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The ethynol (HCCOH) molecule has recently been shown to be present in simulated astrochemical ices possibly linking it to molecular building blocks for interstellar complex organic molecules like amino acids. The proposed reaction mechanism suggests the simultaneous formation of both ketene and ethynol from mixed carbon monoxide/water ice in simulated interstellar conditions. Rigorous anharmonic spectral data within both the IR and microwave regions are needed for possible detection of ethynol in the interstellar medium. This study provides the first such data for this molecule from high-level quantum chemical computations where experiment is currently lacking. Ethynol has a B_{eff} comparable to, but distinct from acetonitrile at 9,652.1 MHz and three notable infrared features with two in the hydride stretching-regions and the C–C stretch at 2,212.8 cm^{-1}. The ketene isomer has already been detected in the interstellar medium, and the possible detection of ethynol made possible by this work may lead to a deeper understanding of the proposed ice formation mechanism involving both species and how this relates to the molecular origins of life.

Keywords: astrochemistry, quantum chemistry, computational spectroscopy, coupled cluster theory, COM formation

1 INTRODUCTION

Structural isomers of complex organic molecules (COMs) are telling of the chemical and physical traits of interstellar environments and are useful testers of molecular cloud chemical models (Turner et al., 2020). Therefore, the ability to accurately recognize the abundance of COM building blocks in interstellar environments is critical for the prediction of interstellar chemical pathways. Two promising reactants to form larger COMs are ethynol (Zasimov et al., 2019), also known as hydroxyacetylene, and ketene, both members of the C_2H_2O isomer family. Ketene has a carbon=carbon double bond as well as a carbon=oxygen double bond. Ethynol has a carbon–carbon triple bond and an accompanying hydroxyl group. Previous *ab initio* computations have shown ethynol to lie 150.9 kJ/mol above the more stable ketene (Tanaka and Yoshimine, 1980). A third C_2H_2O isomer, oxirene, is suspected to be a possible intermediate structure facilitating some isomerization between the more stable structures of ethynol and ketene (Turner et al., 2020). Visual representation of these three molecules can be seen in **Figure 1**. Of these three molecules, only ketene and its ketenyl radical have been observed in the interstellar medium (ISM) with the former first detected toward Sgr B2 (Turner, 1977). However, the downhill pathway for the formation of ethynol from the same starting materials as ketene implies that it should have non-negligible abundance. Furthermore, detection of ethynol giving the ketene/ethynol pair would imply that mixed CO/H$_2$O ices could be the provenance of both molecules including the known ketene molecule.

FIGURE 1 | From left to right: ethynol, oxirene, and ketene.
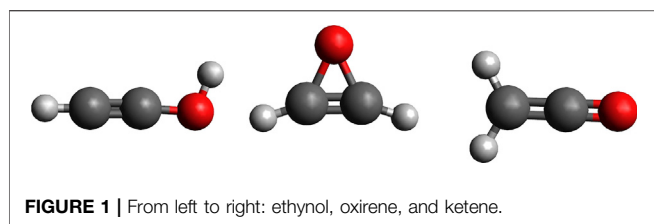
In addition to ice experiments, part of the previous work by Turner et al. (2020) explored quantum chemical reaction schemes at the coupled cluster singles, doubles, and perturbative triples [CCSD(T)] level beginning with dicarbon monoxide in the presence of free hydrogen and found barrier free pathways producing both ketene and ethynol. The ketenyl radical is an intermediate along this pathway. The addition of hydrogen to the carbon of the ketenyl radical is strongly preferred and leads to the formation of ketene. The addition of hydrogen to the oxygen of the radical is feasible, however extremely disfavored, and leads to the formation of ethynol. This barrier free pathway was then tested experimentally and resulted in the first identification of ethynol in interstellar ice analogs (Turner et al., 2020). Preceding work has also experimentally shown the reversible conversion of ketene into ethynol via photolysis in an argon matrix (Hochstrasser and Wirz, 1990). However, energy must be put into the system for this conversion to take place. Regardless, considering these reaction pathways and that ketene and the ketenyl radical have been previously observed in the ISM, ethynol is likely present in detectable quantities as even tautomers that are less stable than HCCOH compared to their global minima are known to persist in the ISM if their barriers to rearrangement are high enough (Dommen et al., 1987). Before it can be detected, however, highly-accurate anharmonic vibrational frequencies and/or rotational spectroscopic data for ethynol must be produced in order to provide the necessary reference data for comparison to any subsequent experiments or observations. This is the primary objective of the current work.

An early theoretical study on the rotational and vibrational characteristics of ethynol was carried out by DeFrees and McLean (1982). Using Hartree-Fock and a 3–21G basis set, they obtained harmonic vibrational frequencies that they suggested could be scaled by a previously-derived empirical factor (Pople et al., 1981) to obtain values comparable to experiment. They further computed CISD+Q/DZ+P equilibrium rotational constants and accompanying scaling factors derived from the experimental rotational constants of HNCO and HN₃ (DeFrees et al., 1982). Later work on ethynol offered rotational constants at the third-order Møller-Plesset perturbation theory (MP3) level with a 6–31G** basis set (Brown et al., 1985). The MP3 values were then scaled using factors obtained from experimental ketene data, yielding constants that were in good agreement with those computed by DeFrees and McLean (Brown et al., 1985).

Later theoretical work by Dommen et al. (1987) produced vibrational frequencies based on an MP2/6–31G** harmonic force field, with the force constants scaled based on empirical

corrections from similar computations on methanol and acetylene (Dommen et al., 1987). Dommen et al. (1987) also questioned the proposed multiplicative scaling scheme of DeFrees and McLean, instead suggesting that the equilibrium rotational constants should be divided by the scaling factors (Dommen et al., 1987). The scaled vibrational frequencies and re-scaled rotational constants presented by Dommen and coworkers are the most accurate theoretical data currently available for ethynol, revealing the need for new, high-level computational data. In the meantime, some progress has been made on the experimental characterization of ethynol, with five of its vibrational frequencies observed in an argon matrix in 1989 (Hochstrasser and Wirz, 1989). More recently, its ground-state C rotational constant was detected at 9553 MHz in 2019 (Martin-Drumel et al., 2019). The authors therein also report scaled CCSD(T)/cc-pVQZ principle rotational constants for comparison (Martin-Drumel et al., 2019). In spite of these previous computational results, more rigorous theoretical treatment is necessary to complement further experimental and observational work in the gas phase.

The current approach to obtaining high-level, theoretical vibrational frequencies is via a fourth-order Taylor series expansion to the internuclear potential with composite CCSD(T) energies making considerations for complete basis set extrapolation, core electron correlation, and scalar relativity (Huang and Lee, 2008; Huang and Lee, 2009; Huang et al., 2011). Such a scheme is referred to as "CcCR". The rigor of this method makes it very attractive, with it producing vibrational frequencies within 1.0 cm^{-1} of gas-phase experimental values in many cases (Huang and Lee, 2008; Huang and Lee, 2009; Huang et al., 2011; Fortenberry et al., 2012b; Huang et al., 2013; Fortenberry et al., 2014; Zhao et al., 2014; Fortenberry et al., 2015; Kitchens and Fortenberry, 2016; Bizzocchi et al., 2017; Fortenberry, 2017). However, its high computational cost makes this method less viable as molecules become larger and more complex. For this reason, a less complete but commensurately less computationally demanding method utilizing explicit correlation with a triple-ζ basis set is used as a point of comparison (Huang et al., 2010; Agbaglo et al., 2019; Agbaglo and Fortenberry, 2019a; Agbaglo and Fortenberry, 2019b), as it typically provides vibrational frequencies to within 7.0 cm^{-1} of gas-phase experimental values. The rotational constants, on the other hand, still require the more expensive composite approach in order to provide high-accuracy values (Agbaglo et al., 2019; Agbaglo and Fortenberry, 2019a; Agbaglo and Fortenberry, 2019b).

Cheaper methods do exist for determining relatively accurate rotational constants, such as the procedures outlined by Lee and McCarthy (2020). However, even in the best case outlined therein of the MP2/cc-pVQZ B rotational constants, the average deviation from experiment is 0.65%, while the performance of CcCR relative to experiment for the B and C rotational constants was recently shown to be 0.12% (Gardner et al., 2020), albeit for a much smaller selection of molecules. Additionally, the rotational constants from the CcCR methodology come at virtually no additional cost with the fundamental vibrational frequencies, making even marginal accuracy gains in these constants worth the increased computational demand when anharmonic frequencies are desired.

Both the aforementioned CcCR and explicitly correlated procedures are utilized within the current work to produce accurate vibrational frequencies for ethynol. By using the high-level anharmonic vibrational frequencies proposed in the current work, the search for interstellar ethynol may continue with more clarity in the regions in which ketene has been previously detected such as Sgr B2 (Turner, 1977); Orion KL (Johansson et al., 1984); and TMC-1 (Matthews and Sears, 1986).

2 COMPUTATIONAL DETAILS

Optimized geometries, dipole moments, and harmonic frequencies are computed using the MOLPRO 2015.1 software package (Werner et al., 2015) with canonical CCSD(T) and CCSD(T) within the F12 explicitly correlated construction [CCSD(T)-F12b] (Raghavachari et al., 1989; Crawford and Schaefer, 2000; Adler et al., 2007; Shavitt and Bartlett, 2009). As mentioned above, anharmonic frequencies are produced by a fourth-order Taylor series expansion of the internuclear portion of the Watson A-Reduced Hamiltonian referred to as a quartic force field (QFF). Two QFFs are utilized. The CCSD(T)-F12/cc-pVTZ-F12 version (Adler et al., 2007; Peterson et al., 2008; Yousaf and Peterson, 2008; Knizia et al., 2009) will be referred to as the F12-TZ QFF. The second QFF is the composite approach mentioned previously. This methodology is defined as the CcCR QFF since it includes complete basis set extrapolation ("C") using a three-point formula from aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z basis sets (Martin and Lee, 1996); core electron correlation ("cC") using the Martin-Taylor (MT) core correlating basis set (Martin and Taylor, 1994); and scalar relativity ("R") using Douglas-Kroll basis sets (Douglas and Kroll, 1974; de Jong et al., 2001). Recent results show that the F12-TZ QFF produces comparable anharmonic data to the CcCR QFF but with significantly lower computational costs (Agbaglo and Fortenberry, 2019a).

For both QFFs, an optimized reference geometry is required. For the F12-TZ QFF, this optimization is carried out at the CCSD(T)-F12/cc-pVTZ-F12 level. For the CcCR QFF, structural optimizations are determined at the canonical CCSD(T) level using the aug-cc-pV5Z basis set (Dunning, 1989; Kendall et al., 1992; Peterson and Dunning, 1995) as well as the MT core correlating basis set (Martin and Taylor, 1994). The difference in the bond lengths and angles between the CCSD(T)/MT computations with and without the core correction is then added to the respective variables within the optimized CCSD(T)/aug-cc-pV5Z geometry in order to correct for core correlation.

From the previously discussed reference geometries, displacements of 0.005 Å for bond lengths, 0.005 radians for bond angles, and 0.005 unitless displacements of LINX/LINY coordinates (Fortenberry et al., 2012b), which are necessary for the near-prolate structure of ethynol, are used to generate a QFF of 3,161 points using the following coordinate system:

$$S_1 = r(H - C) \tag{1}$$

TABLE 1 | Structural data and rotational constants for HCCOH.[a]

	Units	CISD+Q/DZ+P[b]	F12-TZ	CcCR
r(H–C)	Å	1.067	1.04922	1.05946
r(C–C)	Å	1.213	1.20637	1.20103
r(C–O)	Å	1.327	1.31690	1.31213
r(O–H)	Å	0.966	0.97184	0.96082
∠(H–C–C)	Deg	180.1	180.000	180.000
∠(C–C–O)	Deg	177.5	179.561	176.737
∠(C–O–H)	Deg	108.2	109.280	109.320
A_e	MHz	652,843	670,787.1	674,112.4
B_e	MHz	9,546	9,701.3	9,749.6
C_e	MHz	9,408	9,562.8	9,610.7
A_0	MHz	706,200	672,972.8	676,470.9
B_0	MHz	9,678	9,678.9	9,726.8
C_0	MHz	9,525	9,530.2	9,577.2
A_1	MHz		643,738.9	646,947.9
B_1	MHz		9,675.3	9,723.2
C_1	MHz		9,521.4	9,568.5
A_2	MHz		672,870.1	676,353.1
B_2	MHz		9,653.4	9,701.6
C_2	MHz		9,505.5	9,552.6
A_3	MHz		672,151.1	675,615.0
B_3	MHz		9,621.9	9,670.1
C_3	MHz		9,474.8	9,522.3
A_4	MHz		711,570.5	715,785.4
B_4	MHz		9,686.0	9,734.0
C_4	MHz		9,525.8	9,573.0
A_5	MHz		671,768.4	675,291.5
B_5	MHz		9,638.8	9,686.6
C_5	MHz		9,487.3	9,534.3
A_6	MHz		700,420.6	700,318.2
B_6	MHz		9,692.6	9,740.9
C_6	MHz		9,532.2	9,579.6
A_7	MHz		670,993.1	674,828.0
B_7	MHz		9,685.2	9,733.4
C_7	MHz		9,549.5	9,596.7
A_8	MHz		639,270.3	645,838.7
B_8	MHz		9,693.8	9,740.9
C_8	MHz		9,561.9	9,608.0
A_9	MHz		678,343.8	681,950.5
B_9	MHz		9,718.2	9,765.4
C_9	MHz		9,547.6	9,594.0

[a]Vibrationally-excited rotational constants are provided in the same order as vibrational frequencies. Structural parameters provided at the CISD+Q/DZ+P level are equilibrium values, while those provided for F12-TZ and CcCR are zero-point corrected.
[b]Geometrical parameters and equilibrium rotational constants are from Ref.13, and principle-rotational constants are from Ref.14, using the equilibrium rotational constants and the scaling factors reported in Ref.13.

$$S_2 = r(C - C) \tag{2}$$

$$S_3 = r(C - O) \tag{3}$$

$$S_4 = r(O - H) \tag{4}$$

$$S_5 = LINX(H - C - C) \tag{5}$$

$$S_6 = \angle(C - C - O) \tag{6}$$

$$S_7 = \angle(C - O - H) \tag{7}$$

$$S_8 = LINY(H - C - C - O) \tag{8}$$

$$S_9 = \tau(C - C - O - H) \tag{9}$$

TABLE 2 | Quartic and sextic spectroscopic constants.

	Units	MP2/6–31G**[a]	F12-TZ	CcCR
Δ_J	kHz	3.3	3.2167	3.2373
Δ_K	kHz	250,000	253,080	259,350
Δ_{JK}	kHz	560	622.16	617.68
δ_J	Hz		41.641	42.022
δ_K	Hz		275,980	274,600
Φ_J	Hz		0.31476	0.29727
Φ_K	Hz		145,020	152,580
Φ_{JK}	Hz		3.4790	3.2803
Φ_{KJ}	Hz		52,787	48,214
ϕ_j	mHz		0.2328	0.2500
ϕ_{jk}	mHz		1,937.4	1,849.6
ϕ_k	mHz		68,713,000	66,530,000
μ_X	D		1.50	
μ_Z	D		0.51	
μ	D		1.58	

[a]From Ref.14.

From this coordinate system, single point energies are computed for the composite method using the definition described above. The F12-TZ method only relies on CCSD(T)-F12/cc-pVTZ-F12. Once the single point energies are computed for both of the QFFs, they are fit using a least squares procedure with a sum of squared residuals less than 3×10^{-16} a.u.^{2} for both CcCR and F12-TZ. Next, the force constants' simple internal coordinates are converted into Cartesian coordinates using the INTDER program (Allen, 2005). These Cartesian coordinates are then fed into the SPECTRO program (Gaw et al., 1991) in which rotational, rovibrational, and vibrational perturbation theory at second order (VPT2) (Mills, 1972; Watson, 1977; Papousek and Aliev, 1982) are used to obtain the fundamental vibrational frequencies and spectroscopic constants. The CcCR force constants themselves are available in **Supplementary Table S1** of the **Supplementary Material**.

Combinations of ν_5 and ν_3, ν_6 and ν_5, ν_7 and ν_5 are considered as type 1 Fermi resonances. Combinations of ν_5, ν_3, and ν_2 are treated as type 2 Fermi resonances as well as combinations of ν_5, ν_4, and ν_3. Polyads of the Fermi resonances are also handled. Finally, Coriolis resonances are included, with the combinations of ν_7 and ν_6, ν_9 and ν_7, ν_9 and ν_8 all resulting in A-type Coriolis resonances.

3 RESULTS AND DISCUSSION

3.1 Structure and Rotational Spectroscopic Constants

The optimized structures at both the F12-TZ and CcCR levels are given in **Table 1**. The optimized bond lengths computed at both levels of theory agree to within 0.02 Å when compared to one another and previous computations at the MP2/6–31G** level of theory (Dommen et al., 1987). The quartic and sextic A-reduced Hamiltonian spectroscopic constants of ethynol are given in **Table 2** alongside dipole moments. Ethynol's vibrationally-excited rotational constants are provided in **Table 1** in the same order as the fundamental vibrational frequencies. Due to ethynol's considerable dipole moment of 1.58 D, as shown in **Table 2**, its rotational transitions should be easily observable via rovibrational spectroscopy.

A useful point of comparison for ethynol's equilibrium rotational constants would be with those of acetonitrile. Acetonitrile is a prolate molecule that compares nicely to ethynol's near-prolate structure and has a nearly equivalent molecular weight to that of ethynol. As seen in **Table 1**, ethynol has CcCR B_0 and C_0 values of 9726.8 and 9576.9 MHz, respectively. Previous work has shown CcCR rotational constants to be accurate within 20 MHz of experimental values for closed shell molecules (Gardner et al., 2020). Acetonitrile has equivalent B_0 and C_0 values of 6,200.9 MHz (Herzberg, 1966). As expected, ethynol has B_0 and C_0 values higher than those of acetonitrile due to its near-prolate, as opposed to fully prolate, nature. These similarities will make acetonitrile a useful sign-post for the observation of ethynol in the ISM, but, because acetonitrile has a larger dipole moment (3.92 D), observed rotational modes of ethynol will have considerably lower intensity than those of acetonitrile.

3.2 Vibrational Frequencies
Vibrational frequencies for ethynol are given at the F12-TZ and CcCR levels of theory alongside experimental values in **Table 3**. F12-TZ and CcCR anharmonic frequencies compare well to each other, with a mean absolute error of less than 8 cm^{-1} between the two methods. Although gas-phase experimental data are currently unavailable for ethynol, argon matrix experimental data (Hochstrasser and Wirz, 1989) correlates in expected fashion with theoretical values presented in this work. Namely, all but ν_5 are shifted to the red in the matrix results, in line with the typical behavior of a matrix (Anderson and Ogden, 1969). Of the nine vibrational frequencies present in ethynol, only the five most intense have experimental data. The others are too weak to be observed. This is corroborated by MP2 intensities presented alongside F12-TZ harmonic frequencies in **Table 3**, which are seen to drastically drop off after ν_5.

Of ethynol's vibrational frequencies, ν_1, ν_2, and ν_3 have the three brightest intensities. These modes are described in **Table 3** using the coordinate system established in the Computational Details section and are attributed to the O–H, C–H, and C–C stretching modes, respectively. Comparison of ethynol's anharmonic frequencies to known values of similar structures in the gas-phase may be useful in aiding the vibrational assignment of ethynol in the ISM. The CcCR ν_3, corresponding to the C–C stretching mode, occurs at 2,212.8 cm^{-1} or 4.519 μm and is the brightest vibrational mode present in ethynol, making it a critical resource for the future assignment of ethynol in the ISM. The C–N triple bond stretch present in acetonitrile, a molecule of, again, similar structure and weight to ethynol that is known to be present in the ISM (Solomon et al., 1971), is observed at 2,267 cm^{-1} or 4.411 μm in gas-phase experiment (Shimanouchi, 1972). The reported CcCR frequency for ν_3 is redshifted 0.108 μm from the experimental acetonitrile C–N stretch. This redshifting is to be expected as ethynol is a slightly more massive system.

With only a slightly lower intensity than ν_3, the CcCR ν_1 is observed at 3,635.2 cm^{-1} or 2.751 μm. As ν_1 is attributed to the O–H stretch of ethynol, a reasonable mode to compare as an analog is the O–H stretch present in methanol, which is well

TABLE 3 | Vibrational frequencies (in cm^{-1}) of ethynol.

Mode	Description	Symmetry	Experiment[a]	Previous harmonic[b]	F12-TZ		CcCR	
					Harmonic[c]	Fundamental	Harmonic	Fundamental
1	$(1.000)S_4$	a'	3,501.3	3,798.2	3,819.7 (138)	3,628.4	3,828.1	3,635.2
2	$(0.957)S_1 + (0.042)S_2$	a'	3,339.6	3,474.0	3,478.9 (93)	3,347.8	3,482.9	3,354.7
3	$(0.772)S_2 + (0.187)S_3$	a'	2,198.3	2,230.4	2,243.3 (139)	2,203.3	2,251.5	2,212.8
4	$(0.980)S_7$	a'	1,232.1	1,270.2	1,272.6 (85)	1,235.9	1,273.9	1,236.1
5	$(0.822)S_3 + (0.175)S_2$	a'	1,072.1	1,062.0	1,069.5 (85)	1,052.8	1,074.0	1,058.7
6	$(0.870)S_5 + (0.128)S_6$	a'		610.3	622.7 (47)	629.2	631.3	639.1
7	$(1.093)S_8 - (0.093)S_9$	a"		527.3	537.8 (54)	548.4	544.4	558.0
8	$(1.093)S_9 - (0.093)S_8$	a"		378.4	401.6 (4)	417.1	416.6	432.3
9	$(0.867)S_6 + (0.116)S_5$	a'		355.0	368.3 (10)	386.1	377.8	393.5

[a]Argon matrix experimental data from Ref. 26.
[b]CCSD(T)/aug-cc-pVTZ harmonic frequencies from Ref. 55.
[c]Double-harmonic MP2/6–31+G* intensities (in km mol^{-1}) in parentheses.

known in the ISM (Ball et al., 1970). This methanol stretching mode is observed in gas-phase experiment at 3,681 cm^{-1} (Shimanouchi, 1972) or 2.717 µm. When comparing ν_1 to this stretching mode in methanol, the CcCR ν_1 exhibits a redshift of 0.034 µm away from methanol's stretching mode.

Of the three brightest vibrational frequencies present in ethynol, ν_2, observed at 3,354.7 cm^{-1} or 2.980 µm, is considerably dimmer than ν_1 and ν_3 but still has potential to serve as a useful indicator in future detection. As ν_2 is attributed to the C–H stretching mode of ethynol, a practical mode for comparison would be that of the C–H stretching mode of the ethynyl radical, which has also been previously observed in the ISM (Tucker et al., 1974). This gas-phase stretching mode is observed at 3,298.85 cm^{-1} or 3.031 µm (Stephens et al., 1988). Similar to ν_1 and ν_3, ν_2 is shifted by 0.051 µm when compared to the C–H stretch present in the ethynyl radical.

Positive anharmonicities are present for ν_6–ν_9 in **Table 3**. These positive anharmonicities range from 6.5 to 17.8 cm^{-1} when examining ν_6 and ν_9, respectively. This behavior in the anharmonicities arises due to the nearly linear nature of the H–C–C–O backbone present in ethynol and has been documented previously in molecules of similar near-prolate construction (Fortenberry et al., 2012a; Fortenberry et al., 2012b; Fortenberry et al., 2013).

The high intensity stretching modes ν_1–ν_5 are observed in the region of previously identified peaks (Peeters et al., 2004). However, the ν_1–ν_5 frequencies occur in regions not typically attributed to polycyclic aromatic hydrocarbons or dust, thus making these regions less well confined in terms of potential molecular provenance. Although far from conclusive, ethynol's distinct vibrational peaks combined with their high intensities show promise for IR spectroscopy identifying the molecule in the ISM. Additionally, its notable dipole moment is encouraging for rotational observation, thus providing even more avenues of detection.

4 CONCLUSION

Considering that ethynol has already been shown to form in interstellar ice analogs and that the related ketene molecule

(Turner et al., 2020) is known to be present in the ISM, the high-level vibrational and rotational data provided here may lead to the detection of ethynol in various astrophysical regions, especially those where ketene and its dehydrogenated radical are known to exist. Detection of ethynol through rotational spectroscopy should be possible due to its 1.58 D dipole moment. Further, detection is also feasible via mid-IR spectroscopy due to the bright nature of vibrational frequencies ν_1–ν_3, leading to multiple spectral regions for detection. Once ethynol has been detected in the ISM, investigation of relative populations of ethynol compared to ketene within certain regions will increase understanding of the recently proposed mechanism by Turner et al. (2020). This knowledge may then further augment models exploring COM formation in the ISM and help the collective understanding of how small molecules like ethynol and ketene relate to the molecular origins of life in the ISM.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

JD and BW performed the computations. JD wrote the draft. JD, BW, and RF edited the manuscript. RF provided conceptualization, oversight, methodology, and provision of funds.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fspas.2020.626407/full#supplementary-material.

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