

Electronic Structure of $(\text{CS}_2)_2^-$

Andrei Sanov* and W. Carl Lineberger

JILA, National Institute of Standards and Technology and University of Colorado, and
Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0440

Kenneth D. Jordan

JILA, National Institute of Standards and Technology and University of Colorado,
Boulder, Colorado 80309-0440, and Department of Chemistry, University of Pittsburgh, Pennsylvania 15260

Received: January 30, 1998

We investigate theoretically the electronic structure of $(\text{CS}_2)_2^-$. Five different low-lying forms of the anion are identified. These include the ion–molecule complex and a covalently bonded dimer anion, both of which have electronic configurations consistent with electron attachment to the LUMO of the van der Waals dimer. The other species, including the most stable form of the anion, all have cyclic structures and can be viewed as arising from electron capture by cyclic covalently bonded neutral dimers, with electronic configurations doubly excited with respect to the van der Waals dimer. Vertical detachment energies are calculated for the various anions and lead us to reassign the features in the observed photoelectron spectra of $(\text{CS}_2)_2^-$.

The structures and electronic configurations of the low-lying states of $(\text{CS}_2)_2^-$ have been the subject of considerable discussion. Bowen and Eaton obtained the anion photoelectron spectrum with 2.54 eV photon energy.¹ Their spectrum displayed a peak at an electron binding energy (eBE) of 1.4 eV that was attributed to the $\text{CS}_2^- \cdot \text{CS}_2$ complex form of the anion. More recently, Tsukuda et al. obtained the photoelectron spectrum of $(\text{CS}_2)_2^-$ at a photon energy of 4.66 eV and observed features at eBE = 1.65, 2.7, 3.2, and 3.7 eV.² These authors also attributed the lowest energy peak to the ion–molecule complex and assigned the 2.7 eV feature to photodetachment of a C_{2v} symmetry cyclic form of the anion with C–C and S–S chemical bonding between the two CS_2 moieties. This cyclic form of the anion had been predicted by Hiraoka et al.,³ on the basis of ROHF/6-31G calculations, to be 0.6 eV more stable than the $\text{CS}_2^- \cdot \text{CS}_2$ ion–molecule complex. Further evidence for a low-energy cyclic form of $(\text{CS}_2)_2^-$ was provided by the recent observation⁴ of the C_2S_2^- product channel in the photodissociation of $(\text{CS}_2)_n^-$, $n = 2-4$ clusters.

The photodissociation and theoretical results both indicate that the most stable form of $(\text{CS}_2)_2^-$ contains a C_2S_2 ring and is not the $\text{CS}_2^- \cdot \text{CS}_2$ ion–molecule complex. This, together with the fact that the 1.4 eV peak in the photoelectron spectrum of $(\text{CS}_2)_2^-$ is narrower than that observed in the photoelectron spectrum of CS_2^- ,¹ leads us to raise the possibility that the low binding energy peak in the photoelectron spectrum of the dimer anion is due to a covalently bound anion. In order to address this possibility, we have undertaken a detailed theoretical study of the low-energy forms of $(\text{CS}_2)_2^-$. Our calculations reveal that this system is far more complex than has been recognized. Specifically, we find that there are *four* covalently bound forms of $(\text{CS}_2)_2^-$, all of which lie energetically below the ion–molecule complex. Three of these are cyclic structures with electronic configurations best viewed as arising from electron attachment to a doubly excited neutral dimer. The vertical detachment energies (VDE) of the various anions are calculated

and used to assign the features in the photoelectron spectrum of $(\text{CS}_2)_2^-$.

In the present study, second-order Møller–Plesset perturbation theory (MP2)^{5–7} was used to characterize the anionic and neutral dimers of CS_2 . The calculations on the open-shell species were based on the spin-unrestricted Hartree–Fock method.^{8–10} Geometries were optimized using analytical gradients, and vibrational frequencies were calculated for the various optimized structures to assure that they correspond to local potential energy minima. All calculations were carried out with a 6-31+G(d) basis set¹¹ using the Gaussian 94 package.¹²

The optimized structures are shown in Figure 1, and the relative energies of the different anion structures and the associated VDE's are summarized in Figure 2. Structures I and II correspond, respectively, to the ion–molecule complex³ and the covalently bound D_{2d} structure, both of which have electronic configurations consistent with electron attachment to the LUMO of the neutral van der Waals dimer. The corresponding structures of the valence isoelectronic $(\text{CO}_2)_2^-$ ion are the only low-energy forms of that anion.^{13–16}

The remaining $(\text{CS}_2)_2^-$ structures, III–V, are cyclic. Of these, anions III and IV have C_{2v} symmetry structures with both C–C and S–S bonding between the CS_2 monomers (see Figure 1) and are nearly isoenergetic. Anion III has a $^2\text{B}_1$ electronic configuration and is the species studied previously by Hiraoka et al.³ and Maeyama et al.⁴ The electronic wave function of anion IV has $^2\text{B}_2$ symmetry. To the best of our knowledge, the latter anion has not been previously reported. Examination of the electronic configurations of III and IV reveals that they have a $[\dots 16(a_1)^2 14(b_2)^2 4(b_1)^2 4(a_2)^2]$ core with the odd electron occupying out-of-plane $5b_1$ and in-plane $15b_2$ orbitals, respectively. This core configuration is doubly excited ($15(b_2)^2 \rightarrow 16(a_1)^2$) with respect to the van der Waals CS_2 dimer (constrained to C_{2v} symmetry). This suggests that the neutral dimer possesses a low-lying cyclic structure with the $[\dots 16(a_1)^2 14(b_2)^2 4(b_1)^2 4(a_2)^2]$ configuration. Our calculations show that this

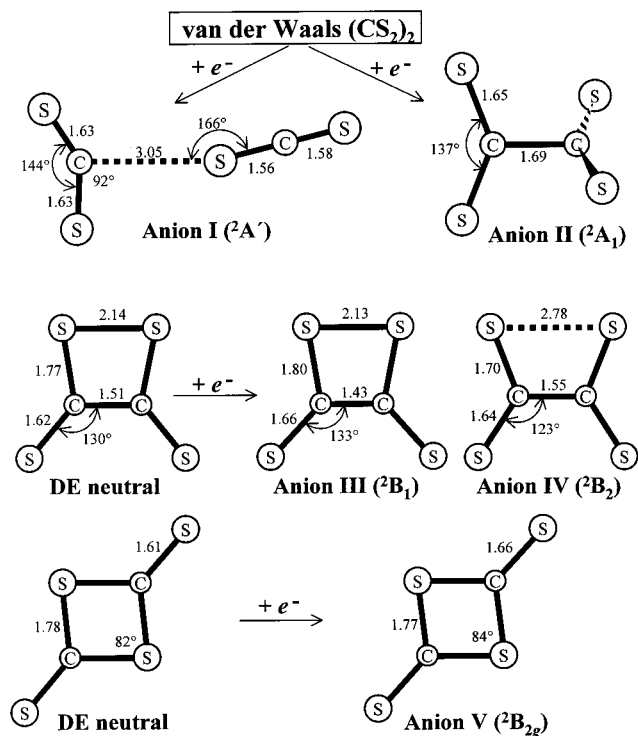


Figure 1. MP2/6-31+G(d)-optimized structures of the five most stable forms of $(\text{CS}_2)_2^-$. Optimized geometries of the doubly excited (DE) neutral species are also shown. Bond lengths are in angstroms and bond angles in degrees.

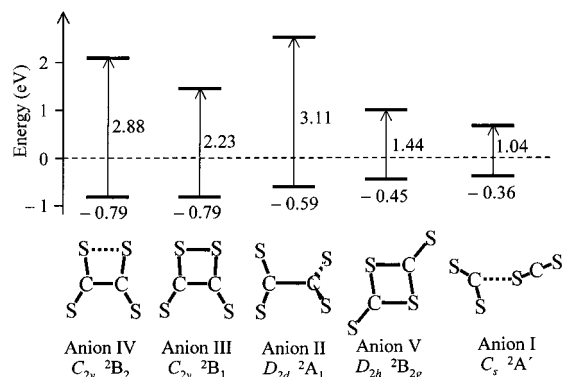


Figure 2. Relative energies (lower solid lines) and VDE's (vertical arrows) of the low-lying forms of $(\text{CS}_2)_2^-$. The zero of energy (dashed line) indicates the $\text{CS}_2 + \text{CS}_2^-$ asymptote. Upper solid lines denote neutral energies at the anion geometries.

is indeed the case, with the cyclic neutral dimer (see Figure 1) lying only 1.5 eV above the van der Waals dimer. This species, which has a short 2.14 Å S-S bond, corresponding to a bond order of 1, is analogous to the elusive dioxetane dione C_2O_4 molecule.¹⁷ Hereafter, we refer to this cyclic form of the neutral dimer as ${}^1A_1(\text{DE})$, where the "DE" denotes "doubly excited".

The ${}^1A_1(\text{DE})$ species can be viewed as arising from coupling of two CS_2 molecules in excited 3B_2 states. The triplet excitation energy of CS_2 is calculated to be 3.2 eV (linear singlet to bent triplet). All but 1.5 eV of the energy required to promote two CS_2 molecules to the lowest triplet state is recovered by formation of the C-C and S-S bonds in the ${}^1A_1(\text{DE})$ species. The ${}^1A_1(\text{DE})$ cyclic form of $(\text{CS}_2)_2$ lies much lower in energy than that of $(\text{CO}_2)_2$ because of the much lower singlet \rightarrow triplet excitation energy of CS_2 compared to CO_2 .¹⁴

The final anion studied, V, has D_{2h} symmetry, with the ring consisting of four equivalent C-S bonds. The electronic wave

function has ${}^2B_{2g}$ symmetry and also has an electronic configuration consistent with electron attachment to a doubly excited neutral dimer. Our calculations show that the doubly excited neutral dimer has a D_{2h} global potential energy minimum (structure shown in Figure 1), lying only 1.1 eV above the van der Waals dimer.

The relative energies of the various forms of $(\text{CS}_2)_2^-$ together with their VDE's are reported in Figure 2. According to our MP2 calculations, the most stable anions are the nearly isoenergetic C_{2v} 2B_2 and 2B_1 species with VDE's of 2.88 and 2.23 eV, respectively. On the basis of these results, the 2B_2 anion is the most viable candidate for the 2.7 eV peak in the $(\text{CS}_2)_2^-$ photoelectron spectrum.²

The lowest binding energy peak in the photoelectron spectrum of $(\text{CS}_2)_2^-$ (eBE = 1.4 eV in the spectrum of Bowen and Eaton¹ and 1.65 eV in the spectrum of Tsukada et al.²) was previously assigned to the ion-molecule complex, for which our calculations give a VDE of 1.04 eV. We believe it more likely that the 1.4 eV peak is due to the ${}^2B_{2g}$ D_{2h} $(\text{CS}_2)_2^-$ anion, for which our calculated VDE is 1.44 eV. This assignment is consistent with the fact that the 1.4 eV peak in the photoelectron spectrum of $(\text{CS}_2)_2^-$ is substantially narrower¹ than the peak in the photoelectron spectrum of CS_2^- . The photoelectron spectrum² of $(\text{CS}_2)_2^-$ also displays a small peak at eBE = 3.2 eV, which may be due to the noncyclic 2A_1 D_{2d} form of $(\text{CS}_2)_2^-$, calculated to have a VDE of 3.11 eV.

It is interesting to speculate how the cyclic anions with "doubly excited" core electronic configurations are formed. The most likely scenario involves conversion of anions with van der Waals cores. This could happen with high probability if there are energetically accessible crossings or avoided crossings between the two types of anion states. Our calculations indicate that a crossing between the 2B_2 C_{2v} and 2A_1 D_{2d} anion surfaces lies substantially lower in energy than that involving the 2B_1 C_{2v} and 2A_1 D_{2d} surfaces.¹⁴ This may lead to a greater abundance of 2B_2 anions compared to 2B_1 anions in the ion beam. It is also possible (but unlikely) that the electron impact sources used in the experiments produced copious triplet CS_2 molecules that recombined to form the cyclic neutral dimers that, in turn, underwent nondissociative electron capture to produce the cyclic anions with doubly excited core configurations. This mechanism would favor formation of the ${}^2B_{2g}$ D_{2h} anion since the corresponding form of the neutral dimer is predicted to be the global minimum of the "doubly excited" neutral potential energy surface.

In conclusion, we have identified theoretically five different low-lying forms of $(\text{CS}_2)_2^-$, two of which have electronic configurations consistent with electron attachment to the van der Waals dimer, while the other three, including the most stable forms of the anion, can be viewed as arising from electron capture by covalently bonded neutral dimers with electronic configurations doubly excited with respect to the van der Waals dimer. Calculated VDE's of the various forms of the anion are used to reassign the features in the observed^{1,2} photoelectron spectra of $(\text{CS}_2)_2^-$.

Acknowledgment. The authors have benefited from enlightening discussions with Professor G. Barney Ellison. This work is supported by the National Science Foundation (Grants CHE97-03486 and PHY95-12150) and the Air Force Office of Scientific Research (AASERT program). K.D.J. acknowledges the support of a Visiting Fellowship at JILA.

References and Notes

- (1) Bowen, K. H.; Eaton, J. G. Photodetachment Spectroscopy of Negative Cluster Ions. In *The Structure of Small Molecules and Ions*;

Naaman, R., Vager, Z., Eds.; Plenum: New York, 1988; p 147.

(2) Tsukuda, T.; Hirose, T.; Nagata, T. *Chem. Phys. Lett.* **1997**, 279, 179.

(3) Hiraoka, K.; Fujimaki, S.; Aruga, G.; Yamabe, S. *J. Phys. Chem.* **1994**, 98, 1802.

(4) Maeyama, T.; Oikawa, T.; Tsumura, T.; Mikami, N. *J. Chem. Phys.* **1998**, 108, 1368.

(5) Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, 46, 618.

(6) Pople, J. A.; Seeger, R.; Krishnan, R. *Int. J. Quantum Chem. Symp.* **1977**, 11, 149.

(7) Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, 32, 359.

(8) Roothan, C. C. J. *Rev. Mod. Phys.* **1951**, 23, 69.

(9) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1959**, 22, 571.

(10) McWeeny, R.; Dierksen, G. *J. Chem. Phys.* **1968**, 49, 4852.

(11) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, 4, 294.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Kieth, T.; Petersson, G.

A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Rev. E.1; Gaussian, Inc.: Pittsburgh, PA, 1994.

(13) Fleischman, S. H.; Jordan, K. D. *J. Phys. Chem.* **1987**, 91, 1300.

(14) Sanov, A.; Lineberger, W. C.; Jordan, K. D. To be published.

(15) DeLuca, M. J.; Niu, B.; Johnson, M. A. *J. Chem. Phys.* **1988**, 88, 5857.

(16) Tsukuda, T.; Johnson, M. A.; Nagata, T. *Chem. Phys. Lett.* **1997**, 268, 429.

(17) Rauhut, M. M.; Bollyky, L. J.; Roberts, B. G.; Loy, M.; Whitman, R. H.; Iannotta, A. V.; Semsel, A. M.; Clarke, R. A. *J. Am. Chem. Soc.* **1967**, 89, 6515.