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Structural Studies of Higher Energy Conformers by Millimeter-Wave Spectroscopy: Oxalic Acid

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We have detected a polar conformer of oxalic acid and investigated its structure using Stark-modulated free jet microwave spectroscopy. By comparing observed and ab initio predicted spectroscopic rotational constants and deuteration isotopic substitution coordinates, the species has been identified with the cis, trans, trans conformer (cTt), in which one of the carboxyl hydrogen atoms is involved in an intramolecular hydrogen bond with the carbonyl oxygen of the other carboxyl group. Stark effect measurements yielded electric dipole moment values of $\mu_a = 2.850(6)$ D; $\mu_b = 1.148(3)$ D, $\mu_c = 0.0$ D (assumed), and hence $\mu_{total} = 3.073(6)$ D. Ab initio calculations at the MP2/6-311++G(d,p) level predict and experiment confirms that no other polar conformers occur in detectable concentrations in the vapor at the experiment spectral search scan preexpansion temperature of 458 K. However, two undetectable species, one nonpolar (tTt), the other of low polarity (c“T”c, $\mu = 0.6$ D) are predicted to be present in greater concentrations than the observed species. Predicted relative stabilities of the different conformers are appreciably affected by the inclusion of Gibbs free energy corrections via the vibrational partition function. Large amplitude anharmonic vibrations, for which numerical integration of the vibrational Schrödinger equation is required for obtaining the correction, have an important influence on predicting relative stabilities of the oxalic acid conformers.

Introduction

The structure of oxalic acid has been the subject of many studies, both experimental and theoretical. X-ray crystallographic studies of oxalic acid crystals,[1] which exist in two forms (α and β), reveal a symmetric planar structure for the two carboxyl groups, the two groups being arranged trans with respect to the central C−C bond and the HO−CO groups of each carboxyl having the O−H cis to the C═O. The individual oxalic acid molecules are linked throughout the crystal in layers (α), or chains (β), by intermolecular hydrogen bonds joining each OH group to an adjacent C═O group. In contrast, an electron diffraction study[2] of oxalic acid vapor at about 430 K was analyzed on the assumption (based on IR detection of two weak intramolecular hydrogen bonds) that free oxalic acid molecules have both carboxyl groups in a trans arrangement of HO−CO and likewise the two groups are trans in respect of the C−C bond.

Theoretical studies of varying degrees of sophistication indicate that the configuration of lowest energy[3] has the symmetrical planar trans arrangement of the carboxyl groups and that within each carboxyl group the arrangement is trans, in harmony with the electron diffraction study − tTt (see Figure 1). It appears that the internal hydrogen bonding made possible by the trans arrangement of each carboxyl group lowers the energy more than enough to compensate for the cis/trans relative stability of an isolated carboxyl group (for which our calculations on formic acid at the MP2/6-311++G(d,p) level yield relative electronic energies of 1623 cm^{-1} [i.e., 20 kJ mol^{-1}] in favor of the cis arrangement of HO−CO). In the crystal, however, the intermolecular hydrogen bonding is sufficiently strong to be decisive in determining the conformation of the acid molecules.

The theoretical studies also indicated that some other conformers of oxalic acid (see Figure 1) would be stable but with higher energies, the next lowest being cTt with an estimated relative energy [MP2/6-31G(d,p)] of 8.5 kJ mol^{-1} above tTt. This would imply that even at, say, 450 K (temperatures needed to produce oxalic acid vapor for electron diffraction or spectroscopic studies) the proportion of cTt would be no more than 1/10 of the amount of tTt present. A more recent theoretical study[4] at the B3LYP level, which included zero-point energy corrections, yielded essentially the same results.

Nieminen et al.[5] studied the photolysis of matrix isolated oxalic acid. From the rise and fall in intensities of IR bands ascribed to O−H stretch in matrix-isolated oxalic acid, they concluded that two conformers were present, one being the most stable all-trans conformer, the other having one of the carboxyl groups in a cis arrangement. They used ab initio calculations to identify the second conformer and estimated that it was higher in energy, by about 7 kJ mol^{-1}, than the all-trans species.

This suggested that a second conformer might be detectable as a minor constituent of oxalic acid vapor by rotational spectroscopy, especially because the most stable species, being nonpolar, has no rotational spectrum.

We now report a successful experimental detection of a polar conformer of oxalic acid in the vapor phase, together with a systematic ab initio theoretical study of possible conformers of the acid, from which the shape of the polar conformer can be unambiguously identified. Our study adds to the now substantial circumstantial evidence for the relaxation of less stable conformers to more stable ones during supersonic jet expansions.[6] As has recently been discussed more fully,[6(e)] whenever the barrier to relaxation is less than about 1000 cm^{-1}, for molecules of roughly the size of oxalic acid (as now demonstrated in seven other cases), relaxation in the jet is to be expected.

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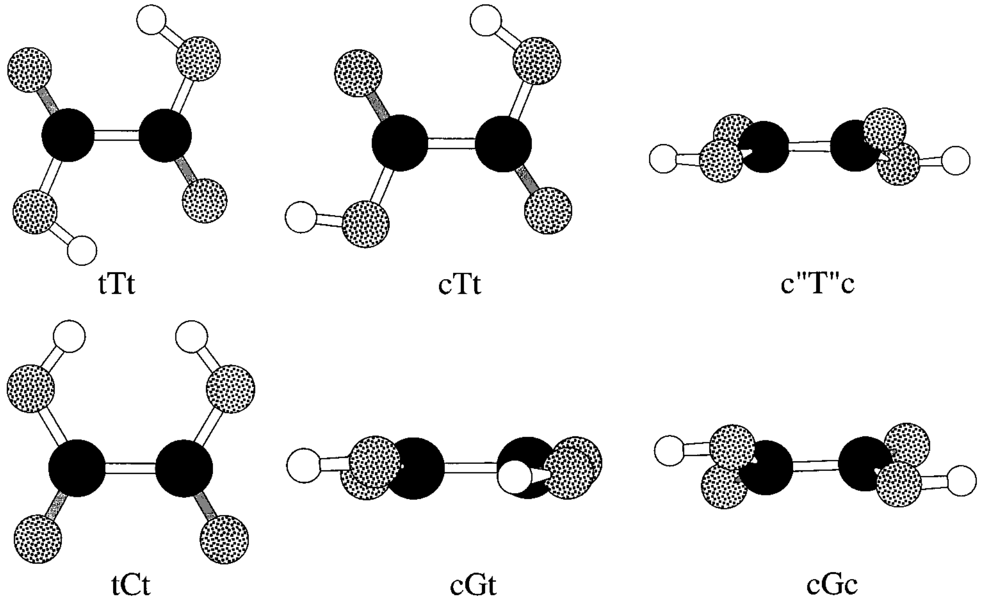

Figure 1. Theoretically predicted structures from ab initio MP2/6-311++G(d,p) calculations and adopted nomenclature of the conformers of oxalic acid. All are stable minima except conformer tCt which is a saddle point 84.1 kJ mol^{-1} above conformer tTt.

Methodology

Experimental. The free-jet expansion, Stark-modulated spectrometer used in the present study is based on a design that has previously been described.[7] Oxalic acid solid was vaporized at 185 °C in a stream of argon. Following free-jet expansion the rotational temperature was found to be ca. 10 K under the conditions employed. Deuterated samples of oxalic acid were prepared by recrystallization from 100% D_2O for the dideutero and from 50% heavy water to maximize the proportion of monodeutero compound.

The microwave absorption spectrum was first investigated via an extended spectral search scan over a wide frequency range (48−72 GHz). Once located via the wide search scan, each detected line was digitally acquired via repetitively averaged narrow-band scans, and line frequencies measured by least-squares fitting of a Lorentzian function to each line profile.

The 33 kHz square-wave Stark modulation system employed parallel-plate electrodes with a separation of ca. 3.5 cm. The square wave modulation field was established by opposed polarity equal amplitude ground-clamped voltage waveforms applied to the opposing electrodes. For dipole moment measurements the various M_J lobes for selected transitions were scanned, digitally acquired and the Stark frequency shift measured by least-squares fitting a Lorentzian line shape profile. The preset Stark voltages were measured via a precision a/d converter. The effective electrode spacing, which includes allowance for any scale factor error in the voltage measurement, was calibrated from a series of Stark shift measurements on SO_2 for which a precise dipole moment has been determined via molecular beam electric resonance.[8]

Theoretical. Predictive ab initio calculations of molecular structure, conformational energy and electric dipole moments were performed on all of the feasible oxalic acid conformers to assist in the rotational assignment of the observed spectrum and to serve as a guide to the identification of the species present in the expanding jet. Following the nomenclature of Nieminen et al.[5] the various possible conformers for oxalic acid are conveniently designated by C or T for the cis or trans arrangement of the carbonyl groups of the two carboxyls with respect to the C−C bond and then by t or c for the relative dispositions of the carbonyl and hydroxyl components of each carboxyl group, as shown in Figure 1. In the present study deviations from planarity have been encountered, and in these cases “T” and G have been used for species nearer to T, or, respectively, to C. Ab initio calculations were performed using the *Gaussian 94* package[9] at the MP2/6-311++G(d,p) level. To estimate vibrational and thermal contributions to the relative stabilities of conformers, conventional ab initio harmonic vibrational frequency calculations were performed at the MP2/6-31G(d,p) level on all conformers studied. For the thermochemical calculations a vibrational frequency empirical scaling factor of 0.9910, previously found optimal for calculations on histamine,[6(b)] was used.

To guide us as to possible conformational relaxations during the jet expansion within the spectrometer the torsional potential energy barriers between adjacent conformers were explored via constrained optimizations at the MP2/6-311++G(d,p) level.

In the case of the species c“T”c, cGc, and cGt, our calculations of the potential energy curve for the torsional motion about the central C−C bond indicated significant anharmonicity and the possibility of large-amplitude motion (LAM). We used a numerical integration of the vibrational Schrödinger equation for the ab initio predicted potential energy function to estimate the vibrational contributions to Gibbs free energy corrections for these vibrations. The Gibbs energy correction was obtained via explicit summation of the partition function for this anharmonic torsion and added to the correction estimated in the harmonic approximation at the 6-31G(d,p) level for the remaining degrees of freedom. No empirical scaling factor was used in evaluating the Gibbs energy correction for the anharmonic modes.

We also undertook ab initio calculations at the MP2/6-311G++(d,p) level to search for energy minima corresponding to two tautomers of oxalic acid that have been suggested as intermediates in the thermal decomposition to CO_2 and HCOOH.

Results and Discussion

Experimental. We observed 38 lines in the frequency range 52−68 GHz that we were able to assign to an asymmetric rotor. No unassigned lines were detected in the wide-band search

TABLE 1: Experimentally Derived Rotational and Centrifugal Distortion Constants[a] for the Observed Conformer of Oxalic Acid and for the Corresponding Monodeutero and Dideutero Isotopomers

	normal isotopomer	cis-deutero	trans-deutero	dideutero
A/MHz	5951.2806(44)	5913.0607(36)	5751.293(11)	5719.906(44)
B/MHz	3683.7867(20)	3536.7817(29)	3666.4216(24)	3517.316(15)
C/MHz	2276.0555(25)	2213.7803(18)	2239.7326(12)	2178.721(6)
D_j/kHz	0.000549(13)	0.4987(93)	0.5705(66)	0.572(45)
D_{jk}/kHz	not fitted	0.032(46)	not fitted	-0.82(60)
D_k/kHz	0.00081(21)	0.893(77)	0.44(30)	not fitted
d_1/kHz	−0.0002510(40)	−0.2256(56)	−0.2650(46)	−0.225(33)
d_2/kHz	−0.0000479(26)	−0.0446(24)	−0.0511(15)	−0.017(19)
no. lines in fit	38[b]	53[b]	37[b]	21[b]
rms residual/MHz	0.023	0.029	0.015	0.033

[a] The numbers in parentheses are one standard deviation in units of the least significant quoted digit. [b] Observed frequencies, assigned quantum numbers and residuals from the fitting calculations are listed in Tables 1S−4S.

TABLE 2: Experimentally Derived Principal Axis Dipole Moment Components for the Observed Conformer of Oxalic Acid[a]

μ_a/D	2.8502(62)
μ_b/D	1.1476(26)
μ_c/D	0 [assumed]
μ_{total}/D	3.073(6)
no. transitions used	2
no. Stark shift measurements	15
rms residual /MHz	0.05

[a] The numbers in parentheses are one standard deviation in units of the least significant quoted digit. Stark shifts at a series of voltages were measured for the transitions $8_{2,6} - 7_{2,5}$ and $8_{4,4} - 7_{4,3}$. Voltages, observed Stark shifts, M_J quantum numbers, and residuals from the dipole moment fitting calculation and from the Stark electrode spacing calibration are detailed in Tables 5S and 6S, respectively.

scans. It is a characteristic of the collisional cooling process in the free-jet expansion that all low frequency vibrational modes are efficiently cooled, and hence the torsional vibrational satellites that are a major complicating feature of past conventional ambient or higher temperature microwave spectroscopy studies are not detected in our spectrometer. Table 1 lists the spectroscopic constants (I^R representation, S reduction[10]) derived by a least-squares fit to these lines. A full listing of the observed transitions and the least-squares fit residuals is given in Table 1S. Similarly are listed in Table 1 the spectroscopic parameters derived from the measurement of 21 lines assigned to the dideutero isotopomer of the same species and 37 and 53 lines of two different monodeutero species. The full listing of observed transitions is given in Tables 2S−4S of the Supporting Information.

Principal axis dipole moment component values were determined from the analysis of Stark effect measurements on the transitions $\{8_{44} \leftarrow 7_{43}\}$ and $\{8_{26} \leftarrow 7_{25}\}$ via our own Stark effect least-squares computer program STARKFIT that treats any rotational near-degeneracies explicitly. The resulting best-fit dipole moment components [based on $\mu(SO_2) = 1.63305$ D] are presented in Table 2.

As a first step in identifying the observed conformer of oxalic acid, we note that the derived spectroscopic constants of the observed species agree much more closely with those predicted for cTt than for any of the other conformers (see Table 3). As further independent confirmation of this identification, the spectroscopic constants of the two observed monodeutero and the dideutero species also agree more closely with those predicted for the cTt species than any other. The fact that there are two distinct monodeutero species indicates that one of the carboxyl groups must be cis and the other trans. By using Kraitchman's equations to derive the substitution coordinates of the two different hydrogens (see Table 4) we have a clear identification of the conformer as cTt.

TABLE 3: Predicted Geometric and Spectroscopic Parameters from ab Initio MP2/6-311++G(d,p) Calculations for Oxalic Acid

	conformer					
parameter[a]	tTt	tTc	c"T"c	cGt	cGc	observed
O═C−C═O, τ_1/°	180	180	153.9	0	29.1	
HO−C═O, τ_2/°	180	0	−0.5	2.4	0.6	
HO−C═O, τ_3/°	180	180	−0.5	180.3	0.6	
E_{rel}/kJ mol^{-1}	0	7.92	9.79	18.62	10.92	
A/MHz	5773.7	5902.4	5995.7	5872.7	5974.0	5951.3
B/MHz	3813.4	3684.0	3514.1	3643.6	3480.2	3683.8
C/MHz	2296.6	2268.3	2292.2	2248.5	2315.8	2276.1
rms(O−C)[b]	231	29	102	53	120	
μ_a/D	0	3.2	0	3.3	0	2.9
μ_b/D	0	1.3	0	4.2	3.1	1.1
μ_c/D	0	0	0.6	0	0	(0)
μ_{tot}/D	0	3.5	0.6	5.3	3.1	3.1

[a] A complete listing of ab initio predicted geometric parameters is given in Table 7S. [b] Root-mean-square deviation in MHz between the observed and ab initio rotational constants.

TABLE 4: Experimental(Kraitchman) and Theoretical Hydrogen Atom Coordinates of Oxalic Acid [MP2/6-311++G(2d,p)]

		$\|a\|$/pm	$\|b\|$/pm	$\|c\|$/pm	rms (o.-c.)
exp	H(7)	83.1	172.2	0	
	H(8)	240.6	74.1	0	
c"T"c	H(7)	83.7	83.7	13.7	89.6
	H(8)	235.3	235.3	13.7	161.9
cGc	H(7)	99.9	99.9	29.2	198.9
	H(8)	224.4	224.4	29.2	153.9
tTt	H(7)	174.8	174.8	0	432.4
	H(8)	80.1	80.1	0	160.6
cTt	H(7)	81.0	174.0	0	2.7
	H(8)	237.7	77.3	0	4.3
cGt	H(7)	105.3	177.8	0	188.5
	H(8)	222.8	63.7	0	20.6

Finally, the measured dipole moment components are in significantly closer agreement with those predicted by our molecular orbital calculations for cTt than for the other species. As a further check on the validity of this assignment it is useful to consider whether any other species of oxalic acid might have been detectable spectroscopically. For this we have to turn to consideration of the results of the ab initio calculations. These are discussed in the next section.

Theoretical. The predicted MP2/6-311++G(d,p) ab initio structures of three of the six constrained planar conformers of oxalic acid are shown, together with the nomenclature adopted in this work, in Figure 1. Full geometric parameters for the five energy minima conformers are given in Table 7S of the Supporting Information. Six planar species would have been predicted from simple arguments based on planarity of each carboxyl group (preferred because of π-electron delocalization)

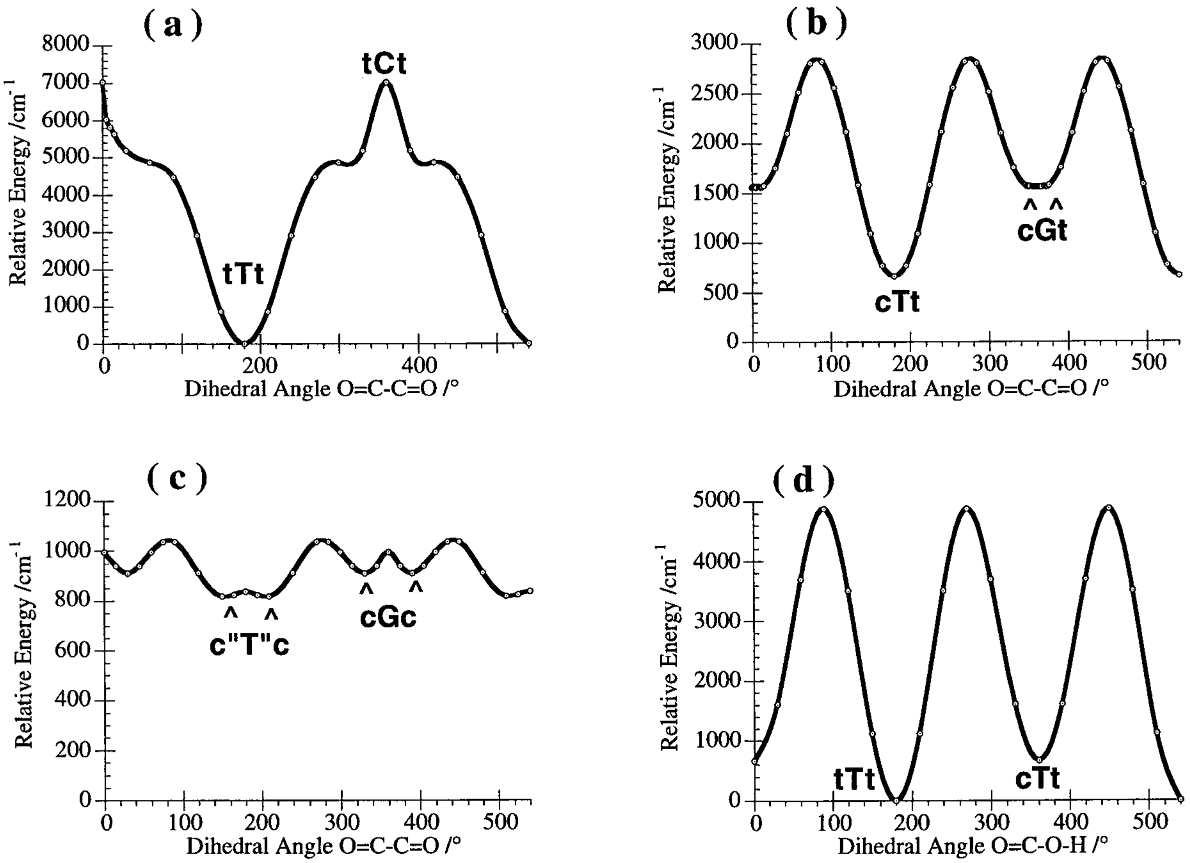

Figure 2. Interconformational energy profiles predicted from ab initio MP2/6-311++G(d,p) calculations on oxalic acid constrained in a single geometric parameter. For (a), (b), and (c) C−C torsion is involved, while in (d), CC−OH torsion. The low barriers shown in (c) for the cGc conformer will enable efficient relaxation of cGc to c“T”c during the jet expansion in argon. Similarly, the low barrier shown in (b) for the cGt conformer will enable relaxation from cGt to cTt. The significantly higher barriers shown in (d) involving the cis−trans rearrangement of the carboxyl groups preclude relaxation between species differing in the cis−trans conformation of the carboxyl groups.

and on coplanarity of the two carboxyl groups (preferred because of π-electron delocalization across the central C−C bond). When the geometry optimization allows nonplanar distortions it is found that three of these planar “conformers” must be reconsidered. The structure cCc (see Figure 2) is found to be a local maximum (barrier height ca. 85.4 cm^{-1}) between two equivalent gauche minima, cGc, having O═C−C═O torsional angles of ± 29°.

Similarly cTc (see Figure 2) is found to be a local maximum (barrier height 21.9 cm^{-1}) between two equivalent near-trans minima c“T”c having O═C−C═O torsional angles of 154° and 206°. The barrier separating cGc from c“T”c is so low (131.4 cm^{-1}, see Figure 2) that in the present context it is best regarded as vibrationally excited c“T”c rather than a separate species. When calculating the vibrational partition function for the O═C−C═O torsion of c“T”c at a temperature of 458 K, we had to include levels well above the top of the barrier, up to about 1800 cm^{-1} to obtain convergence. At this level of excitation the species c“T”c and cGc are interconverting by free rotation about the C−C bond. Thus we shall designate this as a single species c“T”c-cGc. We also note that the direct numerical evaluation of the vibrational energy levels (see Table 9S) gives a zero-point energy of 13.2 cm^{-1}, below the central potential maximum of 21.9 cm^{-1}, and so the most probable geometry,[11] r_P, is not planar but twisted ±20° from the plane (the vibrational wave function is actually almost constant over the range 150°−210°).

For cGt also there is a very shallow double-minimum in the potential energy curve, the central maximum being just 5.8 cm^{-1} above the minima. In this case the zero-point vibrational level (see Table 8S) was found to be 15.8 cm^{-1} above the minima, which is above the central maximum and so the most probable geometry falls at the symmetric planar position.

In the case of tCt, this form is a saddle point with no adjacent minima, the energy decreasing monotonically from tCt to tTt (see Figure 2a). Thus at this level of ab initio calculation we conclude that there is no stable conformer in the vicinity of tCt, that at 458 K cGc is not a distinct species and so, effectively, only four stable conformers are relevant at this temperature.

Our searches at the MP2/6-311++G(d,p) level for potential energy minima corresponding to the tautomers (approaching dihydroxycarbene) that have been suggested[3,5] as intermediates in the thermal decomposition of oxalic acid were unsuccessful. We conclude that while suggested by the results of lower level ab initio calculations, such nuclear configurations in reality do not constitute physically stable intermediates or tautomers of oxalic acid.

The relative energies are listed in Table 5, which also gives relative energies including vibrational zero-point energy (i.e., Gibbs free energies at 0 K) and Gibbs energies at 458 K, the preexpansion temperature used for the experimental search scan of the rotational spectrum. These vibrational corrections have to be treated with some care because the computed potential energy curves for rotation about the central C−C bond (see below) reveal that the minima corresponding to conformers c“T”c, cGt, and cGc deviate substantially from simple harmonic potentials. Thus vibrational energies and Gibbs energy corrections computed with the harmonic approximation for frequencies (as provided by *Gaussian 94*[9]) will be quite unreliable. For the C−C torsional modes of these three species the vibrational

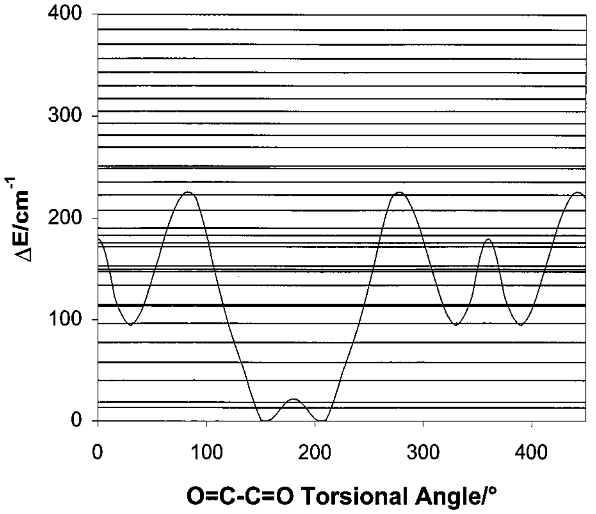

Figure 3. Computed torsional energy levels of the highly anharmonic c“T”c-cGc potential function.

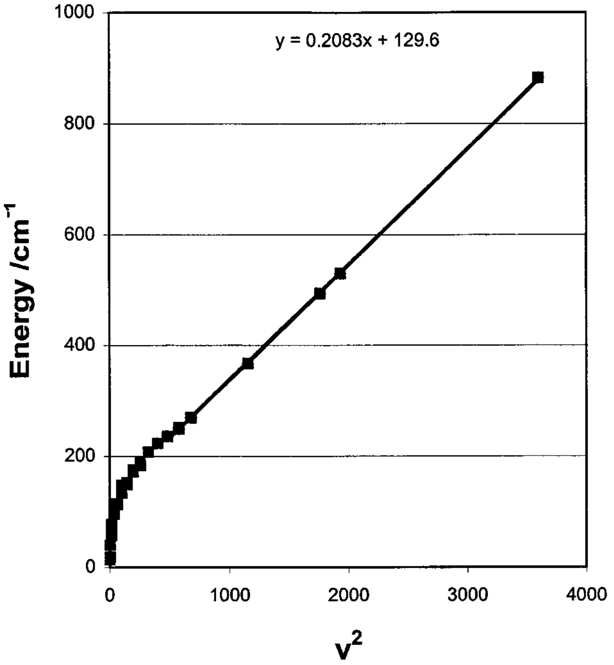

Figure 4. Computed torsional energy versus the square of the vibrational quantum number for the anharmonic c“T”c-cGc potential function. It can be seen that the energy levels substantially above the torsional barriers (>300 cm^{-1}) fit closely to a vertically displaced free rotor energy formula.

TABLE 5: Predicted Relative ab Initio Energies for the Conformers of Oxalic Acid Optimized at the MP2/6-311++G(d,p) Level and the Corresponding Mole Fractions under Experimental Conditions

species	ΔE_{MP2} kJ mol−1	$\Delta E_{MP2} + ZPE$[a] kJ mol^{-1}	ΔG_{458K}[a] kJ mol^{-1}	mole fraction[b] 458 K[c]	mole fraction[b] 10 K[d]
tTt	0.00	0.00	0.91	0.36	0.36
cTt	7.92	7.28	4.19	0.15	0.18
cGt	18.62	16.56	11.21	0.02	0.00
cCt	18.70[e]	na	na		
c“T”c	9.79	8.58	0.00[g]	0.46	0.46
cTc	10.05[e]	na	na		
cGc	10.92	9.340	na[g]		
cCc	11.94[e]	na	na		
tCt	84.08[f]	na	na		

[a] For conformers tTt and cTt the vibrational zero-point and thermal Gibbs energy contributions are predicted from *Gaussian 94* harmonic force field calculations performed at the MP2/6-31G(d,p) level. For conformers cGt and c“T”c, the vibrational zero-point and thermal Gibbs energy contributions are predicted from numerically determined torsional eigenvalues (see Figures 3 and 4 and Tables 8S and 9S) of the anharmonic ab initio torsional potential functions at the MP2/6-311++G(d,p) level (see Figure 2). [b] Calculated from the theoretical relative Gibbs energies. [c] In heated $T = 458$ K preexpansion chamber. [d] After relaxation from $T = 458$ K during argon jet expansion. [e] Not a local minimum in potential energy, but a local maximum in a double-minimum potential well. [f] Not a local minimum in torsional potential energy; nearest accessible minimum is tTt. [g] In calculating the anharmonic torsional Gibbs correction, the torsional levels of conformer cGc were treated as excited states of c“T”c.

energy eigenvalues have therefore been estimated by numerical integration and are listed in Tables 8S and 9S of the Supporting Information, the energy levels for the c“T”c- cGc potential also being shown in Figure 3. For this potential it was possible to fit a few of the higher energy levels to a modified free rotor formula, simplifying the calculation of further levels in this energy range. This fit is illustrated in the plot of torsional energy versus the square of the torsional quantum number shown in Figure 4. The derived Gibbs energies are included in Table 5. It is of interest to note that in the case of the cGc-c“T”c torsion, not only is the anharmonicity extreme but at 458 K ca. 50% of the torsional partition function actually arises from the doubly degenerate free rotor states residing above the potential maxima.

On the basis of the zero-point energies of the conformers tTt and cTt, the most stable species is predicted to be the tTt conformer followed by the cTt conformer at an energy higher by 7.3 kJ mol^{-1}. Although this is a large enough separation to severely limit the proportion of the cTt species in the jet, this ignores the effect of thermal free energy. At the preexpansion chamber temperature of 458 K cTt is higher in free energy than tTt by only 3.3 kJ mol^{-1} which corresponds to a cTt abundance of 15% of the vapor. After expansion in the supersonic jet the relaxation effects discussed below result in predicted approximate mole fractions in the jet vapor of 18% for cTt, which is to be compared with 36% for tTt and 46% for c“T”c. (It is notable that the impact of the Gibbs energy correction on abundance can be substantial when a LAM is involved, as is the case for c“T”c where in the absence of this correction a mole fraction of only 6% would be predicted.)

We would therefore expect cTt to be readily detectable in the spectrometer (since it is quite unsymmetrical and hence strongly polar). But what of the other conformers?

The computed electronic energy of c“T”c is higher than that of cTt. However, the substantial Gibbs energy corrections at the preexpansion temperature and the high interconformational energy barrier (effectively preventing relaxation to cTt at lower temperatures) combine to predict that both before and after jet expansion c“T”c is actually the most abundant species (at 46%). However, c“T”c is of low polarity ($\mu = 0.6$ D), so the intensities of rotational spectral lines will be about 30 times less intense than cTt and difficult to Stark-modulate. Since the lines assigned to cTt were detected at a signal/noise of ca. 10 or less under search scan conditions, c“T”c is well below the level of detectability in a search scan with our spectrometer.

Conformer cGc is predicted to be higher in electronic energy than tTt but again is favored by Gibbs energy corrections. However, on considering the potential energy variation for the interconversion of cGc to c“T”c (Figure 2) it is evident that the barrier to relaxation to the more stable (in terms of zero-point energy) c“T”c is very low, so that we predict complete relaxation to the latter during the jet expansion. Similar considerations apply to cGt, complete relaxation to cTt being predicted.

TABLE 6: Internuclear Distances (pm) Derived by ab Initio MP2/6-311++G(d,p) Calculations for Oxalic Acid Conformers and Several Comparison Molecules

parameter	tTt	cTt	c“T”c	cGc	cTc	HCOOH	CH_2O	CH_3OH	CHO−CHO	elec. diff.[a]
C═O	121.0	120.2 (t) 121.5 (c)	120.7	120.5	120.7	119.8 (t) 120.5 (c)	121.3		121.5(t) 121.1(c)	120.8(1)
C−O	132.7	133.9(t) 132.8 (c)	134.2	134.4	134.1	135.5 (t) 134.8 (c)		142.2		133.9(2)
C−C	154.3	154.2	153.4	153.3	153.7				152.2(t) 153.8(c)	154.8(4)
O1··O′1	356.2	354.6	347.9	262.2	351.7					
O2··O′2	348.1	350.0	348.4	287.1	351.8					
C··O′1	240.3	238.3(t) 239.1(c)	235.8	238.6	236.0					
C··O′2	240.5	242.9(t) 241.1(c)	242.7	240.5	243.2					
O2··O′1	270.6	273.4 267.2	272.7	346.0	268.9					271.7(5)

[a] From Reference 2. Standard errors (in parentheses) are probably unreliable, see text.

Based on the predicted Gibbs energies of tTt, cTt, and c”T”c in the preexpansion chamber at 458 K and then allowing for relaxation of cGt to cTt in the jet expansion (thus augmenting the mole fraction of the latter), we estimate that the relative proportions of the three will be 36:18:46.

Accordingly we expect the spectrum of cTt to be the only detectable rotational spectrum and so on this basis identify our experimentally observed species as cTt. This analysis successfully explains why no lines other than those assignable to cTt were observed although at first sight it seemed necessary to consider several other polar conformers of oxalic acid.

We conclude that our identification of the observed species as the cTt conformer of oxalic acid is secure.

The conclusion that the hot vapor will consist of four species of oxalic acid with three (tTt, cTt, and c“T”c) predominating means that tTt is less than 40% of the vapor. This has a consequence for consideration of the electron diffraction data on oxalic acid for which an effusive nozzle at 433 K was used.[2] In this study it was assumed that oxalic acid was in the tTt form but, if it is actually a mixture of several conformers then the derived geometrical information will in reality be an average over these species. Scrutiny of the radial distribution function (ref 2, Figure 3) and comparison with our internuclear distances predicted by the ab initio calculations (see Table 6) reveals that the other conformers would have produced maxima for distances such as O2··O′2, C··O′2, etc. differing just a few pm from those in the tTt conformer, even for the nonplanar c“T”c conformer. Distances involving H would have yielded scarcely perceptible slight bumps on the radial distribution curve and so presumably have been overlooked, but we notice a small positive deviation of the experimental radial distribution function from the theoretical curve of Nahlovska et al.[2] in the region between 400 and 450 pm where a conformer with a trans carboxyl group would display the longest H··O distance (our ab initio calculations for the cTt conformer predict this distance to be 423 pm). Thus the standard errors, reproduced in Table 6, for the experimental geometrical data on oxalic acid must be treated with some reserve.

A comment about the relative stabilities of cis and trans carboxyl groups is in order. Because in formic acid the cis shape of the HOCO is considerably more stable than the trans (by ca. 1700 cm^{-1}) we might expect that this would also be the energetically more favored configuration for the two carboxyl groups in oxalic acid. In the case of glycine[6a] (aminoacetic acid) an internal hydrogen bond of the OH to the N of the amino group in glycine is sufficient to make the carboxyl trans configuration (in glycine-2) almost as stable as the cis (in glycine-1). Internal hydrogen bonding is also possible in oxalic acid, and our calculations indicate that the situation is similar to that in glycine in that the thermodynamically most stable species in hot oxalic acid vapor is c“T”c. At 458 K it has virtually the same Gibbs energy as tTt and so the cis and trans arrangements of the carboxyl groups are approximately balanced. When thermally excited C−C torsion is taken into account, the intracarboxyl hydrogen bonds and the intercarboxyl hydrogen bonds produce virtually the same stabilizing effects.

Geometry and π-Electron Conjugation. It is widely accepted that the carboxyl group, e.g., in formic acid, contains a delocalized group of four π-electrons, the consequence of which is that the C−O bond is somewhat shorter than an unconjugated C−O bond and that there is slight lengthening of the C═O bond. Selected geometrical data from our MP2/6-311++G(d,p) ab initio calculations (given in full in Table 7S) are presented in Table 6 together with data, computed at the same level of MO calculation, for some comparison molecules. For cis-formic acid the C═O bond length is 120.5 pm and the C−O length is 134.8 pm, while in the less stable trans conformer the lengths are 119.8 pm and 135.5 pm. For comparison, at the same level of sophistication of the calculations, the C═O length in formaldehyde is 121.3 pm and the C−O length in methanol is 142.2 pm. These values indicate that the only noticeable geometric effect of conjugation is in the C−O bond, which shortens by about 7 pm.

In oxalic acid it would be expected that the two carboxyl groups are further conjugated into an eight π-electron system through the central C−C bond. If so, this should be apparent not only through the lengths of the C−O bonds but also through the C−C bond length. However, there is no shortening from the ethane value of 152.9 pm (to be compared with the best experimental value[12] of 152.2(2) pm), rather a lengthening to ca. 154 pm. In the case of glyoxal the C−C distance remains close to the ethane value. Nevertheless there is a clear energetic preference for near-planarity, seen uncomplicated by the possible influence of hydrogen bonding in the case of the c“T”c-cGc conformer pair (see for example Figure 2c). It is unclear whether this should be attributed to π-electron conjugation.

Conclusion

We have detected via microwave spectroscopy and rotationally assigned the spectrum of an unsymmetrical conformer of oxalic acid. Our identification of this species, based on spectroscopic constants, coordinates of hydrogen atoms, dipole moments, and free energy calculations, shows that it is the same species as that tentatively identified in an earlier matrix isolation study.[5] In that study it was possible only to decide that the second species contained one (or more) trans carboxyls from the experimental IR data and the particular species was inferred on the basis of ab initio calculations of relative energies. Our present work shows that one cannot always rely on relative electronic energies alone to decide on the relative stabilities of conformers at elevated temperatures because the Gibbs energy corrections can, especially when LAMs are present, differ appreciably between conformers.

From the ab initio torsional potential energy curves relating to interconversion of conformers, we infer that (a) at 458 K the species cGc effectively is not a separate conformer but represents vibrationally excited c“T”c; (b) relaxation of conformer cGt to the more stable species cTt occurs during the jet expansion. This adds to the already substantial circumstantial evidence that such conformer relaxations occur in the jet expansion whenever the barrier to relaxation falls below a critical value (for species of this kind in argon carrier gas it is estimated to be ca. 1000 cm^{-1}).

Theory predicts then that the only polar species present in amounts readily detectable via microwave absorption in the jet-expanded vapor is cTt, in agreement with our experimental study. However it is predicted that oxalic acid vapor at 458 K contains four conformers with three of them dominating. This throws into question the electron diffraction data on oxalic acid[2] obtained with a nozzle temperature of 433 K that were interpreted on the assumption that the vapor consisted of only a single species.

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Supporting Information Available: Collection of Tables 1S − 9S containing all of the measured and assigned microwave transition frequencies used to derive the rotational constants reported in this work, all the measured and assigned Stark shifts used to derive the dipole moment components reported in this work, the complete ab initio optimized geometries for each equilibrium structural form of oxalic acid, and the calculated torsional energy levels of the anharmonic conformers. This material is available free of charge via the Internet at http://pubs.acs.org

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