

Theoretical rotational constants and IR signatures of protonated polycarbon dioxides OC_nO

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Abstract. This study considers the possibility of astronomical detection of members of the $C_nO_2H^+$ series; these are possible tracers of the parent polycarbon dioxide molecules, OC_nO . Direct radio detection of these molecules is not possible owing to non-existent or too small dipole moments. The structures of all stable isomers were determined according to protonation sites. Rotational constants and dipole moments for the most stable protonated species were predicted by molecular electronic structure calculations and the error bar was estimated using a combination of observed data on the starting member of the series, $HOCO^+$, and the closely related family of polycarbon monoxides, C_nO . These molecular constants, accurate to within 0.2%, along with the calculated IR spectra, should assist in the identification of these species in the laboratory and in tentative assignments of interstellar lines.

Key words: Magnetohydrodynamics (MHD) – molecular data – radio lines: ISM

1. Introduction

Hydrogen is by far the most abundant chemical element in space; thus, protonation processes are thought to play an important role in the synthesis of interstellar species. In this context, any neutral molecule can be seen as a proton acceptor while, reciprocally, any protonated ion is a possible proton carrier. Some of these ions have been known for a long time: HCO^+ , HCS^+ , HNN^+ ; others, such as $HCNH^+$ or $HCCCNH^+$, have been identified more recently. Protonated ions may also be useful tracers of their neutral parents for a variety of reasons. For example, if astrochemical models predict the existence of a neutral molecule which cannot be detected in radio because its dipole moment is too small or equal to zero for symmetry reasons, then the protonated derivative is a natural target for observations. There are two examples of indirect detection: the first is HNN^+ , the second is $HOCO^+$ which is the tracer of the first term of the OC_nO series. The present study involves the latter example.

The usual procedure for identification of a molecule in space relies on the perfect match of the observed radio emission lines with a laboratory microwave spectrum. Such a procedure is

hardly possible for systems that are too unstable to survive in laboratory experiments. It is therefore important to know which among the possible isomers is the most stable. Since the OC_nO chain presents non equivalent protonation sites, an extensive study of all possible adducts was performed for each molecule to determine the most energetically favored product of the protonation process. Moreover, to be a good candidate, the ion should have a dipole moment large enough to allow sufficient intensity of the rotational bands and thus be observable while taking into account the small abundances expected for such species.

This paper considers the possibility of astronomical detection of the $C_nO_2H^+$ series and estimates the rotational constants and dipole moments that enable identification. IR spectra of the most likely candidates are reported to complete the spectral signature at shorter wavelengths.

The first of these compounds is CO_2H^+ . Its identification in space followed the now classical interdisciplinary approach starting with the observation of a set of related radio lines (Thaddeus et al. 1981). Subsequent comparison with ab-initio calculations on a number of plausible molecules cut the list of candidates down to $HOCO^+$ and $HNCO$ with a better match for the former species (DeFrees et al. 1982). The final proof that the radio lines observed in space were effectively due to $HOCO^+$, came from submillimeter wave spectra (Bogey et al. 1984, 1986), a result confirmed by independent IR experiments (Amano & Tanaka, 1985).

To the best of our knowledge, the following terms of the series have not been studied, neither theoretically nor experimentally. The prediction of the rotational constants of the $C_nO_2H^+$ series could be improved neither by the knowledge of experimental data on isoelectronic compounds of similar mass (DeFrees et al. 1982) nor by extrapolation of the results obtained on the first members of the series as previously done for long chain molecules such as cyanopolyynes, $H - (CC)_n - CN$ (DeFrees & McLean, 1989) or linear radicals HC_n and C_nN (Pauzat et al. 1991). We used a two step approach instead. A converging series of calculations on the leading system $HOCO^+$ was performed to define a precise and cost effective level of theory. This level of theory was then applied to the closely related series, C_nO , of similar electronic structure and masses in order to obtain an estimate of the uncertainty on the calculated spectroscopic constants.

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2. Computational methods

Several levels of ab-initio molecular orbital theory and density functional theory (DFT) were used. Each employed the split-valence polarized 6-311G** basis set of triple-zeta quality. Calculations were performed at the single configuration level (HF), increasing levels of perturbation theory, (MP2 and MP3 with and without frozen core approximation, MP4) and finally the coupled cluster level (CCSD(T)). For this last level of wavefunction, two additional basis sets of larger dimension were used to reach convergence in the results for the smallest system, i.e. 6-311++G** and AUG-cc-pVTZ. DFT calculations used the hybrid B3LYP functional with the same three basis sets. All the calculations were performed using the methods as implemented in GAUSSIAN94.

3. Tests and calibration

Prediction of rotational constants by quantum mechanical methods alone to an accuracy such that it can be used to support identification of unknown molecules in space is at the limits of applicability of present computational chemistry. Calculations were performed in the rigid rotor approximation, meaning that A_e , B_e and C_e estimates could be obtained for the equilibrium geometries with a 1% accuracy (see for example Botschwina et al. 1993). However it should be remembered that it is A_0 , B_0 and C_0 which are the quantities needed to reproduce radio signatures.

It has been shown that adjustments of the raw predictions of the quantum mechanical calculations were possible in order to achieve the 0.1% accuracy usually required for identification. Several types of empirical corrections have been applied successfully in the past, all of which combine the calculated values with experimental data on known species.

One such approach is applicable to the rotational constants directly, using laboratory spectra of known isoelectronic systems of similar mass. The basic assumption made is that the ratio $B_{iso}(theory)/B_{iso}(exptl)$, where B_{iso} is any of the rotational constants A , B or C of the isoelectronic benchmark, is independent of the molecule considered for a given level of theory. This procedure has given remarkable results in the isoelectronic series HOCN, HNNN, HNCO and HOCO⁺, leading to the identification of the last species (DeFrees et al. 1982).

Another approach is to use a set of bond length and angle corrections obtained by comparing calculated structural parameters with experimental ones for a range of small and well suited systems. This technique was also employed for HOCO⁺ and its sulphur containing analogs HOCS⁺, HSCO⁺ and HSCS⁺ (Taylor & Scarlett, 1985).

A different type of approach, which can be used for a series of molecules whose leading terms are known, relies on extrapolation techniques. A quadratic least-squares fit of the computed rotational constants to the experimental values in the form

$$B_0 = a + bB_e(theory) + cB_e(theory)^2$$

can be obtained for each level of theory. In a second step, the fit is used to predict the rotational constants of the next mem-

bers of the series. This was the procedure employed to predict the rotational constants in the cyanopolyyne series (DeFrees & McLean, 1989). A closely related scheme was used by Pauzat et al. (1991) who found that, in the C_nH long chain radicals, the $B_0(observed)/B_e(theory)$ ratio converges toward a constant value as n increases. This approach made it possible to predict the rotational constants of C_nH radicals ($n=7-10$). Based on these values, recent identifications of C_7H (Travers et al. 1996), C_8H (McCarthy et al. 1996a) and C_9H (McCarthy et al. 1996b) in the laboratory and detections of C_7H (Cernicharo & Guélin, 1996) and C_8H (Guélin et al. 1997) in space provided independent confirmations that the theoretical predictions were accurate within 0.1%.

One common conclusion from all these strategies is that careful calibration is needed, and calibration depends on the method used for the calculation of the equilibrium geometries. These geometries, as well as the calculated rotational constants, are sensitive to the evaluation of electronic correlation. The amplitude of the correction depends on the level of theory. Lower levels of wavefunctions such as MP2 and particularly MP3, when properly corrected for the systematic errors, sometimes provide better predictions than sophisticated methods such as MP4 or CCSD(T) which give results that are too close to the exact values for the remaining errors to be adjusted for in a systematic way. The emergence of Density Functional Theory (DFT) calculations has opened a new area of applications which has not yet been thoroughly investigated. As shown below, extremely good results are obtained (compared to experiments) and it is not clear how the results can be further improved.

None of the strategies presented above were well adapted to the problem of the $C_nO_2H^+$ ions. Only one term of the series was studied experimentally: CO_2H^+ . It is helpful to determine a level of theory for the calculations but not useful for an evaluation of the uncertainties for the higher members of the series. For that purpose a well-known and closely related series, C_nO , was used. It presents enough similarities (structural parameters and mass) to be compared with the target series considered in this study.

3.1. Tests on HOCO⁺

This molecular ion has been the subject of extensive theoretical studies in the past in order to determine its most stable geometry. All studies agree that the stable form is the O-protonated species, HOCO⁺ (Seeger et al. 1978; Frisch et al. 1985; Yu et al. 1986; Pauzat et al. 1986); Frisch et al. (1985) showed that the C_s O-protonated isomer is the only observable form of CO_2H^+ when it is produced by addition of H^+ on CO_2 and under most other conditions. Yu et al. (1986) studied the rearrangement path for the proton shift between carbon and oxygen and obtained 8.47 kcal/mol for the energy barrier by MCSCF methods.

In the present study we were mainly interested in the determination of the equilibrium geometry of HOCO⁺ and its rotational constants. The calculations are tabulated (Table 1) with the level of theory increasing from top to bottom for both

Table 1. Computed energies and spectroscopic constants of OCOH⁺

method / basis set	energy (a.u.)	dipole (D)	rotational constants (GHz)		
ab-initio					
HF / 6-31G*	-187.844278	3.391	821.380	11.0700	10.9228
HF / 6-311G**	-187.904470	3.361	813.175	11.2230	11.0702
MP2(FC) / 6-311G**	-188.416194	3.515	740.298	10.6641	10.5127
MP2 / 6-311G**	-188.472500	3.517	743.854	10.6806	10.5294
MP3(FC) / 6-311G**	-188.402025	3.389	749.401	10.8927	10.7366
MP3 / 6-311G**	-188.459700	3.390	752.115	10.9077	10.7518
MP4 / 6-311G**	-188.502219	3.535	738.712	10.5515	10.4029
CCSDT/ 6-311G**	-188.435101	3.459	736.076	10.6797	10.5269
CCSDT/ 6-311++G**	-188.438841	3.435	734.701	10.6733	10.5205
CCSDT/AUG-cc-pVTZ	-188.555455	3.420	734.693	10.6738	10.5201
DFT					
B3LYP/ 6-311G**	-188.854658	3.393	797.402	10.8140	10.6693
B3LYP/ 6-311++G**	-188.856635	3.375	799.855	10.8083	10.6642
B3LYP/ AUG-cc-pVTZ	-188.876190	3.301	793.385	10.8041	10.6590
experiments					
Bogey et al. 1986			788.629 ($\delta=3.070$)	10.7737221 ($\delta=0.0000087$)	10.6094435 ($\delta=0.0000089$)
Bogey et al. 1984				10.7710 ($\delta=0.010$)	10.6120 ($\delta=0.010$)

ab-initio and DFT approaches. The experimental values were taken from the submillimeter spectrum by Bogey et al. (1986).

Considering the raw values of the computed rotational constants A_e , B_e and C_e (without any scaling procedure), it can be seen that the quality of the results improved when the amount of electronic correlation incorporated in the ab-initio wavefunction increased from HF to MP2 and MP3 levels of theory (MP3 values being the closest to the experimental A_0 , B_0 and C_0). However, the expensive MP4 calculations were of poorer quality than trivial MP2. The CCSD(T) calculations, by far the most sophisticated and time consuming, stood also in the same range as MP2 and very little influence could be seen when the flexibility of the basis set was increased beyond polarized triple-zeta quality.

The best results were obtained using density functional theory. The B3LYP set of calculations were the closest to the experimental values, showing some improvement in the A values with the basis set extension; the remaining 0.5% difference between the best computed values (B_e) and the experimental results (B_0) could be considered as mainly coming from the vibrational contribution, whose exact evaluation is far beyond reach for the series of molecules considered here.

Table 2 presents the geometries through the successive levels of calculations. The DFT/B3LYP calculations leading to the best molecular constants B_e correspond to bond lengths and angles converging within less than 10^{-3} Å and 0.3° respectively. Any further improvement falls into background noise. The conclusion which could be drawn from this study of the first term of the series is that using DFT/B3LYP calculations had a double advantage. It was the most cost-effective method for the size of molecules studied here and, at the same time, it avoided the deli-

cate step of calibration of geometrical parameters (bond lengths and angles). The question of the level of the basis was still open at that point and some more tests were necessary to determine an eventual scaling factor and/or an error bar.

3.2. Tests on the C_nO

Considering the previous results, we limited the second series of test calculations to the DFT method with the B3LYP functional. Two basis sets were used, 6-311G** and AUG-cc-pVTZ which were useful to get an estimate of the accuracy of the results by comparison with the experiments on the singlet C₃O (Brown et al. 1985), C₅O, C₇O, C₉O (Ogata et al. 1995) and triplet C₂O, C₄O, C₆O, C₈O (Ohshima et al. 1995) series. The calculations with the larger basis were limited to 6 carbon atoms in the chain. This was believed to be sufficient to decide which basis to use in forthcoming studies.

The results reported in Table 3 showed that the calculated rotational constants obtained with the 6-311G** and the extended AUG-cc-pVTZ basis set, were largely within 1% of the available experiments.

The present B3LYP/6-311G** calculations also provided a test of the functional to be used in such calculations. Comparison with the BLYP/6-311G** results (Table 4), obtained using a less evolved functional and the same basis set (Moazzen-Ahmadi & Zerbetto, 1995), showed that the B3LYP functional used in the present study rendered much more accurate rotational constants due to a better description of the bond lengths (systematically overestimated at the lower level of functional).

The comparison of the two basis sets at the B3LYP level showed that the larger AUG-cc-pVTZ basis, which was de-

Table 2. Computed geometries of OCOH^+

method / basis set	energy (a.u.)	geometry (Ang.; deg.)				
		OH	CO ₁	CO ₂	COH	OCO
ab-initio						
HF / 6-31G*	-187.844278	0.9743	1.2111	1.1021	121.011	175.745
HF / 6-311G**	-187.904470	0.9675	1.2051	1.0933	120.054	176.093
MP2(FC) / 6-311G**	-188.416194	0.9847	1.2282	1.1349	117.071	174.026
MP2 / 6-311G**	-188.472500	0.9842	1.2269	1.1340	117.249	174.099
MP3(FC) / 6-311G**	-188.402025	0.9788	1.2234	1.1138	117.110	174.771
MP3 / 6-311G**	-188.459700	0.9783	1.2224	1.1130	117.247	174.839
MP4 / 6-311G**	-188.502219	0.9842	1.2330	1.1433	116.938	173.820
CCSDT / 6-311G**	-188.435101	0.9837	1.2315	1.1301	116.704	174.170
CCSDT / 6-311++G**	-188.438841	0.9843	1.2324	1.1300	116.670	174.056
CCSDT/AUG-cc-pVTZ	-188.555455	0.9843	1.2324	1.1300	116.669	174.040
DFT						
B3LYP / 6-311G**	-188.854658	0.9877	1.2187	1.1227	120.735	174.241
B3LYP / 6-311++G**	-188.856635	0.9880	1.2191	1.1228	120.855	174.251
B3LYP / AUG-cc-pVTZ	-188.876190	0.9882	1.2203	1.1224	120.527	174.321

Table 3. Experimental and computed spectroscopic constants of C_nO in their ground singlet (S) and triplet (T) states.

molecule		experiments				calculations					
		Oshima et al. (1995)		this work		Moazzen-Ahmadi and Zerbetto (1995)			this work		
		Bo (MHz)		B3LYP/6-311G**		BLYP/6-311G**			B3LYP/Aug-cc-pVTZ		
		Be (MHz)	$\Delta B\%$	μ (D)	Be (MHz)	$\Delta B\%$	μ (D)	Be (MHz)	$\Delta B\%$	μ (D)	
CO	S	57635.9660(17)	58037.22	0.7	0.121				58154.55	0.9	0.095
C ₂ O	T	11545.5970(7)	11578.94	0.3	1.354				11624.49	0.7	1.341
C ₃ O	S	4810.8864(2)	4801.812	0.19	2.188	4715.053	2.0	2.191	4816.985	0.1	2.268
C ₄ O	T	2351.2625(2)	2349.320	0.08	2.560	2310.456	1.7	2.577	2357.745	0.3	2.631
C ₅ O	S	1366.84709(6)	1364.760	0.15	3.457	1343.801	1.7	3.376	1369.780	0.2	3.575
C ₆ O	T	849.75709(6)	849.2431	0.06	3.661	836.548	1.6	3.630	852.3000	0.3	3.774
C ₇ O	S	572.94105(5)	572.6526	0.05	4.585	564.262	1.5	4.417			
C ₈ O	T	400.64183(8)	400.6327	0.00	4.729	394.931	1.4	4.629			
C ₉ O	S	293.73611(4)	293.7576	0.01	5.694	289.600	1.4	5.421			

signed for the purpose of correlated ab-initio calculations, did not seem to improve the DFT results. This was due to the fact that we were in the range of uncertainty where the vibrational and centrifugational corrections (neglected in these calculations) canceled with the electronic correlation defect and the incompleteness in the basis set still remaining at this level of calculation. This balance of effects happened to be at its best for the B3LYP/6-311G** calculations. Any further scaling or extrapolation was likely to deteriorate the results. Moreover, the residual error was not systematic and determining a scaling factor to be applied to the geometry or directly to the rotational constants, was no longer a reliable procedure. Therefore the best choice for our study was to use the B3LYP/6-311G** method with no correction.

An evaluation of the error bar was done in fine by comparing the computed values to the experimental ones. Both singlet and triplet series showed improved quantitative agreement to the observed values when the length of the chain increased. The error done with a B3LYP/6-311G** optimization decreased from

0.3% for $n=2$ (number of carbons) to less than 0.01% for $n=8-9$. This effect was already observed in the C_nH series (Pauzat et al. 1991) where the ratio of the calculated to the experimental rotational constant tended toward an asymptotic value. This could be attributed to a levelling of the bond lengths with the increase of the carbon chain. Transferring the uncertainty from the $\text{C}_{(n-1)}\text{O}$ compound to the OC_nO of closest mass, we assigned a conservative error bar of 0.2% for $n=3,4$ and 0.1% for $n=5-8$.

4. Predicted structures for protonated polycarbon dioxides

Owing to symmetry reasons, two different series corresponding to odd and even numbers of carbons can be identified. For the odd series, there are $(n/2 + 1)$ C-protonated and 1 O-protonated possible isomers. There is always a central carbon and the remaining carbons are symmetry related, one on each side. For the even series, there is no central atom and pairs of carbons are then defined with respect to the central CC bond, which leads to $n/2$

Table 4. Computed geometries of C_nO (bond lengths in Å). All entries are triple: upper - B3LYP/6311G** (this work); medium - BLYP/6311G** (taken from Moazzen-Ahmadi & Zerbetto (1995)); lower - B3LYP/Aug-cc-pVTZ (this work).

molecule/state	OC ₁	C ₁ C ₂	C ₂ C ₃	C ₃ C ₄	C ₄ C ₅	C ₅ C ₆	C ₆ C ₇	C ₇ C ₈	C ₈ C ₉
C ₃ O S	1.1498	1.2947	1.2709						
	1.1653	1.3017	1.2838						
	1.1486	1.2942	1.2662						
C ₄ O T	1.1644	1.2840	1.2840	1.3089					
	1.1796	1.2913	1.2940	1.3202					
	1.1616	1.2829	1.2815	1.3038					
C ₅ O S	1.1564	1.2839	1.2617	1.2920	1.2788				
	1.1726	1.2897	1.2719	1.2988	1.2988				
	1.1555	1.2826	1.2589	1.2893	1.2738				
C ₆ O T	1.1637	1.2820	1.2758	1.2756	1.2888	1.2981			
	1.1794	1.2889	1.2854	1.2833	1.2980	1.3098			
	1.1629	1.2808	1.2735	1.2731	1.2865	1.2928			
C ₇ O S	1.1591	1.2824	1.2660	1.2815	1.2647	1.2927	1.2809		
	1.1753	1.2884	1.2764	1.2883	1.2747	1.3000	1.2942		
	x								
C ₈ O T	1.1636	1.2814	1.2744	1.2761	1.2795	1.2721	1.2910	1.2928	
	1.1793	1.2882	1.2840	1.2838	1.2880	1.2807	1.2994	1.3051	
	x								
C ₉ O S	1.1604	1.2817	1.2682	1.2799	1.2683	1.2825	1.2650	1.2937	1.2816
	1.1765	1.2880	1.2786	1.2867	1.2784	1.2892	1.2751	1.3010	1.2949
	x								

Table 5. Computed energies and dipole moments of $C_nO_2H^+$ (by B3LYP/ 6-311G**)

molecule	protonation site ^a	singlet		triplet	
		energy (a.u.)	dipole (D)	energy (a.u.)	dipole (D)
CO ₂ H ⁺	O	-188.85466	3.393	-	-
C ₂ O ₂ H ⁺	O	- 226.87759 (diss)		- 226.87189	3.693
C ₂ O ₂ H ⁺	C	- 226.94291 (diss)		- 226.85812	2.178
C ₃ O ₂ H ⁺	O	- 265.05133	3.714	- 264.94498	4.065
C ₃ O ₂ H ⁺	C 1st	- 264.95947	3.546	- 264.96096	2.611
C ₃ O ₂ H ⁺	C 2nd	-265.09336	1.863	- 264.98066	3.726
C ₄ O ₂ H ⁺	O	- 303.08733	3.915	- 303.09589	4.333
C ₄ O ₂ H ⁺	C 1st	- 303.12386	3.228	- 303.06635	2.367
C ₄ O ₂ H ⁺	C 2nd	- 303.14312	3.085	- 303.11884	2.045
C ₅ O ₂ H ⁺	O	- 341.23942	3.871	- 341.15121	3.610
C ₅ O ₂ H ⁺	C 1st	- 341.16786	2.749	- 341.17976	2.672
C ₅ O ₂ H ⁺	C 2nd	- 341.27995	1.734	- 341.19209	3.765
C ₅ O ₂ H ⁺	C 3rd	- 341.20694	3.141	- 341.17579	1.774
C ₆ O ₂ H ⁺	O	- 379.28766	5.411	- 379.29805	4.687
C ₆ O ₂ H ⁺	C 1st	- 379.32103	3.778	- 379.26249	1.045
C ₆ O ₂ H ⁺	C 2nd	- 379.33949	3.999	- 379.33120	2.269
C ₆ O ₂ H ⁺	C 3rd	- 379.32754	3.568	- 379.30804	1.745
C ₇ O ₂ H ⁺	O	- 417.42585	3.955	- 417.35791	5.367
C ₇ O ₂ H ⁺	C 1st	- 417.37075	2.451	- 417.38513	3.307
C ₇ O ₂ H ⁺	C 2nd	- 417.46737	1.699	- 417.39956	4.504
C ₇ O ₂ H ⁺	C 3rd	- 417.36910	1.740	- 417.39113	2.041
C ₇ O ₂ H ⁺	C 4th	- 417.45944	1.362	- 417.38571	2.317
C ₈ O ₂ H ⁺	C 2nd	- 455.53180	4.546	- 455.52905	2.330

^a 1st, 2nd, 3rd, 4th refer to the neighbouring position with respect to oxygen

Table 6. Computed spectroscopic constants of the lowest state of $C_nO_2H^+$

method / basis set	energy (a.u.)	dipole (D)	rotational constants (GHz) (lower line for deuterated)			
$C_3O_2H^+$	S	- 265.09336	1.86	31.458 ± 0.06 25.980	2.6963 ± 0.005 2.6964	2.4835 ± 0.005 2.4429
$C_4O_2H^+$	S	- 303.14312	3.08	35.762 ± 0.07 28.235	1.4554 ± 0.003 1.3929	1.3985 ± 0.003 1.3274
$C_5O_2H^+$	S	- 341.27995	1.73	17.732 ± 0.02 15.708	0.9314 ± 0.0009 0.9267	0.8849 ± 0.0009 0.8751
$C_6O_2H^+$	S	- 379.33949	4.00	15.121 ± 0.01 13.560	0.6197 ± 0.0006 0.6156	0.5953 ± 0.0006 0.5888
$C_7O_2H^+$	S	- 417.46737	1.70	13.691 ± 0.01 12.534	0.4215 ± 0.0004 0.4182	0.4089 ± 0.0004 0.4047
$C_8O_2H^+$	S	- 455.53180	4.55	11.343 ± 0.01 10.531	0.3095 ± 0.0003 0.3067	0.3013 ± 0.0003 0.2980

Table 7. Computed IR spectra of $C_nO_2H^+$

$C_3O_2H^+$		$C_4O_2H^+$		$C_5O_2H^+$		$C_6O_2H^+$		$C_7O_2H^+$		$C_8O_2H^+$	
ν	I	ν	I	ν	I	ν	I	ν	I	ν	I
155	8	95	2	77	1	40	0	49	0	32	0
437	6	152	1	95	3	77	1	65	2	58	1
466	1	246	22	182	1	94	1	112	1	60	0
545	0	434	6	409	3	235	15	164	2	135	0
638	108	527	18	426	5	280	9	220	3	158	5
673	6	585	21	507	0	439	25	404	3	260	13
997	4	643	40	538	35	453	0	417	9	428	3
1421	8	931	42	611	26	529	9	499	2	448	0
2305	1163	981	50	648	73	571	0	539	28	466	0
2379	101	1295	5	821	7	645	33	563	0	471	28
3121	161	1699	27	1077	17	732	38	567	4	506	10
		2257	652	1231	3	771	42	605	26	532	9
		2333	448	1486	164	98	11	654	72	614	12
		3113	23	2194	503	1190	13	719	4	659	22
				2283	2289	1341	45	1001	0	702	23
				2400	1248	1805	76	1120	47	738	37
				3126	111	2118	80	1312	60	941	8
						2300	2562	1533	157	1052	58
						3107	34	2222	5089	1416	98
								2321	121	1817	223
								2369	2256	2058	55
								3134	91	2131	275
										2282	3884
										2330	1510
										3114	40

Frequencies ν are in cm^{-1} and intensities I in Km/mole

C-protonated and 1 O-protonated possible isomers. This parity related classification, however, did not help in the interpretation of the results as it did for the non protonated C_nO species where the two series belong to different multiplicities. For that reason it was found more appropriate to refer to the protonation sites by their neighbouring order to the terminal oxygen, i.e. 1st, 2nd, 3rd,... neighbour.

All possible isomers, for each molecule of the series up to $n=7$, in the lowest singlet and triplet states were considered. All geometries were fully optimized in order to determine the most energetically favored isomer. The energy results are reported in Table 5 for molecules with 1 to 8 carbon atoms. Only the rotational constants and dipole moments of the most likely candidates to be studied in the laboratory in view of telescope search in the interstellar medium or circumstellar envelopes are

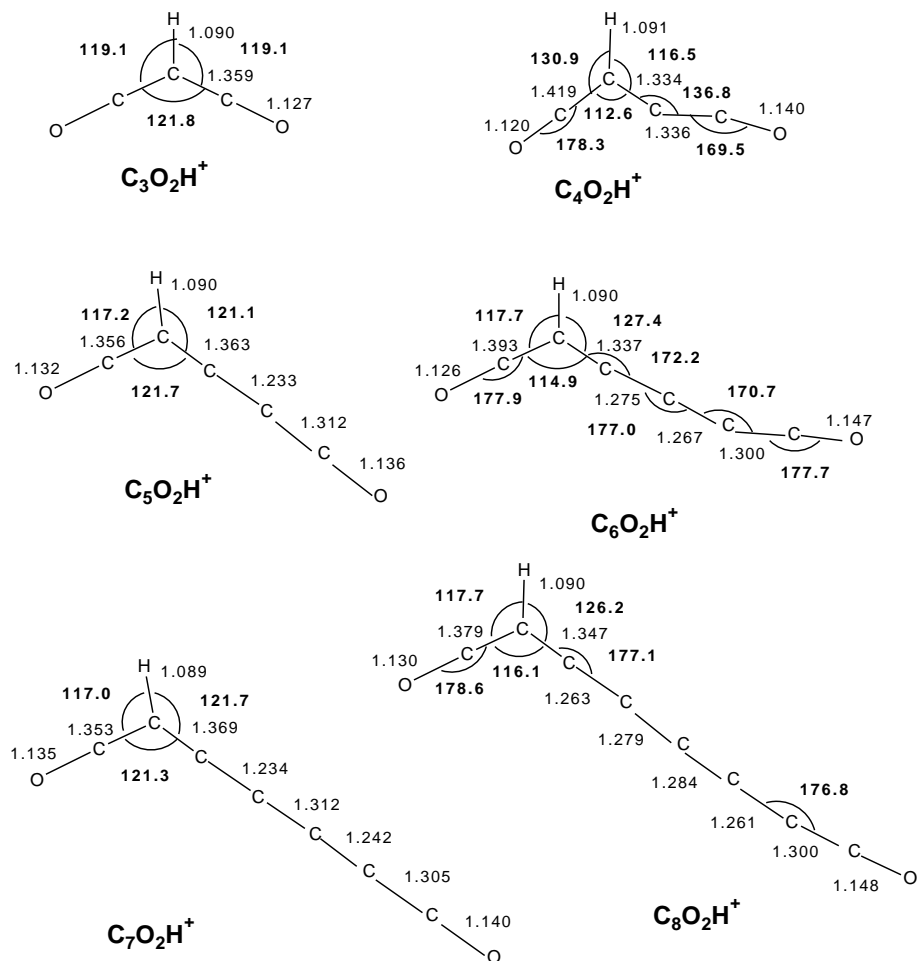


Fig. 1. Computed geometries of $C_nO_2H^+$ (bond lengths in Å, angles in deg.)

tabulated in Table 6; the corresponding geometrical structures are displayed in Fig. 1. The IR frequencies and intensities are listed in Table 7. Details about the metastable isomers and excited states are beyond the purpose of this paper and will be published elsewhere.

4.1. Protonated adducts of OC_2O

Previous theoretical studies have shown that C_2O_2 is bound only in an excited triplet state (Haddon et al. 1975) and that the ground state dissociates spontaneously to give 2 CO molecules (Raine et al. 1983). Protonation does not change the picture since the most stable arrangements of $C_2O_2H^+$ are weakly interacting long distance complexes of singlet multiplicity (CO, HCO^+) and (CO, COH^+). Only triplet states are bound but, since they are excited states, they cannot be considered reasonable candidates. Thus, these species were not included in the even series.

4.2. Protonated adducts of the odd series

OC_3O : Two C-protonated and one O-protonated isomers were expected from this neutral compound. The most stable one is protonated on the central carbon, i.e. on the 2nd neighbour to the

oxygen. It is a singlet state. The other C-protonated compound (on the 1st neighbour to oxygen) is slightly more stable in the triplet state. The O-protonated structure is more stable in the singlet state. All these structures are found to be more stable than C_3O_2 and the dissociation products observed in the interstellar space ($C_2O + HCO^+$, $C_2O + COH^+$, $C_2O + CO + H^+$) (Mann & Williams, 1980). Indeed, the least stable adduct of C_3O_2 is still more stable than the most stable products of dissociation ($C_2O + HCO^+$) by 23.7 kcal/mole. Thus the C_3O_2 protonated adducts are likely candidates for interstellar observation, the most probable one being the singlet C-central protonated isomer with a reasonable dipole moment of almost 2 Debye.

OC_5O : Three distinct C-protonated (central, intermediate and O-linked) and one O-protonated isomers were expected. Contrary to the preceding member of the series, protonation of the central atom does not yield the most stable isomer. However, the situation is similar if we consider the rank of the protonated carbon in the chain: the most stable structure corresponds to the 2nd neighbour to the oxygen; it is also a singlet state with a dipole moment of about 1.7 Debye, which is an encouraging result for an experimental study. As previously, the structure in which the proton is attached to the 1st neighbour is more stable in the triplet state and the O-protonated structure is found to be more stable in the singlet state.

OC₇O: There were four C-protonated and one O-protonated isomers to consider in this case. The most stable isomer is still a singlet state with the proton attached to the 2nd neighbour to the oxygen with a dipole moment of 1.7 Debye. The O-protonated species is also more stable in the singlet state and the structure in which the proton is attached to the 1st neighbour is found to be more stable in the triplet state.

4.3. Protonated adducts of the even series

OC₄O: Two C-protonated and one O-protonated isomers were expected here. The C-protonated singlet structures are more stable than the corresponding triplets. Contrary to the preceding series, the O-protonated structure is more stable in the triplet state. All these isomers are stable with respect to the dissociation products. The most stable one corresponds to the protonation of the central CC bond, i.e. the proton was attached to the 2nd neighbour to the oxygen as in the odd series. The dipole moment of 3 Debye seems favorable for eventual observation.

OC₆O: Here protonation could lead to three distinct C-protonated and one O-protonated isomers. The situation is identical to that of the preceding member of the series. Singlet C-protonated structures are more stable than the corresponding triplets and the opposite is found for the O-protonated structure. The most stable isomer does not correspond to protonation of the central CC bond but the common point is that this most stable structure has the proton attached to the 2nd neighbour to the oxygen as in the preceding case. The dipole moment of 4 Debye is encouraging for eventual observation.

OC₈O: Assuming that the most stable isomer remained the protonated on the 2nd neighbour to the oxygen when the length of the chain increases, only this isomer was optimized. Once again, the singlet state is more stable than the triplet. The dipole moment, 4.5 Debye, has increased by 0.5 Debye with the addition of two carbons in the chain.

5. Concluding remarks

This quantum mechanical study based on Density functional Theory, using a flexible basis set, shows that the odd and even series of OC_nOH⁺ are well identified although they both lead to preferential protonation on the 2nd neighbour to the oxygen with singlet multiplicity.

For the odd series, the most stable compounds are planar with a common ketene fragment HC=C=O and a linear arrangement of the longer C=C... C=O branch with alternating long and short CC bonds. Dipole moments are very close with medium values around 1.7–1.8 Debye, and they are sufficient for spectroscopic measurements. Similarities appear again in the IR spectra where they all exhibit large intensities for the CH vibrations (stretching, in-plane bending and out-of-plane bending respectively around 3000 cm⁻¹, 1450 cm⁻¹, 650 cm⁻¹); however the CC vibrations (in the 2100–2400 cm⁻¹ range) are intense for all molecules regardless of the number of carbons.

For the even series, the most stable compounds are also planar with the same ketene fragment (slightly bent by 2°)

and a floppy arrangement of the longer C=C... C=O branch with nearly equivalent CC bonds. By contrast, dipole moments are much larger and increase with the number of carbons (3 to 4 and 4.5 Debye for 4, 6 and 8 carbons respectively) which is encouraging for experiments in the laboratory and observations. Similarities appear again in the IR spectra where large intensities are predicted only for the CC vibrations (in the 2100–2400 cm⁻¹ range) which are intense for all molecules. However the last member, i.e. C₈O₈H⁺, begins to present less well defined characteristics; in particular, the longer branch tends towards a linear structure and the IR spectrum shows intensities increasing for the CH in-plane bending, bringing both series closer to each other.

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