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Relative energies, structures, vibrational frequencies, and electronic spectra of pyrylium cation, an oxygen-containing carbocyclic ring isoelectronic with benzene, and its isomers

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Abstract: We have studied relative energies, structures, rotational, vibrational and electronic spectra of the pyrylium cation, an oxygen-containing six-membered carbocyclic ring, and its six isomers, using *ab initio* quantum chemical methods. Isoelectronic with benzene, the pyrylium cation has a benzenoid structure and is the global minimum on the singlet potential energy surface of $C_5H_5O^+$. The second lowest energy isomer, the furfuryl cation, has a five membered backbone akin to a sugar, and is only 16 kcal mol^{-1} above the global minimum computed using coupled cluster theory with singles, doubles and perturbative triple excitations (CCSD(T)) with the correlation consistent cc-pVTZ basis set. Other isomers are 27, 30, 37, 59, and 64 kcal mol^{-1} above the global minimum, respectively, at the same level of theory. Lower level methods such as density functional theory (B3LYP) and second order Møller-Plesset perturbation theory performed well when tested against the CCSD(T) results. The pyrylium and furfuryl cations, although separated by only 16 kcal mol^{-1}, are not easily interconverted, as multiple bonds must be broken and formed, and the existence of more than one transition state is likely. Additionally, we have also investigated the asymptotes for the barrierless ion-molecule association of molecules known to exist in the interstellar medium that may lead to formation of the pyrylium cation.

I.   Introduction

Pyrylium cation, **1**, is an isomer of $C_5H_5O^+$ with a six-membered carbocyclic ring that incorporates an oxygen atom and is isoelectronic with benzene. A CH group in benzene is replaced with O^+ in the pyrylium cation. The oxygen heteroatom in the pyrylium cation introduces major physical and spectroscopic perturbations relative to benzene. Astronomers have identified benzene in the interstellar medium (ISM).[1] A similar identification of pyrylium cation in an oxygen rich environment would be an exciting new development in the identification of oxygen containing cyclic molecules in the ISM and could also help unravel how or if oxygen atoms are incorporated into the carbon ring framework in polycyclic aromatic hydrocarbons (PAHs). Pyrylium cation is also isoelectronic with pyridine, wherein the oxygen atom is replaced by a nitrogen atom (and the molecule is neutral). Pyridine has not been identified in the interstellar medium thus far.

The interstellar abundance of oxygen is comparable to the abundance of carbon. Although much interstellar oxygen is locked up in carbon monoxide, carbon dioxide and silicates, many carbon and oxygen containing molecules have been identified in the interstellar medium – mainly straight chain alcohols, aldehydes, and carboxylic acids. Cyclic molecules, in which oxygen is involved in the cyclic framework, are as yet unobserved. Oxygenated polycyclic aromatic hydrocarbons (PAHs) may exist in oxygen-rich areas of the interstellar medium, but have never been identified because of limited high-quality theoretical and experimental laboratory data.[2,3] Oxygen can be involved in the PAH molecules as a hydroxy-cyclopentadiene, cyclopentenone, carboxylic acid functional group, or as a part of a ring, as in furan or pyran. Hudgins et al. have

investigated the vibrational spectra of oxygen, and nitrogen, substituted circumcoronene cations.[4]

Pyrylium cation, **1**, has a pyranose structure, as shown in Figure 1. There are many other higher energy isomers of $C_5H_5O^+$, some of which are shown in Figure 2. One of those, 2-methylene-2H-furanium or furfuryl ion, **2**, has the framework of a ribose sugar of nucleotides. Direct analysis in real-time (DART) mass spectrometry of nucleotides reveals that they fragment when introduced into a high temperature (200-250C) helium gas stream.[5] One of the common ionic fragments observed in these experiments has a mass of 81 amu, representing $C_5H_5O^+$. The deoxyribose sugar moiety of nucleotides dissociate from the nucleobase and the phosphate group in this experiment. This $C_5H_5O^+$ ion is proposed to be 2-methylene-2H-furanium ion by Curtis et al.,[5] though no structural information was available from the experiment.

A few other experimental and theoretical studies[6,7] have investigated heteroatom insertion in carbocyclic rings in general, and oxygen insertion in the rings in particular, and proved that these species can form in the gas phase. Solano et al. predicted, based on electron impact mass spectra, that the furfuryl ion, **2**, is synthesized during the dissociation of N-(2-furylmethyl) anilines.[8] Espinoza and Navarez studied[9] unimolecular rearrangements of methyl furan and pyran ions by DFT and RRKM theories, and predicted that the pyrylium ion is the most likely fragment-ion produced during the meta-stable decomposition of methyl furan. The mechanism of unimolecular rearrangement of pyrylium and furfuryl ions is, however, not understood. In yet another study, Chai and Pfefferle reported that the oxidation of benzene in lean-fuel conditions produces cyclopentadienonyl radical (C_5H_5O), which has the same chemical formula but one more

electron, among other products.[10] Shock waves also oxidize cyclopentadiene – cyclopentadiene has not been observed in the ISM thus far – to form the C_5H_5O radical.[11] These are only some of the ways C_5H_5O species could be synthesized from pure carbon compounds. Many more unexplored routes via ion-molecule reactions will exist, as ion-molecule reactions are one of the most effective ways large molecules can be synthesized in the ISM.[12-15] Crystal structures of pyrylium salts and the aromatic character of the pyrylium ring have been studied before as pyrylium salts are very common in heterocyclic chemistry.[16] However, accurate structural parameters for the pyrylium cation, **1**, furfuryl cation, **2**, and the other higher energy isomers shown in Figure 2 have thus far not been determined nor even investigated.

This system ($C_5H_5O^+$) is of potential astrophysical interest for several reasons: 1) pyrylium cation, **1**, is an oxygen-containing six membered aromatic ring that is isoelectronic with benzene and will therefore share its aromatic stability, and therefore might exist in the interstellar medium; 2) the 2-methylene-2H-furanium cation (furfuryl), **2**, is a conjugated oxygen-containing five-membered ring which is also quite stable, and no five membered rings have been observed in the ISM thus far; and 3) **2** has the structure of a sugar and the identification of a sugar backbone in the ISM would be significant. Thus the goal of the present study is to thoroughly characterize the structural and spectroscopic parameters of both **1**, **2**, and the other higher energy isomers of Figure 2.

In this study we have investigated relative energies and structural and spectroscopic parameters of the low-lying isomers of the $C_5H_5O^+$ cation. We have also computed the binding energies for the formation of the global minimum (which is the

pyrylium cation) from association of known ISM molecules and cations. We have compared the computed spectroscopic parameters of pyrylium cation with those of commonly known molecules such as benzene. We hope that these data will be useful in the future experimental identification and, potentially, the eventual astronomical observation of the pyrylium cation and/or its isomers.

II.   Theoretical Methods

We obtained accurate geometrical parameters using coupled cluster singles and doubles with perturbative triples [CCSD(T)][17] along with Dunning's correlation consistent valence triple zeta basis set (cc-pVTZ).[18] Coupled cluster calculations were performed using the MOLPRO 2008 quantum chemistry code.[19]

As a prelude to future studies of the growth of larger oxygen containing molecules, we also compared the performance of more computationally affordable methods. We used restricted second order Møller-Plesset perturbation theory (MP2) to optimize the geometries of the pyrylium cation and its isomers. We computed the harmonic vibrational frequencies and intensities using MP2/cc-pVTZ.

Finally, we also optimized geometries with the B3LYP[20,21] density functional approach using a very fine grid of 75 radial points and 590 angular points. We computed the electronic spectra of the complexes employing time dependent density functional theory (TDDFT) with ωB97X,[22] a range-separated density functional due to Chai and Head-Gordon. We employed the Q-Chem 3.2[23] quantum chemistry package for all the MP2 and DFT computations. In order to identify all low-lying isomers, we performed a stochastic search to locate minima on the singlet potential energy surface of $C_5H_5O^+$.[24,25]

III. Results

In the following sub-sections we will discuss the relative energies of the isomers (A), geometrical parameters (B), rotational constants (C), association energies (D), harmonic vibrational frequencies (E), and electronic excitation spectra (F) for singlet-singlet transitions of the seven lowest energy isomers of the $C_5H_5O^+$ shown in Figure 2.

III.A. *Relative energies*

In Table 1 we present the relative energies upon geometry optimization using the MP2, B3LYP and CCSD(T) methods together with the cc-pVTZ basis set. All CCSD(T)/cc-pVQZ energies are single point energies computed at the CCSD(T)/cc-pVTZ optimized geometries. Pyrylium cation, **1**, which incorporates the oxygen atom into the six-membered ring, is the global minimum, and is planar with C_{2v} symmetry as shown in Figure 1. The second lowest-energy isomer, **2**, (2-methylene-furanium or furfuryl cation) is 16.0 kcal/mol above the global minimum at the CCSD(T)/cc-pVQZ level. The third lowest-energy isomer, **3**, 3-methylene furanium is 25.4 kcal/mol above the global minimum at the same level of theory. The fourth lowest-energy isomer, **4**, hydroxy-cyclopentadiene cation, is very close to its nearest energy isomer, being 25.8 kcal/mol above the global minimum. The fifth, sixth, and seventh lowest-energy isomers, cyclopentenone (**5**), methyl-cyclopropenylidene ketone (**6**), and meta-cyclopentenone ion (**7**), are 37.3, 59.2, and 64.5 kcal/mol above the global minimum, respectively. Both MP2 and B3LYP predict the same relative energy order for the isomers, and there is very little difference between the relative CCSD(T) energies computed using either the cc-pVTZ or cc-pVQZ basis sets. B3LYP/cc-pVTZ, for most of these closed shell cations, comes very close, compared to CCSD(T)/cc-pVQZ, to predicting the relative energies. The largest

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error in B3LYP/cc-pVTZ relative energies is 3.7 kcal/mol for **4**. MP2 slightly overestimates the relative energies.

III.B. Structures

Structural features of the pyrylium cation are seen in Figure 1: **1** has C_{2v} symmetry and a $^1A_1$ electronic ground state. The oxygen atom forms two equal but short C-O single bonds on each side. In fact, the C-O bond distance is almost exactly between a typical C-O single bond and a C=O double bond. The C-C bonds between the 2 and 3 carbons, and the 5 and 6 carbons are equal and elongated double bonds at 1.376 Å. C-C distances between the 3 and 4, and 4 and 5 carbons are very short single bonds at 1.400 Å. The C-C bond distances in **1** show only slight deviations from the C-C distances found in benzene. The aromatic all-equal C-C bond distances in benzene are 1.3976 Å at the CCSD(T)/cc-pVTZ level of theory.[26] Pyrylium cation has two equivalent Kekule resonance structures with alternating single and double bonds. The lowering of the symmetry (from D_{6h} in benzene to C_{2v} in pyrylium) due to the introduction of the oxygen heteroatom means that there are sets of equal bond distances and angles on both sides of the reflection plane perpendicular to the molecular plane, as seen in Figure 1. In fact the bond distances and angles in pyrylium show a similar trend as seen in pyridine, which is also aromatic. Pyridine has one set of equal C-N bonds (1.3402 Å) and two sets of equal C-C bonds (1.3945 and 1.3944 Å) across the reflection plane.[27]

The near perfect aromatic COC bond angle of pyrylium cation – a deviation of 1.1º from the ideal CCC bond angles of benzene – indicates that the oxygen atom takes part in aromaticity which helps to explain its thermal stability. A slight widening of the COC and OCC bond angles are compensated by the squeezing of the CCC bond angles

on the other side of the ring. According to a natural population analysis, the positive charge in pyrylium cation is highly delocalized being concentrated mainly on the hydrogen atoms, while the charges on the carbon atoms and oxygen atom mostly cancel each other out (natural charges for all isomers are given in the Supplementary Material). In a DFT and RRKM theoretical study, Espinoza et al. proposed that the $C_5H_6O^+$ ion dissociates into primarily hydrogen atom and pyrylium isomer, but they did not provide any structural information for the dissociated $C_5H_5O^+$ fragment.

The second lowest energy isomer, **2**, is the furfuryl cation shown in Figure 2. **2** is a five-membered cyclic molecule that includes the oxygen atom in the ring, and has an exocyclic methylene group at the 2-position. The geometry is planar, and has C_s symmetry and a $^1A'$ electronic ground state. **2** is 16, 18.6 and 16.2 kcal/mol above the global minimum at CCSD(T), MP2 and B3LYP levels (all with the cc-pVTZ basis set) respectively. In contrast to the pyrylium cation, **1**, the two C-O bonds of **2** are quite unequal in length, 1.388 Å and 1.304 Å respectively, although both are shorter than a regular C-O single bond distance. The external methylene group forms a 1.340 Å C=C double bond with the ring-carbon. C=C double bonds appear in the bond between the exocyclic carbon and C2, and between C3 and C4. The C2=C3, and C4=C5 bonds appear considerably shortened from standard single bond distances but longer than a typical C=C double bond. The <COC bond angle (106.7º) is also considerably smaller than the <COC bond angle in ethyl ether (112.1º). These structural parameters suggest that the single resonance structure with three alternating double bonds is most important, whilst also showing that there is some π-conjugation (i.e. contributions from resonance structures with only 2 double bonds) within the 5-membered cyclic framework that extends to the

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exocyclic C of the methylene group. This conjugation also serves to delocalize the net charge. Indeed, a natural population analysis again shows that the positive charge is mainly spread out amongst the hydrogen atoms, while the negative charge on the oxygen atom is mostly canceled by positive charges on its adjacent carbon atoms. The structural and spectroscopic parameters presented here could be used to identify the products obtained in the DART mass spectrometric study by Curtis et al., if further comparable experimental data were available. Further, it will be of interest to determine whether isomer **2**, produced in the DART experiment retains its sugar framework or rearranges to the lower energy global minimum pyrylium cation.

The third lowest energy isomer, **3**, of $C_5H_5O^+$, 3-methylene-furanium cation, (see Figure 2) is a five membered cyclic molecule that includes the oxygen atom in the ring and has an exocyclic methylene group at the 3-position. This isomer is also planar, with C_s symmetry and a $^1A'$ electronic ground state. The two C-O bonds are very unsymmetric, one being an elongated C=O double bond (1.286 Å) and the other being a standard C-O single bond (1.429 Å). In fact, **3** exhibits approximately alternating single and double bonds starting from the exocyclic methylene group. However, the C=C double bonds (1.359 Å for the exocyclic CC bond and 1.342 Å for C4=C5) are slightly elongated and the C-C single bonds (1.462 Å for C3-C4 and 1.430 Å for C2-C3) are slightly shortened, while the methylene group forms a long C=C double bond (1.359 Å) with the ring at the 3-position. Based on this structural data, the single resonance structure with three double bonds dominates, while again there is conjugation within, and outside the ring, to partially delocalize the net positive charge similar to **2**. In terms of resonance theory, this amounts to contributions from resonance structures with two double bonds. A natural

population analysis for **3** is also similar to that for **2**; that is the positive charge is spread out amongst the hydrogen atoms while the negative charge on the oxygen atom is balanced by its adjacent carbon atoms.

The fourth lowest-energy isomer, **4**, hydroxy-cyclopentadiene cation (Figure 2) has a cyclopentadiene cyclic framework. A hydrogen atom in cyclopentadiene is replaced with an OH^+ group to obtain this isomer. The oxygen atom forms a double bond with the cyclopentadiene carbon atom and a proton is attached to the oxygen. The oxygen atom and the proton attached to it lie in the same plane as the cyclic framework – hence the molecule has C_s symmetry. The external C=O bond is an elongated double bond at 1.274 Å. The C2-C3 and C2-C5 single bonds are shorter than a standard C-C single bond, while the two C=C double bonds are slightly elongated relative to ethylene. The structure again suggests that there is conjugation throughout the ring, extending to the exocyclic oxygen atom. The positive charge resides primarily on the C1 carbon atom and the proton attached to the oxygen based on a natural population analysis.

A fuel-lean oxidation study of benzene produced the C_5H_5O radical, and according to Chai and Pfefferle[10] it is the cyclopentenone radical – an assertion, however, based on mass spectrometric data only. The analogous cyclopentenone cation, **5**, (Figure 2) is 37.3 kcal/mol above the global minima and is the fifth lowest-energy isomer on the singlet $C_5H_5O^+$ potential energy surface. It is 37.3, 41.5 and 37.5 kcal/mol above the global minimum, **1**, using CCSD(T), MP2 and B3LYP methods, respectively, with the cc-pVTZ basis set. Cyclopentenone cation has a five membered ring, a cyclopentene moiety, with an exocyclic oxygen atom that is doubly bonded to one of the ring C atoms. This is a tautomer of the hydroxy-cyclopentadiene isomer, **4**, (Figure 2) – the hydrogen

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atom attached to the oxygen atom in **4** has moved to the C2 atom in **5**. The bonds between C4-C5 (1.407 Å) and C5-C6 (1.381 Å) share partial double bond character. All the C-C single bonds are shorter than the typical single bond distance found in ethane.

The sixth lowest energy isomer, **6**, methyl-cyclopropenyl ketone ion (Figure 2) is 59.2 kcal/mol above the global minimum, and possesses C_s symmetry If we replace one of the methyl groups of acetone by a cyclopropenylidene group we get this isomer. Carbon monoxide is one of the most abundant molecules in the ISM and cyclopropenylidene has been observed in the ISM as well as many other astrophysical environments[28] (see Ref. 26 for a discussion). The positive charge in **6** resides primarily in the cyclopropenylidene moiety and the carbonyl carbon based on a natural population analysis. The C-C distance between the carbonyl carbon and the cyclopropenylidene ring carbon is 1.511 Å, a short C-C single bond. The C-O distance is 1.204 Å, shorter than the C-O distance in H_2CO. The C-C single bond between the carbonyl and methyl carbons is also a short C-C single bond at 1.476 Å. The C-C bonds within the cyclopropenylidene ring are all elongated double bands at 1.340 and 1.367 Å, respectively.

The highest energy isomer, **7**, shown in Figure 2, is over 65 kcal/mol above the global minimum. This isomer is similar in structure to the cyclopentenone isomer, **5**, a tautomer. In this case the hydrogen has moved from C3 to the C4 carbon atom. The C4 atom is sp^3 hybridized. The C4-C5 bond distance, 1.342 Å, is close to a typical double bond distance. The other C-C bonds are all short single bonds ranging from 1.421 Å to 1.513 Å. The external C-O bond is a typical C-O double bond distance.

There are a few more isomers that are higher lying on the singlet potential energy surface, and thus, not included here. For example, an interesting cage structure was found

that is much higher in energy compared to the seven lowest energy isomers of $C_5H_5O^+$, approximately 120 kcal/mol above the global minimum. The heavy-atoms form the six vertices of a prism in this cage structure. The carbon atoms bond one hydrogen atom each, and are connected to three other carbons atoms. The oxygen atom is bonded to three carbon atoms.

III.C. *Rotational Constants*

All the isomers investigated in this work are asymmetric tops. The rotational constants and dipole moments of the 7 studied isomers of $C_5H_5O^+$ are presented in Table 2. All values have been computed with respect to the molecule's center of mass (for the main isotopologue) using the CCSD(T)/cc-pVTZ optimized geometries. The rotational constants of pyrylium cation, **1**, are 5.9413 (A), 5.7784 (B) and 2.9294 (C) GHz, while its dipole moment is 0.94 Debye (with the origin at the center of nuclear mass for the main isotopologue; the dipole moment of charged species depends linearly on the origin). The rotational constants of **2** are 8.6123 (A), 3.9599 (B), and 2.7136 (C) GHz, while its dipole moment is 0.99 Debye.

The rotational constants of the 3-methylene furanium ion, **3**, are 8.6105 (A), 3.7948 (B), and 2.6345 (C) GHz, and its dipole moment is 2.38 Debye. The rotational constants and dipole moment for **4** are 7.9284 (A), 3.8186 (B) and 2.5773 (C) GHz, and its dipole moment is 1.65 Debye. Rotational constants of the cyclopentenone isomer, **5**, are 7.8460 (A), 3.7349 (B), and 2.5704 (C) GHz. This relatively high-energy isomer has a large dipole moment of 4.01 Debye. Methyl cycloproyl ketone, **6**, has a very large dipole moment of 6.03 Debye. Its rotational constants are 7.7397 (A), 2.5952 (B) and 2.2536 (C)

GHz. Isomer **7**, meta-cyclopentenone cation, has a dipole moment of 3.28 Debye, and the rotational constants are 7.8811 (A), 3.6855 (B) and 2.5488 (C) GHz.

Importantly, the rotational constants for all of the isomers exhibit significant differences between one another, suggesting that the different isomers would be easily distinguished using either rotational spectroscopy or high-resolution rovibrational spectroscopy. Further, all of the isomers possess significant dipole moments indicating that they should be observable provided their concentration is large enough.

III.D. *Association energies*

We turn our attention to the association energies of fragments leading to the global minimum, **1**, the pyrylium cation. We are interested in the stability of the pyrylium cation relative to known molecules/ions in carbon and oxygen rich environments of the ISM. How the pyrylium cation might be synthesized in the ISM is of great interest as it is a six-membered ring similar to benzene. We note that in a favorable association reaction, the excess energy would need to be eliminated, and this typically occurs either via radiative attachment or dissociative attachment. However, it is not the purpose of the present study to investigate all possible formation mechanisms and pathways, rather in this section we present various asymptotes of association of precursors leading to the pyrylium cation merely to determine its thermodynamic stability relative to other possible products. We could conceive of ion-molecule reactions of two types of precursors: closed shells and radicals. In both cases we found strong and favorable association energies, as presented in Table 3. We computed association energies with B3LYP, MP2, and CCSD(T) in conjunction with the cc-pVTZ basis set. Association energies computed

using all three methods are very similar to each other for each set of association asymptotes. The first four rows represent ion-molecule association of closed-shell species. The last two rows represent radical-radical association energies and, therefore, yield larger association energies (i.e. coming from higher energy asymptotes).

HCCH, HCO, HCO^+ and HCCHO have been observed in the ISM. Cyclic C_4H_4 can attach with HCO^+ and produce $C_5H_5O^+$ with 140.8 kcal/mol energy release. In other words, the C_4H_4 and HCO^+ association is energetically favorable by 140.8 kcal/mol. HCCH can combine with two different precursors, $HCCHCHO^+$ or $HCCHOCH^+$, to form the pyrylium cation with association energies of 135.6 and 205.2 kcal/mol, respectively. Cyclobutadiene cation is a stable isomer on the potential energy surface of $C_4H_4^+$. The association energy of cyclobutadiene cation with HCO, both radicals, is 141.0 kcal/mol. Association of the HCCHCHO and $HCCH^+$ radicals leads to an even larger energy release of 203.9 kcal/mol. The association energies in Table 3 show that formation of pyrylium cation is thermodynamically favorable relative to many asymptotes.

III.E. Vibrational Frequencies

Harmonic vibrational frequencies of all the isomers of $C_5H_5O^+$ were computed at the MP2/cc-pVTZ level of theory and are presented in Tables 4, 5 and 6. In Table 4, the symmetries of the vibrational modes, the harmonic vibrational frequencies, and the infrared intensities (using the double harmonic approximation) of the pyrylium cation are presented. A large-intensity bending mode appears at 668 cm^{-1}, and a couple of large-intensity modes appear near the C-O stretching region at 1538 and 1692 cm^{-1}. These

harmonic vibrational frequencies could act as good reference points for verification of future experimental detection of pyrylium cation, **1**.

Benzene has a pair of degenerate CH stretching modes at 3199.7 cm^{-1} (e_{1u}) and 3183.1 cm^{-1} (e_{2g}), and non-degenerate frequencies at 3209.9 cm^{-1} (a_{1g}) and 3173.1 cm^{-1} (b_{1u}) according to harmonic frequencies computed at the CCSD(T) level of theory.[26] **1** has five unique frequencies in the CH stretching region, and two of them, 3309 cm^{-1} (A_1) and 3319 cm^{-1}, (B_2) have appreciable intensities, while the other three at 3289, 3306 and 3323 cm^{-1} have smaller intensities. It is interesting that the C-H stretch frequencies for **1** are all higher in energy than those in benzene, at least for the comparisons made here.

The B_1 symmetry mode at 668 cm^{-1} (Table 4) with large intensity is an asymmetric rocking motion of the COC and CCC moieties. The A_1 symmetry mode at 990 cm^{-1} is a symmetric stretch of the two CO bonds. An asymmetric CC stretch is responsible for the B_2 symmetry mode at 1538 cm^{-1} with a large intensity of 76.6 km/mol, and a symmetric CC stretch is responsible for the A_1 symmetry band at 1692 cm^{-1} with an intensity of 61.8 km/mol. Further refinement of the vibrational spectra incorporating anharmonicity and a dipole moment surface for the intensities would provide more accurate vibrational frequencies but is beyond the scope of this work.

Table 5 reports the harmonic vibrational frequencies, with corresponding normal mode symmetries, of the C_s symmetry planar isomers – furfuryl (**2**), 3-methylene furanium (**3**), and hydroxy-cyclopentadiene (**4**) cations. **2** has one large-intensity C-O feature near the C-O stretching region at 1497 cm^{-1} (intensity 134 km/mol), and a few medium intensity features – one at 845 cm^{-1} and another at 1460 cm^{-1} stand out.

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The vibrational frequencies of the C_s symmetry non-planar (two hydrogen atoms out-of-plane) isomers (**5,6,7**) are presented in Table 6. These vibrational frequencies should be useful for identification of the corresponding isomers in future laboratory experiments and in the interstellar medium.

III.F. *Electronic spectra*

Electronic excitation spectra of the 7 isomers of $C_5H_5O^+$ were computed using the range-separated ωB97X density functional with the cc-pVTZ basis set at the CCSD(T)/cc-pVTZ optimized geometries. The electronic excitation lines are plotted against wavelength (in nm) in Figure 3 (a table of excitation energies is given in the Supplementary Material). Pyrylium cation, **1**, has two large intensity excitation peaks: one at 162 nm with oscillator strength 0.5, and the other at 237 nm with oscillator strength 0.1. These oscillator strengths are significantly larger – mainly due to the presence of heteroatom oxygen – compared to the oscillator strengths of electronic transitions of benzene. Furfuryl ion (**2**) also has two strong – but weaker than **1** – electronic excitations: one at 242 nm with oscillator strength of 0.25, and the other at 264 nm with an oscillator strength of 0.22. The 3-methylene-furan cation, **3**, has three relatively strong electronic excitations: the first and most intense one at 170 nm with oscillator strength of 0.4; the second one at 215 nm with 0.25; and the third one at 325 nm with 0.1 oscillator strength.

Some of the electronic transitions for pyrylium cation, **1**, possess large oscillator strengths due to an n to π* type transition from an oxygen lone-pair to the π* of the aromatic ring. These oscillator strengths of transitions for absorption lines are large

enough that they can be observed easily. We have seen earlier[15] that the agreement between the positions of the excitation transitions estimated using time dependent density functional theory and those estimated using the EOM-CCSD method are within 0.3 eV if they are not of the charge transfer type excitation. Furthermore, these excitation transitions, computed using a range separated density functional ωB97X, are not affected by charge transfer type excitation, and thus should be reliable.

IV.   Concluding remarks

We have studied the structures, relative energies, association energies and spectroscopic properties of the seven lowest energy isomers on the potential energy surface of $C_5H_5O^+$. The global minimum, pyrylium cation, **1**, is an oxygen containing six-membered carbocyclic ring. The second lowest-energy isomer, **2**, the furfuryl cation (2-methylene-furanium cation) is only 16 kcal/mol above **1**. Curtis et al. proposed that **2** is the 81 amu fragment unit formed during DART analysis of deoxyribose decomposition. The accurate structural parameters, and rotational, vibrational, and electronic spectra computed in this work may be useful to identify these two very important isomers from laboratory experimental data.

Another aspect of this research was to compare lower level methods such as MP2 and density functional theory (B3LYP) with the results obtained from the state-of-the-art coupled cluster theory methods (CCSD(T)). In all cases the agreement, in predicting relative energies, between the CCSD(T)/cc-pVQZ, CCSD(T)/cc-pVTZ, MP2/cc-pVTZ and B3LYP/cc-pVTZ levels of theories is good. B3LYP comes very close to predicting the relative energies predicted by CCSD(T) using the same basis set, cc-pVTZ. MP2, in

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all cases, slightly overestimates the relative energies (by up to thirteen percent in the case of the hydroxy-cyclopentadiene isomer) when compared with the CCSD(T) results.

Experimentally obtained rotational constants of benzene are 5.68407 (0.18960 cm^{-1}), 5.68407 (0.18960 cm^{-1}) and 2.84203 (0.09480 cm^{-1}) GHz.[29] We computed the rotational constants of the isoelectronic pyrylium cation (**1**) to be (A) 5.9413, (B) 5.7784 and (C) 2.9294 GHz. The A and B rotational constants, although not identical due to the oxygen substitution, are very close to the rotational constants of benzene. The rotational constants of **1**, although in the vicinity of benzene, are sufficiently different to allow for identification. The experimentally obtained rotational constants of ^{13}-C-pyridine are (A) 5.9629, (B) 5.7587 and (C) 2.9289 GHz.[27] **1** could, therefore, be distinguished from benzene and pyridine, and identified by rotational spectroscopy. Thus these rotational constants may be useful in the future detection of **1** in the interstellar medium or in laboratory studies.

V.   **Acknowledgements**

VI.   Tables

Table 1. Table of relative energies (kcal/mol) of the isomers of $C_5H_5O^+$.

	Isomer	B3LYP/ cc-pVTZ	MP2/ cc-pVTZ	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVQZ*
1	pyrylium	0.0	0.0	0.0	0.0
2	2-methylene-furanium	16.2	18.6	16.0	16.0
3	3-methylene-furanium	27.0	28.3	25.3	25.4
4	hydroxy-cyclopentadiene	30.1	31.0	26.1	25.8
5	cyclopentenone	37.5	41.5	37.3	37.3
6	methyl cyclopropyl ketone	59.6	62.2	59.6	59.2
7	meta-cyclopentenone	66.0	70.8	65.0	64.5

 * Energies calculated using the CCSD(T)/cc-pVTZ optimized geometries

Table 2. Rotational constants (GHz) and dipole moments (a.u.) of isomers of $C_5H_5O^+$ calculated using CCSD(T)/cc-pVTZ on the optimized geometries obtained at the same level of theory

	Isomer	Rotational Constants (GHz)			Dipole Moment (Debye)
		A	B	C	
1	pyrylium	5.9413	5.7784	2.9294	0.94
2	2-methylene-furanium	8.6123	3.9599	2.7136	0.99
3	3-methylene-furanium	8.6105	3.7948	2.6345	2.38
4	hydroxy-cyclopentadiene	7.9284	3.8186	2.5773	1.65
5	cyclopentenone	7.8460	3.7349	2.5704	4.01
6	methyl-cyclopropyl ketone	7.7397	2.5952	2.2536	6.03
7	meta-cyclopentenone	7.8811	3.6855	2.5488	3.28

Table 3. Association energies (kcal/mol) of fragments leading to pyrylium cation. Molecules in italics have observed in the ISM.

Fragments		B3LYP/ cc-pVTZ	MP2/ cc-pVTZ	CCSD(T)/ cc-pVTZ
$HCCHCH^+$	*HCCHO*	108.5	123.4	115.8
$HCCHCHO^+$	*HCCH*	137.8	139.5	136.5
C_4H_4	HCO^+	152.2	151.6	140.8
$HCCHOCH^+$	*HCCH*	229.6	221.3	205.2
$C_4H_4^+$	*HCO*	138.3	141.4	141.0
$HCCHCHO$	$HCCH^+$	200.2	206.6	203.9

Table 4. Vibrational frequencies (cm^{-1}) of the pyrylium cation, **1**, computed at the MP2/cc-pVTZ level of theory; intensities in italics in km/mol.

Pyrylium cation		
Symmetry	Frequency	*Intensity*
A_2	380	*0.0*
B_1	379	*2.0*
A_1	583	*5.2*
B_2	660	*0.0*
B_1	682	*47.7*
B_1	788	*45.2*
A_2	914	*0.0*
A_1	982	*25.5*
B_1	983	*0.5*
A_2	1009	*0.0*
A_1	1045	*1.5*
B_1	1058	*0.2*
B_2	1084	*0.4*
A_1	1087	*1.3*
B_2	1193	*3.1*
A_1	1244	*1.7*
B_2	1330	*0.1*
B_2	1389	*0.3*
A_1	1499	*12.3*
B_2	1525	*80.1*

B_2	1620	*12.7*
	1670	*60.2*
A_1		
	3241	*1.7*
A_1		
	3261	*4.2*
B_2		
	3264	*28.5*
A_1		
	3276	*41.8*
B_2		
	3379	*3.5*
A_1		

Table 5. Vibrational frequencies (cm^{-1}) of the planar C_s isomers of $C_5H_5O^+$ computed at the MP2/cc-pVTZ level of theory; intensities, in *italics*, are expressed in km/mol.

isomer	**2**		**3**		**4**	
name	2-methyl-furanium		3-methyl-furanium		hydroxy-cyclopentadiene	
Symmetry	Freq	Int	Freq	Int	Freq	Int
A″	223	*12.5*	204	*2.9*	186	*3.62*
A′	344	*5.4*	324	*0.4*	432	*11.6*
A″	500	*7.9*	501	*8.4*	390	*5.4*
A″	633	*9.3*	633	*31.6*	660	*45.1*
A′	713	*3.1*	696	*3.1*	657	*1.0*
A″	755	*1.7*	694	*0.2*	722	*15.9*
A″	845	*44.4*	807	*39.5*	808	*42.0*
A′	875	*1.7*	841	*4.4*	686	*19.9*
A′	902	*38.6*	946	*20.1*	893	*10.9*
A′	959	*5.3*	979	*4.4*	965	*2.1*
A″	978	*1.5*	901	*0.0*	841	*135.7*
A″	996	*0.6*	948	*7.4*	970	*0.3*
A″	1044	*25.8*	1093	*20.9*	979	*0.1*
A′	1090	*15.1*	999	*19.1*	1101	*86.7*
A′	1120	*11.7*	1129	*16.2*	1113	*3.5*
A′	1251	*8.2*	1273	*109.0*	1121	*19.8*
A′	1263	*19.6*	1283	*53.4*	1303	*29.6*
A′	1383	*33.1*	1401	*20.3*	1353	*60.4*
A′	1460	*44.6*	1466	*7.7*	1368	*163.2*
A′	1497	*134.3*	1520	*118.5*	1574	*26.2*
A′	1547	*12.9*	1586	*32.3*	1633	*22.3*
A′	1712	*54.5*	1701	*60.8*	1673	*306.3*
A′	3196	*24.6*	3183	*9.2*	3266	*3.1*
A′	3272	*11.2*	3267	*31.2*	3275	*15.3*
A′	3279	*28.9*	3293	*11.3*	3291	*28.7*
A′	3306	*29.5*	3299	*24.5*	3304	*24.1*
A′	3311	*20.5*	3330	*28.5*	3661	*338.3*

Table 6. Vibrational frequencies (cm^{-1}) of the higher isomers of C$_5$H$_5$O$^+$ calculated at the MP2/cc-pVTZ level of theory; intensities, in *italics*, are expressed in km/mol.

isomer	**5**		**6**		**7**	
name	cyclopentenone ion		methyl-cyclopropyl ketone ion		meta-cyclopentenone ion	
Symmetry	Freq	Int	Freq	Int	Freq	Int
A″	137	*6.5*	44	*0.1*	120	*0.2*
A″	264	*0.9*	125	*0.0*	225	*11.5*
A′	447	*5.0*	147	*13.6*	435	*11.5*
A″	447	*12.1*	220	*0.0*	523	*22.2*
A′	642	*4.1*	373	*12.6*	628	*11.1*
A′	768	*0.0*	573	*8.7*	752	*10.6*
A″	769	*19.3*	540	*0.1*	558	*14.6*
A′	829	*0.2*	638	*33.7*	828	*23.3*
A″	873	*12.7*	868	*30.5*	814	*35.5*
A′	978	*34.2*	955	*13.3*	944	*2.3*
A″	1012	*3.3*	994	*24.4*	992	*2.5*
A″	1057	*3.6*	1008	*7.7*	1006	*2.7*
A′	1105	*5.4*	1003	*0.5*	969	*24.9*
A′	1121	*13.8*	1053	*0.0*	1114	*0.3*
A′	1164	*15.3*	1175	*151.2*	1180	*9.9*
A″	1177	*0.5*	1272	*26.1*	1117	*0.0*
A′	1304	*10.6*	1385	*9.9*	1248	*88.5*
A′	1360	*74.5*	1406	*24.8*	1299	*31.0*
A′	1374	*38.3*	1463	*18.6*	1356	*47.3*
A′	1494	*54.4*	1476	*16.7*	1402	*5.3*
A′	1551	*122.7*	1697	*22.8*	1614	*26.7*
A′	1754	*40.8*	1791	*75.1*	1658	*57.2*
A′	3061	*70.0*	3073	*12.1*	2968	*84.7*
A″	3102	*25.1*	3157	*0.9*	2978	*47.1*
A′	3226	*9.3*	3209	*5.2*	3216	*19.9*
A′	3244	*21.2*	3282	*99.2*	3263	*1353*
A′	3279	*24.5*	3320	*44.9*	3287	*26.4*

VII. Figures

Figure 1. Optimized structure of the pyrylium cation, **1**, (the global minimum) is presented at the CCSD(T)/cc-pVTZ level of theory. Bond lengths are in Angstroms and angles are in degrees.

Figure 2. Optimized structure of the next 6 lowest energy isomers of $C_6H_5O^+$, at the CCSD(T)/cc-pVTZ level of theory. In ascending energy order, these isomers are 2-methylene furanium ion or furfuryl cation (**2**), 3-methyl-furanium (**3**), hydroxy-cyclopentadiene (**4**), cyclopentenone ion (**5**), methyl-cyclopropyl ketone ion (**6**), and meta-cyclopentenone ion (**7**). Bond lengths are in Angstroms and bond angles are in degrees.

Figure 3. Electronic excitation lines of the pyrylium cation and its 6 higher isomers, computed at the ωB97x/cc-pVTZ level theory. In the X-axis is wavelength (in nm) and in the Y-axis is oscillator strength in arbitrary units.

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