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Article

H_2CO_3 and Its Oligomers: Structures, Stabilities, Vibrational and NMR Spectra, and Acidities

J. A. Tossell*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

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Although the molecular form of carbonic acid, H_2CO_3, is of very limited stability in aqueous solution, some form of H_2CO_3 is apparently stable as a solid and may be a stable species on acid-treated carbonate mineral surfaces. Experimental vibrational spectra that have been assigned to solid H_2CO_3 have been obtained by several research groups, although there is no information on either the local or long-range structure of this phase and calculated vibrational frequencies for monomeric H_2CO_3 show significant discrepancies with the experimental IR data. Previous calculations have also indicated that H-bonded H_2CO_3 oligomers are more stable than the monomer and have significantly different vibrational spectra, but the accuracy of the spectral calculations was not considered sufficient to reassign the experimental data. We have now calculated the harmonic vibrational spectrum of monomeric H_2CO_3 at the 6-311+G(2d,p) CCSD level and have calculated anharmonic corrections at the CBSB7 B3LYP level (used in CBS-QB3 calculations), combining the two to obtain an accurate description of the fundamental vibrations of gas phase H_2CO_3, which disagree significantly and systematically with the experimental data for solid H_2CO_3. For the H-bonded dimer, $(H_2CO_3)_2$, we have calculated both the harmonic spectrum and anharmonicity corrections at the CBSB7 B3LYP level, finding much better agreement with the experimental spectrum of solid H_2CO_3 than for the monomer, particularly for the C=O and O–H stretching vibrations, which are strongly red-shifted by both H bonding and anharmonic effects in the dimer. The free-energy changes for the formation of the $(H_2CO_3)_n$ ($n = 2$ and 3) oligomers and for the formation of a 1D chain structure of H-bonded monomers are negative in the gas phase, despite an unfavorable entropic contribution. However, in aqueous solution, the free-energy change for the formation of the $n = 2$ and 3 oligomers becomes positive because of the loss of hydration free energy, since the –OH groups of H_2CO_3 are removed from H bonding with the solvent. We have also calculated ^{13}C NMR shieldings for the H_2CO_3 oligomers and some other related molecules, finding that the central C is systematically deshielded by oligomerization.

Introduction

The existence of H_2CO_3 as a discrete molecular species has long been controversial. It has been identified in the gas phase but only by a peak in the mass spectrum[1] of the vapor existing over heated solid NH_4HCO_3, while other related acidic species such as $B(OH)_3$ and HNO_3 have been thoroughly characterized by vibrational spectroscopy both in the gas phase and in matrix isolation. A feature in the Raman spectrum of acidified bicarbonate solutions has been assigned[2] to H_2CO_3, but this feature is almost coincident with one of the frequencies of HCO_3^-, a somewhat unexpected result. An early ^{13}C NMR study[3] of solutions of CO_2 in water did not identify any peaks other than those attributable to CO_2, HCO_3^-, and CO_3^{2-}, although the NMR shift for H_2CO_3 could only be guessed at that time. It is commonly accepted within inorganic solution chemistry and geochemistry[4] that a "carbonic acid" solution, produced by dissolving CO_2 in water, contains only a fraction of a percent of actual H_2CO_3 molecules. An acidity value has also been measured[5] for a transient species produced by the acidification of

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* E-mail: tossell@chem.umd.edu.

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sodium carbonate solutions, which may be H_2CO_3. This species is considerably more acidic (pK_a around 3) than is carbonic acid itself (pK_a around 6), consistent with its instability in solution. The ^{13}C NMR spectrum of carbonates in superacid solutions has been determined[6] and features have been attributed to H_2CO_3 and $H_3CO_3^+$, but the shieldings calculated using the IGLO version of the coupled Hartree−Fock perturbation theory for the assigned species did not match the experimental trends.

In the early 1990's, proton irradiation of icy mixtures of CO_2 and H_2O produced[7] a solid whose IR features seemed qualitatively consistent with those expected for H_2CO_3, particularly in the C═O and O−H stretching regions. Subsequent studies showed that a number of different synthetic approaches[8−13] could produce a solid with qualitatively the same spectral characteristics, although quantitative differences suggested that there were two different polymorphs of the material, which have been labeled α- and β-H_2CO_3(s). Recently, H_2CO_3-like species have been identified on the surface of acid-treated calcite,[14,15] primarily on the basis of their vibrational spectra.

Several theoretical studies[16−20] have shown that gas phase H_2CO_3 had a less negative free energy than the reactants $CO_2 + H_2O$, but other studies have indicated a substantial activation energy barrier for the decomposition of H_2CO_3 in the absence of water,[21] which was greatly reduced when water molecules were added.[21−25] One study calculated the (harmonic) vibrational spectrum[20] of H_2CO_3 at a high quantum mechanical level (6-311^{++}G** MP2) and uncovered systematic quantitative disparities with the experimental data for solid H_2CO_3, which were attributed to unspecified medium effects. Note that the only data available to characterize the solid H_2CO_3 species were IR and Raman spectra. There was no X-ray or neutron diffraction data and no C, O, or H NMR that might substantiate the assignment. The stability of some oligomers of H_2CO_3 has also recently been studied[24,25] using both correlated post-Hartree−Fock and density functional theory (DFT) methods. The small H-bonded oligomers studied were found to have energies per H_2CO_3 unit that were generally lower than those for monomeric H_2CO_3. The DFT study[26] also showed that the calculated C═O and O−H stretching frequencies were lower in the oligomers than in the monomer, but the accuracy of the results was not considered by the authors to be sufficient to definitively reassign the experimental spectra.

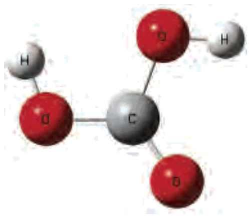

Figure 1. H_2CO_3 s−a conformer.

Recently, we carried out a study[27] of the acidity of a number of aqueous oxyacids, such as $B(OH)_3$, H_2CO_3, and HNO_3. We found that the complex $CO_2 \cdots H_2O$ was the predominant species in “carbonic acid”, roughly 1000 times more abundant than H_2CO_3, in agreement with experiment. Of the three conformers of monomeric H_2CO_3, s−s, s−a, and a−a, we found a−a to be the most stable in the gas phase (in agreement with previous studies, e.g., ref 20), but in aqueous solution, the a−a and s−a conformers were within a couple of kilocalories per mole of each other because of a more negative hydration energy for the less symmetric s−a isomer.[27] The calculated geometry of the s−a isomer of H_2CO_3 is shown in Figure 1. Although we will show below that the dimer and trimer of H_2CO_3 give a much better description of the experimental vibrational spectrum of the solid than does any configuration of the monomer, it is worth noting that for the s−s, s−a, and a−a conformers the C═O stretching frequencies, calculated at the CBSB7 B3LYP level, do vary from 1929 to 1905 to 1853 cm^{-1}, while the two O−H stretching modes vary from 3807 and 3826 to 3802 and 3806 to 3811 and 3815 cm^{-1} along the same series. For comparison, previous 6-311^{++}G** MP2 values[20] for the a−a conformer are 1843 cm^{-1} for the C═O stretch and 3844 and 3845 cm^{-1} for the O−H stretches.

Until recently, there have been important limitations on our ability to accurately calculate vibrational frequencies for species even as small as H_2CO_3 and its small oligomers. These limitations arose from the need for including both electron correlation effects[28] and anharmonic effects[29] to

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accurately describe the fundamental vibrations of even small gas-phase molecules. Additionally, methods were unavailable for incorporating the effects of the surrounding environment on the vibrational spectra of species in condensed phases. Such limitations can now be overcome to a large extent for medium-size molecules using a bootstrapping approach. We still cannot do a highly correlated calculation to directly obtain the anharmonically corrected spectrum for a species such as H_2CO_3 in an explicit nanocluster model for an aqueous solution. However, we can do a highly correlated calculation with a large basis set to obtain very accurate harmonic frequencies, then add anharmonicity corrections obtained at a lower computational level, and then add solvation corrections obtained using a lower-level polarizable continuum model (PCM) simulation. This is admittedly a clumsy procedure, but it is the only one presently feasible for moderate-size molecules in solution and it often seems to give good results. For example, the calculation of anharmonic vibrational properties using DFT seems to produce accurate anharmonic corrections, which can be used either alone or as corrections to harmonic frequencies calculated at higher levels such as CCSD.[30,31] Although this approach is often quite successful[30] in accurately matching experiment, it should be noted that, for very strongly anharmonic cases, such as very low frequency O−H stretches (around 1700 cm^{-1}), in systems with very short O−H⋯O distances (around 2.4 Å), this procedure (as implemented in the *Gaussian* programs) has been shown to give poor results.[32] However, the H-bonded systems that we will later describe have much higher O−H stretching frequencies and much longer O−O distances and so will have smaller anharmonic effects. After performing the vibrational frequency calculations, we calculated accurate total free energies for the different species in the gas phase, using composite methods such as the complete basis set (CBS) approach, and estimate hydration free energies within a PCM approximation.[33] Studying the vibrational spectra and the energetics together makes it easier to identify the species existing in condensed phases.

Computational Methods

For the calculation of gas-phase free energies, we use the CBS-QB3 method,[34] a composite method that determines equilibrium geometries at essentially the 6-311G(d,p) B3LYP level (although using the slightly modified CBSB7 basis set) and uses as its highest-level single-point correlated calculation, a CCSD(T) calculation at the equilibrium geometry with a 6-31+G(d,p) basis. Unfortunately, the computer time required for the highly demanding CCSD(T) step[35] in this method scales as about the seventh power of the number of electrons, so the method becomes extremely demanding for oligomeric species. We have thus applied it to the monomeric and dimeric species only.

The vibrational spectra were obtained at several levels of approximation. First, we use the vibrational frequencies obtained at the CBSB7 B3LYP level during the CBS-QB3 calculation. For the monomer we experimented with the “tightness” of the optimization constraints to determine how much they might affect the results. We then calculated vibrational frequencies at the 6-311+G(2d,p) CCSD level if computationally feasible, which restricts us to the monomeric species. Anharmonic frequencies were then calculated at the CBSB7 B3LYP[36] level using the second-order perturbation theory approach implemented in *Gaussian03* for the monomeric and dimeric species. Finally, we evaluated harmonic frequencies at the CBSB7 B3LYP level within a PCM simulating an aqueous solution (using a dielectric constant of 78.5 appropriate to water at 25 °C and standard water PCM parameters). To evaluate the hydration free energies, we use the conductor polarizable continuum method, CPCM, version[37] of the PCM.

We have also calculated NMR shieldings for a number of the species considered, to establish additional criteria for their identification, using the GIAO version of coupled Hartree−Fock perturbation theory.[38] We have utilized 6-311+G(2d,p) basis sets and Hartree−Fock (HF), MP2, and B3LYP versions of the GIAO method. We have also used the HF and MP2 results together with the scaling procedure of Chesnut to estimate the infinite-order MP result.[39] For several of the molecules, NMR properties and electric field gradients at the nuclei have been calculated both at the normal 0 K equilibrium geometry and at the vibrationally averaged 0 K geometry obtained from the anharmonic frequency analysis.

All calculations were done using *Gaussian03*,[40] and structures were visualized using *GaussView*.[41]

Results and Discussion

Vibrational Spectra of H_2CO_3 and Its Oligomers. Computed vibrational frequencies are given in Table 1 for the s−a conformer of H_2CO_3. Both harmonic and anharmonic frequencies at the CBSB7 B3LYP level are given, along with the harmonic frequencies obtained at the 6-311+G(2d,p)

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Table 1. Calculated Vibrational Frequencies (in cm^{-1}) for the s−a Conformer of Monomeric H_2CO_3, Obtained Using CBSB7 B3LYP (Both Harmonic and Anharmonic) and 6-311+G(2d,p) CCSD (Harmonic Only) Methods along with Estimated 6-311+G(2d,p) CCSD Results Corrected for Anharmonicity[a]

CBSB7 B3LYP harmonic		CBSB7 B3LYP anharmonic		6-311+G(2d,p) CCSD harmonic	6-311+G(2d,p) CCSD results approximately corrected for anharmonicity; columns 3 + 2 − 1, using tight values for columns 1 and 2	intensities (harmonic CBSB7 B3LYP)	
reg	tight	reg	tight			IR	Raman
486	486	474	471	473	458	235.2	1.6
545	545	539	538	557	550	26.9	1.2
571	568	534	538	563	533	15.4	3.5
610	610	605	610	623	623	8.7	2.1
785	785	774	774	809	798	36.0	0.2
967	968	941	948	980	960	38.7	8.1
1153	1153	1017	1121	1187	1159	228.7	1.4
1274	1274	1221	1219	1308	1253	138.2	7.2
1406	1407	1370	1370	1445	1408	293.8	0.4
1905	1905	1859	1860	1909	1864	462.6	5.1
3804	3804	3608	3619	3845	3660	89.3	57.1
3806	3806	3611	3621	3849	3664	75	68.5

[a] IR and Raman intensities from the CBSB7 B3LYP harmonic calculations are also given.

CCSD level. For the CBSB7 B3LYP calculations, we have employed both regular and Opt=Tight, Integral(UltraFine) constraints on the geometry optimization process. Either regular or tight constraints present no serious computational problem for a harmonic calculation on monomeric H_2CO_3, but for the anharmonic calculation, the tight constraints are much more demanding. Employing the regular constraints would be highly desirable if they did not introduce too much error. Relative IR and Raman intensities from the CBSB7 B3LYP harmonic calculations are also given in the last column. It is apparent from the data in Table 1 that the use of tight versus regular constraints has very little effect on the harmonic frequencies but can significantly affect the anharmonic frequencies, some of which (the low-frequency bending modes and the high-frequency stretching modes) show errors of 5−10 cm^{-1} using the regular constraints. As expected based on the general comparison of harmonic oscillator and Morse potentials, the anharmonic stretching frequencies are systematically lower than the harmonic ones, with the largest absolute changes occurring for the O−H stretches around 3000−4000 cm^{-1}, which are reduced by about 200 cm^{-1}. However, the ratio of anharmonic to harmonic frequency shows considerable variation, with only the O−H stretches showing the ratio of about 0.953 that might be expected from the normal scaling factors of 0.95−0.97 used to estimate experimental fundamental frequencies from DFT harmonic frequencies.[36] The harmonic frequencies calculated at the 6-311+G(2d,p) CCSD level are typically 5 and 40 cm^{-1} higher than those calculated at the CBSB7 B3LYP level for the C=O and O−H stretching vibrations, respectively.

Using a procedure like that of Carbonniere et al.[30] and others, we have added to the CCSD frequencies the difference between the CBSB7 anharmonic and harmonic frequencies (both obtained with tight constraints) to obtain estimated fundamental frequencies at (nearly) the CCSD level. Explicitly for the highest energy vibration (a O−H stretch), we add to the 6-311+G(2d,p) CCSD value of 3849 cm^{-1} the CBSB7 B3LYP anharmonic value (with tight constraints) of 3621 cm^{-1} and then subtract the CBSB7 B3LYP harmonic value (with tight constraints) of 3806 cm^{-1} to obtain an approximate anharmonically corrected 6-311+G(2d,p) CCSD value of 3664 cm^{-1}. All of the values just quoted appear in Table 1. Although this bootstrapping procedure certainly will introduce some error, it appears on the basis of previous studies to be accurate enough for us to be sure that the values thus obtained for the C=O stretch and the O−H stretches of monomeric H_2CO_3 (1864 and 3660, 3664 cm^{-1}, respectively; Table 1) are too high to be consistent with experimental values around 1700 cm^{-1} for the C=O stretch and 3200−2600 cm^{-1} for the O−H stretches in H_2CO_3(s).

Table 2. Calculated Vibrational Frequencies (in cm^{-1}) for the s−a Isomer H_2CO_3 in the Gas Phase and in a PCM Simulating Water

CBSB7 B3LYP harmonic		
gas	aqueous solution PCM	solution shift
486	455	−31
545	542	−3
571	555	−16
610	617	+7
785	791	+6
967	992	+25
1153	1158	+5
1274	1256	−18
1406	1395	−11
1905	1815	−90
3804	3426	−378
3806	3443	−363

If the H_2CO_3 species were in an aqueous solution or a water ice environment (because many of them could well be based on their methods of preparation), we would expect additional changes in their vibrational frequencies due to H bonding with water molecules and polarization of the water-like solvent. We can crudely estimate this effect by carrying out the CBSB7 B3LYP calculation within a PCM simulating the water environment (with a dielectric constant of 78.5), producing the results shown in Table 2, where we give vibrational frequencies for the free molecule and the molecule inside the PCM, along with the calculated solution shift. This shift is typically small for the lower-frequency bending vibrations and larger and negative for the high-frequency stretching vibrations, with changes on the order of −90 cm^{-1}

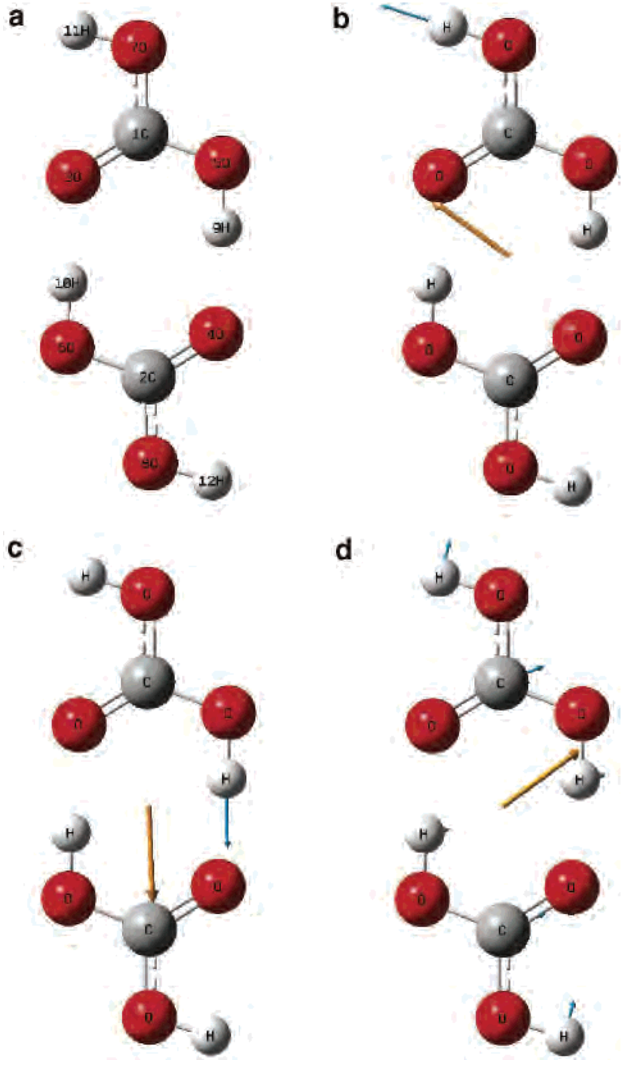

Figure 2. (a) $(H_2CO_3)_2$. (b) $(H_2CO_3)_2$ outer O−H stretch, $\nu = 3807$ cm^{-1} (atom displacement vectors in blue; mode dipole derivatives in brown). (c) $(H_2CO_3)_2$ inner O−H stretch, $\nu = 3232$ cm^{-1}. (d) $(H_2CO_3)_2$ C═O stretch, $\nu = 1798$ cm^{-1}.

for C═O stretches and −370 cm^{-1} for O−H stretches. However, even such additional corrections for a hypothetical hydrated environment are insufficient to bring the calculated C═O and O−H frequencies for monomeric H_2CO_3 into good agreement with the experimental values for H_2CO_3(s). For example, the best value for the C═O stretch of 1864 cm^{-1} from Table 1, when corrected for the solution shift of −90 cm^{-1} in Table 2, is still 1774 cm^{-1}, considerably larger than the experimental values of around 1705−1715 cm^{-1}. The discrepancy is even larger in the O−H stretch region. Thus, we must consider oligomeric species to explain the IR spectra.

The most stable form for the H_2CO_3 dimer has each individual H_2CO_3 unit in an a−a configuration, and its calculated geometry is shown in Figure 2a. We have calculated vibrational frequencies for the dimer, both harmonic and anharmonic and both free and in a PCM simulating an aqueous solution using the CBSB7 B3LYP method. Because of the larger number of atoms in the dimer, frequency calculations at the 6-311+G(2d,p) CCSD level were not feasible. However, remember that for the monomer the CBSB7 B3LYP and 6-311+G(2d,p) CCSD harmonic frequencies never differed by more than 50 cm^{-1} and were within 10 cm^{-1} for the C═O stretches. As seen in Table 3, the calculated C═O and O−H stretches in the dimer are considerably lower in frequency than those in the monomer, as expected because the intramolecular H bonds holding the dimer together occur between the O−H and O═C groups. The average decrease for the C═O stretches from monomer to dimer is about 200 cm^{-1}, while the decrease for the O−H stretches of groups participating in H bonds to C═O is about 600 cm^{-1}. Plots showing the atomic motions in the normal modes for outer O−H, inner O−H, and C═O stretching are shown in Figure 2b−d. Both atomic displacement vectors and dipole derivative vectors are shown. The frequency lowerings arising from anharmonicity for the C═O and O−H stretches are somewhat larger in the dimer than in the monomer, while the lowerings arising from the effects of the PCM are somewhat smaller (because the C═O and O−H groups are protected from the aqueous environment). Raman and IR relative intensities from the harmonic gas-phase CBSB7 B3LYP calculation are also given. All of the experimental data with which we compare have been obtained from IR spectroscopy, so we can concentrate on the IR-active modes in analyzing the match of calculation and experiment.

In Table 4, we summarize the experimental data on the vibrational properties of the two polymorphs of solid

Table 3. Calculated Vibrational Frequencies (in cm^{-1}) for $(H_2CO_3)_2$, Obtained at the CBSB7 B3LYP Level (Harmonic and Anharmonic and in the PCM)[a]

CBSB7 B3LYP			columns 2 + 3 − 1	intensities (harmonic gas phase)	
harmonic	anharmonic	harmonic in the PCM	PCM-corrected anharmonic	IR	Raman
57	60	54	57	0.1	0
74	76	64	66	2.1	0
125	121	121	117	0	0.8
170	161	165	156	0	0.5
186	185	170	169	0	0.1
205	209	183	187	19.4	0
573	566	531	524	0	1.3
577	573	533	529	194	0
578	574	579	575	0	6.1
605	598	608	601	135	0
643	639	640	636	0	6.4
654	648	654	648	45	0
802	794	797	789	0	0.2
804	795	798	789	0.44	0
924	897	875	848	0	0.2
972	947	907	882	264.4	0
1025	1006	1026	1007	25	0
1032	1013	1035	1015	0	21.7
1238	1201	1201	1164	0	2.5
1243	1204	1207	1168	696	0
1390	1343	1375	1328	280	0
1392	1386	1380	1374	0	6.8
1529	1478	1511	1460	404	0
1561	1519	1542	1500	0	17.4
1729	1656	1698	1625	0	8.2
1798	1752	1735	1689	1149	0
3120	2752	3096	2728	0	245.5
3232	2883	3169	2820	2938	0
3807	3624	3414	3231	189	0
3808	3624	3417	3233	0	123.2

[a] IR and Raman intensities are also given.

Table 4. Comparison of Most Accurate Calculated Anharmonic, PCM-Corrected Frequencies for IR-Active Modes of H_2CO_3 and $(H_2CO_3)_2$ with Experimental Values in the IR Spectra of β-H_2CO_3(s) and α-H_2CO_3(s), Taken from the Compilation of Hage et al.[10] (Table 2; All Experimental Values Are for the $H_2{}^{12}CO_3$ Isotopomer)

type of vibration	calcd			
	H_2CO_3	$(H_2CO_3)_2$	β-H_2CO_3(s)	α-H_2CO_3(s)
O−H stretch	3301, 3282	3232, 2820, 2728	3200−2600	2694, 2585
C═O stretch	1774	1689	1705	1715
C−OH antisymmetric stretch	1397, 1235	1460,1328	1501	1477, 1304
C−OH symmetric stretch	1164	1168	1034	1084

H_2CO_3, along with our most accurate calculated values for the vibrational frequencies of H_2CO_3 and $(H_2CO_3)_2$, incorporating correlation, anharmonicity, and hydration effects. As a note of caution, our results are effectively at the CCSD level for the monomer but only at the CBSB7 B3LYP level for the dimer. On the basis of the data for the monomer in Table 1, this should introduce differences of less than 50 cm^{-1} for the O−H stretches and less than 10 cm^{-1} for the C═O stretches. First, we should note that some have suggested that the two different polymorphs of solid H_2CO_3 may simply correspond to the different isomers, a−a, s−a, and s−s, of monomeric H_2CO_3. However, we mentioned previously that the different conformers show fairly small differences in C═O and O−H stretching frequencies. Thus, the experimental spectrum must be attributed to some type of oligomeric species. The calculated spectrum of the H_2CO_3 dimer matches reasonably well against the experimental spectra of both α- and β-H_2CO_3(s). Although there are slight differences between the reported spectra of the α and β polymorphs in many spectral regions, the most significant difference is an additional absorption in the O−H stretch region at higher frequency (a peak around 3050 cm^{-1} and some absorption at frequencies up to 3200 cm^{-1}) in the β form. For the dimer, the anharmonic O−H stretch for the outer −OH group (not internally H-bonded) appears at 3600 cm^{-1} for the free molecule and at about 3200 cm^{-1} for the molecule in the PCM, while the inner H-bonded O−H groups have frequencies of around 2900−2800 cm^{-1} free and 2800−2700 cm^{-1} in the PCM. Thus, the dimer or some other small oligomer in which a significant fraction of the −OH groups lie on the outside of the molecule and are H-bonded only to water could possibly explain the 3050 cm^{-1} feature in the β polymorph. All of the other experimental features in the −O−H stretching region would then correspond to internally H-bonded O−H groups (i.e., bonded to C═O).

For the trimer (shown in Figure 3), the four calculated IR-active inner O−H stretching harmonic frequencies at the CBSB7 B3LYP level are at 3333−3147 cm^{-1}, slightly larger than those for the dimer. Unfortunately, neither the 6-311+G-(2d,p) CCSD harmonic nor the CBSB7 B3LYP anharmonic calculations were feasible for the trimer. Using the latest general scaling factor of 0.968 for frequencies obtained at the 6-311(d,p) B3LYP level from ref 42b, we obtain scaled values of 3226−3046 cm^{-1} for these frequencies. However, if we use the ratio of anharmonic to harmonic CBSB7 B3LYP frequencies found for the inner O−H stretches of the dimer (around 0.89 from Table 3), we would obtain values of 2966−2800 cm^{-1}. This difference of course occurs because H-bonded systems show unusually large anharmonic effects, much larger than those seen in the more normal molecules used to develop standard scaling factors. In any case, the larger inner O−H frequencies in the trimer are consistent with the slightly longer calculated average O−H···O distance in the trimer compared to the dimer (2.659 vs 2.641 Å). There are no calculated O−H stretches in the trimer that seem consistent with the features seen around 2700−2600 cm^{-1} in the experimental spectra of both polymorphs of H_2CO_3(s). However, the IR-active C═O stretches for the trimer are calculated at 1790−1671 cm^{-1}, which when scaled by 0.968 gives values between 1732 and 1618 cm^{-1}, consistent with experiment. Thus, we cannot completely exclude the trimer from consideration as a possible contributor to the spectrum of β-H_2CO_3(s).

Figure 3. $(H_2CO_3)_3$.

For the 1D periodic solid $(H_2CO_3)_\infty$ (shown in Figure 4), the present version of the periodic boundary condition implementation[43] in *Gaussian03* does not support the calculation of vibrational frequencies, but the average O−O distance at equilibrium has increased to 2.670 Å, which would be consistent with an average inner O−H stretch frequency of about 120 cm^{-1} higher than that in the dimer, according to the latest empirical correlations[44] of O−O distance and O−H stretching frequency. Thus, the infinite

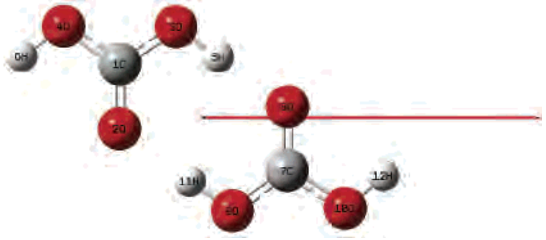

Figure 4. $(H_2CO_3)_\infty$ 1D polymer (two atoms in the unit cell and the translation vector are shown).

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(42) (a) Wong, M. W. *Chem. Phys., Lett.* **1996**, *256*, 391−399. (b) Andersson, M. P.; Uvdal, P. *J. Phys. Chem. A* **2005**, *109*, 2937−2941.

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Table 5. Calculated Relative Energies per H_2CO_3 Unit (in kcal/mol) for H_2CO_3 Oligomers and a 1D Crystal in Gas Phase and an Aqueous Solution Compared to the s−a Isomer of Monomeric H_2CO_3[a]

	ΔE_g for CBSB7 B3LYP	ΔG_{VRT}	$\Delta E_g + \Delta G_{VRT}$	$\Delta G_{CBS-QB3}$	ΔG_{CPCM}	ΔG_{aq}
H_2CO_3 s−a isomer	0	0	0	0	−14.5	−14.5
$(H_2CO_3)_2$	−11.9	+6.6	−5.3	−4.5	−6.7	−11.2
$(H_2CO_3)_3$	−14.6	+8.3	−5.6	na	−6.9	na
$(H_2CO_3)_\infty$ 1D solid	−19.1	na	na	na	na	na

[a] na = not attempted

1D polymer can probably not reproduce the O−H part of the spectrum of H_2CO_3(s).

Energetics for the Formation of Oligomers of H_2CO_3. To support our assignment of the IR spectra of solid H_2CO_3 to oligomeric species, we have considered the energetics for the formation of the dimer, trimer, and 1D crystalline solid starting from monomeric H_2CO_3. A plot of the unit cell of the 1D crystalline solid is shown in Figure 4. Energies and free-energy contributions for the most stable monomer in solution (s−a) and for the dimer, trimer, and 1D crystalline solid are complied in Table 5. We find that the free energy per H_2CO_3 unit does indeed become more negative from the monomer to the dimer at the CBS-QB3 level in the gas phase. The CBS-QB3 calculation was not feasible for the trimer, but the sum of the gas-phase CBSB7 B3LYP energies and the vibrational, rotational, and translational (VRT) contributions to the gas-phase free energy also becomes more negative from monomer to dimer to trimer. In fact, the CBSB7 B3LYP energy per H_2CO_3 unit is even more negative for the infinite 1D crystalline solid. However, the 1D solid is lower in energy than the trimer by only 4.5 kcal/mol, compared to a 12 kcal/mol H_2CO_3 stabilization in going from the monomer to the dimer, so that the stability per H_2CO_3 unit must clearly flatten out with increasing oligomer size.

However, the CPCM hydration free energy is much less negative per H_2CO_3 unit in the dimer and trimer than in the monomer because half of the −OH groups are involved in internal H bonding and are therefore not accessible to solvent. Therefore, the overall solution free energy, ΔG_{aq}, is actually *less* negative for the dimer than for the monomer. This indicates that the dimer, and presumably higher oligomers, is favored in the gas phase or as a fragment of a solid but is not favored in an aqueous solution.

Vibrational Spectra of Solid $KHCO_3$ and $(HCO_3)_2^{2-}$. We can further support our vibrational spectral assignment for H_2CO_3(s) by calculating vibrational spectra for the dimeric anion, $(HCO_3)_2^{2-}$, which exists in solid $KHCO_3$ and has been studied by IR spectroscopy[45] and X-ray diffraction[46] (although the X-ray structure is rather old). The crystal structure indeed shows $(HCO_3)_2^{2-}$ dimeric units, as is shown for the CBSB7 B3LYP-calculated structure in Figure 5. The O−H···O distance in the crystal is reported as 2.61 Å. This distance calculated at the CBSB7 B3LYP level for both the harmonic and anharmonic structures of the free gas-phase dianion is much longer (2.82 and 2.84 Å) because of the uncompensated negative charge, but optimization within the PCM appropriate to an aqueous solution (with a dielectric constant of 78.5) reduces the equilibrium O−H···O distance to 2.66 Å. This suggests that the stabilization provided by the aqueous solution PCM is similar in magnitude to that experienced by the dianion in the crystal. Agreement of other experimental structural parameters with the calculated anharmonic values for the dianion is generally good, although it appears that the difference between the inner C═O and C−OH distances is averaged out in the experiment. The average of the calculated C═O and C−O(H) distances of 1.264 and 1.404 Å is 1.33 Å, in good agreement with the experimental values, which are given as 1.32 and 1.33 Å.

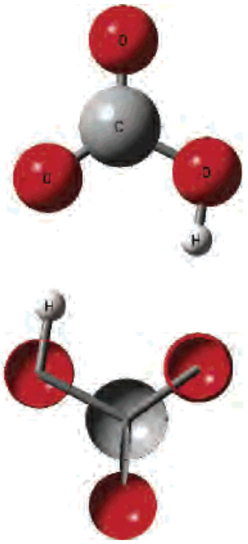

Figure 5. $(HCO_3)_2^{2-}$.

Calculated and experimental IR frequencies are compared in Table 6. Although the IR experiment was done on the crystalline material, we presently have no accurate way to incorporate the effects of the surrounding crystal lattice on the vibrational properties so we have approximated them very crudely through a PCM calculation appropriate to an aqueous environment. The electrostatic influence of the polarizable continuum scales as the quantity $1 - 1/D$, where D is the dielectric constant. This quantity is not that much different for $D = 78.5$, appropriate to water, and $D = 5$, which might be appropriate to the environment in $NaHCO_3$ or some similar ionic crystal [the experimental value of $D \approx 5$ for NaF(s)]. Thus, the exact value of the dielectric constant should not exert that large an influence on the magnitude of the effect. To support this idea, we have also calculated the frequencies in a PCM with a dielectric constant of 5, and these values are included in Table 6 in parentheses. It is apparent that the shifts from the gas-phase results are smaller in the PCM calculation with the smaller dielectric constant, but by only 10−30%.

Note first that in the dianion there are no O−H groups that are not H-bonded, so all of the O−H stretches are reduced to slightly more than 2900 cm^{-1}, with no higher energy features. The C═O stretch is slightly lower in energy than that in $(H_2CO_3)_2$, around 1600 cm^{-1} rather than 1700

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Table 6. Comparison of Calculated Frequencies for IR-Active Modes of $(HCO_3)_2^{2-}$ with Experimental Values of Strong Features in the IR Spectra of $KHCO_3$(s) (Nakamoto et al.[45])

mode	CBSB7 B3LYP harmonic	anharmonic	harmonic PCM $D = 78.5$ ($D = 5$)	harmonic PCM $D = 78.5$ + anharmonic − harmonic	$KHCO_3$ expt
O−H stretch	3402	3154	3186 (3209)	2938	2920
C═O stretch	1734	1695	1640 (1667)	1601	1618
C−OH stretch	1395, 1344, 958	1355, 1303, 935	1390, 1357, 988 (1401, 1361, 982)	1350, 1316, 965	1367, 1283, 1029

cm^{-1}. This is exactly the difference seen between the C═O stretches in the experimental spectra of H_2CO_3(s) and $NaHCO_3$(s). The difference occurs because the outer O has been deprotonated in the dianion, so that it acquires partial double-bond character and so the inner C═O therefore loses part of its double-bond character. The agreement of calculated and experimental frequencies is thus quite good in the O−H, C═O, and C−OH stretching regions. This suggests that if we knew the detailed structure of solid H_2CO_3, we could probably calculate its vibrational spectrum very accurately at the present computational level.

The accuracy of our procedures is also supported by the good agreement of our calculated anharmonic value for the C═O stretch in the cis−cis conformer of $(CH_3)_2CO_3$ (a species like H_2CO_3 but without its H-bonding capabilities) of 1782 cm^{-1} (at the CBSB7 B3LYP level), compared to an experimental value[47] of 1774 cm^{-1}. The calculated harmonic value of the C═O stretch for this molecule is 1814 cm^{-1}, so that anharmonicity lowers the stretching frequency by 32 cm^{-1}, similar to the 45-cm^{-1} lowering seen in H_2CO_3 (Table 1).

Energetics for Dimerization of H_2CO_3 and HCO_3^- in Solution. It is instructive to compare the energetics for the formation of the two dimeric species $(H_2CO_3)_2$ and $(HCO_3)_2^{2-}$, as shown in eqs 1 and 2.

$$2H_2CO_3 \Rightarrow (H_2CO_3)_2 \qquad (1)$$

$$2HCO_3^- \Rightarrow (HCO_3)_2^{2-} \qquad (2)$$

For these two reactions (with H_2CO_3 in its most stable s−a conformer), the gas-phase free energy changes are −9.0 and +55.8 kcal/mol, respectively (at the CBS-QB3 level), while the CPCM hydration free-energy contributions are +15.6 and −45.7 kcal/mol, respectively. Thus, both reactions are unfavorable in aqueous solution, although the overall ΔG_{aq} (the sum of the gas-phase free-energy change and the hydration free-energy change) is only about half as large (+6.6 vs +10.1 kcal/mol) for the neutral case, eq 1, as for the anion, eq 2. If we reoptimize reactant and product geometries at the CBSB7 B3LYP level within the PCM, the overall reaction free energies become +10.1 and +5.7 kcal/mol, respectively, somewhat different from those for the first approach employing the gas-phase geometries and single-point CPCM calculations at those geometries. In any case, it is clear that the free energies for dimerization in solution are positive for both neutral and anion, but by fairly modest amounts. One could also imagine an environment intermediate between the gas phase and a uniform aqueous environment, where reactants and products could be partially hydrated, which could give dimerization free energies even closer to zero for the neutral case. We have also calculated CPCM energies appropriate to a methanol solution (D = 32.6) and find that the solution energetics are changed by no more than 1.0 kcal/mol. Thus, we would not expect the relative stabilities of monomers and dimers to differ significantly between water and a methanol solution.

Table 7. Calculated ^{13}C NMR Shieldings Obtained from CBSB7 B3LYP Geometries, Using the HF, MP2, and B3LYP Versions of the GIAO Method and 6-311+G(2d,p) Basis Sets

	σ_{HF}		σ_{MP2}		σ_{B3LYP}		σ_{corr}	
molecule	σ_{HF}	δ_{HF}	σ_{MP2}	δ_{MP2}	σ_{B3LYP}	δ_{B3LYP}	σ_{corr}	δ_{corr}
$Si(CH_3)_4$, reference for C shieldings	192.3	0	197.3	0	183.1	0	195.6	0
CO_2	53.2	139.1	67.6	129.7	52.7	130.4	62.8	132.8
$CO_2\cdots H_2O$	51.9	140.4	66.7	130.6	51.7	131.4	61.8	133.8
H_2CO_3, a−a isomer	32.5	159.8	39.6	157.7	31.6	151.5	37.2	158.4
HCO_3^-	29.9	162.4	38.2	159.1	20.9	162.2	35.4	160.2
$H_3CO_3^+$	22.3	170.0	28.6	168.1	12.7	170.4	26.5	169.1
$(H_2CO_3)_2$	25.3	166.9	32.5	164.8	15.4	167.7	30.1	165.5
$(H_2CO_3)_3$ inner	21.2	172.1	na		171.4		na	
$(H_2CO_3)_3$ outer	25.6	166.7			15.5	167.6		
$(HCO_3)_2^{2-}$	22.9	169.4	31.0	166.3	13.9	169.2	28.3	167.3

[a] na = not attempted because of the size of the necessary calculation.

NMR Spectra for H_2CO_3 and Its Oligomers. In addition to vibrational spectroscopy, ^{13}C NMR spectroscopy may be a useful way to characterize H_2CO_3 and its oligomers. Characterization of these species by ^1H and ^{17}O NMR is more difficult because the synthesis procedure usually involves an aqueous environment with an abundance of water and/or ice, which overwhelms the ^1H and ^{17}O NMR from the carbonate species. Using the CBSB7 B3LYP-optimized geometries and the anharmonic vibationally averaged geometries, we have calculated ^{13}C NMR shieldings, σ, and shifts, δ [with respect to $Si(CH_3)_4$], at the HF, B3LYP, and MP2 levels using the GIAO method and 6-311+G(2d,p) basis sets and extrapolated to the infinite-order MP level. These results are presented in Table 7 for several different species and graphically in Figure 6 for $(H_2CO_3)_2$. For the C atoms in Figure 6, we give only the shieldings, evaluated both for the harmonic structure and for the anharmonic structure at 0 K. For the O and H atoms, we give both the shieldings and (on the line below them) the electric field gradients (in atomic units) because they can be measured by NMR for these quadrupolar nuclides. We also give in bold the harmonic and anharmonic values for the O−H and O−H···O distances. Note that the anharmonicity effects on the H shieldings, electric field gradients, and distances are not negligible. Our calculated shift with respect to $Si(CH_3)_4$ is in good agreement with experiment[48] for CO_2. We find

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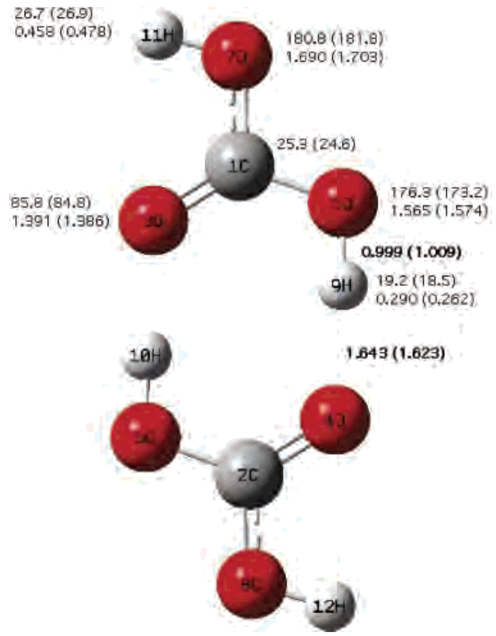

Figure 6. $(H_2CO_3)_2$ with calculated NMR shieldings and electric field gradients, for both reference and vibrationally averaged geometries, with distances given in bold.

that the a−a isomer of monomeric H_2CO_3 is deshielded with respect to CO_2 by about 25 ppm and that oligomerization deshields the C by about another 7−10 ppm, depending upon how “deep” the C is within the oligomer chain. For example, the inner C and outer C’s of $(H_2CO_3)_3$ differ in shift by about 4 ppm. In the anionic dimer $(HCO_3)_2^{2-}$, the deshielding is larger than that in the neutral dimer, by a few parts per million. Thus, we should find different ^{13}C NMR signatures depending upon the types of oligomers present and their charge.

As expected, the presence of H bonding also affects the NMR shieldings and the electric field gradients at the O and H atoms. It is well established that deshielding of H and reduction of the electric field gradient at the attached O are correlated with a reduction of the O−H···O distance[49] in H-bonded systems. Our calculations at the 6-311+G(2d,p) HF level using the harmonic geometries give 26.9 ppm for the ^{1}H shielding in the a−a isomer of the monomer and 19.2 ppm for the ^{1}H shielding of the H-bonded proton in the dimer. The electric field gradient at the H nucleus also decreases from 0.460 to 0.290 au, from the free to the H-bonded proton. There is also a reduction in the shielding of O in the O−H group (from about 188 to 176 ppm) and an increase in the shielding of O in the C═O group (from around 47 to 86 ppm). Thus, the O atoms of the O−H and C═O groups become more alike in shielding and electric field gradient as they participate in the −C═O···H−O- bonding arrangement.

Calculation of pK_a’s for Carbonic Acid Species. We have recently[27] calculated pK_a values from first principles for a number of species expected to occur in carbonic acid solutions. We have used the procedure described by Liptak and Shields in ref 50, employing CBS-QB3 for the gas-phase free energies, the CPCM method to calculate hydration free energies, and a free energy of −269.0 kcal/mol for the proton in solution (corrected for standard state as explained in ref 50). Several other researchers are presently evaluating pK_a values in solution computationally.[51,52] We correctly reproduce the experimental result that the dominant species, CO_2 complexed with water, has a calculated pK_a of 7.2, near the experimental value of 6.3, while monomeric H_2CO_3, a minor species, gives pK_a values near 3 (depending upon the conformer), consistent with the results on transient species in ref 5. We have obtained analogous results for the dimer, for ionization of both the inner and outer H’s, and present them in Table 8. We report gas-phase free energies, hydration free energies, total free energies for the acid dissociation in an aqueous solution, and pK_a values. We see that the outer H’s have lower pK_a’s, near the value of around 3 observed[5] for the monomer, while the inner H-bonded protons have larger pK_a values, around 6.

Table 8. Calculated Free Energies (in kcal/mol) and pK_a’s at 25 °C for Acid Dissociation Reactions of the $CO_2 \cdots H_2O$ Complex and for Monomeric and Dimeric Carbonic Acids[a]

reaction	ΔG_g for CBS-QB3	$\Delta\Delta G_{CPCM}$	$\Delta G_g - \Delta\Delta G_{CPCM} - 269.0$	calcd pK_a
$H_2O \cdots CO_2 \Rightarrow HCO_3^- + H^+$	348.7	−69.9	+9.8	7.2
$H_2CO_3 \Rightarrow HCO_3^- + H^+$				
a−a	336.2	−62.0	+5.2	3.8
s−a	335.1	−61.2	+4.9	3.6
s−s	326.7	−54.7	+3.0	2.2
$(H_2CO_3)_2 \Rightarrow H_3C_2O_6^- + H^+$				
outer	315.8	−43.2	+3.6	2.6
inner	328.2	−50.3	+8.0	5.9

[a] Gas-phase free energies are obtained from CBS-QB3 calculations, and hydration free energies are obtained from CPCM calculations.

Conclusions

It has been known for more than 15 years that species with stoichiometry H_2CO_3 are stable, thermodynamically or at least kinetically, in solid or film polymorphs. Vibrational spectra have been measured for these phases and qualitatively assigned, but the experimental spectra are considerably different from those calculated for gas-phase monomeric H_2CO_3 at moderate quantum mechanical levels. We have extended this work by calculating the harmonic spectra for the H_2CO_3 monomer and dimer, and related molecules, at considerably higher quantum mechanical levels, using CBSB7 B3LYP or 6-311+G(2d,p) CCSD methods. We have also evaluated both anharmonic corrections and solution corrections as obtained from a PCM aqueous solution simulation. Our more accurate vibrational frequency calculations show clearly that monomeric H_2CO_3 cannot explain the experimental IR spectra. On the other hand, in the H-bonded dimer, $(H_2CO_3)_2$, the calculated frequencies in the

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O—H and C═O stretching regions are much lower as a result of the internal H bonding and in much better agreement with experiment, indicating that oligomeric species must exist in the film or solid versions of H_2CO_3. This interpretation is supported by our calculated energetics, which show that the oligomers have lower free energy than a collection of monomers in the gas phase while having higher free energies in an aqueous solution, a consequence of their reduced hydration free energies. It is also consistent with the good agreement of our calculated frequencies with experiment for crystalline $KHCO_3$, a material that contains $(HCO_3)_2^{2-}$ units. As far as we know, no one has ever before calculated the vibrational spectra of the $(HCO_3)_2^{2-}$ species. Finally, to assist in the definitive characterization of these species, we have calculated the ^{13}C NMR shieldings of a variety of monomeric and oligomeric H_2CO_3 species and related compounds, finding that ^{13}C in the oligomeric species is systematically deshielded compared to that in the monomer. Calculated pK_a's for the H_2CO_3 dimer are around 3 for the outer H's and around 6 for the inner H's.

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