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# Pinning the most stable $H_xC_yO_z$ isomers in space by means of high-level theoretical procedures

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## ABSTRACT

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It has been recently demonstrated that there is a high statistical correlation between the relative energies of isomers and their relative abundances in the interstellar medium (ISM). In the present work we use the high-level W2–F12 thermochemical protocol to obtain accurate isomerization energies for a set of 109  $H_xC_yO_z$  isomers, 18 of which have been observed in the ISM so far. We use our benchmark isomerization energies to (i) rationalize the presence of the isomers that have been detected, and (ii) predict which new isomers are likely to be detected in the future. We find that the energetically most stable isomers of  $H_2C_3O$  (1,2-propadien-1-one),  $H_8C_3O$  (2-propanol), and  $H_6C_3O_2$  (propanoic acid) have not been observed, despite the fact that higher-energy isomers of these chemical formulas have been detected in the ISM. The dipole moments of these isomers are sufficiently large that these species should be observed using microwave spectroscopy techniques.

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Keywords: organic molecules • interstellar medium • isomerization energies • computational thermochemistry • W2–F12 theory

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## 1. Introduction

The search for organic molecules in the ISM is an important branch of astrochemistry that has been gaining increasing attention over the past two decades.<sup>1,2,3,4,5</sup> To date, about 180 molecules have been detected in our galaxy, about 30% of which are organic molecules containing 6–13 atoms.<sup>6</sup> This total, which is constantly increasing, does not include numerous isotopologues (e.g. of <sup>2</sup>H, <sup>13</sup>C, and <sup>18</sup>O). Each new molecule that is identified in the ISM is an additional piece in the very large puzzle of how organic molecules are being synthesized in space. However, this puzzle is far from complete.<sup>1,2,3,4,5</sup>

Recently, Lattalais *et al.*<sup>7,8</sup> calculated the relative energies of molecules that have been detected in the ISM in two or more isomeric forms. They showed that, with few exceptions, (i) the most abundant isomers of the same chemical formula are the most stable isomers, and (ii) there is a statistical correlation between the relative energies of the isomers and their observed abundances in certain regions of the ISM. They called this relationship between the observed abundances and relative energies of the isomers the “minimum energy principle” (MEP).

In the present work, we obtain accurate isomerization energies for a set of 109  $H_xC_yO_z$  isomers by means of the high-level W2–F12 composite thermochemical protocol.<sup>9</sup> W2–F12 represents a layered extrapolation to the relativistic, all-electron CCSD(T) (coupled cluster with singles, doubles, and quasiperturbative triple excitations) basis-set-limit energy, and can achieve ‘benchmark accuracy’ (arbitrarily defined as 1 kJ mol<sup>-1</sup>) for isomerization energies.<sup>9,10</sup>

The isomers of 14 chemical formulas are considered:  $H_2C_2O$ ,  $H_4C_2O$ ,  $H_6C_2O$ ,  $H_2C_2O_2$ ,  $H_4C_2O_2$ ,  $H_6C_2O_2$ ,  $H_2C_3O$ ,  $H_4C_3O$ ,  $H_6C_3O$ ,  $H_8C_3O$ ,  $H_2C_3O_2$ ,  $H_4C_3O_2$ ,  $H_6C_3O_2$ , and  $H_8C_3O_2$ . To date, isomers of ten of these  $H_xC_yO_z$  molecular formulas have been detected in the ISM. We show that the isomers of  $H_2C_3O$ ,  $H_8C_3O$ , and  $H_6C_3O_2$  that have been detected in the ISM are not the most stable isomers. The more stable isomers are lower in energy than the lowest-laying isomer that has been detected by 2.5 (1,2-propadien-1-one,  $H_2C_3O$ ), 53.4 (2-propanol,  $H_8C_3O$ ), 36.6 (1-propanol,  $H_8C_3O$ ), and 41.5 (propanoic acid,  $H_6C_3O_2$ ) kJ mol<sup>-1</sup>. We also find that one isomer of  $H_4C_2O_2$  (1,1-ethenediol) is more stable by 3.2 kJ mol<sup>-1</sup> than an  $H_4C_2O_2$  isomer that has been detected in the ISM (glycoaldehyde). These results suggest that the abovementioned (yet undetected) isomers are likely to exist in the ISM, and that their spectroscopic signatures should be searched for in the ISM.

## 2. Computational Methods

In order to obtain reliable isomerization energies, calculations have been carried out using the high-level, ab initio W2–F12 procedure with the Molpro 2012.1 program suite.<sup>11</sup> W2–F12 theory<sup>9</sup> (and its earlier versions W2 and W2.2 theories<sup>12,13</sup>) represent layered extrapolations to the CCSD(T) infinite basis-set-limit energy. These composite theories include scalar-relativistic, first-order spin-orbit coupling, diagonal Born–Oppenheimer, zero-point vibrational energy, and enthalpic corrections and can achieve ‘near-benchmark accuracy’ for atomization reactions (e.g., W2–F12 theory is associated with a mean absolute deviation of 1.3 kJ mol<sup>-1</sup> for a set of 140 very accurate atomization energies).<sup>9,10,12,13,14,15,16</sup> Nevertheless, it should be pointed out that for isomerization reactions these theories yield even better performance due to a larger degree of systematic error cancelation between reactants and products.<sup>10,16,17,18,19</sup>

W2–F12 theory combines explicitly correlated F12 methods<sup>20</sup> with extrapolation techniques in order to approximate the CCSD(T) basis-set-limit energy. Due to the drastically accelerated basis-set convergence of the F12 methods,<sup>21,22</sup> W2–F12 is superior to the original W2 and W2.2 methods in terms of computational cost.<sup>9</sup> The computational protocol of the W2–F12 method has been specified and rationalized in detail in Ref. 9. In brief, the Hartree–Fock component is calculated with the VQZ-F12 basis set (where VQZ-F12 denotes the cc-pVQZ-F12 basis set of Peterson *et al.*,<sup>21</sup> that was specifically developed for explicitly correlated calculations). Note that the complementary auxiliary basis (CABS) singles correction is included in the SCF energy.<sup>23,24,25</sup> The valence CCSD-F12 correlation energy is extrapolated from the VTZ-F12 and VQZ-F12 basis sets, using the  $E(L) = E_\infty + A/L^\alpha$  two-point extrapolation formula, with  $\alpha = 5.94$ . Optimal values for the geminal Slater exponents ( $\beta$ ) used in conjunction with the VnZ-F12 basis sets were taken from Ref. 22. The quasiperturbative triples, (T), corrections are obtained from standard CCSD(T)/VTZ-F12 calculations (i.e., without inclusion of F12 terms) and scaled by the factor  $f = 0.987 \times E^{\text{MP2-F12}}/E^{\text{MP2}}$ . This approach has been shown to accelerate the basis set convergence.<sup>9,26</sup> In all of the explicitly correlated coupled cluster calculations the diagonal, fixed-amplitude 3C(FIX) ansatz<sup>24,27,28,29</sup> and the CCSD-F12b approximation are employed.<sup>25,26</sup> The CCSD inner-shell contribution is calculated with the core-valence weighted correlation-consistent aug'-cc-pwCVTZ basis set of Peterson and Dunning,<sup>30</sup> whilst the (T) inner-shell contribution is calculated with the cc-pwCVTZ(no f) basis set (where cc-pwCVTZ(no f) indicates the cc-pwCVTZ basis set without the f functions). The scalar relativistic contribution (in the second-order Douglas–Kroll–Hess approximation)<sup>31,32</sup> is obtained as the difference between non-

relativistic CCSD(T)/A'VDZ and relativistic CCSD(T)/A'VDZ-DK calculations.<sup>33</sup> The diagonal Born–Oppenheimer corrections are calculated at the HF/A'VTZ level of theory using the CFOUR program suite.<sup>34</sup>

The geometries of all structures have been obtained at the B3LYP–D3/A'VTZ level of theory,<sup>35,36</sup> where A'VTZ indicates the combination of the standard correlation-consistent cc-pVTZ basis sets<sup>37</sup> on H, and the aug-cc-pVTZ basis sets<sup>38</sup> on C and O. Harmonic vibrational analyses have been performed to confirm each stationary point as an equilibrium structure (i.e., all real frequencies). Zero-point vibrational energy and enthalpic corrections have been obtained from such calculations. Unless otherwise indicated, only the lowest-energy conformer is being considered. All geometry optimizations and frequency calculations were performed using the Gaussian 09 program suite.<sup>39</sup>

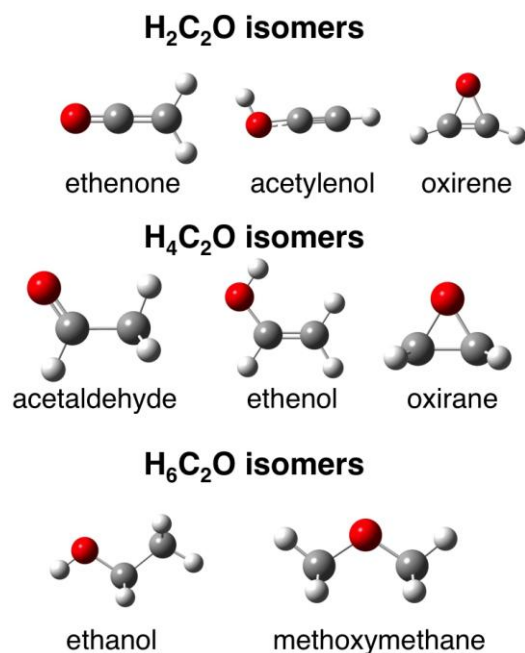
### 3. Results and Discussion

#### 3.1. Isomers observed in the interstellar medium

**3.1.1.  $H_{2n}C_2O$  isomers.** Table 1 summarizes the relative enthalpies at 0 K ( $\Delta H_{0K}$ ) for the  $H_{2n}C_2O$  isomers ( $n = 1-3$ ). The  $H_{2n}C_2O$  isomers are shown in Fig. 1. The three  $H_2C_2O$  isomers span a relatively wide energetic range. The W2–F12 relative energies are: 0.0 (ethenone), 140.5 (acetylenol), and 317.6 (oxirene) kJ mol<sup>-1</sup>. Of these, ethenone is the only isomer that has been detected in the ISM, specifically in the galactic Sgr B2(OH) region,<sup>40</sup> dark clouds,<sup>41</sup> translucent clouds,<sup>42</sup> and Orion.<sup>43</sup>

**Table 1.** Isomerization enthalpies at 0 K ( $\Delta H_0$ , W2–F12, kJ mol<sup>-1</sup>) and dipole moments (B3LYP–D3/A'VTZ, Debye) for the  $H_{2n}C_2O$  isomers ( $n = 1-3$ ).

Formula	Isomer	$\Delta H_0$	$\mu$	Detected
$H_2C_2O^a$	ethenone	0.0	1.52	[40,41,42,43]
	acetylenol	140.5	1.65	
	oxirene	317.6	2.41	
$H_4C_2O$	acetaldehyde	0.0	2.88	[44,45,46,47,48]
	ethenol	41.7	0.97	[49]
	oxirane	114.8	1.93	[50,51,52]
$H_6C_2O$	ethanol	0.0	1.58	[53,54]
	methoxymethane	50.9	1.28	[54,55,56,57]



**Fig. 1.** B3LYP–D3/A'VTZ optimized geometries for the H<sub>2n</sub>C<sub>2</sub>O isomers ( $n = 1–3$ ). Atomic color scheme: H, white; C, gray; O, red.

The three H<sub>4</sub>C<sub>2</sub>O isomers span a much narrower energetic range of 114.8 kJ mol<sup>-1</sup> (Table 1), and all three isomers have been observed in the ISM. Acetaldehyde, the most stable isomer, was one of the early polyatomic molecules to be detected in space. It has been detected in the Sagittarius constellation,<sup>44</sup> Sgr B2 molecular cloud,<sup>45,46</sup> cold dust clouds,<sup>47</sup> and translucent clouds.<sup>48</sup> Ethenol is higher in energy than acetaldehyde by 41.7 kJ mol<sup>-1</sup>, and has been detected in the Sgr B2(N) molecular cloud near the center of the Milky Way galaxy.<sup>49</sup> The cyclic oxirane isomer is the least stable H<sub>4</sub>C<sub>2</sub>O isomer (114.8 kJ mol<sup>-1</sup>), and has been detected in Sagittarius B2(N),<sup>50</sup> the hot core (HII) region,<sup>51</sup> and galactic center molecular clouds.<sup>52</sup>

Ethanol, the lowest-energy H<sub>6</sub>C<sub>2</sub>O isomer, has been detected in the star-forming region Sagittarius B2(OH),<sup>53</sup> and in galactic center molecular clouds.<sup>54</sup> Methoxymethane, which lies 50.9 kJ mol<sup>-1</sup> above ethanol, has been detected in galactic center molecular clouds,<sup>54</sup> Orion,<sup>55</sup> and hot cores.<sup>56,57</sup>

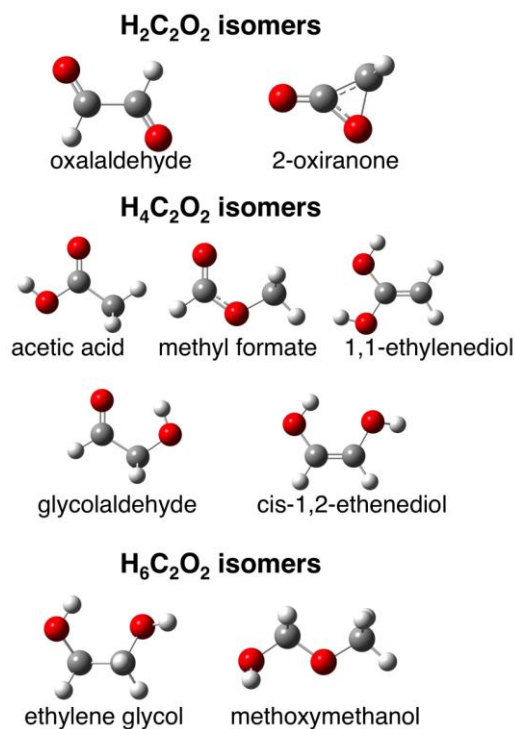
**3.1.2.  $H_{2n}C_2O_2$  isomers.** The relative isomerization enthalpies ( $\Delta H_0$ ) for the  $H_{2n}C_2O_2$  isomers ( $n = 1-3$ ) are given in Table 2. The isomers are shown in Fig. 2. The two  $H_2C_2O_2$  isomers oxalaldehyde and 2-oxiranone are separated by  $42.5 \text{ kJ mol}^{-1}$ . Oxalaldehyde (also known as glyoxal) has no permanent dipole moment and therefore cannot be detected by radio astronomy techniques. To date, 2-oxiranone has not been detected in the ISM.

**Table 2.** Isomerization enthalpies at 0 K ( $\Delta H_0$ , W2-F12,  $\text{kJ mol}^{-1}$ ) and dipole moments (B3LYP-D3/A'VTZ, Debye) for the  $H_{2n}C_2O_2$  isomers ( $n = 1-3$ ).

Formula	Isomer	$\Delta H_0$	$\mu$	Detected
$H_2C_2O_2^a$	oxalaldehyde	0.0	0.00	
	2-oxiranone	42.5	3.37	
$H_4C_2O_2^a$	acetic acid	0.0	1.79	[58,59]
	methyl formate	72.1	1.95	[54,56,60]
	1,1-ethenediol	110.5	1.72	
	glycolaldehyde	113.7	2.45	[52,61,62,63,64,65]
	cis-1,2-ethenediol <sup>b</sup>	144.7	2.37	
$H_6C_2O_2^a$	ethylene glycol	0.0	2.41	[52,66,67,68]
	methoxymethanol	27.8	2.08	

<sup>a</sup>See the supplementary data for isomers with relative energies  $> 150 \text{ kJ mol}^{-1}$ .

<sup>b</sup>The relative energy of the trans-1,2-ethenediol isomer is  $163.3 \text{ kJ mol}^{-1}$ .



**Fig. 2.** B3LYP–D3/A'VTZ optimized geometries for the H<sub>2n</sub>C<sub>2</sub>O<sub>2</sub> isomers ( $n = 1–3$ ). Atomic color scheme: H, white; C, gray; O, red.

Acetic acid is the most stable H<sub>4</sub>C<sub>2</sub>O<sub>2</sub> isomer, and has been detected in the Sagittarius B2 North Large Molecule Heimat (Sgr B2(N-LMH)) star-forming region,<sup>58</sup> as well as in the W51e2 hot core.<sup>59</sup> Methyl formate is higher in energy by 72.1 kJ mol<sup>-1</sup>, and has been detected in molecular clouds,<sup>54,60</sup> and hot core regions.<sup>56</sup> Lattalais *et al.*<sup>7,8</sup> noted that the higher relative abundance of methyl formate is one of the few exceptions of the MEP principle. The next two isomers on the potential energy surface are 1,1-ethenediol (110.7 kJ mol<sup>-1</sup>) and glycolaldehyde (113.5 kJ mol<sup>-1</sup>). Despite the fact that 1,1-ethenediol is more stable than glycolaldehyde by 3.2 kJ mol<sup>-1</sup>, only the latter has been detected in the ISM so far. Specifically, in galactic center molecular clouds,<sup>52</sup> the Sgr B2(N-LMH) hot core region,<sup>61,62,63,64</sup> and solar-type protostars.<sup>65</sup>

The two lowest lying H<sub>6</sub>C<sub>2</sub>O<sub>2</sub> isomers, ethylene glycol and methoxymethanol, are separated by 27.8 kJ mol<sup>-1</sup>. Ethylene glycol, the energetically more stable isomer, has been detected in galactic center molecular clouds,<sup>52</sup> in the outflow of the comet Hale-Bopp,<sup>66</sup> and in the Sgr B2(N-LMH) region.<sup>67,68</sup>



**3.1.3.  $H_{2n}C_3O$  isomers.** Table 3 summarizes the isomerization enthalpies ( $\Delta H_{0K}$ ) for the  $H_{2n}C_3O$  isomers ( $n = 1-4$ ). Fig. 3 shows selected low-energy isomers. The three  $H_2C_3O$  isomers (1,2-propadien-1-one, propiolaldehyde, and 2-cyclopropen-1-one) span a narrow energetic range of only  $29.2 \text{ kJ mol}^{-1}$ . 1,2-Propadien-1-one (also known as 1-allenone) is the energetically most stable isomer. Propiolaldehyde is higher in energy by just  $2.5 \text{ kJ mol}^{-1}$ , and the strained 2-cyclopropen-1-one isomer is higher in energy by  $29.2 \text{ kJ mol}^{-1}$ . Interestingly, only propiolaldehyde and 2-cyclopropen-1-one have been detected in the ISM. Propiolaldehyde was the first aldehyde to be detected in the ISM, specifically in the cold cloud TMC-1,<sup>69</sup> and later towards the Sgr B2(N)<sup>70</sup> and galactic center molecular clouds.<sup>52</sup> 2-Cyclopropen-1-one has been detected toward Sgr B2(N) molecular cloud.<sup>71</sup>

The two most stable  $H_4C_3O$  isomers, acrylaldehyde and 1-propen-1-one, are nearly isoenergetic. 1-propen-1-one lies just  $1.2 \text{ kJ mol}^{-1}$  above acrylaldehyde. So far, only acrylaldehyde has been detected in the ISM, specifically towards the Sgr B2(N)<sup>70</sup> and the galactic center molecular clouds.<sup>52</sup>

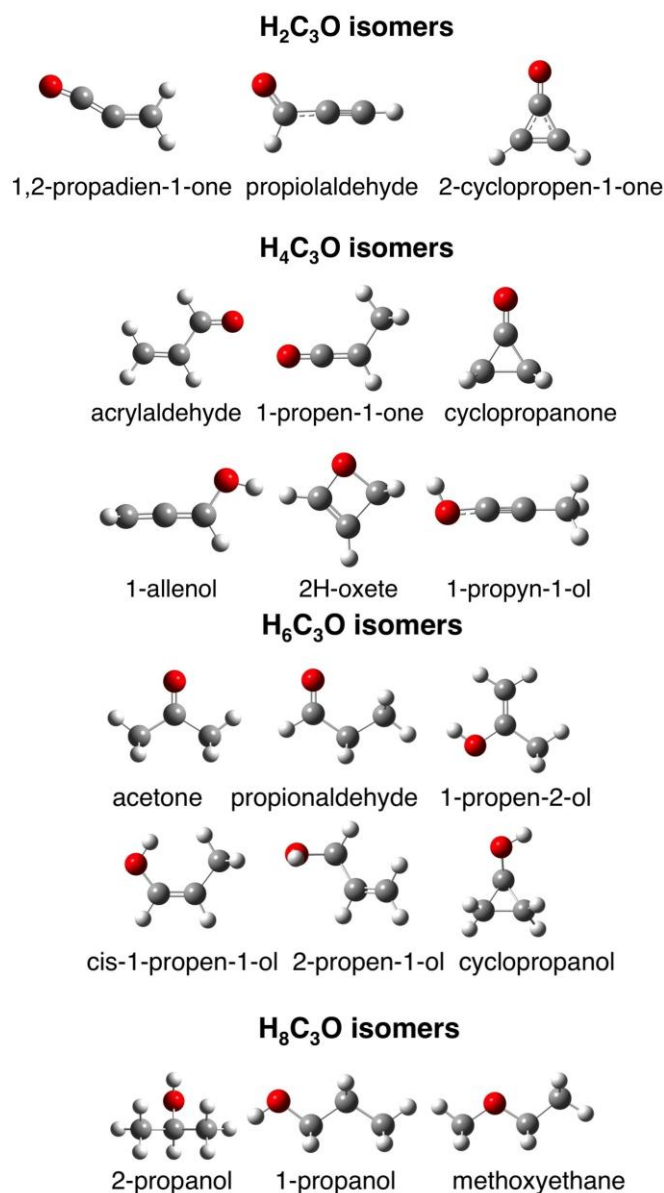
**Table 3.** Isomerization enthalpies at 0 K ( $\Delta H_0$ , W2-F12, kJ mol<sup>-1</sup>) and dipole moments (B3LYP-D3/A'VTZ, Debye) for the H<sub>2n</sub>C<sub>3</sub>O isomers ( $n = 1-4$ ).

Formula	Isomer	$\Delta H_0$	$\mu$	Detected
H <sub>2</sub> C <sub>3</sub> O	1,2-propadien-1-one	0.0	2.56	
	propionaldehyde	2.5	3.00	[52,69,70]
	2-cyclopropen-1-one	29.2	4.33	[71]
H <sub>4</sub> C <sub>3</sub> O <sup>a</sup>	acrylaldehyde <sup>b</sup>	0.0	3.40	[52,70]
	1-propen-1-one	1.2	1.95	
	cyclopropanone	84.8	3.03	
	1-allenol	109.6	1.61	
	2H-oxete	119.4	1.37	
	1-propyn-1-ol	120.5	1.45	
	2-propyn-1-ol	120.8	1.88	
	2-methyleneoxirane	128.6	1.73	
	acetone	0.0	3.08	[72,73,74]
	propionaldehyde	29.8	2.78	[52,70]
H <sub>6</sub> C <sub>3</sub> O	1-propen-2-ol	48.9	0.53	
	cis-1-propen-1-ol <sup>c</sup>	66.6	1.44	
	2-propen-1-ol	91.6	1.59	
	cyclopropanol	117.2	1.54	
	methoxyethene	119.6	1.73	
	2-methyloxirane	124.8	2.02	
	oxetane	139.6	1.99	
H <sub>8</sub> C <sub>3</sub> O	2-propanol	0.0	1.68	
	1-propanol	16.8	1.49	
	methoxyethane <sup>b</sup>	53.4	1.19	[75]

<sup>a</sup>See the supplementary data for isomers with relative energies > 150 kJ mol<sup>-1</sup>.

<sup>b</sup>Note that these detections are marked as tentative detections in Ref. 6.

<sup>c</sup>The relative energy of the trans-1-propen-1-ol isomer is 67.6 kJ mol<sup>-1</sup>.



**Fig. 3.** B3LYP–D3/A'VTZ optimized geometries for selected H<sub>2n</sub>C<sub>3</sub>O isomers ( $n = 1–4$ ). Atomic color scheme: H, white; C, gray; O, red.

Acetone is the most stable H<sub>6</sub>C<sub>3</sub>O isomer, it has been detected toward Sgr B2 cloud,<sup>72,73</sup> and towards the high-mass star-forming region Orion KL.<sup>74</sup> Propionaldehyde is higher in energy by 29.8 kJ mol<sup>-1</sup>, and has been detected towards the Sgr B2(N),<sup>70</sup> and the galactic center molecular clouds.<sup>52</sup>

The three saturated H<sub>8</sub>C<sub>3</sub>O isomers are: 2-propanol, 1-propanol, and methoxyethane. The most stable isomer is 2-propanol, followed by 1-propanol (16.8) and methoxyethane

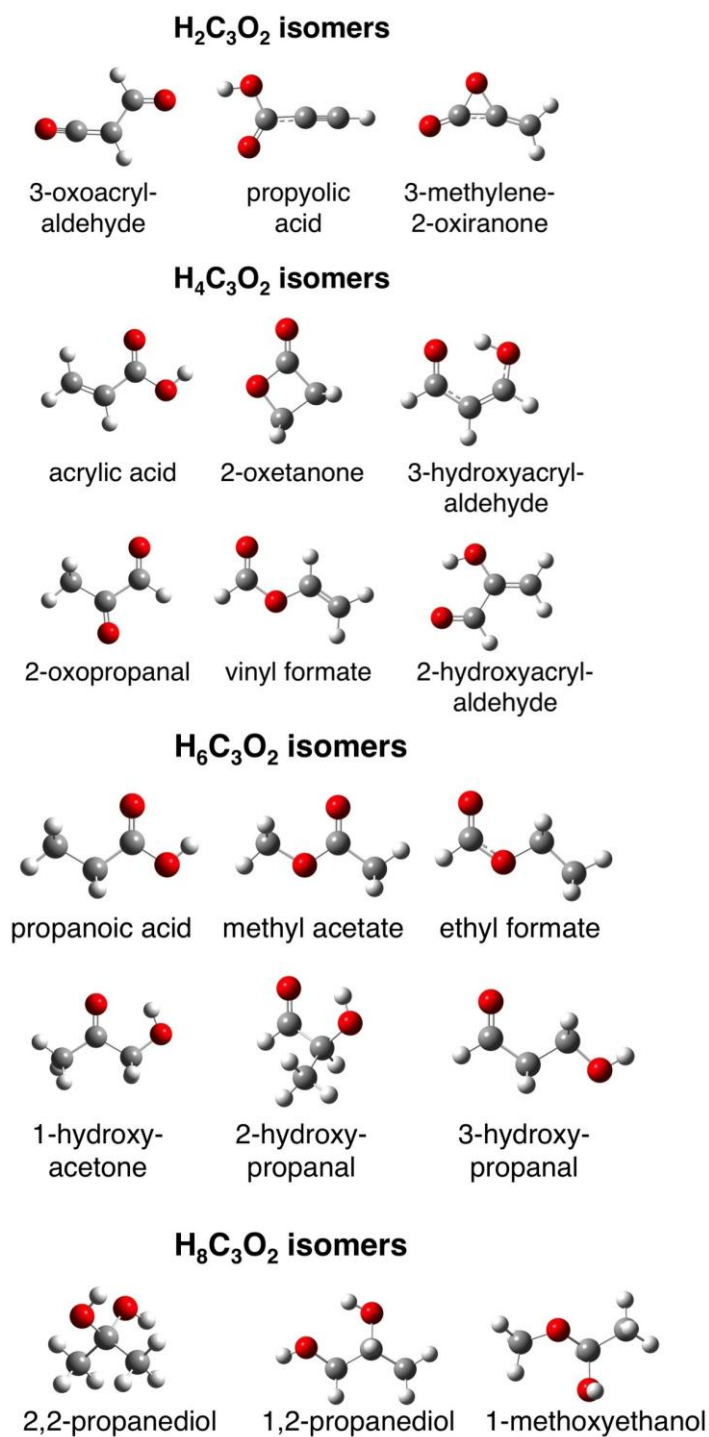
(53.4 kJ mol<sup>-1</sup>). So far, only the latter has been detected in the ISM, specifically, towards the W51e2 hot core.<sup>75</sup>

**3.1.4. H<sub>2n</sub>C<sub>3</sub>O<sub>2</sub> isomers.** The isomerization enthalpies for the H<sub>2n</sub>C<sub>3</sub>O<sub>2</sub> isomers ( $n = 1-4$ ) are summarized in Table 4, and selected low-lying isomers are depicted in Fig. 4. So far, none of the H<sub>2</sub>C<sub>3</sub>O<sub>2</sub>, H<sub>4</sub>C<sub>3</sub>O<sub>2</sub>, or H<sub>8</sub>C<sub>3</sub>O<sub>2</sub> isomers have been detected in the ISM. Very recently, the H<sub>6</sub>C<sub>3</sub>O<sub>2</sub> isomers, methyl acetate and ethyl formate, have been observed in Orion.<sup>76</sup> Ethyl formate has also been detected in the star-forming Sagittarius B2(N) region.<sup>77</sup> Nevertheless, propanoic acid, which is more stable than these isomers by appreciable amounts (specifically, 41.5 and 60.7 kJ mol<sup>-1</sup>, respectively) has not been detected.

**Table 4.** Isomerization enthalpies at 0 K ( $\Delta H_0$ , W2-F12, kJ mol<sup>-1</sup>) and dipole moments (B3LYP-D3/A'VTZ, Debye) for the H<sub>2n</sub>C<sub>3</sub>O<sub>2</sub> isomers ( $n = 1-4$ ).

<b>Formula</b>	<b>Isomer</b>	<b><math>\Delta H_0</math></b>	<b><math>\mu</math></b>	<b>Detected</b>
H <sub>2</sub> C <sub>3</sub> O <sub>2</sub> <sup>a</sup>	3-oxoacrylaldehyde	0.0	2.44	
	propionic acid	46.7	1.73	
	3-methylene-2-oxiranone	117.2	3.09	
H <sub>4</sub> C <sub>3</sub> O <sub>2</sub> <sup>a</sup>	acrylic acid	0.0	1.62	
	2-oxetanone	41.2	4.32	
	3-hydroxyacrylaldehyde	47.1	2.71	
	2-oxopropanal	48.8	1.06	
	vinyl formate	61.8	1.70	
	2-hydroxyacrylaldehyde	62.4	2.01	
	malonaldehyde	69.3	2.01	
	3-hydroxy-2-propenal	82.4	3.14	
	3-oxetanone	141.7	0.99	
	1,3-dioxole	144.8	0.54	
H <sub>6</sub> C <sub>3</sub> O <sub>2</sub> <sup>a</sup>	propanoic acid	0.0	1.65	
	methyl acetate	41.5	1.92	[76]
	ethyl formate	60.7	2.24	[76,77]
	1-hydroxyacetone	79.3	3.22	
	2-hydroxypropanal	98.6	2.58	
	3-hydroxypropanal	117.2	1.38	
	1-propene-1,2-diol	121.7	2.01	
	1-propene-1,1-diol	130.1	0.19	
	2-propene-1,2-diol	140.5	2.18	
1-propene-1,3-diol	145.5	2.95		
H <sub>8</sub> C <sub>3</sub> O <sub>2</sub> <sup>a</sup>	2,2-propanediol	0.0	2.34	
	1,2-propanediol	40.7	2.37	
	1-methoxyethanol	53.1	0.41	
	1,3-propandiol	58.1	3.52	
	ethoxymethanol	74.4	2.10	
	2-methoxyethanol	97.7	2.32	
	dimethoxymethane	140.7	2.42	

<sup>a</sup>See the supplementary data for isomers with relative energies > 150 kJ mol<sup>-1</sup>.



**Fig. 4.** B3LYP–D3/A'VTZ optimized geometries for selected H<sub>2n</sub>C<sub>3</sub>O<sub>2</sub> isomers ( $n = 1-4$ ). Atomic color scheme: H, white; C, gray; O, red.

### 3.2. New isomers that are likely to exist in the ISM

Based on our W2–F12 benchmark isomerization energies (Tables 1–4) and the MEP principle outlined by Lattelais *et al.*,<sup>7,8</sup> we can predict which of the  $H_xC_yO_z$  isomers that have not been observed are likely to exist in the ISM. We can group the undetected isomers into two classes:

- 1) Undetected isomers that are energetically more stable than isomers of the same chemical formula that have been detected in the ISM. According to the MEP principle there is a high probability that isomers that belong to this class will be present in the ISM (or otherwise, their absence should be explained based on kinetics arguments).<sup>7,8</sup> This class of isomers is discussed in Section 3.2.1.
- 2) To date, isomers of  $H_2C_2O$ ,  $H_4C_2O$ ,  $H_6C_2O$ ,  $H_4C_2O_2$ ,  $H_6C_2O_2$ ,  $H_2C_3O$ ,  $H_4C_3O$ ,  $H_6C_3O$ ,  $H_8C_3O$ , and  $H_6C_3O_2$  have been detected in the ISM (Tables 1–4). Of these, the isomers with the highest isomerization energies are oxirane (114.8, Table 1) and glycoaldehyde (113.7  $\text{kJ mol}^{-1}$ , Table 2). These relative energies may serve as an empirical guide as to which  $H_xC_yO_z$  isomers are likely to be present in the ISM. Thus, the second class of undetected isomers consists of isomers with isomerization energies below 115  $\text{kJ mol}^{-1}$ . This class of isomers is discussed in Section 3.2.2.

**3.2.1. Undetected isomers that are energetically more stable than isomers that have been detected.** We find five species in this class of isomers. Three of which are the energetically most stable isomers of their chemical formula, namely: 1,2-propadien-1-one ( $H_2C_3O$ ), 2-propanol ( $H_8C_3O$ ), and propanoic acid ( $H_6C_3O_2$ ). The other two are not the lowest-energy isomers, but still lie lower in energy than isomers that have been detected, namely: 1,1-ethenediol ( $H_4C_3O_2$ ) and 1-propanol ( $H_8C_3O$ ). We make the following observations:

- i) **1,2-Propadien-1-one.** The three  $H_2C_3O$  isomers (Table 3, Fig. 3) and their relative energies are: 1,2-propadien-1-one (0.0), propionaldehyde (2.5), and 2-cyclopropen-1-one (29.2  $\text{kJ mol}^{-1}$ ). The latter two have been detected in the ISM. However, the most stable isomer (1,2-propadien-1-one) has not yet been observed. Based on the small energy difference between 1,2-propadien-1-one and propionaldehyde the MEP principle predicts that both isomers should have similar abundances.
- ii) **2-Propanol and 1-propanol.** The three saturated  $H_8C_3O$  isomers (Table 3, Fig. 3) and their relative energies are: 2-propanol (0.0), 1-propanol (16.8), and methoxyethane (53.4  $\text{kJ mol}^{-1}$ ). Of these, only the least stable isomer has been

detected in the ISM. Given the relatively large energy separations between methoxyethane and the more stable isomers, we expect that 2-propanol (and to a lesser extent also 1-propanol) should be present in the ISM.

- iii) **Propanoic acid.** The three most stable  $\text{H}_6\text{C}_3\text{O}_2$  isomers (Table 4, Fig. 4) and their relative energies are: propanoic acid (0.0), methyl acetate (41.5), and ethyl formate (60.7  $\text{kJ mol}^{-1}$ ). Very recently, the latter two have been detected in the ISM. Given the relatively large energy separations between these two isomers and propanoic acid, the MEP principle predicts that propanoic acid should be present in the ISM.
- iv) **1,1-Ethenediol.** Three  $\text{H}_4\text{C}_2\text{O}_2$  isomers have been detected in the ISM (Table 2, Fig. 2), namely: acetic acid (0.0), methyl formate (72.1), and glycoaldehyde (113.7  $\text{kJ mol}^{-1}$ ). However, 1,1-ethenediol which is energetically more stable than glycoaldehyde by 3.2  $\text{kJ mol}^{-1}$  has not been detected in the ISM so far.
- v) The dipole moments of the above-mentioned isomers are sufficiently large that these species should be observed using microwave spectroscopy techniques. Specifically, at the B3LYP-D3/A'VTZ level of theory, they are: 1,2-propadien-1-one (2.56), 2-propanol (1.68), 1-propanol (1.49), propanoic acid (1.65), and 1,1-ethenediol (1.72 Debye).

**3.2.2. Undetected isomers with isomerization energies up to 115.0  $\text{kJ mol}^{-1}$ .** As mentioned above, the detected isomers with the highest isomerization energies are: oxirane (114.8) and glycoaldehyde (113.7  $\text{kJ mol}^{-1}$ ). We can take 115  $\text{kJ mol}^{-1}$  as an empirical upper limit for the isomerization energy of isomers that might be expected to be present in the ISM. Inspection of Tables 1–4 reveals that there are 28 isomers that satisfy this selection criterion (excluding the isomers already discussed in Section 3.2.1). We offer the following general observations:

- i)  **$\text{H}_{2n}\text{C}_2\text{O}$  isomers.** All the  $\text{H}_{2n}\text{C}_2\text{O}$  ( $n = 1-3$ ) isomers with isomerization energies below 115  $\text{kJ mol}^{-1}$  have been detected in the ISM (Table 1, Fig. 1).
- ii)  **$\text{H}_{2n}\text{C}_2\text{O}_2$  isomers.** Three  $\text{H}_{2n}\text{C}_2\text{O}_2$  ( $n = 1, 3$ ) isomers that have not been detected in the ISM have isomerization energies below 115  $\text{kJ mol}^{-1}$  (Table 2, Fig. 2). The two  $\text{H}_2\text{C}_2\text{O}_2$  isomers oxalaldehyde (0.0) and 2-oxiranone (42.5), and the  $\text{H}_6\text{C}_2\text{O}_2$  isomer methoxymethanol (27.8  $\text{kJ mol}^{-1}$ ).
- iii)  **$\text{H}_{2n}\text{C}_3\text{O}$  isomers.** Six  $\text{H}_{2n}\text{C}_2\text{O}_2$  ( $n = 2, 3$ ) isomers that have not been detected in the ISM have isomerization energies below 115  $\text{kJ mol}^{-1}$  (Table 3, Fig. 3). The three



H<sub>4</sub>C<sub>3</sub>O isomers 1-propen-1-one (1.2), cyclopropanone (84.8), and 1-allenol (109.6); and the three H<sub>6</sub>C<sub>3</sub>O isomers 1-propen-2-ol (48.9), cis-1-propen-1-ol (66.6), and 2-propen-1-ol (91.6). One obvious candidate that has a good chance of being present in the ISM is 1-propen-1-one, since it lies only 1.2 kJ mol<sup>-1</sup> above acrylaldehyde which has already been detected.

- iv) **H<sub>2n</sub>C<sub>3</sub>O<sub>2</sub> isomers.** As much as nineteen H<sub>2n</sub>C<sub>3</sub>O<sub>2</sub> ( $n = 1-4$ ) isomers that have not been detected in the ISM have isomerization energies below 115 kJ mol<sup>-1</sup> (Table 4, Fig. 4). It is worth pointing out that none of the energetically most stable H<sub>2n</sub>C<sub>3</sub>O<sub>2</sub> isomers have been detected in the ISM so far (namely, 3-oxoacrylaldehyde, acrylic acid, propanoic acid, and 2,2-propanediol).

#### 4. Conclusions

We have obtained benchmark isomerization energies for a set of 109 H<sub>x</sub>C<sub>y</sub>O<sub>z</sub> isomers. We considered the following 14 molecular formulas: H<sub>2</sub>C<sub>2</sub>O, H<sub>4</sub>C<sub>2</sub>O, H<sub>6</sub>C<sub>2</sub>O, H<sub>2</sub>C<sub>2</sub>O<sub>2</sub>, H<sub>4</sub>C<sub>2</sub>O<sub>2</sub>, H<sub>6</sub>C<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>C<sub>3</sub>O, H<sub>4</sub>C<sub>3</sub>O, H<sub>6</sub>C<sub>3</sub>O, H<sub>8</sub>C<sub>3</sub>O, H<sub>2</sub>C<sub>3</sub>O<sub>2</sub>, H<sub>4</sub>C<sub>3</sub>O<sub>2</sub>, H<sub>6</sub>C<sub>3</sub>O<sub>2</sub>, and H<sub>8</sub>C<sub>3</sub>O<sub>2</sub>. We find that in some cases isomers that have not (yet) been detected in the ISM are separated by only a few kJ mol<sup>-1</sup> from isomers that have been observed, for example acrylaldehyde and 1-propen-1-one (1.2), 1,2-propadien-1-one and propiolaldehyde (2.5), and 1,1-ethenediol and glycolaldehyde (3.2 kJ mol<sup>-1</sup>). We therefore obtain our isomerization energies by means of the high-level W2-F12 composite protocol that has been shown to provide benchmark accuracy for isomerization energies. We use these benchmark isomerization energies to see if there are molecules whose presence in the ISM might be surprising and to predict which of the isomers that have not been observed are expected to be present in the ISM. We offer the following conclusions:

- i) Of the 14 sets of isomers that were considered in the present work, isomers in 10 sets were detected in the ISM. In seven of these sets (H<sub>2</sub>C<sub>2</sub>O, H<sub>4</sub>C<sub>2</sub>O, H<sub>6</sub>C<sub>2</sub>O, H<sub>4</sub>C<sub>2</sub>O<sub>2</sub>, H<sub>6</sub>C<sub>2</sub>O<sub>2</sub>, H<sub>4</sub>C<sub>3</sub>O, and H<sub>6</sub>C<sub>3</sub>O) the most stable isomer has been detected in the ISM. Whereas in three of the sets (H<sub>2</sub>C<sub>3</sub>O, H<sub>8</sub>C<sub>3</sub>O, and H<sub>6</sub>C<sub>3</sub>O<sub>2</sub>) the lowest-energy isomer has not yet been detected. According to the MEP principle, the lowest-energy isomers of each set are likely to be present in the ISM.
- ii) We also find that the isomers 1-propanol (H<sub>8</sub>C<sub>3</sub>O) and 1,1-ethenediol (H<sub>4</sub>C<sub>2</sub>O<sub>2</sub>) lie lower in energy than H<sub>8</sub>C<sub>3</sub>O and H<sub>4</sub>C<sub>2</sub>O<sub>2</sub> isomers that have been detected in the ISM, respectively. Again, according to the MEP principle, this suggests that 2-propanol and 1,1-ethenediol are likely to exist in the ISM.

- iii) In four of the 14 sets of isomers (namely,  $\text{H}_2\text{C}_2\text{O}_2$ ,  $\text{H}_2\text{C}_3\text{O}_2$ ,  $\text{H}_4\text{C}_3\text{O}_2$ , and  $\text{H}_8\text{C}_3\text{O}_2$ ) no isomers have been detected in the ISM so far. The energetically most stable isomers in these four sets are: oxalaldehyde ( $\text{H}_2\text{C}_2\text{O}_2$ ), 3-oxoacrylaldehyde ( $\text{H}_2\text{C}_3\text{O}_2$ ), acrylic acid ( $\text{H}_4\text{C}_3\text{O}_2$ ), and 2,2-propanediol ( $\text{H}_8\text{C}_3\text{O}_2$ ).
- iv) Apart from oxalaldehyde which has no permanent dipole moment, the above-mentioned undetected isomers have relatively large dipole moments (ranging between 1.49 and 2.56 Debye) which should ease their detection by radio astronomy techniques.

### Appendix A. Supplementary data

Isomerization energies for isomers with relative energies  $> 150 \text{ kJ mol}^{-1}$  (Table S1); component breakdown of the final W2–F12 isomerization energies for all the isomers considered in the present work (Table S2); absolute energies used for deriving the final W2–F12 isomerization energies for all the isomers considered in the present work (Table S3); B3LYP–D3/A'VTZ optimized geometries for all the species considered in the present work (Table S4); and full references for Ref. 11 (Molpro 2012), Ref. 34 (CFOUR), and Ref. 39 (Gaussian 09). Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2014.xx.xxx>.

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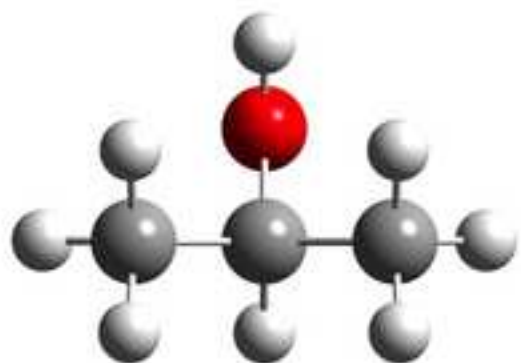
## TOC Graphic 1

Which  $H_xC_yO_z$  isomers are likely to be detected in the interstellar medium?

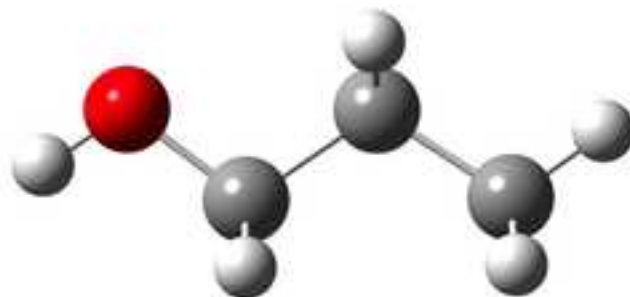


2-Propanol    1-Propanol    Propionic acid

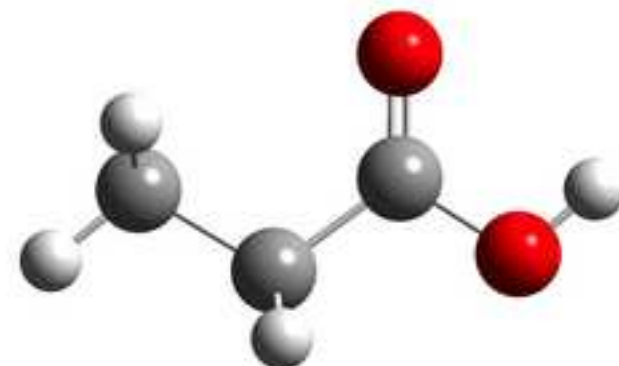
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2-Propanol



1-Propanol



Propionic acid



**Supplementary Materials**

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