Electronic Structure Calculations for $ArCO_2^+$ and $ArCO_2$

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Ab initio calculations are performed for $ArCO_2^+$ and $ArCO_2$. Between the two configurations of $ArCO_2^+$ the orbital interactions and the higher order correlation calculations favor the T-shape, and their interaction energies are calculated to be approximately half the experimental values using 6-31G* basis set. In $ArCO_2$, the calculations qualitatively favor the T-structure, which is compatible with the experiment. However, the true interaction energy is obscured since it is within the BSSE limit at this basis set size and the correlation level. Addition of sp type diffuse functions increase the interaction energies by a considerable amount, but the BSSE estimated by CP method are responsible for the significant portion of the difference. The possible equilibrium structure of the Ar^+-CO_2 complex, where the charge is localized on Ar, is suggested as having a linear structure. The potential energy surface and the amount of charge transfer are shown to be sensitive to the type and balancing of basis set.

Introduction

The informations about the interactions of carbon dioxide with other atoms and molecules are important in a variety of problems. In atmospheric chemistry of CO_2, various properties are almost certainly resulted from the relative strengths of weak interactions. These weakly bound complexes are species that can be thought of as being similar to a collision complex, which is intermediate between reactants and products. Unfortunately, since the collision complex is a transitory species, it is extremely hard to obtain direct experimental observations. Recently, however, several experiments have been progressed to directly observe properties of such transitory species.[1-3] Nevertheless, there are still several difficulties in experimentally obtaining all the data necessary for clear interpretations of structures and reaction mechanisms of weakly bound clusters. For these reasons, in this work we perfmon series of the standard quantum chemical calculations for CO_2^+-Ar cluster ion. The study of this cluster ion is also potentially important due to the role they might play in solution and vapor-to-liquid transitions[4] and due to their bonding character, which is intermediate between van der Waals molecules and covalent bonds. In addition, several experimental studies are available for $ArCO_2^+$ and $ArCO_2$.[5,6,7] The shape of $ArCO_2^+$ is not clearly determined from experiments and one of the main subjects of this work.

The determination of accurate interaction potential for weakly bound species is extremely difficult in practically unavoidable approximations of quantum mechanics.[8] This is because the determination of electron correlation, which accounts for the major part of attraction in these correlation bound complexes, is still nontrival and has limitations such as the truncation of multiple orbital excitations and the use of an incomplete basis set. Moreover, the relative errors in the van der Waals interaction energy are even larger since the interaction energy is composed of attractive correlation contribution which is in a tiny percentage of the total energy and the repulsive HF contributions. The size and quality of basis sets which are always important in any ab initio calculations becomes even more crucial for these species.

HF and MP2 calculations with 6-31G* basis set are the starting points for the present study and further correlation calculations of $ArCO_2^+$ and also $ArCO_2$ are performed for comparison of the interaction energies. We also study the basis set superposition error(BSSE) and other basis set effects. In section 2, the computational methods will be briefly discussed. In section 3, the results of calculations and in section 4, summary and discussions will be given.

Methods of Computation

For weakly bound molecules, potential energy surface is sensitive to the distribution of valence electrons, so the use of split valence basis set is essential. Most calculations are performed using 6-31G* basis set.[9-12] In a few selected cases, sp type diffuse functions[11,13] are added in the basis set in order to study the effect of basis set and to obtain better description of the bonding.

The starting point for electronic structure calculations is Hartree-Fock(HF) for closed shell molecules and unrestricted HF(UHF) for open shell systems. Correlations are included using perturbational methods, MP2, MP3 and MP4, where MP stands for Moller-Plesset[8,14] and the numbers refer to second, third and fourth orders, respectively. BSSE are estimated by the counter poise (CP) method.[15]

All the methods used in the present study are quite standard, and detailed derivations of the theory and computational methods are available in the literature. All the calculations are carried out using GAUSSIAN 82 program developed by Pople and coworkers.

Results

The available experimental values for $ArCO_2$, CO_2^+, and CO_2 are summarized in Table 1. Various experiments have been reported for $ArCO_2^+$.[6,7] Assuming that the appearance potential is identical to the adiabatic ionization potential, the Ar-CO_2^+ bond dissociation energy is calculated to be 0.26 ± 0.04eV[6] using the relation $D_0(ArCO_2^+) = IP(CO_2) + D_0(ArCO_2) - IP(ArCO_2)$. The experimental ground state geo-

Table 1. The Experimental Values of the Bond Dissociation Energy(D_0), the Ionization Potential(IP) and the Equilibrium Bond Distances(r_0) of $ArCO_2$, CO_2, and CO_2^+

Ar-CO_2	$D_0 = 0.02 \pm 0.01$eV[a]
Ar-CO_2	IP = 13.53 ± 0.03eV[a]
CO_2	IP = 13.773 ± 0.002eV[a]
Ar-CO_2(C_{2v} symmetry)	r_0 = 3.493A[b](3.16A)[a]
CO_2	r_0 = 1.162A[c]
CO_2^+	r_0 = 1.177A[c]

[a] reference 6. [b] reference 5. [c] reference 16.

Table 2. MP2 Equilibrium Energies with 6-31G* basis-set(in hartrees). All Electrons are Correlated in MP2 level

	E_{HF}	E_{MP_2}	$E_{corr} = E_{MP_2} - E_{HF}$
Ar	-526.77375	-526.91999	-0.14625
CO_2	-187.62841	-188.11836	-0.48995
CO_2^+	-187.17630	-187.59159	-0.41528
$ArCO_2(C_{2v})$	-714.40198	-715.03886	-0.63687
$ArCO_2(C_{\infty v})$	-714.40205	-715.03867	-0.63662
$ArCO_2^+(C_{2v})$	-713.95075	-714.51439	-0.56365
$ArCO_2^+(C_{\infty v})$	-713.94500	-714.51700	-0.57201

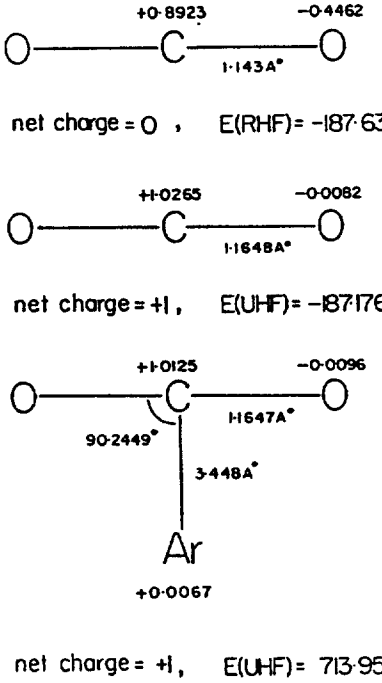

Figure 1. Calculated equilibrium geometries, total energies and partial charges at HF level. (6-31G* basis set).

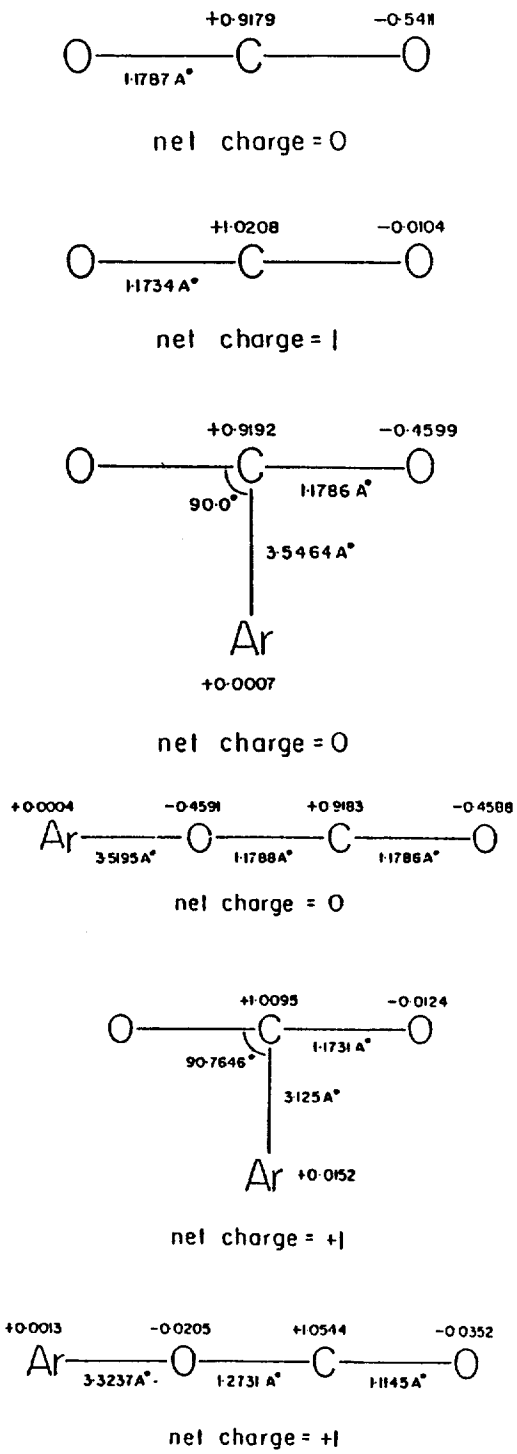

Figure 2. Calculated equilibrium geometries at MP2 level and partial charges calculated at HF level. All electrons are correlated at MP2 level. 6-31G* basis-sets are used.

metry of neutral $ArCO_2$ is T-shaped with small modifications in CO_2 structure. There are two values of Ar-C distance reported as shown in Table 1. No experimental determination of the $ArCO_2^+$ geometry has been made. Figure 1 shows the HF optimized geometries of CO_2, CO_2^+ and $ArCO_2^+$ using 6-31G* basis set. Among the $ArCO_2$ species, only the $ArCO_2^+$ shows a minimum at HF level. The other complexes have purely repulsive potential energy curves at HF level, which is the characteristic of the correlation bound complexes, since the dispersion force, which is the origin of attractive force in van der Waals molecules, comes from the correlation effects. The magnitudes of correlation effect shown in Table 2, varies from -0.146 a.u.(Ar) to about -0.6 a.u.. One can see that most of the attractions in $ArCO_2$ species including Ar-CO_2^+ originate from the correlation energies. Partial charges are calculated from the Mulliken population analysis. For the CO_2 molecule, the total energy is lower by 0.0013 a.u. than that of Mota and Novoa at HF level[17], because the energy by Mota *et al* is calculated at the equilibrium geometry without geometry optimization. For both CO_2 and CO_2^+ in Figure 1,

Table 3. Interaction Energies of Complexes at MP2 Optimized Geometries in eV (6-31G* basis-set), $\Delta E(CP)$ is the BSSE Corrected one by the CP method

	ΔE_{MP2}	$\Delta E(CP)_{MP2}$	BSSE
$ArCO_2(C_{2v})$	-0.0136	0.0018	-0.0154
$ArCO_2(C_{\infty v})$	-0.0086	0.0010	-0.0096
$ArCO_2^+(C_{2v})$	-0.0766	-0.0489	-0.0277
$ArCO_2^+(C_{\infty v})$	-0.1477	-0.1402	-0.0075
$ArCO_2^+(C_{2v})^a$	-0.1102	-0.0603	-0.0499
$ArCO_2^+(C_{\infty v})^a$	-0.1910	-0.1585	-0.0325

[a] 6-31G* + diffuse function on C,O. The calculations are done at MP2 optimized geometries using 6-31G*.

the calculated equilibrium bond lengths are slightly shorter than the experimental values. The ground state electronic configuration of CO_2 is $(1\sigma_u)^2(1\sigma_g)^2(2\sigma_g)^2(3\sigma_g)^2(2\sigma_u)^2(4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^4$. When CO_2 is positively charged, the ejected electron comes from the nonbonding HOMO $1\pi_g$, mainly composed of p_π orbitals of both oxygens. As a result, structures of CO_2 and CO_2^+ are very similar. Since the ionization potential of CO_2 is 13.773eV, which is smaller than the ionization potential of Ar(15.760eV), the positive charge is expected to belong to CO_2 for the ionic cluster of Ar and CO_2. The charge transfer to Ar is expected to be very small. These expectations are compatible with the result of HF calculations as shown in Figure 1.

MP2 optimized geometries are summarized in Figure 2. Neutral complexes, which are purely repulsive at HF level, now become weakly bound. However, the magnitudes of interaction energies of neutral complexes are all comparable with BSSE as shown in Table 3, making it very hard to judge whether the equilibrium structures are mathematical artefacts or not. Since the CP method slightly overestimates BSSE, it is still possible that neutral complexes are slightly bound at MP2 level with 6-31G* basis set.

MP2 calculations indicate that T-shape $ArCO_2(C_{2v}$ symmetry) is more stable than the linear type($C_{\infty v}$), in agreement with the experiment, if CP correction of BSSE is neglected. Since we do not understand the exact nature of BSSE at present, BSSE will be neglected in the main analysis of $ArCO_2$ and $ArCO_2^+$ followed. Calculated dissociation energy of 0.014 eV for $ArCO_2$ is somewhat smaller than the experimental value of 0.02eV. The calculated Ar-C distance of 3.55Å is considerably longer than the experimental value of 3.16Å by Pratt and Dehmer[6], but in reasonable agreement with the other experimental value of 3.47Å by Steed, Dixon and Klemperer.[5] Although additional electron correlations can reduce the bond length, it is not likely to be shortened close to 3.16Å even at MP4 level with the present basis set. Therefore, bond length of 3.49Å seems more reasonable. Then, the present scheme of MP2 calculations with 6-31G* basis set yield qualitatively correct results for van der Waals complex like $ArCO_2$, when BSSE is not considered. It is noted in passing that the less stable linear structure has Ar-O bond length of 3.52Å which is shorter than Ar-C distance in the T-shape $ArCO_2$.

For $ArCO_2^+$, the linear structure is calculated to be more stable at MP2 level as shown in Table 3. As in $ArCO_2$, BSSE estimated by CP method is larger for the T-shape than the linear shape for $ArCO_2^+$. Furthermore, magnitudes of BSSE are considerably larger as Ar and CO_2^+ get closer. Thus BSSE corrected results favor the linear shape even more. In the linear $ArCO_2^+$ in Figure 2, the geometry of CO_2^+ fragment is modified from the isolated CO_2^+. C-O distance for CO bond on Ar side increases to 1.273Å and that on the other side of C decreases to 1.115Å compared to MP2 optimized CO_2^+ distance of 1.173A. Apparently, formation of weak bond between Ar and O reduces the bond strength of CO bond on one side and CO bond on the other side counteracts, but the exact analysis including bond order is difficult because of the complicated correlation effects. The geometry change of the CO_2^+ fragment in the T-shape $ArCO_2^+$, also shown in Figure 2, is very small. CO bond length remains almost the same and the angle $\angle ArCO = 90.8°$, is only slightly larger than the right angle.

Table 4. MP2, MP3, MP4, CISD total Energies of $ArCO_2^+$ at MP2 Optimized Geometry. Energies are in Hartrees. (6-31G* basis set) Only in CISD, all Electrons are Correlated. The other ones are Calculated in Frozen core Approximation

	E_{MP2}	E_{MP3}	E_{MP4SDQ}	E_{CISD}
$ArCO_2^+(C_{2v})$	-714.49481	-714.5144	-714.53111	-714.55441
$ArCO_2^+(C_{\infty v})$	-714.49764	-714.51312	-714.52817	-714.53662

The additions of sp diffuse functions on C and O atom increase the dissociation energies of both the linear and the T-shape as shown in Table 3. Although geometries are not fully optimized with diffuse functions added, preliminary calculations indicate that effects of diffuse functions on geometry will be very small. Calculated dissociation energies for T-shape $ArCO_2^+$ are 0.077eV and 0.11eV without and with diffuse functions, respectively and these for linear shape $ArCO_2^+$ are 0.15eV and 0.19eV without and with diffuse functions, respectively. Therefore, dissociation energy for the linear shape approaches experimental value of 0.26eV with increasing size of basis set. In the absence of further calculations, one might conclude that $ArCO_2^+$ is linear in the lowest state. Unfortunately, higher order correlation energies computed with 6-31G* basis set lower the energy of T-shape $ArCO_2^+$ more than that of the linear $ArCO_2^+$. The energies with higher order correlation terms included, MP3, MP4 and CISD at the MP2 optimized geometries, are summarized in Table 4 and clearly favor T-shape $ArCO_2^+$. Calculations at several grids on the potential energy surface imply that geometry changes due to higher order correlation terms are very small.[18] Although the present study of correlation effects are not exhaustive, i.e. multireference calculations are not attempted, it is reasonable to conclude that $ArCO_2^+$ is more stable as a T-shape with 6-31G* basis set.

As expected from the slight covalent bonding of Ar with CO_2^+, Ar-C distances shown in Figure 2 are significantly shorter for $ArCO_2^+$ than for $ArCO_2$ both in T-shape and linear shape. Charges from Mulliken population analysis of HF orbitals are also given in Figure 2 for reference. When these charges are referred, one should bear in mind that descriptions can be considerably different at MP2 level.

A crude study of Ar^+-CO_2 is also performed, since Ar^+-CO_2 is likely to be an intermediate in the photodissociation of $ArCO_2^+$. When energies of Ar^+-CO_2 are estimated from orbital energies of $ArCO_2$ using Koopmans' theorem,[18] the linear Ar^+-CO_2 is likely to be more stable than the T-shape. If we assume that electrostatic interaction between Ar^+ and

negatively charged O atom of CO_2 fragment are responsible for most of bonding interaction in Ar^+-CO_2, the preference of the linear shape is easy to comprehend. This result is in line with calculations reported for K^+CO_2 and Na^+CO_2.[17] We note that similar argument will favor the linear structure for $ArCO_2^+$, since Ar is slightly positive and O is still negative (Figure 1 and 2) in $ArCO_2^+$. $ArCO_2$ which is T-shape and not ionic has the same valence shell structure as K^+CO_2 and Na^+CO_2. On the contrary, the argument favoring T-shape at MO interaction level can be made based upon the large overlap between Ar p orbitals and nonbonding LUMO of CO_2^+ $1\pi_g$ orbital.[6] Simple analysis based upon MO is useful for many purposes even for systems like $ArCO_2^+$ and $ArCO_2$. Since the present study implies that actual bonding interactions are lot more complicated than what can be pictured from MO's, descriptions based on MO should be exercised with care.

Summary and Discussions

Results of MP2 calculations with 6-31G* basis set for Ar-CO_2 are in qualitative agreement with some of experimental results. Same level of calculations for $ArCO_2^+$ favor the linear shape rather than the T-shape. Addition of diffuse basis set supports the same conclusion. However, higher order correlation effects estimated from MP3, MP4 and CISD calculations with 6-31G* basis set switch the order of stability for $ArCO_2^+$. Although higher order correlation effects are not studied with diffuse functions added, T-shape $ArCO_2^+$ appears to be more stable than the linear shape. The present study is not accurate enough to produce reliable dissociation energies. In the T-shape $ArCO_2$ and $ArCO_2^+$, CO_2 fragments are little changed from isolated CO_2 species, but Ar-C distance becomes considerably shorter in $ArCO_2^+$ compared with $ArCO_2$. Without actual computations of Ar^+CO_2, the lowest state of Ar^+CO_2 is guessed as being linear.

When BSSE's are estimated from CP method and results are corrected accordingly, it is hard to decide whether any of the stable geometries is the artifact of BSSE or not. Under the assumption that CP method overestimates BSSE, BSSE's are reported but not included in the analysis of the result and thus in deriving the above conclusions. More accurate estimate of BSSE is planned but probably requires major theoretical modifications.

Extensions of present calculations to more elaborate methods, such as multireference correlated calculations and/or larger basis sets, are straightforward in theory, but do not seem practical at this moment because of the manifold increase in the required computational time, which is already quite expensive for the present level of the study.

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