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Electron attachment to CO₂ clusters

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Vertical and adiabatic electron attachment to carbon dioxide clusters (CO₂)_N ($N=2-5$) is studied at high *ab initio* levels of theory. As a first step the geometries of neutral and anionic CO₂ clusters are reexamined. The potential energy surfaces of both neutral and anionic CO₂ clusters show many minima, and several isomers have been reported so far. Here we present new lowest-energy isomers for the tetramer and pentamer anion clusters, as well as high-level results for relative and CO₂ evaporation energies. Electron correlation is crucial for the computed properties, and since we had to make certain compromises about the theoretical level in order to include larger clusters, a thorough investigation of different *ab initio* methods is performed for the dimer. The vertical affinities of the investigated (CO₂)_N clusters are found to be clearly negative; i.e., vertical attachment into valence orbitals leads to temporary anion states. The energies of these resonances as well as the associated autodetachment lifetimes are computed using complex absorbing potentials at the frozen-orbital and correlated second-order Green's function levels. Whereas the cluster environment has a surprisingly weak influence on the negative vertical affinities, solvation has a strong effect on the adiabatic electron affinities. The computed trends suggest that the tetramer is at the brink of stability and that the pentamer cluster is the smallest species possessing an appreciable positive electron affinity. Our findings have profound implications for the interpretation of the low-energy electron attachment experiments and provide a basis for the discussion and modeling the attachment process. © 2003 American Institute of Physics. [DOI: 10.1063/1.1609395]

I. INTRODUCTION

Despite the long-standing interest in electron attachment to CO₂ clusters and the long-lived cluster anions originating from this process, there are still many open questions regarding the attachment mechanism as well as the nature of the produced anions. Carbon dioxide cluster anions have been studied in many experiments (see, e.g., Refs. 1–5 and references therein), and a thorough discussion is far beyond the scope of the present communication. Since we focus in particular on the electron binding energies of different CO₂ cluster types, in the following, we confine ourselves to a brief outline of the results from photoelectron spectra that directly address the structure of the long-lived cluster anions as well as to high-resolution electron attachment studies that provide direct information on the attachment process.

Starting with Rossi and Jordan's work,⁶ two types of (CO₂)_N[−] clusters have been discussed. In type-I clusters the extra electron is—similar to the bent long-lived CO₂[−] anion^{7–10}—attached to a single, bent CO₂ monomer unit, and the other CO₂ molecules of the cluster can be viewed as a solvent. In contrast, type-II cluster anions are characterized by a dimer anion core similar to the oxalate monoanion, and the additional CO₂ molecules are again essentially solvating the anion core. Spectroscopic information about these cluster anion types has been obtained in the form of photoelectron (photodetachment) spectra (see Refs. 2 and 3 and references therein). Cluster anions (CO₂)_N[−] prepared by colliding neutral aggregates with high-energy (>100 eV) electrons have

been investigated, and it was found that with increasing cluster size N the anion core type switches twice: For $2 \leq N \leq 5$ exclusively dimer cores are found, for $7 \leq N \leq 13$ monomer cores prevail, and for $14 \leq N \leq 15$ again dimer cores are observed. The only cluster size where both anion types are present is $N=6$.

Understanding the observed core switches in the light of recent¹¹ calculations and our findings presented below is not easy. Previously, and our *ab initio* results, suggest that type-I and type-II clusters are very close in energy and that the relevant energy differences are smaller than the CO₂ evaporation energies from the cluster anions. Thus, instead of a clear preference for a specific structure type, from the calculations one would rather expect a mixture of isomers. Moreover, further *ab initio* studies¹² suggest fast transitions between the different minima on the potential energy surface of the cluster anions and therefore a fluctuating or floppy system. Finally, a dynamic explanation put forward in Ref. 11 is invalidated by the type-I pentamer structure presented in Sec. VI, and at the present stage there seems to be no straightforward explanation for the experimentally observed structural preferences.

Aspects of the attachment process itself were studied very recently by colliding slow electrons of well-defined energies in the 0–200 meV range with neutral CO₂ clusters.^{4,5} In the associated anion yields a series of sharp resonances (widths between 10 and 30 meV) was observed, and the energy differences between the resonance positions were found to correspond to the vibrational level spacing of the CO₂ monomer. Accordingly, these resonances have been interpreted as vibrational Feshbach resonances, suggesting that in the initial step of the attachment process the kinetic energy

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of the incoming electron is transferred to intramolecular vibrational degrees of freedom of the cluster and that the electron is—at least initially—trapped in a diffuse surface state.^{4,5}

In the present contribution we investigate electron attachment to small (CO₂)_N clusters ($N=2-5$) using high-level *ab initio* methods. On the one hand, vertical attachment is considered by examining what becomes of the short-lived ²Π_u resonance in a cluster environment, and on the other hand, the trends in the adiabatic attachment energies of the two cluster anion types are studied. To our best knowledge the vertical attachment energies to CO₂ clusters have not been considered before, and adiabatic electron affinities (EAs) are only known for the dimer. Our results shed some light on the reactants and products of the attachment process and provide a basis for the discussion of its mechanism and for setting up models for the attachment dynamics, for example, along the lines suggested by Tsukada *et al.*¹³ or more recently by Thoss and Domcke.¹⁴

The paper is organized as follows. Details of the *ab initio* calculations are described in Sec. II, and a careful study of different theoretical levels using three prototypical dimers is presented in Sec. III. For the calculations of the vertical and adiabatic electron attachment energies one needs to know the geometrical structures of the neutral and anionic carbon dioxide clusters, and in these two fields much work has been done. We discuss earlier work and our results for the geometries of neutral and anionic CO₂ clusters in Secs. IV and VI, respectively. The resonance energies associated with vertical attachment are presented in Sec. V, and the adiabatic EAs of (CO₂)_N clusters are considered in Sec. VII. Finally, our conclusions are discussed in Sec. VIII.

II. COMPUTATIONAL DETAILS

In this section we describe the *ab initio* methods used in this work. In the first place, the standard bound-state techniques employed to compute geometrical parameters and total energies of the neutral and long-lived anionic clusters are outlined, and in the second place, the calculation of the energies and lifetimes of the resonance states associated with vertical electron attachment are discussed.

For most of the standard calculations two basis sets have been used: Pople's 6-31G* split-valence set¹⁵ and the DZPD set that consists of Dunning's [4s2p1d]-polarized double-ζ set^{16,17} augmented with an *sp* set of diffuse functions (exponents at C: $\alpha_s=0.047$, $\alpha_p=0.036$ and at O: $\alpha_s=0.086$, $\alpha_p=0.064$). Basis set effects are studied in Sec. III using the considerably larger augmented correlation-consistent valence double- and triple-ζ sets¹⁸ (aug-cc-pVDZ and aug-cc-pVTZ).

Geometries have mostly been optimized at the second-order Møller-Plesset perturbation theory (MP2) level of theory. This is the lowest theoretical level that takes into account dispersion effects which is absolutely essential for weakly bound CO₂ clusters and cluster anions. In contrast, self-consistent-field (SCF) and currently available density functional techniques, which do not account for dispersion, are expected to be inadequate, and that is indeed what our experience shows (see also Refs. 11, 19, and 20 and cf. Secs. IV and VI). Higher correlation effects on the geometries

have been examined at the coupled cluster with single and double excitations (CCSD) and at the CCSD plus noniterative triples [CCSD(T)] levels of theory (Sec. III). In all correlated calculations the 1s core orbitals have been frozen and the anticore orbitals of the DZPD basis set have been discarded. Spin-restricted Hartree-Fock (RHF) reference wave functions have been used for the neutral closed-shell clusters and the calculations for the anionic open-shell species were mostly based on the spin unrestricted Hartree-Fock (UHF) approach. Spin contamination in the UHF wave functions was found to be small, and the expectation value for s^2 never exceeded 0.78. Moreover, at the different coupled-cluster levels the results obtained with RHF and UHF reference functions are virtually identical, and the associated differences in the EA values are much smaller than most other influences (typically 0.04 eV at the MP2 and 0.01 eV at the CCSD level). The calculations have been performed using the Aces II (Ref. 21) as well as the GAUSSIAN 98 (Ref. 22) packages of programs.

At the equilibrium geometries of the (CO₂)_N clusters ($N=2-4$) we did not find any bound anionic states. Vertical electron attachment into valencelike orbitals leads to temporary or resonance states, and no hint at a diffuse or surface state was found during the investigation of the resonance states where very diffuse basis sets have been employed.

The temporary anion states associated with the empty valence orbitals of the neutral clusters have been investigated using complex absorbing potentials (CAPs). The absorbing potential method^{23,24} is a general and flexible technique to describe decay processes. One adds an absorbing potential $-iW$ to the molecular Hamiltonian H and works with a parametrized non-Hermitian complex-symmetric Hamilton operator

$$H(\eta) = H - i\eta W, \quad (1)$$

where W is typically a real "soft"-box-like potential in the "dissociation coordinate" R —e.g., R^2 or R^4 —and η is a strength parameter. The resonance parameters are obtained *directly* as a complex eigenvalue

$$E_{\text{res}} = E_r - i\frac{\Gamma}{2} \quad (2)$$

of $H(\eta)$, and the associated resonance wave function is square integrable (\mathcal{L}^2). Loosely speaking, a CAP is added to the Hamiltonian to absorb the outgoing electron, and it is straightforward to combine the CAP method with existing electronic structure codes.²⁵ Here, on the one hand, the CAP was added to the static exchange Hamiltonian—i.e., the neutral cluster is treated within the frozen orbital approximation—and, on the other hand, the one-particle Green's-function-based ADC(2) method,²⁶ which includes orbital relaxation as well as electron correlation effects, has been used. More details on combining the ADC method with absorbing potentials can be found in Refs. 27 and 28.

In the CAP calculations large diffuse basis sets are needed, and for the calculations at the frozen-orbital level we employed Dunning's double-ζ basis set¹⁶ augmented with one *d*-type polarization function ($\alpha_d=0.75$ and 0.85 for C and O, respectively) and a (1s6p)/[1s5p] set of diffuse

functions [$\alpha_s=0.077$ and 0.14 for C and O, respectively, even-scaled p exponents (scaling factor 1.6) starting from the smallest exponents in the DZP set]. In the ADC calculations the one-particle basis set was Dunning's $[5s3p]$ valence triple- ζ set¹⁷ augmented with a d -type polarization function ($\alpha_d=0.72$ and 1.28 for C and O, respectively) and a $(1s10p)/[1s8p]$ set of diffuse functions ($\alpha_s=0.077$ and 0.14 for C and O, respectively, even-scaled p exponents, scaling factor 1.4), yielding a $[6s11p1d]$ set of contracted Gauss-type functions.

The first step in the CAP computations is an SCF calculation for the neutral CO_2 cluster, and the SCF has been performed with the MOLCAS 5 suit of programs.²⁹ The specific CAP form is the box-CAP suggested in Ref. 30, where the CAP box size has been set to the maximum component of the respective nuclear coordinates plus 2.5 bohrs in each Cartesian direction. The required matrix elements of the ADC and CAP matrices have been computed using our own codes, and the eigenpairs with the lowest energies [$\text{Re}(E_{\text{res}})$] have been obtained with standard numerical routines from the LAPACK library and a block-Davidson program adapted to the complex symmetric case,³¹ respectively. The second step consists of diagonalizing the CAP Hamiltonian repeatedly for different values of the CAP strengths η . Resonance states can be identified from the η trajectories of their complex energies that stay close to the real axis and show stabilization cusps. In contrast, η trajectories belonging to pseudocontinuum states accelerate quickly into the complex plane. With our basis sets it was possible to unambiguously identify the π^* -like resonances, and a satisfying stabilization behavior of the corresponding η trajectories was obtained.

III. DIMER AS A TEST CASE

In order to study trends in the electron attachment energies one needs to treat the species in question at a common theoretical level, and for the investigation of CO_2 clusters consisting of up to five monomer units we had to make certain compromises. In particular, we had to settle for MP2/6-31G* geometries and CCSD(T)/DZPD energies (MP2/DZPD energies for $N=5$), and the results discussed in this section are primarily intended to provide an idea of the effects that can be expected if higher levels of theory were used.

In the following we present an extended study of the CO_2 dimer (C_{2h} symmetry) and two dimer anions (C_{2v} and D_{2d} symmetry) using several *ab initio* methods and basis sets. The geometrical structures of the three dimers are shown in Fig. 1. The two anionic isomers are prototypical for the type-I and type-II cluster anions discussed in Sec. VI, and at this point we only note that in the C_{2v} isomer the two CO_2 moieties are only bound by weak intermolecular forces whereas the D_{2d} isomer shows a well-defined carbon-carbon bond (Fig. 1). Both dimer anions have been studied before at the SCF (Refs. 6 and 32) and at the MP2 levels of theory,^{11,20,33} and our MP2 results agree with the previous results. To our best knowledge this is the first time geometry optimizations have been performed at different coupled-cluster levels.

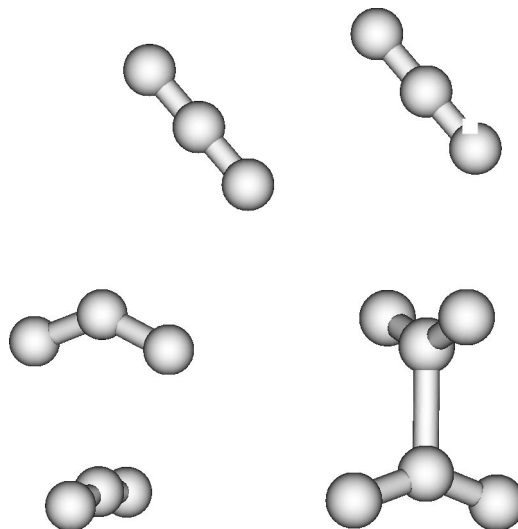


FIG. 1. Geometrical structures of the C_{2h} symmetrical neutral dimer $(\text{CO}_2)_2$ and the two C_{2v} and D_{2d} symmetrical dimer anions $(\text{CO}_2)_2^-$ discussed in Sec. III.

To begin with let us state that the intermolecular interactions between the constituting monomers in both neutral and anionic clusters are governed by dispersion effects. It is therefore crucial to take electron correlation into account, and SCF and current implementations of density functional theory are inadequate for the computation of equilibrium structures and the interaction energies of these clusters.^{11,19,20} Indeed, we found that the intermolecular interactions are drastically underestimated at these levels, leading to extremely flat potential energy surfaces (PESs) and tremendous difficulties in the search for minimal energy structures of the higher clusters.

Table I collects selected distances of the three prototypical dimers obtained from geometry optimizations at the MP2, CCSD, and CCSD(T) levels using different basis sets. Let us begin with the neutral C_{2h} dimer. Clearly, the intramolecular C–O bond lengths are rather insensitive to the particular theoretical level and basis set, and the values at the different levels differ by only 0.01 Å. In contrast, substantial differences in the order of up to 0.15 Å are found for the intermolecular distance, underlining the theoretical challenge to describe the weak intermolecular bonding accurately. Undoubtedly owing to fortuitous error compensation, the MP2 results are very close to the CCSD(T) lengths, whereas somewhat longer distances are predicted at the CCSD level. Similar with the correlation effects, we cannot make out any obvious basis sets trend, and our “best” intermolecular distances are about 0.1 Å shorter than the experimental D_e value.³⁴

Very similar tendencies are found for the two investigated dimer anions. For both isomers the intramolecular C–O bond lengths are more or less independent of the theoretical level, whereas the computed long C–C distances show for both anions substantial variations. In the C_{2v} anion (type I) this distance is close to 3 Å, and one can think of this dimer as a CO_2 molecule loosely attached to a bent CO_2 anion. For this species the C–C length is rather insensitive to

TABLE I. Bond distance dependence on the theoretical level. The geometries of the neutral C_{2h} symmetrical (CO₂)₂ and the two anionic (CO₂)₂[−] (C_{2v} and D_{2d} symmetry) clusters (cf. Fig. 1) have been optimized at different correlated levels of theory using the 6-31G*, DZPD, AUG-cc-pVDZ, and AUG-cc-pVTZ basis sets. All bond distances are given in angstroms.

| | | | $R(C-C)$ | $R(C-O)$ | $R'(C-O)$ |
|----------|-------------|---------|----------|----------|-----------|
| C_{2h} | 6-31G* | MP2 | 3.494 | 1.181 | 1.178 |
| | | CCSD | 3.556 | 1.172 | 1.169 |
| | | CCSD(T) | 3.509 | 1.178 | 1.175 |
| | DZP+1s1p | MP2 | 3.594 | 1.182 | 1.180 |
| | | CCSD | 3.638 | 1.173 | 1.170 |
| | | CCSD(T) | 3.579 | 1.180 | 1.177 |
| | AUG-cc-pVDZ | MP2 | 3.470 | 1.181 | 1.178 |
| | | CCSD | 3.537 | 1.171 | 1.168 |
| | | CCSD(T) | 3.465 | 1.178 | 1.175 |
| | AUG-cc-pVTZ | MP2 | 3.489 | 1.172 | 1.169 |
| | | Expt. | 3.602 | ... | ... |
| C_{2v} | 6-31G* | MP2 | 2.879 | 1.256 | 1.182 |
| | | CCSD | 2.896 | 1.251 | 1.173 |
| | | CCSD(T) | 2.868 | 1.256 | 1.180 |
| | DZP+1s1p | MP2 | 3.082 | 1.253 | 1.182 |
| | | CCSD | 3.089 | 1.247 | 1.174 |
| | | CCSD(T) | 3.054 | 1.252 | 1.180 |
| | AUG-cc-pVDZ | MP2 | 3.004 | 1.252 | 1.180 |
| | | CCSD | 3.022 | 1.245 | 1.171 |
| | | CCSD(T) | 2.982 | 1.251 | 1.178 |
| | AUG-cc-pVTZ | MP2 | 3.005 | 1.241 | 1.172 |
| D_{2d} | 6-31G* | MP2 | 1.849 | 1.231 | ... |
| | | CCSD | 1.884 | 1.222 | ... |
| | | CCSD(T) | 1.868 | 1.229 | ... |
| | DZP+1s1p | MP2 | 1.863 | 1.233 | ... |
| | | CCSD | 1.915 | 1.222 | ... |
| | | CCSD(T) | 1.897 | 1.230 | ... |
| | AUG-cc-pVDZ | MP2 | 2.145 | 1.223 | ... |
| | | CCSD | 1.944 | 1.219 | ... |
| | | CCSD(T) | 1.920 | 1.228 | ... |
| | AUG-cc-pVTZ | MP2 | 1.898 | 1.220 | ... |

the theoretical level, but very basis set dependent. Specifically, too small distances are found if the employed basis set does not contain any diffuse functions. In contrast to the type-I dimer, in the type-II D_{2d} anion the two monomers are linked by a long C–C bond of roughly 1.9 Å. The corresponding bond length depends strongly (differences of up to 0.2 Å) on the employed method and on the basis set, but there are again no clear trends. From these findings (Table I) it is obvious that computing a reliable intermolecular distance of neutral or anionic CO₂ clusters is by no means straightforward, and that high levels of electron correlation and large basis sets will be needed to obtain accurate values for these parameters. Yet the associated interactions are weak and the PES is correspondingly flat. Thus—as discussed in the next paragraph—computed EAs are essentially independent of the precise geometrical structures employed to compute the energies of the clusters, and even if low-level geometries are used, the associated errors in the EA values are much smaller than other basis set and correlation effects.

Adiabatic electron attachment energies of the two dimer anions computed at various different levels are collected in Table II. In particular, we compare results that have been obtained using the same theoretical level for geometry optimization and calculation of the EA (right-hand columns)

with EA values obtained at the MP2/6-31G* equilibrium structures (left-hand columns). As mentioned above the different geometries make hardly any difference while the influences of theoretical level and basis set are far more pronounced. Three points are worth noting: (1) As expected, diffuse functions are absolutely crucial for computing EAs. (2) Contrary to expectation, larger basis sets do not automatically stabilize the anion in the sense that lower attachment energies are found. In going from the augmented correlation consistent double- ζ to the corresponding triple- ζ set the computed attachment energies slightly increase, which indicates a “destabilisation” of the anions. (3) For the C_{2v} anion and all other type-I clusters the effect of triple excitations on the coupled-cluster attachment energies is considerably smaller than for the D_{2d} isomer and all other type-II anions. All in all, our results show that it is essential to employ high levels of electron correlation and that one should rather compromise about the basis set than about the theoretical level. Computing attachment energies at the CCSD(T)/DZPD level using MP2/6-31G* geometries is a workable compromise and should be reasonably accurate in comparison with far more costly CCSD(T)/aug-cc-pVTZ values.

TABLE II. Dependence of the electron detachment energy on the theoretical level. The electron detachment energies of two $(\text{CO}_2)_2^-$ (C_{2v} and D_{2h} symmetry) cluster anions (cf. Fig. 1) have been computed at the correlated MP2, CCSD, and CCSD(T) levels of theory using several different basis sets. On the one hand, the relevant energies have been evaluated at the MP2/6-31G* geometries (left hand columns: 6-31G*), and for comparison the equilibrium geometries obtained at the respective levels have been employed (right hand columns: opt). All values are given in eV without zero-point corrections.

| | | C_{2v} isomer | | D_{2d} isomer | |
|---------|-------------|-----------------|------|-----------------|------|
| | | 6-31G* | Opt. | 6-31G* | Opt. |
| MP2 | 6-31G* | 1.45 | 1.45 | 1.10 | 1.10 |
| | DZP+1s1p | 0.69 | 0.67 | 0.45 | 0.43 |
| | AUG-cc-pVDZ | 0.58 | 0.54 | 0.34 | 0.22 |
| | AUG-cc-pVTZ | 0.62 | 0.55 | 0.35 | 0.30 |
| CCSD | DZP+1s1p | 0.45 | 0.45 | 0.37 | 0.37 |
| | AUG-cc-pVDZ | 0.39 | 0.39 | 0.31 | 0.32 |
| | AUG-cc-pVTZ | 0.44 | ... | 0.33 | ... |
| CCSD(T) | DZP+1s1p | 0.45 | 0.45 | 0.30 | 0.30 |
| | AUG-cc-pVDZ | 0.35 | 0.35 | 0.20 | 0.19 |
| | AUG-cc-pVTZ | 0.40 | ... | 0.21 | ... |

IV. NEUTRAL CLUSTERS

Much work has been devoted to the weak interactions in and the potential energy surfaces of small CO_2 clusters (see, e.g., Refs. 19 and 35–37 and references therein for earlier work). It is now accepted that the CO_2 dimer has only one C_{2h} symmetrical minimum, but already for the trimer there are several isomers that are very close in energy, showing differences on the order of or even less than 10 meV.^{19,35} Clearly, the larger neutral clusters will also show very flat PESs with several or even many minima of comparable energies. Owing to this characteristic of neutral CO_2 clusters, if one is interested in the electron affinities, one does not need to aim at a particularly accurate description of the weak interactions or at finding the absolute minimum. For the present purpose—computing vertical and adiabatic electron attachment energies—it is sufficient to find one of the low-lying minima and a reasonably accurate geometry, since the errors in the attachment energies stemming from electron correlation effects are one order of magnitude larger than the small energy differences between the neutral isomers (cf. Sec. III and Table II).

We have studied the five trimer structures discussed in Ref. 35, and for the tetramer and pentamer it is also not difficult to find several minima on the PES. At the MP2/6-31G* level the lowest tetramer structure we found has a pseudotetrahedral and the lowest pentamer structure has a pseudotrigonalbipyramidal geometry: i.e., the carbon atoms of the tetramer form a distorted tetrahedron and the carbon atoms of the pentamer form a distorted trigonal bipyramid. The two latter structures are displayed in Fig. 2 together with the C_{2h} symmetrical dimer as well as with the lowest C_{3h} symmetrical trimer. Let us note that these isomers can be understood as the lowest members of the class of “icosahedral” structures that have been suggested to represent the most stable structures for small N whereas in the range $19 < N < 55$ a crossover to cubic-bulk-like morphology is expected (see, e.g., Refs. 38–40 and references therein).

The CO_2 binding and CO_2 evaporation energies one could obtain from our calculations are certainly not very ac-

curate, but it is instructive to look at the contributions from vibrational and higher electronic effects. Starting from the MP2 evaporation energies as a base line (on the order of 100–200 meV) there are two corrections: the difference in the zero-point energies and higher electron correlation effects estimated as the difference of the CCSD(T) energies. For the dimer both contributions are similar (about 10 meV), but for the trimer correlation effects are 3 times larger than the corresponding zero-point correction, and for the tetramer the correlation effects are about 25% larger than the zero-point correction. Thus, if one were interested in the details of the weak binding energies of CO_2 clusters, one should spend at least as much effort on including electron correlation at a high level as on computing particularly accurate zero-point energies.

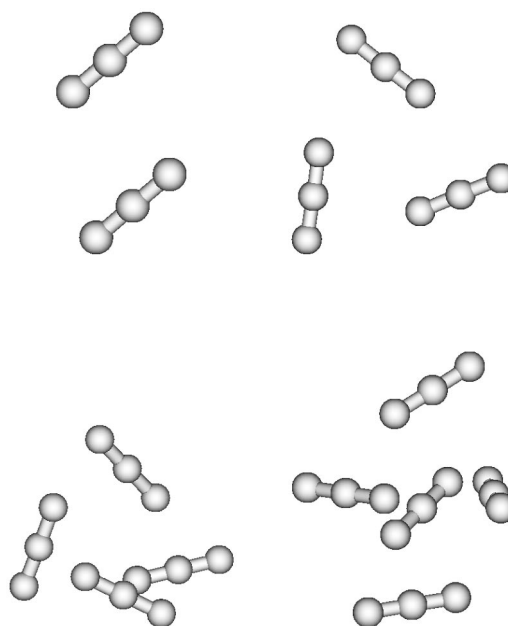


FIG. 2. Geometrical structures of the “polyhedral” $(\text{CO}_2)_N$ isomers ($N = 2-5$) discussed in Sec. IV.

TABLE III. Siegert energies corresponding to vertical electron attachment to CO₂ and (CO₂)_N clusters ($N = 2-4$). The static exchange results have been obtained using the DZP basis set augmented with a $1s5p$ set of diffuse functions, whereas the TZVP set augmented with a diffuse $1s8p$ set has been employed for the ADC(2) calculations. The symmetry of the resonance state is indicated in the second column and all values are given in eV.

| | | Static exchange | | Second order | |
|----------|---------|-----------------|----------|--------------|----------|
| | | E_r | Γ | E_r | Γ |
| Monomer | π_u | 5.26 | 0.70 | 4.21 | 0.21 |
| Dimer | b_u | 4.88 | 0.20 | 3.65 | 0.14 |
| | b_g | 4.92 | 0.52 | 3.82 | 0.18 |
| | a_u | 5.31 | 0.40 | 4.01 | 0.21 |
| | a_g | 5.67 | 0.38 | 4.23 | 0.25 |
| Trimer | e' | 4.93 | 0.31 | ... | ... |
| | e'' | 4.94 | 0.37 | ... | ... |
| | a'' | 5.31 | 0.34 | ... | ... |
| | a' | 5.70 | 0.25 | ... | ... |
| Tetramer | a | 4.51 | 0.44 | ... | ... |
| | a | 4.57 | 0.25 | ... | ... |
| | a | 4.74 | 0.37 | ... | ... |
| | a | 4.86 | 0.32 | ... | ... |
| | a | 5.02 | 0.27 | ... | ... |
| | a | 5.02 | 0.54 | ... | ... |
| | a | 5.50 | 0.25 | ... | ... |
| | a | 5.63 | 0.37 | ... | ... |

Another issue worth mentioning at this point is that apart from the long distances between the CO₂ monomers, the weak intermolecular interactions in CO₂ clusters are also reflected in the essentially uncoupled intramolecular vibrations. Similar to the findings for bulk CO₂,^{41,42} the computed vibrational frequencies of the investigated clusters show very sharp bands at the vibrational energies of the CO₂ monomer. Thus, from a structural as well as from a vibrational viewpoint the neutral CO₂ clusters consist of virtually unperturbed monomer units. We will come back to this point in Secs. V and VIII.

V. VERTICAL ELECTRON ATTACHMENT

Electron scattering from the CO₂ molecule is dominated by the $^2\Pi_u$ resonance state that corresponds to attachment of an electron into an empty π^* orbital and by a virtual state of Σ_g symmetry. In this section we investigate electron attachment into the π^* -like valence orbitals of CO₂ clusters that leads to a series of $^2\Pi_u$ -like resonances. For the monomer the energy of the $^2\Pi_u$ resonance is 3.8 eV (corresponding to a negative EA of -3.8 eV) and the corresponding fixed-nuclei width Γ is about 0.3 eV, translating into an autodetachment lifetime $\tau = \hbar/\Gamma$ of 2 fs (see, e.g., Refs. 43–45). The question how these parameters change in a cluster environment has to our best knowledge not been considered before.

We have employed complex absorbing potentials at the frozen-orbital or static-exchange level (the electrons of the neutral CO₂ cluster are frozen in their SCF orbitals) to study the trends of the resonance energies and lifetimes in small (CO₂)_N[−] ($N = 1-4$) clusters. This method directly yields the Siegert energies $E_{\text{res}} = E_r - i\Gamma/2$ of the resonances as a complex eigenvalue of a complex-symmetric Hamiltonian,²⁴ and these calculations are far more involved than standard *ab*

initio calculations for bound states (cf. Sec. II). While the frozen-orbital resonance positions and lifetimes are only rough approximations, a reasonable description of the trends for different cluster sizes N is expected. Orbital relaxation effects and electron correlation, which are both missing in the frozen-orbital treatment, have been included for the dimer cluster at an electron-propagator-based second-order perturbation theory level [ADC(2)]. The results are collected in Table III, and the static-exchange resonance positions are displayed in Fig. 3.

At the frozen-orbital level resonance positions are usu-

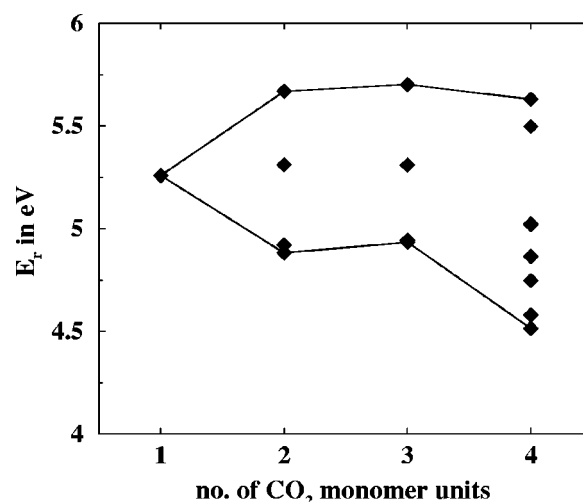


FIG. 3. Positions of the CO₂ $^2\Pi_u$ resonance state and the $^2\Pi_u$ -like resonance states of the (CO₂)_N clusters ($N = 2-4$) at the frozen-orbital level. These temporary anion states correspond to occupation of the π^* -like orbitals at the geometries of the neutral clusters (see Fig. 2). The associated decay widths can be found in Table III.

ally overestimated, and the $^2\Pi_u$ resonance of CO_2 is found near 5.3 eV. In clusters (we only consider the polyhedral structures displayed in Fig. 2) the corresponding positions of the $^2\Pi_u$ -like resonances are split by about 0.8 eV in the dimer and trimer and by about 1.1 eV in the tetramer, but the average resonance position stays close to that of the CO_2 monomer. The situation is similar for the associated decay widths (Table III). All widths are found to be somewhat smaller than the width of the monomer resonance, but the changes are relatively modest: e.g., the widths of the eight tetramer resonances fall into the range between 0.25 and 0.54 eV. It is worth noting that there is no correlation whatsoever between the resonance positions and associated lifetimes. We conclude that placing a CO_2 molecule in a cluster environment has a surprisingly weak influence on the electron accepting properties in the valence region.

This picture is essentially retained at the ADC(2) level. Allowing the target electrons to react to the incoming electron and taking orbital relaxation and electron correlation into account leads—usually—to a “stabilization” of the resonance state in the sense that lower positions and smaller widths are found. For both the CO_2 monomer and dimer we find the expected shifts that exhibit a typical magnitude of 1–1.5 eV for the positions and 0.1–0.2 eV for the widths (Table III). The splitting of the resonance positions of the dimer is found to be somewhat smaller at the correlated level (0.6 eV), yet the energetic order of the resonance states is retained, and apart from the typical shifts we do not expect any qualitative changes of the trends found at the static-exchange level.

Thus, in contrast to the intramolecular vibrational levels that remain essentially uncoupled (cf. Sec. IV), the electronic states exhibit clearly visible interactions, and we find a substantial through-space interaction between the unoccupied valence orbitals of neutral CO_2 clusters. Yet there are no dramatic effects, and similar to the monomer, vertical electron attachment into the empty π^* -like orbitals of CO_2 clusters is predicted to lead to short-lived resonance states with lifetimes in the fs regime and resonance positions well above 2.5 eV.

VI. ANIONIC CLUSTERS

Long-lived CO_2 cluster anions are readily formed in electron collisions with neutral CO_2 clusters, and the properties of the smaller cluster anions have been studied for some time now. The CO_2^- monomer itself shows a bent equilibrium structure with a bond length notably longer than that of neutral CO_2 .^{7–10} This anion is stable with respect to vertical electron loss, but metastable with respect to adiabatic autodetachment, and it possesses a lifetime on the order of 10 μs .^{46,47} Following the first observation of CO_2 cluster anions by Klots and Compton,¹ in a series of papers^{6,20,32} the Jordan group proposed two types of possible structures for the $(\text{CO}_2)_2^-$ dimer anion that turned out to represent prototypes for larger anionic clusters (cf. Fig. 1), and recently this work has been greatly extended by Saeki *et al.*^{11,12,33} who studied the geometrical structures of cluster anions consisting of up to six CO_2 units at the MP2 level. Type-I clusters consist of

a monomer anion core i.e., the extra electron is, similar to the long-lived bent CO_2^- anion, attached to one specific CO_2 unit, and the other CO_2 monomers in the cluster essentially solvate the anion core. In contrast, type-II cluster anions possess a dimer anion core forming an oxalatelike anion (cf. Fig. 1).

Let us reiterate some of the conclusions from Refs. 11, 12, and 33 at this point. First, electron correlation is crucial for obtaining the correct geometrical structures, and similar to neutral CO_2 clusters one may expect many low-energy isomers, since there are several possible positions for the solvating CO_2 units—in particular, for larger N . Second, type-II clusters were predicted to be slightly more stable than their type-I isomers (about 0.3 eV for $N=3, 4$ and about 0.1 eV for $N=6$). No type-I cluster was found for $N=5$, and no other cluster types were found in the examined N range. Third, typical CO_2 evaporation energies were found to be on the order of a few tenths of an eV and to decrease slowly towards higher N .

To compute the adiabatic electron affinities of CO_2 clusters we started out with the most stable structures given in Ref. 11. For $N=3$ we did not find any other low-lying isomers, but for $N=4$ one and for $N=5$ two new isomers were found including, in particular, a type-I pentamer. Moreover, computing the vibrational frequencies for the two C_{2v} pentamer structures from Ref. 11 we found two imaginary values, indicating that these geometries correspond to higher-order saddle points. Since the new structures show the lowest energies and represent true minima, no attempt was made to follow the imaginary modes into a minimum of lower symmetry. The structures of the three new CO_2 cluster anions are shown in Fig. 4. Note that the C_s symmetrical $(\text{CO}_2)_5^-$ anion shows a D_{2d} -like anion core analogous to the type-II dimer, whereas all type-II cluster anions presented in Ref. 11 show planar D_{2h} -like cores.

As a supplement to the electron affinities presented in the next section, let us briefly discuss our findings on the energetics and structural properties of anionic CO_2 clusters. The results for the relative energies and CO_2 evaporation energies are collected in Table IV. Despite the lower-quality basis set used in Ref. 11, the MP2 results agree quite nicely with each other. Yet both higher-order correlation effects and zero-point corrections—both have been neglected in Ref. 11—do have a pronounced influence on the values. Including electron correlation at a higher level—that is, going from MP2 to CCSD(T)—the CO_2 evaporation energies increase by about 10%, and more importantly, the energy differences between type-I and type-II isomers decrease substantially (Table IV). The zero-point corrections, on the other hand, do not have a unique sign. The values themselves are not particularly large, but since the relative energies and evaporation energies are also small, zero-point corrections can make a noticeable difference. For example, for the dissociation of the C_{2v} -symmetrical type-II tetramer into the lowest type-II trimer and CO_2 the zero-point correction is 50 meV or 14% of the uncorrected value, while for the dissociation of the type-I tetramer into the C_s type-I trimer and CO_2 the zero-point correction is –15 meV. In view of the small energy differences we conclude that far more costly calculations will

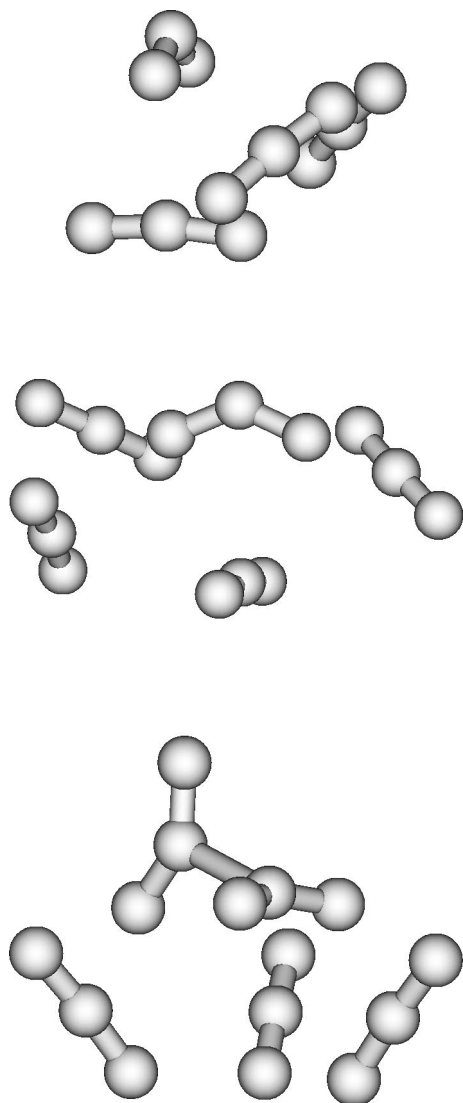


FIG. 4. Geometrical structures of one tetramer and two pentamer cluster anions. From the top: (CO₂)₄[−], type-I, *C_s* symmetry; (CO₂)₅[−], type-I, *C₁* symmetry; (CO₂)₅[−], type-II, *C_{3v}* symmetry.

be required to arrive at precise values, but we are confident that the qualitative trends are correct.

For all cluster sizes considered the energy differences between the lowest type-I and type-II isomers are considerably smaller than the associated evaporation energies. Thus, we predict the (CO₂)_{*N*}[−] cluster anions to be unable to “cool down” into a specific structure by emitting CO₂ units. In view of the small energy differences and the small barriers¹² between the isomers we rather expect that cluster anions produced in an experiment will not exhibit a well-defined structure, since in general several minima will be accessible and can be visited frequently on a mass spectrometric time scale. Even if we assume perfect thermal equilibrium, the small type-I and type-II energy difference of the tetramer (10 meV) will translate into a notable occupation of the type-I minimum at room temperature.

In the light of these findings it is by no means obvious how one could explain the clear-cut structural transition observed in the photoelectron spectra.^{2,3} As far as we can see, there is at best a weak preference for either structure type on

energetic grounds, and the energy difference between the lowest isomers of each type is expected to become smaller with growing *N*. Moreover, the core switch at *N*=6 cannot be explained in terms of a “missing” type-I pentamer.¹¹ Of course, calculations at higher levels of theory including cluster sizes up to *N*=15 might prove us wrong and at this point we can only speculate, but if the photoelectron spectra do show only the lowest-energy structure, implying that the most stable structure type does indeed switch twice (at *N*=6 and between *N*=13 and 14), then there must be an efficient energy dissipation mechanism other than CO₂ evaporation and the effective temperature in the ion source must be very low. At the present time we consider it more likely that there is some kinetic mechanism associated with the ion source that favors the production of certain cluster types. More experimental and theoretical work is needed to clarify this issue.

VII. ADIABATIC ELECTRON AFFINITIES

At this stage we have all the ingredients to study the adiabatic electron affinities of CO₂ clusters. Our results are collected in Table V, and in order to “see” the trends the zero-point corrected affinities are plotted in Fig. 5. Clearly, at the computational levels employed all investigated cluster anions show—similar with the bent CO₂ monomer anion—negative adiabatic EAs, indicating that these species may possess long lifetimes, but will eventually autodetach their extra electron. As discussed in Sec. III for the dimer, the CCSD(T) results are markedly more positive than the MP2 values, yet the trends in the EAs and the solvation shifts are well reproduced at the MP2 level.

Starting from the bent CO₂[−] anion and following the type-I species, the first solvating CO₂ unit stabilizes the anion by slightly more than 0.2 eV. The stabilizing contributions of the second and third CO₂ units are similar in magnitude, and only for the fourth solvating CO₂ monomer is the stabilization slowing down. Since the adiabatic EA of the lowest type-I tetramer is small (−0.1 eV)—though still negative—and in view of the slight underestimation of the EA at the CCSD(T)/DZPD level (cf. Sec. III), we predict the (CO₂)_{*N*}[−] pentamer to be the smallest type-I cluster anion exhibiting a clearly positive adiabatic EA.

For the type-II cluster anions the solvation effects are considerably smaller in line with a larger anion core and a more delocalized charge distribution. The stabilization provided by the first and second solvating CO₂ units, respectively, is about 0.1 eV, and taking into account the findings discussed in Sec. III the lowest type-II tetramer is at the brink of stability. There is little doubt that—using a large basis set—the CCSD(T) value for the EA of the *C_s*-symmetrical type-II pentamer will be clearly positive, though certainly less than 0.2 eV. We predict this isomer to be the smallest type-II (CO₂)_{*N*}[−] cluster anion that is clearly stable with respect to electron autodetachment. Thus, even though the type-I dimer is clearly less stable than the type-II dimer, the onset of electronic stability is predicted at the same cluster size for both types, owing to the larger solvation energies of the type-I anions.

TABLE IV. Energetics of the $(\text{CO}_2)_N^-$ cluster anions. The energies have been computed at the MP2/DZPD and CCSD(T)/DZPD levels of theory using the MP2/6-31G* structures. For both relative energies and CO_2 evaporation energies zero-point corrections obtained at the MP2/6-31G* level are included apart from the two C_{2v} pentamer anions that do not correspond to minima on the PES. For convenience in the third column the label used in Ref. 11 is given. Note that neither structure $5a$ nor $5c$ corresponds to minima on the MP2/6-31G* potential energy surface (see text). All values in eV.

| N | Type | | | Rel. energy | | Evaporation energy | |
|---|------|----------|------|-------------|---------|--------------------|---------|
| | | | | MP2 | CCSD(T) | MP2 | CCSD(T) |
| 2 | I | C_{2v} | | 0.21 | 0.12 | 0.27 | 0.31 |
| | I | C_s | | 0.26 | 0.18 | 0.22 | 0.25 |
| | II | D_{2d} | | 0.0 | 0.0 | ... | ... |
| 3 | I | C_s | $3a$ | 0.18 | 0.09 | 0.24 | 0.27 |
| | I | C_{2v} | $3b$ | 0.22 | 0.10 | 0.25 | 0.28 |
| | II | C_{2v} | $3c$ | 0.0 | 0.0 | 0.22 | 0.24 |
| | II | C_{2v} | $3d$ | 0.02 | 0.03 | 0.19 | 0.21 |
| 4 | I | C_s | | 0.13 | 0.01 | 0.34 | 0.38 |
| | I | C_{2v} | $4a$ | 0.20 | 0.11 | 0.30 | 0.34 |
| | II | D_{2h} | $4b$ | 0.0 | 0.0 | 0.30 | 0.34 |
| | II | D_{2d} | $4d$ | 0.08 | 0.08 | 0.21 | 0.23 |
| | II | C_s | $4c$ | 0.13 | 0.13 | 0.17 | 0.21 |
| 5 | I | C_1 | | 0.16 | ... | 0.38 | ... |
| | II | C_s | | 0.0 | ... | 0.31 | ... |
| | II | C_{2v} | $5a$ | 0.07 | ... | 0.24 | ... |
| | II | C_{2v} | $5c$ | 0.02 | ... | 0.29 | ... |

VIII. DISCUSSION AND CONCLUSIONS

In the preceding sections we studied the electron acceptance properties of carbon dioxide clusters, and in this section we discuss our findings in the light of the slow-electron attachment experiments of Leber *et al.*⁴ and Barsotti *et al.*⁵

The neutral clusters that represent the reactants of the attachment process do most probably not show a well-

defined structure, since starting with the trimer cluster there are several low-lying isomers with energy differences that are considerably smaller than the CO_2 evaporation energy. This explains the inhomogeneous broadening attributed to the observed peaks. Another consequence of the weak van der Waals interaction between the monomer units is the essentially unchanged intramolecular bond lengths and the

TABLE V. Adiabatic electron affinities of the $(\text{CO}_2)_N^-$ clusters. All anions lie energetically above the associated neutral clusters corresponding to negative electron affinities. The values have been obtained at the MP2/DZPD and CCSD(T)/DZPD levels of theory using the MP2/6-31G* structures, and the associated MP2/6-31G* zero-point corrections are listed separately in the last column. Positive zero-point corrections stabilize the anions: i.e., in that case the corrected affinities are more positive than the listed uncorrected values. For the reader's convenience in the third column the labels used in Ref. 11 are given. All values in eV.

| N | Type | | | Electron affinity | | ZPC MP2 |
|---|------|----------|------|-------------------|---------|------------|
| | | | | MP2 | CCSD(T) | |
| 2 | I | C_{2v} | | -0.69 | -0.45 | 0.039 |
| | I | C_s | | -0.76 | -0.53 | 0.057 |
| | II | D_{2d} | | -0.45 | -0.30 | 0.004 |
| 3 | I | C_s | $3a$ | -0.54 | -0.32 | 0.040 |
| | I | C_{2v} | $3b$ | -0.59 | -0.38 | 0.049 |
| | II | C_{2v} | $3c$ | -0.33 | -0.19 | 0.005 |
| | II | C_{2v} | $3d$ | -0.35 | -0.24 | 0.015 |
| 4 | I | C_s | | -0.38 | -0.14 | 0.040 |
| | I | C_{2v} | $4a$ | -0.47 | -0.24 | 0.046 |
| | II | D_{2h} | $4b$ | -0.23 | -0.10 | 0.015 |
| | II | D_{2d} | $4d$ | -0.31 | -0.18 | 0.009 |
| | II | C_s | $4c$ | -0.34 | -0.22 | -0.004 |
| 5 | I | C_1 | | -0.31 | ... | 0.043 |
| | II | C_s | | -0.15 | ... | 0.006 |
| | II | C_{2v} | $5a$ | -0.22 | ... | ... |
| | II | C_{2v} | $5c$ | -0.17 | ... | ... |

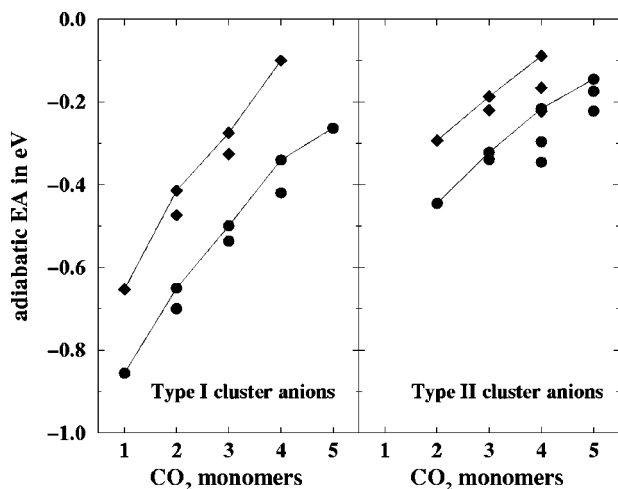


FIG. 5. Adiabatic electron affinities of CO₂ clusters. The values have been computed at the MP2 (circles) and CCSD(T) (diamonds) levels of theory using the DZPD basis set, and in the left and right panels results are shown for type-I and type-II clusters, respectively. The computed zero-point corrections (see Table V) have been included. To show the trends more clearly the values associated with the lowest isomers have been connected by lines.

very weak coupling of the intramolecular vibrational modes. Yet electronically the monomers are clearly coupled as shown by the splitting of the ${}^2\Pi_u$ -like resonance states on the order of 1 eV.

No hint at a diffuse bound state that could support vibrational Feshbach resonances was found despite the extended basis sets employed in the computation of the Siegert energies. Yet, just as the bent minimum structure of CO₂⁻ is stabilized by solvating CO₂ monomers, we expect solvation effects to stabilize a diffuse state. In other words, those parts of the lowest adiabatic potential energy surface of the anion that corresponds to a diffuse surface state¹⁰ are also expected to be “pushed down” by increasing the cluster size. The fact that we have not seen any traces of a surface state in our calculations reveals that the electrostatic potential of the cluster taken into account in the frozen-orbital computations is not sufficient to bind an electron. We have no doubt that if one could use sufficiently extended basis sets at a correlated level of theory (cf. Ref. 10), one will find polarization and correlation bound surface states for the larger clusters.

As possible products of the attachment process, we have studied type-I and type-II cluster anions which possess monomer and dimer anion cores, respectively. These species are known to be formed in “high-energy” attachment processes and have been identified by their photodetachment spectra.^{2,3} The crucial question in the low-energy context is the adiabatic electron affinity of these species, since it determines whether type-I or type-II anions can be formed at all and how much energy is available for evaporative cooling. Our calculations show that all dimer and trimer cluster anions possess clearly negative electron affinities, and consequently these species cannot be formed at threshold. One type-I as well as one type-II tetramer have been found to show adiabatic EAs close to zero, and the onset of stability for both isomer classes is predicted for $N=5$. We note that even though the investigated smaller type-I and -II cluster anions are metastable, their lifetimes will obviously be much

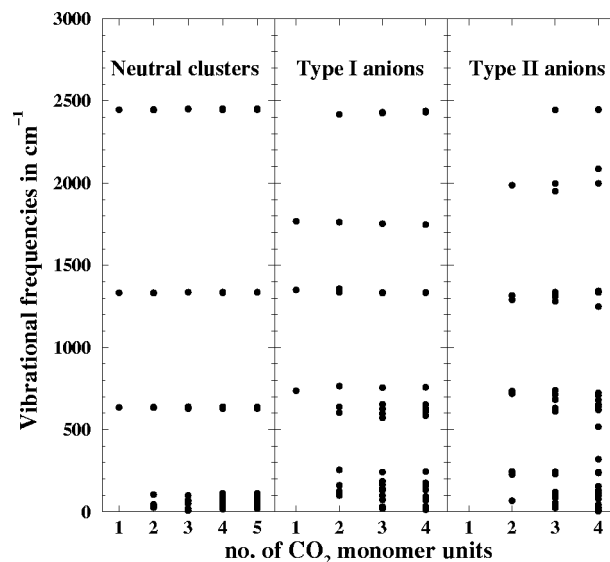


FIG. 6. Harmonic vibrational frequencies of neutral and anionic CO₂ clusters computed at the MP2/6-31G* level.

longer than that of the bent CO₂⁻ monomer anion, and on a mass spectrometric time scale these species will effectively be stable.

If these trends in the EAs continue for another two or three monomer units, then for intermediate-size clusters one or two cooling steps will be possible even at threshold, and any diffuse anion state will most certainly “react” to a compact type-I or type-II cluster. It is a very interesting question at what cluster size the solvation stabilization of the anions saturates and which value it approaches asymptotically.

For the small investigated clusters the computed adiabatic EAs are so small that we cannot draw any conclusions about the nature of the observed (CO₂)_N, $N=4, 5$, clusters. In view of the expected accuracy of our results (cf. Sec. III) it is conceivable that both type-I and type-II anions have been produced, but the attachment process may very well have simply stopped with the vibrational Feshbach resonance. Experimentally, the different anion species including the type-I cluster anions can in principle be distinguished in a straightforward manner either by their photoelectron spectra (owing to their very different vertical detachment energies^{2,3,6,20}) or by their vibrational spectra (cf. Ref. 48). From the harmonic frequencies displayed in Fig. 6 one can see that the antisymmetric stretch fundamentals provide a fingerprint for the anion type. A vibrational Feshbach resonance is expected to show essentially the same vibrational spectrum as a neutral cluster, and in the neutral systems the intramolecular modes are essentially uncoupled. In the type-I clusters the antisymmetric stretching mode of the anion core monomer is downshifted to about 1800 cm⁻¹ (MP2/6-31G* level), whereas in the type-II anions the shift is much smaller and the antisymmetric stretch of the anion core is at about 2000 cm⁻¹. More experimental and theoretical work is required before these questions can be settled. For the time being our results provide a firm basis for the discussion and modeling of the attachment process.

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