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Benzyne in V4334 Sqr: A Quest for the Ring with SOFIA/EXES

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ABSTRACT

Large aromatic molecules are ubiquitous in both circumstellar and interstellar environments. Detection of small aromatic molecules, such as benzene (C_6H_6) and benzyne (C_6H_4), are rare in astrophysical environments. Detection of such species will have major implications for our understanding of the astrochemistry involved in the formation of the molecules necessary for life, including modeling the chemical pathways to the formation of larger hydrocarbon molecules. We conducted a search for the infrared 18 μm spectral signature of benzyne in V4334 Sgr with SOFIA/EXES finding no evidence for a feature at the sensitivity of our observations.

Keywords: Asymptotic giant branch stars (2100): Circumstellar dust (236): Astrochemistry (75)

1. INTRODUCTION

Large hydrocarbon molecules (both aliphatic and aromatic) are now known to be widespread in interstellar and circumstellar environments (Xie et al. 2018; Sloan et al. 2014; Tielens 2008). In particular, Polycyclic Aromatic (carbon-ring structures) Hydrocarbons (PAHs; e.g., the 7-ring coronene $C_{24}H_{12}$) molecules are generally accepted to be the carriers of the ubiquitous "Unidentified Infrared" (UIR) features (Peeters 2011; Tielens 2008).

Small aromatic hydrocarbons however have proven to be more elusive. While benzene (C_6H_6) is known to be common in Solar System environments (Guerlet et al. 2015; Trainer et al. 2013), and may play a role in ice chemistry in the interstellar medium (Sivaraman et al. 2015), the only detection to date in a circumstellar environment has been in the proto-planetary nebula CRL 618 (Cernicharo et al. 2001a,b). Recently, McGuire et al. (2018) reported detection of benzonitrile (c-C_6H_5CN) at radio wavelengths toward the molecu-

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lar cloud TMC-1. Joblin & Cernicharo (2018) argue that benzonitrile likely forms from a reaction of CN with benzene, and hence it may be possible to indirectly infer both the existence of benzene and the abundance of benzene itself.

Dusty, carbon-rich circumstellar environments are laboratories for the detection and study of exotic molecular species (e.g., Zhang et al. 2011). *Benzyne* (C_6H_4) is an aromatic (carbon-ring structure) hydrocarbon with a structure similar to benzene. Benzyne is an example of an aryne (-yne ≡ triple bond), wherein the additional pi bond is formed by the overlap of sp2 hybridized orbitals outside the ring. As the molecule is highly strained, it is a highly reactive intermediate species. on the detection of benzene in CRL 618, Weaver et al. (2007) attempted to detect benzyne in CRL 618 without success.

Here, we present our attempts to detect benzyne in the dusty, dense hydrocarbon-rich circumstellar environment (Evans et al. 2006) of the "Born-Again Giant (BAG)" V4334 Sgr (also known as Sakurai's Object) with SOFIA/EXES.

2. V4334 Sgr AND THE "BAG" PHENOMENON

When a solar-mass star reaches the end of its life and is evolving towards the white dwarf (WD) region of the HR diagram, it may reignite a residual helium shell and be reborn as a giant star: it becomes a BAG. This may occur in as many as 20% of stars, and is a phase of stellar evolution that is very poorly understood (Herwig 2005). For example, observations over the past ∼ 10 years indicate that it takes place far more rapidly than theory predicts. BAGS also may be a primary source of ^{13}C in the interstellar medium (ISM) (Kobayashi et al. 2011).

V4334 Sgr was discovered in 1996 (Nakano et al. 1996). Evidence for its BAG nature are its association with a faint planetary nebula (Eyres et al. 1998; Pollacco 1999), and its low ^{12}C/^{13}C ratio of 4 ± 1 (Evans et al. 2006; Pavlenko et al. 2004). V4334 Sgr subsequently produced an optically thick carbon dust shell that completely obscured the star (visual extinction $\gtrsim 10$ mag). A large mass-loss rate ($\dot{M} \sim 10^{-5}$ M$_\odot$ yr^{-1}) was implied by 1–5 μm spectroscopy (Tyne et al. 2002) and by 450/850 μm photometry (Evans et al. 2002). Observations with the ESO VLTI reveal V4334 Sgr's dust disk, which is nearly edge-on (Chesneau et al. 2009). The rapid rate at which it is evolving has prompted major rethinking about the post-main sequence evolution of low-to-intermediate mass stars (Deneault et al. 2006; Lawlor & MacDonald 2003; Herwig 2001).

Neither *Spitzer* nor SOFIA **spectra show evidence for canonical PAH dust features at mid-infrared wavelengths. Similarly, the 3.28 μm feature is not seen ground-based spectra during the period of 1999 to 2002 (Tyne et al. 2002). The WD in V4334 Sgr certainly is a source of energetic UV photons to excite PAHs, although Li & Draine (2002) argue that such a radiation field may not be required.**

3. OBSERVATION AND DATA REDUCTION

Observations of V4334 Sgr were conducted using the Echelon-cross-echelle Spectrograph for SOFIA (EXES) (Richter et al. 2018) on 2019 April 04.335 UT (MJD = 58577.355), observing at an altitude of 13.11 km (43000 ft) under programs 07_0010 and 06_0095. The instrument was configured in single-order, long-slit mode with a vacuum rest-frame wavelength center of 18.16 μm (550.63 cm^{-1}), in first order using a $25.8'' \times 2.43''$ slit. This configuration yields a resolving power (RP) of $\simeq$ 2240. Because of the high background flux at 18 μm in the EXES low resolution mode, the instrument was operated in subarray mode and at a lower detector bias to avoid saturation. V4334 Sgr was nodded at two positions (AB-nod) separated by $8''$ within the slit to provide for background subtraction. Immediately after the observations of V4334 Sgr, the telluric reference Callisto (a moon of Jupiter) was observed with the same instrumental setup. Data were reduced using the EXES instrument pipeline (REDUX; Clarke et al. 2015), with additional custom routines to deal with the high background photon flux.

We adopted a flux density of 1551.3 Jy at 18.16 μm for Callisto. This flux density was estimated from a standard thermal model (NEATM; Harris 1998), assuming a beaming parameter of 0.756 and a phase coefficient of 0.01 mag per degree (Dotto et al. 2000) using the JPL Horizons values for Callisto's radius and albedo. Details of the observations and SOFIA archive data files used in our analysis are given in Table 1. The EXES spectrum is shown in Fig. 1.

4. DISCUSSION

The infrared (IR) spectral energy distribution (SED) of V4334 Sgr over the last ∼20 yrs is discussed in detail by Evans et al. (2020). The dust shell has cooled, from $\simeq$ 840 K in 1999 (as deduced from ground-based data) to $\simeq$ 180 K in 2016 (SOFIA-based observations). A *Spitzer* IRS spectrum (Evans et al. 2006) revealed the presence of HCN and polyynes (acetylene, C_2H_2; HC_nN) in the 13.5–16.5 μm region. Later epoch SOFIA (+FORCAST) spectra (Evans et al. 2020) show other hydrogenated carbon species are present. The HCN features gave (for 2005) a ^{12}C/^{13}C ratio for the absorbing gas of ∼ 4 (Evans et al. 2006), as recently confirmed by sub-mm observations of the $J = 4 \rightarrow 3$ transition in H^{12}CN

Table 1. EXES Observational Summary

Object	SOFIA DCS Archive File (F0560_EX_SPE_*.fits)	2019 Apr 04 UTC Start (hr:mm:ss)	2019 Apr 04 UTC End (hr:mm:ss)	ITIME [a] (sec)
V4334 Sgr	0600951_NONEEXEECHL_CMB_0069-0082	08:04:12.38	09:36:31.95	1504.00
Callisto	0600953_NONEEXEECHL_CMB_0112	09:49:40.15	09:57:47.88	192.00

[a] Total on-source integration times.

Note—Data files are available through the SOFIA Data Cycle System (DCS) or the Infrared Processing and Analysis Center (IPAC) Infrared Science Archives (IRSA) at https://dcs.arc.nasa.gov or https://www.ipac.caltech.edu/project/irsa respectively.

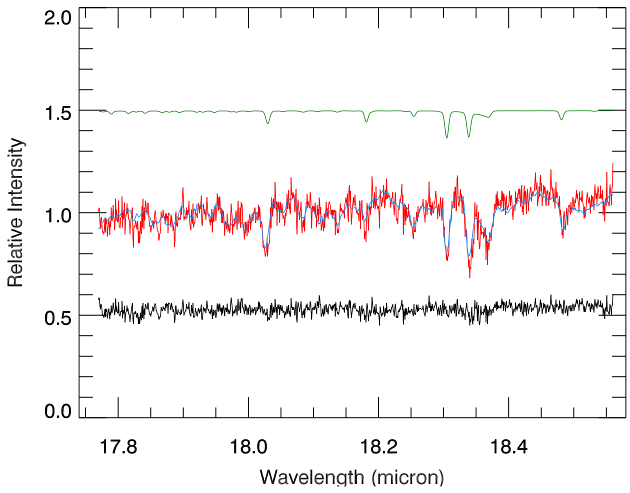

Figure 1. The SOFIA/EXES spectra of V4334 Sgr in the 18 μm region near the 18.28 μm in-plane aromatic ring deformation of benzyne (C_6H_4) observed in terrestrial laboratories. The V4334 Sgr spectrum is the *red* curve, the mean-normalized Callisto (the telluric divisor) spectrum is the *blue* curve, the *black* curve is the division of the two observed spectra multiplied by a factor of 100. The *green* curve is the ATRAN (Lord 1992) transmission model (arbitrarily offset by a factor of 0.5 for clarity). The spectral grasp of our observations does not include the 17.4 μm region in the blue, nor extend to the 18.9 μm region in the red where C_{60} fullerene features are sometimes seen in the dust continuum of objects exhibiting PAH and other UIR bands (Shannon et al. 2015, and references therein).

and $H^{13}CN$ conducted by Tafoya et al. (2017), and a temperature $\simeq 450$ K. SOFIA observations in 2014 and 2016 indicated that the HCN and polyyne features have weakened to invisibility (i.e., non-detectable). Acetylene would just be visible, if present, at the very edge of the FORCAST G111 spectral segment (cf., Herter et al. 2012).

The weak, and temporally varying, absorption features seen in the IR spectra of V4334 Sgr are intriguing, especially those near 10.9 μm and 13.4 μm. Sander et al. (2002) attributes IR meta-benzyne features (Fig. 2) at 10.94 μm to a C−H bend + C−C stretch, 13.37 μm to a C−H wag, and 18.28 μm to an in-plane aromatic ring deformation. The latter is the strongest band, and we suggest that the putative mid-IR features in V4334 Sgr are likely from meta-benzyne. **We expect that benzyne to be in absorption in a similar manner as the observed acteylene features (Evans et al. 2006), which are in absorption, assuming that all molecules and radicals originate in a common zone.** As $^{12}C/^{13}C \sim 4$ in V4334 Sgr, we expect that at least one, and possibly two, of the C atoms in the benzyne will be ^{13}C, which will cause the features to be displaced to longer wavelengths than those ring-chains comprised solely of ^{12}C (i.e., Radziszewski et al. 1992).

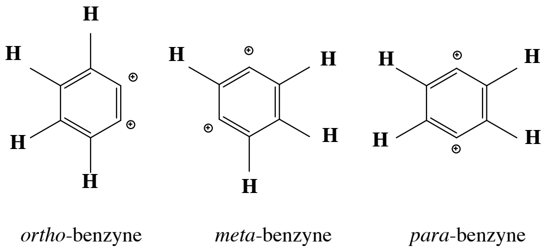

Figure 2. Structure of ortho-, meta- and para-benzyne.

Given the evolution of the hydrocarbon features in V4334 Sgr, is it possible that small hydrocarbon molecules seen in the *Spitzer* spectra (Evans et al. 2006) have undergone reactions to produce the ring molecules?

Benzyne is a highly reactive biradical. Reactions between benzyne molecules, and between benzyne and other molecules, could lead to PAH formation. Any benzyne in V4334 Sgr may evolve along a similar astrochemical pathway into the PAH molecules seen (via the UIR features) in older BAGs such as FG Sge (Evans et al. 2015). If so, detection of benzyne could provide powerful constraints on chemical pathways for aromatic hydrocarbon formation in circumstellar environments, from di- and tri-atomics, to polyynes, to basic rings and thence to the PAHs responsible for the UIR emission.

However, at our spectral sensitivity, median 1σ flux density (upper limit) at 18.16 μm of 25 Jy for our V4334 Sgr data, we find no evidence for benyzene in our EXES spectra. Similarly, no other emission or absorption features are evident (Fig. 1). If benzyne is not present, could the small aliphatic hydrocarbons that are extant in the circumstellar material of V4334 Sgr then have their origins as fragments detached from larger, hydrogenated amorphous carbon (HACs) grains or do they form *in situ* by some other mechanism?

Acetylene is present in V4334 Sgr. Chen & Li (2019) have shown production of carbon nanotubes, formed from benyzene with the presence of C_2H_2 (through a hydrogen-abstraction and acetylene addition reaction) is possible. This could deplete the abundance of benyzene below the level of detectability. However, spectral signatures at the putative wavelengths of carbon nanotubes (cf. Table 1, Chen & Li 2019) are not evident in ***Spitzer*** **or SOFIA spectra of V4334 Sgr. Unlike other BAGS, non-detection of PAHs in V4334 Sgr may suggest that they are not extant in the dusty carbon-rich environment and possibly benyzene quickly transforms into other species.** A more sensitive search (μJy) for benyzene **and other reactive carbon byproducts** in dust environments with the James Webb Space Telescope (JWST) may resolve this issue and the origins of PAH/UIR/HAC species.

5. CONCLUSION

The search for the 18 μm benzyne (C_6H_4) feature in V4334 Sgr with SOFIA/EXES was inconclusive at this epoch (2019) of the evolution of the cool dense circumstellar shell after the 1996 BAG event. However, further pursuit to detect such small hydrocarbons is warranted to advance our understanding of hydrocarbon astrochemistry.

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Facilities: NASA SOFIA (EXES)

Software: REDUX (Clarke et al. 2015)

REFERENCES

Cernicharo, J., Heras, A. M., Pardo, J. R., et al. 2001a, ApJL, 546, L127, doi: 10.1086/318872

Cernicharo, J., Heras, A. M., Tielens, A. G. G. M., et al. 2001b, ApJL, 546, L123, doi: 10.1086/318871

Chen, T., & Li, A. 2019, A&A, 631, A54, doi: 10.1051/0004-6361/201935789

Chesneau, O., Clayton, G. C., Lykou, F., et al. 2009, A&A, 493, L17, doi: 10.1051/0004-6361:200811173

Clarke, M., Vacca, W. D., & Shuping, R. Y. 2015, Astronomical Society of the Pacific Conference Series, Vol. 495, Redux: A Common Interface for SOFIA Data Reduction Pipelines, ed. A. R. Taylor & E. Rosolowsky, 355

Deneault, E. A. N., Clayton, D. D., & Meyer, B. S. 2006, ApJ, 638, 234, doi: 10.1086/498741

Dotto, E., Müller, T. G., Barucci, M. A., et al. 2000, A&A, 358, 1133

Evans, A., Geballe, T. R., Tyne, V. H., et al. 2002, MNRAS, 332, L69, doi: 10.1046/j.1365-8711.2002.05527.x

Evans, A., Gehrz, R. D., Helton, L. A., & Woodward, C. E. 2015, in EAS Publications Series, Vol. 71-72, EAS Publications Series, 281–286, doi: 10.1051/eas/1571063

Evans, A., Tyne, V. H., van Loon, J. T., et al. 2006, MNRAS, 373, L75, doi: 10.1111/j.1745-3933.2006.00246.x

Eyres, S. P. S., Richards, A. M. S., Evans, A., & Bode, M. F. 1998, MNRAS, 297, 905, doi: 10.1046/j.1365-8711.1998.01554.x

Guerlet, S., Fouchet, T., Vinatier, S., et al. 2015, A&A, 580, A89, doi: 10.1051/0004-6361/201424745

Harris, A. W. 1998, Icarus, 131, 291, doi: 10.1006/icar.1997.5865

Herter, T. L., Adams, J. D., De Buizer, J. M., et al. 2012, ApJL, 749, L18, doi: 10.1088/2041-8205/749/2/L18

Herwig, F. 2001, ApJL, 554, L71, doi: 10.1086/320911

—. 2005, ARA&A, 43, 435, doi: 10.1146/annurev.astro.43.072103.150600

Joblin, C., & Cernicharo, J. 2018, Science, 359, 156, doi: 10.1126/science.aar4541

Kobayashi, C., Karakas, A. I., & Umeda, H. 2011, MNRAS, 414, 3231, doi: 10.1111/j.1365-2966.2011.18621.x

Lawlor, T. M., & MacDonald, J. 2003, ApJ, 583, 913, doi: 10.1086/345411

Li, A., & Draine, B. T. 2002, ApJ, 572, 232, doi: 10.1086/340285

Lord, S. D. 1992, A new software tool for computing Earth's atmospheric transmission of near- and far-infrared radiation, Tech. rep.

McGuire, B. A., Burkhardt, A. M., Kalenskii, S., et al. 2018, Science, 359, 202, doi: 10.1126/science.aao4890

Nakano, S., Sakurai, Y., Kojima, T., et al. 1996, IAUC, 6443, 1

Pavlenko, Y. V., Geballe, T. R., Evans, A., et al. 2004, A&A, 417, L39, doi: 10.1051/0004-6361:20040078

Peeters, E. 2011, in IAU Symposium, Vol. 280, The Molecular Universe, ed. J. Cernicharo & R. Bachiller, 149–161, doi: 10.1017/S174392131102494X

Pollacco, D. 1999, MNRAS, 304, 127, doi: 10.1046/j.1365-8711.1999.02300.x

Radziszewski, J. G., Hess, B. A., & Zahradnik, R. 1992, Journal of the American Chemical Society, 114, 52, doi: 10.1021/ja00027a007

Richter, M. J., Dewitt, C. N., McKelvey, M., et al. 2018, Journal of Astronomical Instrumentation, 7, 1840013, doi: 10.1142/S2251171718400135

Sander, W., Exner, M., Winkler, M., et al. 2002, Journal of the American Chemical Society, 124, 13072, doi: 10.1021/ja012686g

Shannon, M. J., Stock, D. J., & Peeters, E. 2015, ApJ, 811, 153, doi: 10.1088/0004-637X/811/2/153

Sivaraman, B., Mukherjee, R., Subramanian, K. P., & Banerjee, S. B. 2015, ApJ, 798, 72, doi: 10.1088/0004-637X/798/2/72

Sloan, G. C., Lagadec, E., Zijlstra, A. A., et al. 2014, ApJ, 791, 28, doi: 10.1088/0004-637X/791/1/28

Tafoya, D., Toalá, J. A., Vlemmings, W. H. T., et al. 2017, A&A, 600, A23, doi: 10.1051/0004-6361/201630074

Tielens, A. G. G. M. 2008, ARA&A, 46, 289, doi: 10.1146/annurev.astro.46.060407.145211

Trainer, M. G., Sebree, J. A., Yoon, Y. H., & Tolbert, M. A. 2013, ApJL, 766, L4, doi: 10.1088/2041-8205/766/1/L4

Tyne, V. H., Evans, A., Geballe, T. R., et al. 2002, MNRAS, 334, 875, doi: 10.1046/j.1365-8711.2002.05561.x

Weaver, S. L. W., Remijan, A. J., McMahon, R. J., & McCall, B. J. 2007, ApJL, 671, L153, doi: 10.1086/525042

Xie, Y., Ho, L. C., Li, A., & Shangguan, J. 2018, ApJ, 860, 154, doi: 10.3847/1538-4357/aac3dc

Zhang, F., Parker, D., Kim, Y. S., Kaiser, R. I., & Mebel, A. M. 2011, ApJ, 728, 141, doi: 10.1088/0004-637X/728/2/141