JOURNAL OF CHEMICAL PHYSICS VOLUME 108, NUMBER 16 22 APRIL 1998

Electron affinities of CO_2, OCS, and CS_2

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(Received 28 August 1997; accepted 16 January 1998)

The structure of the CO_2^-, OCS^-, and CS_2^- anions as well as the adiabatic electron affinities of the corresponding CO_2, OCS, and CS_2 neutral parents are computed using the infinite-order coupled-cluster method with all singles and doubles and non-iterative inclusion of triple excitations (CCSD(T)) and Hartree-Fock-Density-Functional-Theory (HFDFT) levels of theory. The potential energy curves of the CO_2 – CO_2^- and CS_2 – CS_2^- pairs are calculated as a function of the bending angle. All three anions are found to have bent equilibrium configurations. The adiabatic electron affinities of CO_2 and OCS are calculated to be negative, whereas the CS_2^- anion is stable in the linear and relaxed geometries. The existence of CS_2^- at linear geometries can be related to experimental observations of an electric field-induced detachment of an extra electron from the anion in fields of only a few kilovolts per centimeter. *© 1998 American Institute of Physics.* [S0021-9606(98)03415-1]

I. INTRODUCTION

The linear molecules CO_2, OCS, and CS_2 are sixteen valence electron molecules. The addition of an extra electron into the $6a_1$ orbital results in a bent (and extended) anion in accord with Walsh's rules. Experimental studies of free electron attachment and Rydberg electron transfer reactions (RET) of the type

$$X^{**}+CY_2 \rightarrow X^+ + CY_2^-, \quad (1)$$

where X^{**} is a Rydberg atom and Y stands for O or S, have received considerable attention.[1–12] Free electron attachment to either CO_2[1] or CS_2[13] is not observed. The neutral CO_2 and CS_2 molecules are linear, whereas their corresponding anions are highly bent; therefore, a third body is required for the formation of the ground state anions,[6,13] and bending vibrations seem to play an important role in the RET reactions as prompted by a strong isotope effect exhibited by rate constants of the CS_2^- formation in $Cs(ns,nd)+CS_2$ collisions.[8]

Although CO_2^- and CS_2^- are isovalent, they exhibit different behavior. Experimentally, it was found[6] that apparently two types of CS_2^- anions are formed in reactions (1) with $X^{**}=K(nd)$. One type corresponds to relatively long-lived species (lifetime $\geqslant 10$ μs), and ''surprisingly, a fraction of the CS_2^- anions was observed to undergo electric-field-induced detachment when subjected to fields of only a few kilovolts per centimeter.''[6] Such field strengths are characteristic for the field-induced detachment of diffuse dipole-bound electrons (with binding energies of 1 to 10 meV).[9–11] This is puzzling in the case of CS_2^-, because CS_2 has no permanent dipole moment. However, CS_2 is known to possess a rather large quadrupole moment; therefore, it is tempting to attribute this state of CS_2^- to a quadruple-bound state.[12] No such field-induced detachment was observed for either CO_2 or OCS.[6] The (valence) adiabatic electron affinity (EA_{ad}) of CO_2 is negative,[3,4] whereas the EA_{ad} of CS_2 is positive.[4,14–16] CO_2^- anions have only been produced by dissociative electron attachment to organic molecules (e.g., maleic anhydrides[2]) or by fast atom charge transfer.[3,4]

Although electron binding to a molecule through the dipole field is now reasonably well understood theoretically[18–21] and well documented experimentally,[9–11] the binding of an electron to a molecular quadrupole is much less certain. The shorter range of the quadrupole field as compared to the dipole field makes it difficult to predict a ''minimum quadrupole moment'' of a molecule to bind an electron as was done in the dipole case. The minimum quadrupole moment required to bind an electron depends upon the sign and magnitudes of the atomic charges and their separation as well as upon the nature of the repulsive core of the inner electrons. Prasad, Wallis and Herman[22,23] have calculated the binding of an electron to a finite linear electric quadrupole (Q) in two configurations, one of which has two positive charges each of charge $+q$, symmetrically placed about a negative charge of $-2q$ (A) and the other case for the charges reversed (B). Their calculations predict that the minimum quadrupole $Q_{\min}$ to bind an electron is $Q_{\min}$ (A) $=21.0$ a.u. and $Q_{\min}$ (B)$=$ 2.6 a.u.

Theoretical studies have been directed mainly to the study of the ground and low-lying excited states of the neutral species: CO_2,[24–26] OCS,[27–29] and CS_2.[30] The ground-state properties and geometries are well reproduced at the level of both correlated *ab initio*[24–30] and density-functional-theories (DFT).[31–33] The potential energy curves (PEC) as a

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TABLE I. Results of calculations for CO_2 and CS_2 performed at the CCSD(T)/6-311+$G(3df)$ and HFDFT/6-311+$G(3df)$ levels. Total energies are in Hartree, bond lengths are in Å, vibrational frequencies are in cm^{-1}, and the ZPEs are in kcal/mol.

	CO_2			CS_2		
Property	CCSD(T)	HFDFT	Exp[a]	CCSD(T)	HFDFT	Exp[a]
R_e(C–X)	1.1614	1.1642	1.162[b]	1.5576	1.5565	1.5562[c]
$\omega(\pi_u)$	687	660	667	408	409	397
$\omega(\sigma_g)$	1359	1356	1333	675	676	658
$\omega(\sigma_u)$	2417	2393	2349	1568	1589	1535
ZPE	7.36	7.25	7.17	4.37	4.41	4.27
E(HF)	−187.706301	−187.705639	...	−832.959025	−832.959109	...
E(CCSD(T)/B3LYP)	−188.401769	−188.551400	...	−833.851519	−834.394665	...

[a]Experimental frequencies from Ref. 54.

[b]See Ref. 55.

[c]See Ref. 56.

function of the bending angle have been calculated for both CO_2 and CO_2^- by several groups[34–38] using the Hartree-Fock (HF) level of theory. The CO_2^- anion surface was found to lie below the neutral at bending angles smaller than about 150° in all these studies. The computed EA_{ad} values of CO_2 are all negative, but show a rather large variance. The results of correlated calculations[39–42] on the EA_{ad} of CO_2 are in good mutual agreement and also agree with an experimental estimate of -0.6 ± 0.2 of Compton *et al.*[4] To our knowledge, no detailed study was performed for the OCS – OCS^- and CS_2 – CS_2^- pairs.

In order to obtain a qualitative notion about the different behavior of the CO_2^- and CS_2^- anions, we performed coupled-cluster calculations of the PECs of the corresponding neutral-anion pairs as a function of the bending angle keeping in mind that it has been suggested, recently, that the binding of an electron in CS_2^- in a linear geometry could be a result of the relatively large quadrupole moment for the CS_2 molecule.[12] Since both the infinite-order coupled-cluster method with all singles and doubles (CCSD)[46] and noniterative inclusion of triple excitations (CCSD(T))[47,48] and Hartree-Fock-Density-Functional-Theory (HFDFT) approaches proved to be reliable in calculations of small EA_{ad}s,[43,44] we have computed the EA_{ad} for all three members of the series CO_2, OCS, and CS_2 at the CCSD(T) and HFDFT levels. Electric quadruple moments of both neutral and anionic series are calculated at the Hartree-Fock (HF) and CCSD(T) levels.

II. COMPUTATIONAL DETAILS

The present calculations have been performed with the ACES II suite of programs[45] at the (CCSD(T))[47,48] and HFDFT[49–52] levels of theory. Three basis sets have been employed, namely, 6-311+$G(2d)$, 6-311+$G(2df)$, and 6-311+$G(3df)$.[53] The optimizations were carried out until the rms gradients fell below the threshold value of 0.1E−3.

The adiabatic electron affinity (EA_{ad}) measures the energy gain due to the attachment of an additional electron and is defined as the difference in the total energies of the anion and parent ground states. Within the Born-Oppenheimer approximation, one can define the adiabatic EA as

$$EA_{ad}=E_{\rm tot}(N,R_e)+{\rm ZPE}_N-E_{\rm tot}(A,R_e^-)-{\rm ZPE}_A=\Delta E_{el}+\Delta E_{\rm nuc}, \qquad (2)$$

where R_e and R_e^- denote the equilibrium geometrical configurations of the neutral molecule and the anion, respectively. The zero-point vibrational energies (ZPE) can be estimated within the harmonic approximation.

The vertical detachment energy (VDE) of an anion is the minimal energy required for a sudden detachment of an extra electron. It can be defined as the difference in the total energies of the anion and its parent at the equilibrium geometry of the anion

$$\begin{aligned}{\rm VDE}&=E_{\rm tot}(N,R_e^-)+{\rm ZPE}_N-E_{\rm tot}(A,R_e^-)-{\rm ZPE}_A\\&=\Delta E_{el}+\Delta E_{\rm nuc}.\end{aligned} \qquad (3)$$

Usually, one can use the ZPEs estimated for the neutral ground states, i.e., to use the same $\Delta E_{\rm nuc}$ as in Eq. (2).

III. RESULTS AND DISCUSSIONS

A. Ground states

The results of our CCSD(T)/6-311+$G(3df)$ and HFDFT/6-311+$G(3df)$ calculations on the ground states of the CO_2, OCS, CS_2 series and their anions are presented in Tables I–III. Experimental geometries and vibrational frequencies are known for all three neutral molecules and our data are in excellent agreement with the experimental data.[54–61] The dipole moment of OCS is well reproduced at the CCSD(T) level, and the difference with the most reliable experimental value of 0.71521 ± 0.00020 D[57] is only 0.003 D. The geometrical parameters and vibrational frequencies are nearly the same at both the CCSD(T) and HFDFT levels. As expected, the anions are bent as has been established experimentally[59,60] and theoretically,[34–38,62,63] for CO_2^-, and was assumed for CS_2^- [5,8,7,16] by experimentalists. The geometry and vibrational frequencies of the CO_2^- have been measured in matrices and show rather large deviations from our computed values.

TABLE II. Results of calculations for OCS and OCS$^-$ performed at the CCSD(T)/6-311+$G(3df)$ and HFDFT/ 6-311+$G(3df)$ levels. Total energies are in Hartree, bond lengths are in Å, vibrational frequencies are in cm^{-1}, bond angles are in degrees, and the ZPEs are in kcal/mol.

	OCS			OCS$^-$	
Property	CCSD(T)	HFDFT	Exp[a]	CCSD(T)	HFDFT
R_e(C–O)	1.1582	1.1613	1.1562	1.2082	1.2091
R_e(C–S)	1.5656	1.5634	1.5614	1.7035	1.7068
∠ OCS°	180.0	180.0	180.0	136.54	136.32
$\omega(\pi)/\omega(a')$[b]	531	539	520	484	483
$\omega(\sigma)/\omega(a')$[b]	878	889	866	686	692
$\omega(\sigma)/\omega(a')$[b]	2103	2104	2072	1681	1661
ZPE	5.78	5.82	5.69	4.08	4.06
E(HF)	−510.334916	−510.334468	...	−510.320452	−510.320321
E(CCSD(T)/B3LYP)	−511.127200	−511.474089	...	−511.119682	−511.469785

[a] See Ref. 58.

[b] The anion frequency designation.

B. Potential energy curves of the CO_2 – CO_2^- and CS_2 – CS_2^- pairs

In order to see the mutual behavior of the total energies as a function of the bending angle, we performed CCSD(T)/ 6-311+$G(3df)$ and CCSD(T)/6-311+$G(2df)$ calculations for the CO_2 – CO_2^- and CS_2 – CS_2^- pairs, respectively. The bond lengths were optimized at each particular bending angle, which was stepped down by 10°. As is seen from Figs. 1 and 2, the CS_2^- anion is nearly stable towards the autodetachment of an extra electron at the linear geometry, whereas the CO_2^- anion is not. Also, the optimized bond lengths presented in Figs. 3 and 4 show different behavior. If $R(C-S)$ at the linear geometry has a considerable elongation with respect to the bond length of the neutral parent, then $R(C-O)$ of CO_2^- is almost the same as in the neutral CO_2 molecule and moves gradually to the equilibrium bond length of CO_2^- upon bending.

CS_2^- is unstable towards autodetachment by 0.046 eV at the CCSD(T)/6-311+$G(2df)$ level. This value has been obtained according to Eq. (2) for optimized linear configurations of CS_2 and CS_2^- with the anion ZPE determined for the equilibrium angular anion configuration, because the linear configuration of CS_2^- corresponds to a transition state. After recalculating in the same manner at the CCSD(T)/6-311 +$G(3df)$ level, we have obtained the anion to be stable towards autodetachment by 0.016 eV at the reoptimized linear configuration. Such energies are typical for binding an extra electron in dipole-bound states of anions formed by polar molecules.[64–70] Therefore, the extra electron could be autodetached from the linear CS_2^- anion in fields of the same range.

In order to check that there are no excited dipole-bound states at the anion geometries which could be relatively long-lived,[43] we have calculated the dipole moments of CO_2 and CS_2 at the equilibrium geometries of the corresponding anions at the CCSD(T)/6-311+$G(3df)$ level. The dipole moments are found to be rather small: −0.90 and 0.46 D for CO_2 and CS_2, respectively. These values are much smaller then the critical value of ≈2.5 D required for sustaining a dipole-bound state. Our calculations with the EA-EOMCCSD method[71] performed in the same manner as for nitromethane[43] have shown the absence of any excited anionic states at the equilibrium geometries of CO_2^- and CS_2^-. Therefore, the nearly linear configuration of CS_2^- appears to be responsible for experimental observations of the very weakly bound anions.

TABLE III. Results of calculations for CO_2^- and CS_2^- performed at the CCSD(T)/6-311+$G(3df)$ and HFDFT/ 6-311+$G(3df)$ levels. Total energies are in Hartree, bond lengths are in Å, vibrational frequencies are in cm^{-1}, bond angles are in degrees, and the ZPEs are in kcal/mol.

	CO_2^-			CS_2^-	
Property	CCSD(T)	HFDFT	Exp.	CCSD(T)	HFDFT
R_e(C–O)	1.2301	1.2326	1.25[a]	1.6345	1.6300
∠ OCO°	137.93	137.73	127± 8[a], 134[b]	144.01	145.16
$\omega(a_1)$	679	658	849[a]	325	319
$\omega(a_1)$	1222	1181	1424[a]	659	647
$\omega(b_2)$	1769	1723	1671[a], 1658[c]	1198	1214
ZPE	5.25	5.09	...	3.12	3.12
E(HF)	−187.661067	−187.660813	...	−832.968641	−832.968751
E(CCSD(T)/B3LYP)	−188.373949	−188.528557	...	−833.860567	−834.404937

[a] See Ref. 59.

[b] See Ref. 60.

[c] See Ref. 61.

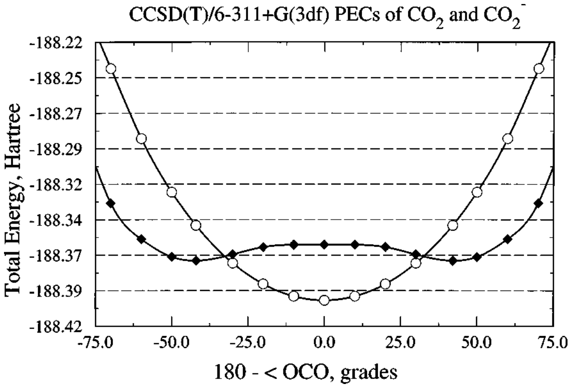

FIG. 1. Potential energy curves of CO_2 (○) and CO_2^- (◇) in C_{2v} symmetry as a function of 180° − ∠OCO° computed at the CCSD(T)/6-311+$G(3df)$ level.

According to the results of the Mulliken analysis, CO_2 has charges (-0.22, $+0.44$, -0.22) that correspond to case B of Prasad *et al.*,[23] whereas CS_2 corresponds to case A, having the opposite charge distribution ($+0.28$, -0.56, $+0.28$). If we use the estimates of Wallis *et al.*[22,23] (i.e., $Q_{\min}$ (A) $= 21.0$ a.u. and $Q_{\min}$ (B)$= 2.6$ a.u.) then one should find the quadrupole binding in linear CO_2^- (where the magnitude of Q_{zz} is computed to be 3.27 a.u., see Table VI), but not in CS_2^-, since CS_2's quadrupole moment is 2.32 a.u. It appears that the theoretical estimates of Prasad *et al.*[23] need corrections to be suitable for real systems, as was the case for the critical dipole moment value required to sustain a dipole-bound state.

Usually, one can simulate the autodetachment of an extra electron by adding more and more diffuse functions[72] in such a manner as not to introduce linear dependencies, e.g., placing the diffuse functions at some distant site.[43] The HF reference function of the linear CS_2^- have all negative orbital eigenvalues, i.e., the anion is stable towards autodetachment in the Koopmans' sense. So, adding diffuse functions does not change the shape of the anionic PEC, resulting only in some lowering with respect to the neutral PEC.

On the contrary, the HOMO of the CO_2^- anion has a positive eigenvalue at bending angles up to 155°. Adding some diffuse functions will result in the disappearance of the inner portion of the anionic curve between two crossing points with the neutral curve[73] (see also a discussion in Ref. 44), and the CO_2^- PEC will consist of two "pockets." The depth of the anionic well, or, in other words, the height of the barrier for matching the neutral PEC or activation energy is about 0.12 eV (1000 cm^{-1}). If to estimate the difference in the energy of zero-point motions (ZPE) as the difference in the harmonic ZPE calculated at the equilibrium configurations of CO_2 and CO_2^-, see Tables I and III, then it adds about 700 cm^{-1}. This seems to be enough for sustaining, at least, the first bending vibration mode with the frequency of about 660 cm^{-1} (see Table I). Our activation energy of about 0.22 eV is in nice accord with the experimentally deduced value of 0.26 eV,[59] and the HF value is about 0.4 eV.[76]

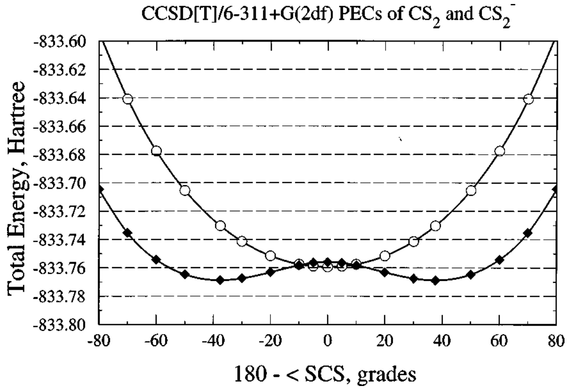

FIG. 2. Potential energy curves of CS_2 (○) and CS_2^- (◇) in C_{2v} symmetry as a function of 180° − ∠SCS° computed at the CCSD(T)/6-311+$G(2df)$ level.

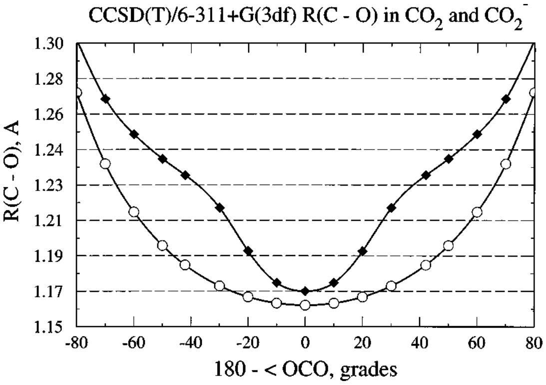

FIG. 3. Bond lengths of CO_2 (○) and CO_2^- (◇) as a function of 180° − ∠OCO° computed at the CCSD(T)/6-311+$G(3df)$ level.

C. Adiabatic electron affinity

The EA_{ad}s of the series calculated according to Eq. 2 at the geometries optimized at the CCSD(T) and HFDFT levels are presented in Table IV. For all the *ab initio* evaluations, the CCSD(T) ZPEs are used and for the HFDFT evaluations, the ZPEs are obtained with the BLYP exchange-correlation functional. In order to see the effect of the basis dependence, the EA_{ad}s of CO_2 and CS_2 are calculated with the 6-311 $+G(2d)$ and 6-311$+G(3df)$ basis sets. As is seen from Table IV, the results are virtually independent of the extension of the 6-311$+G(2d)$ basis set at all the levels of theory.

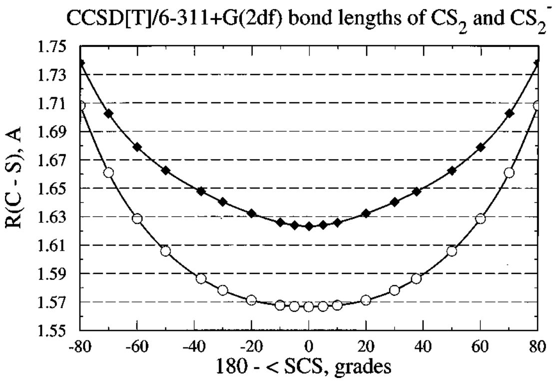

FIG. 4. Bond lengths of CS_2 (○) and CS_2^- (◇) as a function of 180° − ∠SCS° computed at the CCSD(T)/6-311+$G(2df)$ level.

TABLE IV. Adiabatic electron affinities of CO_2, OCS, and CS_2 calculated according to Eq. 2 with different basis sets. All values are in eV.

Level	CO_2		OCS	CS_2	
	6-311+$G(2d)$	6-311+$G(3df)$	6-311+$G(3df)$	6-311+$G(2df)$	6-311+$G(3df)$
HF	−1.190	−1.140	−0.320	0.353	0.316
MBPT(2)	−0.847	−0.845	−0.379	0.002	−0.011
CCSD	−0.684	−0.691	−0.104	0.406	0.382
CCSD+T[a]	−0.657	−0.655	−0.130	0.307	0.301
CCSD(T)	−0.669	−0.666	−0.221	0.306	0.300
HFDFT					
LDA	−0.523	−0.561	−0.170	0.208	0.184
BLYP	−0.527	−0.572	−0.153	0.180	0.155
B3LYP	−0.482	−0.527	−0.041	0.362	0.336
Exp.	−0.4±0.2[b], −0.6±0.2[c]		0.46±0.2[c]	0.5±0.2[d], 1.0±0.2[c], 0.895±0.020[e]	
ΔZPE CCSD(T)	0.089	0.091	0.074	0.051	0.054
ΔZPE HFDFT	0.100	0.094	0.076	0.056	0.056

[a] CCSD+T is a short form of the CCSD+T(CCSD) method (Ref. 47).

[b] See Ref. 2.

[c] See Ref. 4.

[d] See Ref. 15.

[e] See Ref. 16.

The most diffuse functions in the 6-311+$G(2d)$ and 6-311+$G(3df)$ bases have exponents of 0.04. In order to check the dependence of the computed EA_{ad} values on further diffuse extensions of the bases we performed the calculation of the EA_{ad} of CS_2 at the CCSD(T)/GEN level, where GEN denotes the 6-311+$G(2d)$ basis extended with 7 diffuse sp-shells (starting with exponent of 0.005 to 0.000 005[43]) placed at the central atom. The increase in the EA_{ad} value was found to be 0.02 eV only.

Theoretical values of the EA_{ad} have been published for CO_2 only (−0.81 eV,[39] CI/5s3p1d with Davidson's correction;[74] −0.76 eV,[40] MBPT(3)/6-31+$G(d)$; and −0.62 eV,[41,42] G2 level[75]). Our value of −0.67 eV obtained at the CCSD(T) level agrees with the experimental value of −0.6 ±0.2[4] to within the experimental error bars.

The experimentally measured[4,15,16] EA_{ad} of CS_2 have a rather large dispersion. The photodetachment value of 0.895 ±0.020 eV[16] is expected to be the most accurate. However, the EA_{ad} values obtained at the CCSD(T)/6-311+$G(3df)$ and HFDFT/6-311+$G(3df)$ levels, which differ by only 0.036 eV, are in agreement with the lowest boundary of the value of 0.5±0.2 eV obtained by Hughes *et al.*[15] with the use of the endothermic negative-ion charge transfer (ECT) reaction

$$CS_2^- + SO_2 \rightarrow CS_2 + SO_2^- . \tag{4}$$

As no surprise, the EA_{ad} of OCS is between the values for CO_2 and CS_2, being slightly negative (see Table IV).

In order to elucidate the discrepancy between our value of ≈0.3 eV for the EA_{ad} of CS_2 and the values of 0.895 ±0.020 obtained by Oakes and Ellison[16] and the lower limit of 0.8 eV obtained by Schiedt and Weinkauf[17] with the use of laser photodetachment spectroscopy, we performed calculations of the CO_2^-, CS_2^-, and OCS^- VDEs according to Eq. (3). As is seen from Table V, all the anions are stable with respect to detachment of an extra electron at all levels of theory, including HF. The VDEs obtained at the CCSD(T) and HFDFT levels show much larger deviations (up to 0.35

TABLE V. Vertical detachment energies of CO_2^-, OCS^-, and CS_2^- calculated according to Eq. 3 with different basis sets. All values are in eV.

	CO_2^-		OCS^-	CS_2^-	
Level	6-311+$G(2d)$	6-311+$G(3df)$	6-311+$G(3df)$	6-311+$G(2df)$	6-311+$G(3df)$
HF	1.322	1.183	1.624	1.709	1.560
MBPT(2)	1.087	0.766	1.169	0.997	0.946
CCSD	1.127	1.108	1.507	1.470	1.406
CCSD+T	0.933	0.940	1.323	1.230	1.193
CCSD(T)	0.965	0.996	1.353	1.255	1.218
LDA	1.239	1.168	1.508	1.198	1.141
BLYP	1.080	1.012	1.432	1.053	1.001
B3LYP	1.331	1.255	1.598	1.335	1.280

TABLE VI. Electric quadruple moments (in atomic units, 1 a.u.=1.345035 10^{-26} esu) of CO_2, OCS, and CS_2 and their anions calculated at the HF and CCSD(T) levels with the 6-311+$G(3df)$ basis set, and electric dipole moments of CO_2^-, OCS^-, and CS_2^- (in Debye).

Level	CO_2	OCS	CS_2
HF	−3.881	−1.046	2.446
CCSD(T)	−3.269	−0.723	2.316
Exp.	-3.2 ± 0.15^d	-0.22 ± 0.07^d, -0.59 ± 0.01^e -0.65 ± 0.1^f	2.7 ± 0.7^g
HF[a]	−4.300	−1.456	1.468
MCSCF,CI	-3.40^b	-1.01^b,-0.80^c	1.56^b, 2.1 ± 0.5^b
	CO_2^-	OCS^-	CS_2^-
HF			
DM	0.206	0.320	0.095
QM *xx*	4.318	−6.630	5.311
QM *yy*	−6.294	2.238	−8.085
QM *zz*	1.975	4.393	2.774
CCSD(T)			
DM	0.266	0.216	0.017
QM *xx*	3.738	−5.849	5.496
QM *yy*	−4.899	1.541	−7.410
QM *zz*	1.161	4.308	1.915

[a] The basis set is $10s6p/5s3p$ for C,O and $12s9p/6s5p$ for S, see Ref. 79.
[b] Obtained from the results of the MCSCF calculations, see Ref. 80.
[c] The SD-CI result, see Ref. 81.
[d] See Ref. 82.
[e] See Ref. 83.
[f] See Ref. 84.
[g] See Ref. 85.

eV) than the EA_{ad}s presented in Table IV. These deviations decrease as the basis set increases.

Experimental photodetachment spectra of CO_2^- and CS_2^- [77,78] exhibit broad maxima at approximately 1.4 and 1.2 eV, which could be attributed roughly to the vertical detachment energies. The wide vibrational structure shown in these spectra is indicative of large differences in neutral and ionic equilibrium geometries. This structure, whose intensities are determined by Franck-Condon factors, corresponds to the bent neutral parent in different vibrational states left after an extra electron is photodetached. A rather large difference between our value of the EA_{ad} of CS_2 and experimental data[16,17] appears to be due to ''poor Franck-Condon overlap between the bent anionic and the linear neutral molecular structures.''[17]

D. Electric quadruple moments

Electric quadruple moments of the neutral CO_2, OCS, and CS_2 molecules have been determined from both computation[79,80] and experiment.[81–85] However, the results of different studies are in serious disagreement, showing a difference of an order of magnitude.[81] The CCSD(T) method appears to produce rather reliable estimates for first- and second-order molecular properties,[86] which is confirmed also by our CCSD(T)/6-311+$G(3df)$ computations on the permanent dipole moment of OCS. The calculated value of 0.717 D closely matches the experimental value of 0.71521 ±0.00020 D.[57] The electric quadruple moments of all the neutral molecules and their anions are computed at the same, CCSD(T)/6-311+$G(3df)$, level. Comparison of our values to other theoretical and experimental data is shown in Table VI. As is seen, our values are in reasonable agreement with the experimental data for the neutral molecules, which basically have rather wide uncertainties. Since we have used a larger basis than that used in the previous correlated calculations,[80] our values can be recommended as more reliable estimates. The anions are bent, so they have three independent components of the electric quadruple moment. No experimental or previous theoretical data on the quadruple moments of the anions have been reported.

IV. CONCLUSION

We have calculated the structure of the OCS^- and CS_2^- anions at rather reliable CCSD(T) and HFDFT levels of theory and evaluated the adiabatic electron affinities (EA_{ad}) in the CO_2, OCS, CS_2 series. Several conclusions can be drawn from the results of our computations:

(i) Calculations of the ground-state properties (e.g., vibrational frequencies, bond lengths, quadrupole moments, etc.) for CO_2, OCS and CS_2 are in nice accord with experimental data. Only slightly less accuracy should be anticipated for the anions as well.

(ii) The ground-state CO_2^-, OCS^- and CS_2^- anions exist in bent equilibrium configurations. The EA_{ad} is calculated to increase along the series from −0.66 eV in CO_2 and −0.22 eV in OCS to 0.30 eV in CS_2.

(iii) Vertical detachment energies of CO_2^-, OCS^- and CS_2^- are positive and rather large (about 1 eV).

ACKNOWLEDGMENTS

We are appreciative to Professor K. H. Bowen for sending us the reprints with the photodetachment results. This work was supported by the Office of Naval Research Grant Number N00014-95-1-0614 and in part by a grant of HPC time from the DoD HPC Center. R.N.C. was supported by the National Science Foundation (CHE -9508609).

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