

Density functional study of carbonic acid clusters

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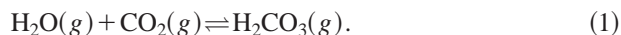
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Density functional calculations on carbonic acid H_2CO_3 are extended to clusters of up to five such units. The most stable forms are the linear, hydrogen-bonded analogs of the dimer with *anti-anti* orientation. We calculate structures and vibration frequencies, as well as the energy required to bend and stretch the linear isomers. Linear chains of up to ~ 20 units should be favored over ring structures, and they have a tensile strength reminiscent of chains of water molecules. We also discuss planar, nonlinear structures as well as three-dimensional isomers. © 2000 American Institute of Physics. [S0021-9606(00)30615-8]

I. INTRODUCTION

The interaction of carbon dioxide with water plays a central role in many biological, ecological, extraterrestrial (particularly cometary), and industrial processes. Carbonic acid (H_2CO_3 , denoted CA), formed by the hydration of CO_2 , dissociates rapidly in water, so that the evidence for its existence is often indirect. There have been numerous calculations of the energetics of the gas phase reaction:^{1,2}



The most extensive calculations indicate that there is an activation barrier for reaction (1) of over 50 kcal/mol,^{1,3} although it is catalyzed by the presence of additional water molecules.³ A peak with mass-to-charge ratio of 62 following thermal decomposition of $(\text{NH}_4)\text{HCO}_3$ (s) has been attributed to gas phase carbonic acid,⁴ and other weakly bound complexes—such as $\text{H}_2\text{O}-\text{CO}_2$ —have been found in the gas phase.⁵

Low temperatures would favor the formation of carbonic acid, and two techniques have been used to synthesize H_2CO_3 at low T and to detect it using infrared (IR) spectroscopy. Moore and Khanna⁶ performed proton irradiation on mixed H_2O and CO_2 ices at 20 K, and carried out IR and mass spectroscopic studies on the products. New features in the IR spectra of the resulting films were assigned to solid H_2CO_3 trapped in the ice matrix. Hage *et al.*^{7,8} formed solid H_2CO_3 by the reaction of K_2CO_3 and HCl (and HBr) at 150 K in vitreous methanol films. Crystallization to a form denoted $\alpha\text{-H}_2\text{CO}_3$ occurred at 190–200 K, and Fourier transform infrared spectroscopy (FTIR) measurements were performed on it. When water was used as solvent, a second metastable polymorph ($\beta\text{-H}_2\text{CO}_3$) could be identified.

The small energy differences involved in the formation of carbonic acid and the metastable nature of many of the structures involved provide challenges to methods for mo-

lecular structure calculations. The H_2CO_3 dimer is a particularly interesting case, as very extensive calculations² indicate that this cluster is remarkably stable. The energy difference between the dimer and the constituent CO_2 and H_2O molecules is, when corrected for zero point energy differences, “astonishingly close to zero.”² The dimer is, therefore, more relevant for investigating the stability of H_2CO_3 than is the monomer. The stability of still larger clusters is a tantalizing question that, to the best of our knowledge, has not yet been addressed.

In an earlier paper,⁹ we discussed the bonding and energy differences of numerous fragments of bisphenol-A polycarbonate (BPA-PC), including the isomers of H_2CO_3 shown in Fig. 1. The most stable is the *trans-trans* isomer, followed by the *cis-trans* and *cis-cis* forms. The calculated frequencies are in reasonable agreement with other calculations and with experimental data. In the present work, we extend these calculations to small aggregates of H_2CO_3 molecules. It continues a study of the applicability of the density functional (DF) method to organic molecules and molecular crystals, as well as to organic polymers. In addition to the intrinsic interest in aggregates of hydrogen-bonded molecules, it is a challenge to theory to provide insight into the presently unknown structures of the carbonic acid polymorphs. Essential details of the calculations are provided in Sec. II, and the results for the structures and vibration frequencies are given in Sec. III. We discuss and summarize our findings in Sec. IV.

II. METHODS OF CALCULATION

The method of calculation has been described previously.^{10,11} The electron-ion interaction is represented by ionic pseudopotentials with the (nonlocal) form suggested by Troullier and Martins.¹² We adopt periodic boundary conditions with a simple cubic cell with lattice constant 36 a.u. and a plane wave basis with a kinetic energy cutoff of 35 a.u., and the expansion of the orbitals uses a single point ($\mathbf{k}=0$) in the Brillouin zone. As in previous work in this series, we use the exchange-correlation energy functional of Perdew, Burke, and Ernzerhof (PBE),¹³ which is relatively simple and free of empirical input. All structures were opti-

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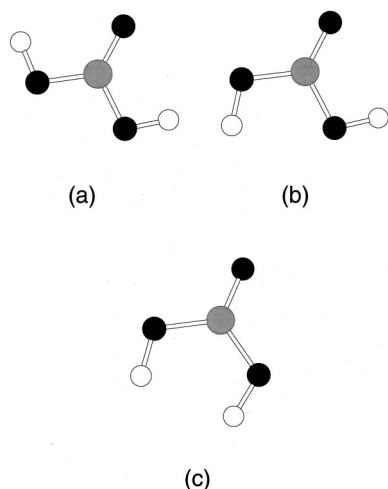


FIG. 1. Molecular structures. (a) *trans-trans* (b) *cis-trans*, and (c) *cis-cis* isomers of carbonic acid. Carbon atoms are gray, oxygen atoms black, hydrogen atoms white.

mized using a combination of DF calculations with molecular dynamics (MD)^{14,15} and a simulated annealing strategy. Optimizations were continued until the magnitude of the *maximum* force on any atom was less than 5×10^{-4} a.u. and the *average* force on the atoms are an order of magnitude less.

The small energy differences involved in hydrogen bonding have provided a challenge for all methods of molecular structure calculations. Tests on the prototype water dimer (H_2O)₂ showed that the local density (LD) approximation to the exchange-correlation energy overbind this system, while both Hartree-Fock and many-body perturbation theory (MBPT) lead to significant underbinding.¹⁶ Gradient corrections to the LD functional lead to dramatic improvements and good agreement with measured structures and vibration frequencies, and these corrections have subsequently been used in numerous studies of hydrogen-bonded systems.¹⁷ In

particular, a thorough study of the Ih phase of ice found that the PBE functional gave excellent results for the sublimation energy, equilibrium volume, and bulk modulus.¹⁸ Finally, a recent study showed that this functional provides a very satisfactory description of atomization energies for the extended G2 set of molecules.¹⁹ All this experience with the PBE functional is very encouraging for the present study of carbonic acid clusters.

The large computational demands of this method mean that it does not suffice to generate starting configurations in organic and other molecules with strong, directional bonds if the structures are unknown. To accelerate the exploration of the potential energy surface, we have used classical molecular dynamics with an empirical force field.²⁰ This allows us to perform extensive simulated annealing on many structures and has provided input to DF calculations of structures that we had not found with other means. Nevertheless, we have concluded that the empirical potential is of limited use for CA_n clusters, since it is difficult to incorporate simply the pronounced tendency to planarity displayed by adjacent hydrogen bonds. As a result, many low-energy structures generated by this method were found to be unstable at the level of DF calculations.

III. RESULTS

A. Monomers, dimer

In Fig. 1 we show the structures of the (a) *trans-trans*, (b) *cis-trans*, and (c) *cis-cis* isomers of H_2CO_3 , which we discussed in Ref. 9. For completeness we provide (Table I) the structural parameters and energy differences calculated using the present method, as well as the results of other calculations.^{1,21}

The small energy differences involved in the reaction of water and carbon dioxide mean that vibrational zero point energy (ZPE) corrections are important.² Our calculations indicate that the reaction $\text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2$ at $T = 0$ K re-

TABLE I. Bond lengths (Å) and angles (degrees), and differences in total and zero point energy ($\Delta E, \Delta E_{\text{ZP}}$, kcal/mol) in carbonic acid isomers. The carbonyl group is C7-O19, and H17 and H18 are attached to O17 and O18, respectively (see Ref. 9). Values in parentheses are HF/6-31G* (Ref. 21) and MP-2 results (Ref. 1), respectively.

Struct. param.	<i>trans-trans</i>	<i>cis-trans</i>	<i>cis-cis</i>
C7-O19	1.217 (1.188, 1.218)	1.208 (1.180, 1.208)	1.202 (1.172, 1.201)
C7-O17	1.353 (1.315, 1.345)	1.371 (1.316, 1.344)	1.371 (1.333, 1.366)
C7-O18	1.353 (1.315, 1.345)	1.351 (1.333, 1.364)	1.371 (1.333, 1.366)
O17-H17	0.984 (0.951, 0.969)	0.985 (0.950, 0.969)	0.982 (0.947, 0.966)
O18-H18	0.984 (0.951, 0.969)	0.985 (0.952, 0.969)	0.982 (0.947, 0.966)
O19-C7-O17	125.8 (125.1, 125.9)	125.4 (124.4, 125.4)	121.6 (122.1, 122.4)
O19-C7-O18	125.8 (125.1, 125.9)	124.1 (124.6, 124.3)	121.6 (122.1, 122.4)
H17-O17-C7	105.0 (107.9, 106.1)	105.6 (108.3, 106.7)	112.5 (115.0, 111.9)
H17... O19	2.320 (2.291, ...)	2.336 (2.299, ...)	3.062 (2.996, ...)
H18... O19	2.320 (2.291, ...)	3.036 (2.975, ...)	3.062 (2.996, ...)
H18... O17	3.022 (2.966, ...)	2.170 (2.993, ...)	2.385 (3.340, ...)
H17... O18	3.022 (2.966, ...)	3.057 (2.159, ...)	2.385 (3.340, ...)
H17... H18	3.720 (3.670, ...)	3.134 (3.096, ...)	2.024 (2.027, ...)
ΔE	0.00	1.50 (2.44, 1.86)	10.0 (12.29, 11.76)
ΔE_{ZP}	0.00	-0.49 (-0.46, -0.38)	-1.78, (-1.90, ...)

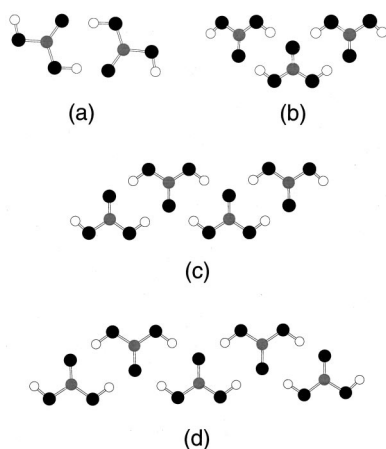


FIG. 2. Structures of planar carbonic acid clusters: (a) dimer, (b) trimer, (c) tetramer, (d) pentamer. Carbon atoms are gray, oxygen atoms black, hydrogen atoms white.

leases 7.1 kcal/mol, with contributions from the potential energy and ZPE of 2.8 kcal/mol and 4.3 kcal/mol, respectively. These results are in fair agreement with those of Ref. 1, but they agree remarkably well with the most extensive calculations performed to date [CCSD(T)].²

A pair of CA molecules can decrease their energy by forming two equivalent hydrogen bonds, as illustrated in Fig. 2(a). The dimer is planar and has a negligible dipole moment, and the structural parameters have standard values ($d_{\text{O-O}} = 2.57 \text{ \AA}$, $\alpha_{\text{O-H-O}} = 178^\circ$). The binding energy per bond (10.3 kcal/mol) is in good agreement with previous estimates using correlated wave functions (MP2, 9.5 kcal/mol)² and a different gradient-corrected functional (B3LYP, 8.9 kcal/mol).² The strength of the two hydrogen bonds is reflected in small but significant changes in the structure of the constituent monomers: the C=O bond increases from 1.22 Å in the monomer to 1.25 Å in the dimer, the C-O bond shrinks from 1.35 Å to 1.32 Å, and the bond angles change slightly to adapt to the formation of the hydrogen bonds. The “external” C-O-H groups have almost identical geometries in monomer and dimer.

Hydrogen-bond formation in the dimer is also reflected in the vibrational frequencies, which display large redshifts from the corresponding modes for the isolated H_2CO_3 molecule: the stretching frequency of the O-H groups involved in the intermolecular bonding decreases by more than 800 cm^{-1} , and the C=O stretching mode softens by more than 60 cm^{-1} . The strong coupling of these modes gives rise to a large splitting for the O-H ($\Delta\omega = 140 \text{ cm}^{-1}$) and the C=O ($\Delta\omega = 100 \text{ cm}^{-1}$) stretching modes. The pronounced tendency of the dimer towards planarity is evident in the fact that the highest frequency out-of-plane mode (1100 cm^{-1}) is associated with the torsion of the OH groups forming hydrogen bonds, while the corresponding modes in the isolated H_2CO_3 molecules occur at much lower frequency (640 cm^{-1}). The combined effect of these changes in the vibrational spectrum is a slight destabilization (by 1 kcal/mol per monomer) of the dimer with respect to two separated monomers.

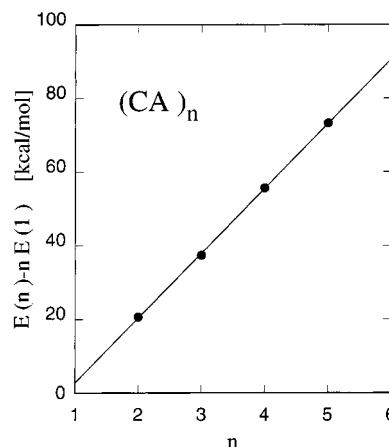


FIG. 3. Cohesive energy of linear clusters of carbonic acid CA_n as a function of n .

B. Linear structures of trimer, tetramer, and pentamer

The regular shape of the dimer suggests an obvious pattern for the growth of CA_n aggregates, as illustrated in Figs. 2(b)–2(e). Our calculations on the ladder structures up to $n = 5$ show that they are very stable, with cohesive energies growing linearly with n (see Fig. 3). Each structure exhibits two sets of hydrogen bonds: the C=O groups in the terminal molecules are involved in a single hydrogen bond, while those in the internal molecules of the ladder participate in two hydrogen bonds (see Fig. 2). As expected, the terminal bonds are slightly stronger than the internal ones, and the cohesive energy E_n of the CA_n molecule can be represented by $E_n = 20.6 + 17.0(n-2)$ kcal/mol.²² In Fig. 3 we show that this linear relation provides a very accurate fit to the calculated cohesive energies, and it can be used to predict the properties of longer linear CA structures. The structural trends observed in the dimer are also present in the larger species, with changes due to the presence of the two hydrogen-bond types described above: The internal C=O and C-O bonds ($d_{\text{C=O}} = 1.27 \text{ \AA}$, $d_{\text{C-O}} = 1.31 \text{ \AA}$) expand and shrink, respectively, while the external hydrogen bonds and the extremal C-O-H groups are the same as in the dimer. The dipole moments of the clusters are very close to zero for even values of n and are small for odd values.²³

The evolution of the vibrational spectrum with increasing n is shown in Fig. 4. The formation and the growth of the band representing the stretching of the O-H groups involved in an intramolecular hydrogen bond is evident in the $2400\text{--}3000 \text{ cm}^{-1}$ frequency interval, as is the progressive hybridization of the C=O stretching modes (1780 cm^{-1} in the isolated monomer) with the bending modes of the OH groups (in the $1200\text{--}1400 \text{ cm}^{-1}$ range in the monomer). The highest frequency band (at 3530 cm^{-1}) is associated with the extremal OH groups. It is not affected by the formation of the intermolecular hydrogen bonds and changes little with increasing size. We note that the calculated vibration frequencies are generally consistent with the infrared data of the solid phases,^{6,7} but a detailed comparison between theory and experiment is made difficult by the lack of structural information in the latter and error bars of $\sim 30 \text{ cm}^{-1}$ in the former.

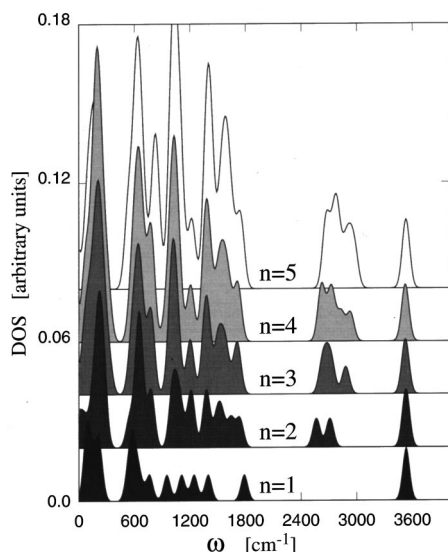


FIG. 4. Vibrational densities of states of linear clusters of carbonic acid CA_n for $n=1-5$. The states are broadened with a Gaussian of width 20 cm^{-1} .

Linear structures are favored for clusters of some elements up to a certain size, beyond which the additional bond formed in a ring structure overcomes the energy cost of bending. An example is provided by carbon clusters C_n , where this transformation takes place at $n \sim 8$.²⁴ The same effect should be evident in CA_n clusters, where an energy lowering of $\sim 20\text{ kcal/mol}$ should result from the saturation of the external hydrogen-bond sites. The size of the ring where the gain in potential energy overcomes the cost of bending the linear geometries can be estimated by considering the pentamer and constraining the carbonyl groups of the central and extremal CA molecules to lie on a circle of radius R . The energy increase with respect to the linear geometry has been computed by relaxing all other degrees of freedom. The result, shown in Fig. 5 as a function of $1/R^2$, indicates that the stiffness of the linear structure is such that ring formation is unfavorable up to $n \sim 20$. Entropy considerations render unlikely the formation of rings of this size.

Hydrogen bonding is often cited as the source of the tensile strength of water that helps plants transport liquids from the roots to the topmost branches and leaves.²⁵ To study whether linear clusters of CA display an analogous mechanical strength, we have evaluated the energy of a tetramer CA_4 by fixing the distance between the outermost car-

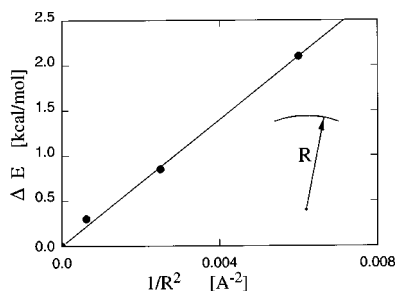


FIG. 5. Energy change on bending CA_5 as a function of $1/R^2$, where R is the radius of curvature of the structure (see text).

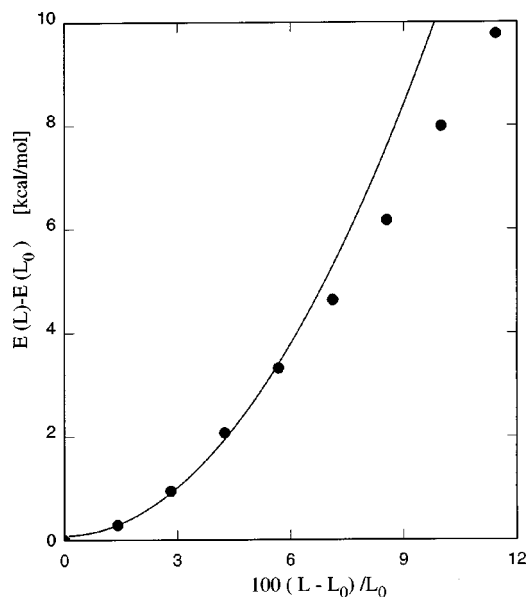


FIG. 6. Energy change in CA_4 on increasing the separation L between the outermost carbonyl groups (see text). L_0 is the equilibrium value of L .

bonyl groups to be larger than the equilibrium value, and relaxing all other degrees of freedom. Figure 6 shows that the deformation of the cluster is remarkably elastic up to $\sim 6\%$ of the original length. The curvature of the elastic part leads to an estimate of the molecular elastic modulus ($1.4 \times 10^{11}\text{ N/m}^2$) that is similar to that found in well-annealed ice samples.^{26,27}

C. Nonlinear isomers

Two crystalline forms of carbonic acid have been identified,⁶⁻⁸ and it is natural to ask whether three-dimensional structures can be derived from CA clusters. Linear chains of CA can clearly give rise to extended solids bound by van der Waals interactions, but the absence of structural information suggests that we also investigate nonlinear isomers of CA clusters, even if they are less stable than their linear counterparts. The systematic search for isomers is notoriously difficult, and we have noted that the use of a simple interatomic potential (see Sec. II) is of limited value: the large gain in the speed of searching configuration space is offset by the fact that many isomers are unstable or very high in energy when studied with DF calculations. Without making any claim to completeness, we now present several examples of these isomers.

A nonlinear, planar isomer of CA_3 is illustrated in Fig. 7(a). It has a single hydrogen bond per monomer, and it is not surprising that it is only marginally stable with respect to dissociation into the dimer and an isolated monomer (the binding energy with respect to three monomers is 24.3 kcal/mol). On the other hand, this isomer has three sites for binding an additional monomer, and we show a typical planar structure built on it in Fig. 7(b). Unfortunately, the addition of monomers to this CA_3 isomer results in low-symmetry structures that are unlikely building blocks for simple crystal forms. Moreover, these structures usually include one or

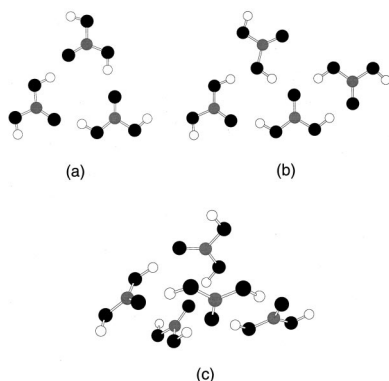


FIG. 7. Nonlinear isomers of carbonic acid clusters: (a) planar trimer, (b) planar tetramer, (c) a three-dimensional structure.

more dimers, suggesting that it may in fact be the most stable building block, not only in the linear clusters.

To investigate the possibility of bridging different linear chains by additional CA molecules, we have relaxed the system obtained by adding a single CA monomer close to the center of a linear CA_5 cluster. A weak bond forms between a monomer hydrogen and an oxygen atom in the CA_5 ladder, which remains stable and almost undeformed. The resulting three-dimensional geometry is a possible structural element for linking linear CA_n segments, but the cohesive energy of this bond is only 4.5 kcal/mol, and it is probably less important than the van der Waals contribution. Other 3D structures generated by Car–Parrinello simulation or by performing DF calculations on structures produced by the model potential had cohesive energies well above those of the linear structures, and none had a symmetry suggesting the 3D crystals. An example of a 3D structure is shown in Fig. 7(c).

IV. DISCUSSION AND CONCLUDING REMARKS

We have carried out an extensive series of density functional calculations on clusters of carbonic acid H_2CO_3 with up to five structural units. The calculations extend our earlier work on the monomer and other fragments of polycarbonate,⁹ and they appear to be the first calculations for clusters larger than the dimer.⁸ In addition to the geometrical structures, we calculate vibration frequencies and the energy cost of bending and stretching the clusters.

The most stable isomers are hydrogen-bonded, planar chains that follow the pattern found in the dimer. This is similar to that found in crystalline formic acid,^{28,29} where long chains of molecules linked by hydrogen bonds are held together by van der Waals forces. We know of no experimental evidence for the existence of such long chains in carbonic acid, which is a transient species in most environments, but we have shown that the chain structure is both stable against bending (a structure with $\sim 20 \text{H}_2\text{CO}_3$ units is needed before a ring becomes more stable than a chain) and has a substantial tensile strength. It would be most interest-

ing to see whether such chain structures can be prepared. The structures of the carbonic acid polymorphs remains a challenge to theory and experiment.

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