^{-\bullet}$ carbons have Mulliken charge densities of +0.749 and −0.757, respectively. Thus the δ^+ C^1 and δ^- C^2 come together to form planar **E**, which then undergoes rotation of the CC bond to form $\mathbf{2}^{-\bullet}$. Radical anion $\mathbf{2}^{-\bullet}$ is formed with an excess energy of 187 kJ mol^{-1}, so unless this radical anion is collisionally stabilised, it will dissociate by one, or both of the processes shown in Scheme 2.

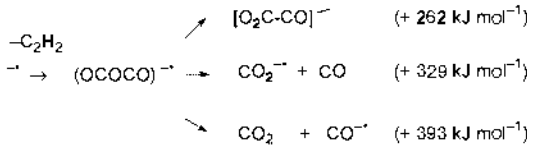
$$[O_2CCO]^{-\bullet} \rightarrow CO^{-\bullet} + CO_2\ (+126\ \text{kJ mol}^{-1})$$

$$[O_2CCO]^{-\bullet} \rightarrow CO + CO_2^{-\bullet}\ (+59\ \text{kJ mol}^{-1})$$

Scheme 2

If an energised maleic anhydride molecular anion fragments *via* a decomposing species $[OCOCO]^{-\bullet}$, the three processes shown in Scheme 3 might, in principle, be operative. We have calculated the thermochemistry for these three overall processes from the maleic anhydride radical anion at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory. Results are shown in Scheme 3.

Peak maxima for *m*/*z* 72 (from dissociation of maleic anhydride radical anions) were observed by Compton and Cooper using electrons of energies 0.1 eV (10 kJ mol^{-1}), 1.2 eV (116 kJ mol^{-1}), 2.2 eV (212 kJ mol^{-1}) and 2.7 eV (260 kJ mol^{-1}). Insufficient energy is available to effect either of the dissociation processes shown in Scheme 3, however the peak at *m*/*z* 72 could, in principle, correspond to $[O_2CCO]^{-\bullet}$ [rearrangement process, Scheme 3, +262 kJ mol^{-1}] when the energy of the captured electrons is 2.7 eV. It must be stressed that the results of calculations shown in Scheme 3 provide the thermochemistries of the three overall processes; they do not provide data concerning individual steps or barriers.



Scheme 3

Conclusions

Theoretical calculations indicate that: (*i*) triplet OCOCO should be a stable species provided it can be formed with an excess energy less than 41 kJ mol^{-1}; (*ii*) the radical anion and radical cation of OCOCO are unstable species, and as a consequence cannot be used as precursors of triplet OCOCO using neutralisation–reionisation; (*iii*) the species *m*/*z* 72 observed by Compton and Cooper following dissociative electron capture from maleic anhydride cannot be $[OCOCO]^{-\bullet}$. If electrons captured by maleic anhydride have energies of ⩾2.7 eV (⩾260 kJ mol^{-1}) the initially formed (and unstable) species $[OCOCO]^{-\bullet}$ could, in principle, rearrange *via* a barrierless exothermic process to yield the isomer $[O_2CCO]^{-\bullet}$.

Experimental

A Mass spectrometric methods

For a detailed description of the experiment and the instrument used see ref. 29. In brief, the experiments were performed using a two-sector modified VG ZAB 2HF mass spectrometer with BE configuration, where B and E represent magnetic and electric sectors, respectively. The maleic anhydride radical anion was generated by electron capture in the chemical ionisation source operating in the negative ion mode, with typical source conditions as follows: source temperature 200 °C, repeller voltage −0.5 V, ion extraction voltage 7 kV, mass resolution $m/\Delta m$ ⩾ 1500. Maleic anhydride (available commercially) was placed in a small glass capillary tube which was then drawn out in a flame to create a very fine aperture, allowing for a slow steady release of sample vapour upon heating. The capillary was inserted into the CI source *via* the direct probe; the probe tip was heated to 60 °C to generate a background pressure of *ca.* 10^{-5} Torr inside the source housing. The collision induced spectrum of the maleic anhydride radical anion was effected using argon as the target gas in the first collision gas after the magnetic sector. The pressure of argon in the cell was maintained such that 80% of the parent ion beam was transmitted through the cell. This corresponds to an average of 1.1–1.2 collisions per ion.[30] Product ions resulting from CID were recorded by scanning E.

B Theoretical methods

Geometry optimizations were carried out with the Becke 3LYP method[31,32] using a modest 6-31+G(d) basis within the GAUSSIAN 98 suite of programs.[33] Stationary points were characterised as either minima (no imaginary frequencies) or transition structures (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures. The minima connected by a given transition structure were confirmed by intrinsic reaction coordinate (IRC) calculations. The calculated frequencies were also used to determine zero-point vibrational energies which were then scaled[34] by 0.9804 and used as a zero-point correction for the electronic energies calculated at this and higher levels of theory. B3LYP/6-31+G(d) has previously been used for geometry optimizations of anions and has demonstrated good correlation with structures calculated using high level coupled-cluster approaches.[35,36] Some problems have been highlighted in the literature regarding the use of the B3LYP method for the accurate prediction of molecular energies for carbon clusters,[37] even though the method continues to be used with success.[38,39] More accurate energies for the B3LYP geometries were determined using the CCSD(T) method[40–45] together with the Dunning aug-cc-pVDZ basis set.[46,47] The CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) approach predicts the adiabatic electron affinity of linear C_4 to be 3.65 eV[29] which is in reasonable agreement with the experimentally measured value of 3.88 eV.[48,49] All calculations were carried out on the AlphaServer SC at the Australian National University Supercomputing Facility (Canberra).

Acknowledgements

We thank the Australian Research Council for continuing financial support of our ion chemistry program, and the Australian National University for a generous allocation of time on their AlphaServer super computer.

References

1 G. P. Smith, P. C. Cosby and J. T. Mosely, *J. Chem. Phys.*, 1977, **67**, 3838.
2 G. G. Jones and J. W. Taylor, *J. Chem. Phys.*, 1978, **68**, 1768.
3 S. H. Linn and C. Y. Ng, *J. Chem. Phys.*, 1981, **75**, 4921.
4 A. J. Illies, M. F. Jarrod, W. Inagner-Redeker and M. T. Bowers, *J. Chem. Phys.*, 1988, **88**, 5204.
5 M. J. DeLuca, B. Niu and M. A. Johnson, *J. Chem. Phys.*, 1988, **88**, 5857.
6 T. Tsukuda, M. A. Johnson and T. Nagata, *Chem. Phys. Lett.*, 1997, **268**, 429.
7 M. E. Jacox and W. E. Thompson, *J. Chem. Phys.*, 1989, **91**, 1410.
8 W. E. Thompson and M. E. Jacox, *J. Chem. Phys.*, 1991, **95**, 735.
9 M. E. Jacox and W. E. Thompson, *J. Phys. Chem.*, 1991, **95**, 2781.
10 W. E. Thompson and M. E. Jacox, *J. Chem. Phys.*, 1999, **111**, 4487, and references cited therein.
11 L. B. Knight and J. Steadman, *J. Chem. Phys.*, 1982, **77**, 1750.
12 E. Giamello, D. Murphy, L. Marchese, G. Marta and A. Zeechina, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 3715.
13 L. B. Knight, D. Hill, K. Berry, R. Babb and D. Fetter, *J. Chem. Phys.*, 1996, **105**, 5672.
14 M. F. Zhou and L. Andrews, *J. Chem. Phys.*, 1999, **110**, 2414.
15 M. F. Zhou and L. Andrews, *J. Chem. Phys.*, 1999, **110**, 6820.
16 A. C. Legon and A. P. Suckley, *J. Chem. Phys.*, 1989, **91**, 4440.
17 R. W. Randall, J. P. L. Summersgill and B. J. Howard, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 1943.
18 Y. Xu, A. R. W. McKellar and B. J. Howard, *J. Mol. Spectrosc.*, 1996, **179**, 345.
19 J. S. Muenter and R. Bhattacharjee, *J. Mol. Spectrosc.*, 1998, **190**, 290.
20 V. Raducu, B. Gauthierroy, R. Dahoo, L. Abouafmarguin, J. Langlet, J. Caillet and M. Allavena, *J. Chem. Phys.*, 1995, **102**, 9235.
21 J. Langlet, J. Caillet, M. Allavena, V. Raducu, B. Gauthier-Roy, R. Dahoo and L. Abouaf-Marguin, *J. Mol. Struct.*, 1999, **484**, 145.
22 Structures drawn in the text or the figures indicate the bond connectivity and the overall geometry. These structures do not indicate the bond order except when indicated to the contrary [*e.g.* in eqn. 1]. Bond lengths are listed in Tables 1 and 3–5. S. Peppe, S. Dua and J. H. Bowie, *J. Chem. Phys. A.*, in the press.
23 S. Peppe, S. Dua and J. H. Bowie, *J. Chem. Phys. A*, in the press.
24 C. Wesdemiotis and F. W. McLafferty, *Chem. Rev.*, 1987, **26**, 805; J. L. Holmes, *Mass Spectrom. Rev.*, 1989, **8**, 513; for recent reviews of the neutralisation–reionisation technique and nomenclature see; C. A. Shalley, G. Hornung, D. Schröder and H. Schwarz, *Int. J. Mass Spectrom. Ion Processes*, 1998, **172**, 181; D. V. Zagorevskii and J. L. Holmes, *Mass Spectrom. Rev.*, 1999, **18**, 87.
25 C. D. Cooper and R. N. Compton, *J. Chem. Phys.*, 1973, **59**, 3550.
26 R. N. Compton, P. W. Reinhardt and C. D. Cooper, *J. Chem. Phys.*, 1975, **63**, 3821.
27 D. Yu, A. Rauk and D. A. Armstrong, *J. Phys. Chem.*, 1992, **96**, 6031.
28 A. Schaftenaar and J. H. Noordik, *J. Comput.-Aided Mol. Des.*, 2000, **14**, 123.
29 S. J. Blanksby, D. Schröder, S. Dua, J. H. Bowie and H. Schwarz, *J. Am. Chem. Soc.*, 2000, **122**, 7105 and references cited therein.
30 J. L. Holmes, *Org. Mass Spectrom.*, 1985, **20**, 169.
31 A. D. Becke, *J. Phys. Chem.*, 1993, **98**, 5648.
32 P. J. Stevens, F. J. Devlin, C. F. Chablowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
33 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Peterson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales and J. A. Pople, GAUSSIAN 98, Gaussian Inc., Pittsburgh, PA, 1998.
34 M. W. Wong, *Chem. Phys. Lett.*, 1996, **256**, 391.
35 J. Szczepanski, S. Ekern and M. Vala, *J. Phys. Chem.*, 1997, **101**, 1841.
36 T. D. Crawford, J. F. Stanton, J. C. Saeh and H. F. Schaefer, *J. Am. Chem. Soc.*, 1999, **121**, 1902.
37 D. A. Plattner and K. N. Houk, *J. Am. Chem. Soc.*, 1995, **117**, 4405.
38 L. M. L. Martin, J. El-Yazal and J.-P. Trancois, *Chem. Phys. Lett.*, 1996, **252**, 9.
39 E. E. Masqualine and M. Lopez, *Chem. Phys. Lett.*, 2000, **320**, 415.
40 J. Cizek, *Adv. Chem. Phys.*, 1969, **14**, 35.
41 J. A. Pople, R. Krishnan, H. B. Schlegel and J. S. Binkley, *Int. J. Quantum Chem.*, 1978, **4**, 545.
42 C. Hampel, K. Peterson and H.-J. Werner, *Chem. Phys. Lett.*, 1992, **190**, 1.
43 J. D. Watts, J. Gauss and R. J. J. Bartlett, *J. Chem. Phys.*, 1993, **98**, 8718.
44 P. J. Knowles, C. Hampel and H.-J. Werner, *J. Chem. Phys.*, 1993, **99**, 5219.
45 M. J. O. Deegan and P. J. Knowles, *Chem. Phys. Lett.*, 1994, **227**, 321.
46 T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007.
47 D. E. Woon and T. H. Dunning, *J. Chem. Phys. A*, 1993, **98**, 1358.
48 D. W. Arnold, S. E. Bradforth, T. N. Kitsopoulos and D. M. Neumark, *J. Chem. Phys.*, 1991, **95**, 8753.
49 C. Xu, G. R. Burton, T. R. Taylor and D. M. Neumark, *J. Chem. Phys.*, 1997, **107**, 3428.