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Theoretical prediction of new dipole-bound singlet states for anions of interstellar interest

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Anions that exhibit dipole-bound singlet states have been proposed as a potential class of molecules that may be identified in the interstellar medium. Using high-level coupled cluster theory, we have computed the dipole moments, electron binding energies, and excited states of 14 neutral radicals and their corresponding closed-shell anions. We have calibrated our methods against experimental data for CH_2CN^- and CH_2CHO^- and demonstrated that coupled cluster theory can closely reproduce experimental dipole moments, electron binding energies, and excitation energies. Using these same methods, we predict the existence of dipole-bound excited states for six of the 14 previously unknown anions, including CH_2SiN^- , SiH_2CN^- , CH_2SiHO^- , SiN^- , $CCOH^-$, and $HCCO^-$. In addition, we predict the existence of a valence-bound excited state of CH_2SiN^- with an excitation wavelength near 589 nm. © 2011 American Institute of Physics. [doi:10.1063/1.3576053]

I. INTRODUCTION

Electronically excited states of molecular anions may play a significant role in the chemistry of the interstellar medium (ISM).¹ If an additional electron is bound to a neutral molecule, chemical intuition suggests that the energy needed to remove the extra electron from the bound system is small. This implies that any possible excitation would be low energy since the excitation energy must typically be less than the electron binding energy. Such long wavelength transitions are not as common as they are for neutral or cationic molecular species, but, as explained by Simons,² some anions do exhibit excited states below the deionization limit.

Excited states of anions have been known to exist in highly controlled laboratory experiments and have been studied theoretically for more than 50 years. Fermi and Teller³ were the first to put the lower limit on the permanent dipole moment necessary to bind an electron—a dipole-bound state—at 1.625 D, and this result has been elaborated upon several times in the literature.^{4–6} Although this hard limit has been modified throughout the years due to numerous factors,^{7–13} it is accepted that a relatively large dipole moment must exist in order for the positive component of the molecular dipole of a given neutral molecule to bind the additional electron to the system. While other factors may play a role in the stability of the excited state, the dipole moment strength is the key.²

Most anions have such small binding energies that any extant electronic transitions would appear well into the infrared.^{2,13,14} However, some anions possess electronic excitation energies just beneath the electron detachment level—sometimes referred to as "threshold resonances"—in energy ranges that are much closer to the visible. Most notably, CH_2CN^- (Refs. 15 and 16) and CH_2CHO^- (Refs. 17 and 18) are well-known to exhibit such higher-energy electronic

transitions. The corresponding neutral species of $CH_2CN^$ and CH_2CHO^- are radicals with large dipole moments. Naturally, electronic attachment to a valence orbital in a neutral radical is more stable than attachment to a loosely bound orbital in an already closed-shell neutral molecule. Hence, the electron binding energy (eBE) will be greater in the resulting closed-shell anions than open-shell anions, and this increases the probability that an excited state will exist below the eBE. The large dipole moment is still necessary, however, since the virtual orbital(s) accepting the electron in an excitation is(are) typically a very diffuse orbital, and the positive component of the dipole holds the excited electron within the system.²

In 2000, Sarre¹ proposed that dipole-bound states of anions should be examined as potential carriers of the diffuse interstellar bands (DIBs). This series of interstellar absorption peaks has been known for roughly 90 years,¹⁹ but not a single line has been conclusively linked to a molecular carrier²⁰ (although there is much discussion of a recent correlation between the excited states of CCCH₂ and several DIB features as proposed by Maier and co-workers²¹). Even so, Sarre¹ noticed that the 8 037.78 Å absorption wavelength for the 1 ${}^{1}B_{1} \leftarrow \tilde{X} {}^{1}A'$ transition of CH₂CN⁻ (Ref. 15) was nearly coincident with the DIB at the same wavelength (8 037.8 $\pm 0.15 {}^{1}A).^{22}$ This hypothesis was further explored by Cordiner and Sarre²³ through additional laboratory experimentation and interstellar examination with promising results, although many questions remain unanswered.

Such a tantalizing result for a "coincidence"²⁴ between the laboratory band of CH_2CN^- and the DIB has opened up the potential for a new direction of DIB research. Molecular anions have been thought to exist in the ISM since 1979 when Soifer and co-workers²⁵ tentatively resolved OCN⁻ in the 4–8 μ m spectrum of protostar W33 A in the constellation Sagittarius, an assignment that is supported by recent laboratory studies by Bennett *et al.*²⁶ Concerns remain that the ambient radiation field of background starlight might cause efficient ionization of such species, thus precluding their

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appearance as DIB carriers, though recent work by McCarthy and co-workers has shown that anions are actually more abundant and long-lived in the ISM than originally thought.²⁷ Other work has already proposed and cast doubt on a dipolebound state of CCCH₂⁻ as a carrier of some DIBs.^{28,29} However, there are still innumerable unexamined anions that could exhibit dipole-bound excited states that may yet show correlation between their absorption features and the DIBs.

Anions in experimentally simulated interstellar environments are difficult to study in the laboratory due to the low molecular densities generally created in the experiment, although newer experimental techniques promise to decrease this difficulty.²⁷ Hence, theory and computation are logical tools for the examination of such fleeting species. Methods that account for electron correlation effects have played a role in the determination of excited states for molecular anions since 1980 when a clear evidence for a dipole-bound state of CH₂CHO⁻ was finally shown using configuration interaction wave functions.³⁰ A recent theoretical interstellar study of OCN⁻ and its CNO⁻ isomer considered whether higherenergy electronic states for these anions could exist, though this seems unlikely given their low eBEs.³¹

In this study, we examine 12 anions for their potential to possess dipole-bound singlet excited states: CH₂SiN⁻, SiH₂CN⁻, CH₂SiHO⁻, SiH₂CHO⁻, CN⁻, C₃N⁻, SiN⁻, C₂F⁻, CCOH⁻, HCCO⁻, CH₂NO⁻, and CH₂OH⁻ shown in Figs. 1 and 2. High accuracy coupled cluster methods and large diffuse basis sets are used to compute dipole moments, eBEs, and excitation energies. As a first step, we calibrate the methods against experimental data for the two well-studied species, CH₂CN⁻ and CH₂CHO⁻. The performance of our methods with CH₂CN⁻ and CH₂CHO⁻ gives us a measure of certainty about the properties computed for the new anions that have not been fully explored. The new anions chosen for this study are either simple linear molecules with a σ orbital extending beyond the end of the chain, or the corresponding neutral radicals of the anions possessing a singly occupied valence orbital with an out-of-the-plane methylene or analogous silvlene group, comparable to the calibration molecules. The anions examined here may yet hold significance for further interstellar studies.

II. COMPUTATIONAL DETAILS

Computations on the neutral radical species were undertaken using spin-unrestricted (UHF) (Refs. 32 and 33) wave functions, while computations of the closed-shell anions used spin-restricted (RHF) (Ref. 34) wave functions. Ground state geometries of both the neutral radicals and anions were optimized using coupled cluster theory at the singles, doubles, and perturbative triples [CCSD(T)] (Ref. 35) level of theory. Previous theoretical work on dipole-bound states of anions by Skurski, Gutowski, and Simons³⁶ suggests the need for the use of Dunning's correlation-consistent basis sets augmented with higher angular momentum functions, the aug-cc-pVXZ series,^{37,38} for geometry optimizations and adiabatic eBEs.³⁹ Hence, the triple-zeta variant of these basis sets, aug-cc-pVTZ (Refs. 37 and 38) and aug-cc-pV(T + d)Z for the molecules containing silicon,⁴⁰ were used in this work. Dipole moments were computed using CCSD/aug-ccpVTZ at the CCSD(T)/aug-cc-pVTZ geometries. Both vertical and adiabatic excited states were computed in the equation of motion (EOM) formalism⁴¹ with coupled cluster theory^{42–44} at the singles and doubles (CCSD) level and at the additional approximate triples (CC3) (Refs. 45–47) levels of theory. CCSD adiabatic excitation energies were computed as the difference between the energies of the ground and desired excited states at their respective optimized geometries.^{48–50}

We have employed basis sets with increasing numbers of diffuse functions—including the aug-cc-pVXZ, d-aug-ccpVXZ, t-aug-cc-pVXZ, and q-aug-cc-pVXZ basis sets, with X = D, T—in order to examine how such functions affect the accuracy of the transition energies.^{48,49} The most diffuse exponents of each angular momentum of the d-aug-ccpVDZ and d-aug-cc-pVTZ basis sets^{37,38} were extrapolated in an even-tempered fashion in order to obtain the t-augcc-pVDZ, t-aug-cc-pVTZ, and q-aug-cc-pVDZ basis sets. In systems reported in this work where Si is present, *n*-aug-ccpVXZ actually refers to the *n*-aug-cc-pV(X+d)Z basis set⁴⁰ on the Si atoms. This nomenclature is used for the ease of discussion.

All EOM-CCSD adiabatic excited states were computed with the d-aug-cc-pVDZ basis set. Core orbitals were frozen in all coupled cluster computations: $1s^2$ for carbon, oxygen, and nitrogen and $1s^22s^22p^6$ for silicon. All coupled cluster computations were undertaken using PSI3,⁵¹ apart from EOM-CC methods for ionized states (EOMIP-CCSD and EOMIP-CCSDT) for selected species,⁵² which were carried out using the CFOUR package.⁵³ Density functionals available in the GAUSSIAN 03 package⁵⁴ were employed to examine their effectiveness in predicting the energies of dipole-bound excited states of anions. Becke's three-parameter exchange functional⁵⁵ with the Lee–Yang– Parr correlation functional⁵⁶ in the form of B3LYP,⁵⁷ as well as the 1996 Perdew–Burke–Ernzerhof functional (PBE),^{58,59} were utilized in this study.

III. RESULTS AND DISCUSSION

A. Calibration against known anions

CH₂CN⁻ and CH₂CHO⁻ are used as our benchmarking and calibration species since the properties of interest (eBEs and excitation energies) are well known for these molecules. Our computational results shown in Table I match well with the previously existing computational and experimental data. For the CH_2CN class of molecules shown in Figs. 1(a) and 2(a), the neutral radical is a $C_{2\nu}$ molecule while the anion has a C_s symmetry, which corroborates previous studies.^{14,16} The ground state Hartree-Fock configuration of CH₂CN⁻ is (core) $1a''^27a'^28a'^22a''^29a'^2$, and the key virtual orbitals are Rydberg-like 3s, 4s, and 5s orbitals. The neutral radical has a singly occupied b_1 orbital with a substantial amount of its density above and below the methylene group with the other two lobes above and below the cyano group. This orbital can be straightforwardly understood to correspond to the nearly identical 9a' HOMO of the anion.



FIG. 1. CCSD(T)/aug-cc-pVTZ optimized structures of the ground states of the closed-shell anions (top values) and neutral radicals (bottom values) of: (a) CH₂CN⁻ (1¹A' & 1²B₁, respectively) (The geometry shown is the C_s 1¹A' ground state of the anion, but the 1²B₁ radical ground state is C_{2v} .); (b) CH₂SiN⁻ (1¹A₁ & 1²B₁); (c) SiH₂CN⁻ (1¹A' & 1²A'); (d) C₃N⁻ (1¹\Sigma⁺ & 1²\Sigma⁺); (e) CN⁻ (1¹\Sigma⁺ & 1²\Sigma⁺); (f) SiN⁻ (1¹\Sigma⁺ & 1²\Sigma⁺); (g) C₂F⁻ (1¹\Sigma⁺ & 1²A') (The anion of C₂F⁻ is $C_{\infty v}$ and the neutral radical is C_s); (h) CCOH⁻ (1¹A' & 1²A'); (i) HCCO⁻ (1¹A' & 1²A'); (j) CH₂CHO⁻ (1¹A' & 1²A''); (k) CH₂SiCHO⁻ (1¹A' & 1²A''); (l) SiH₂CHO⁻ (1¹A & 1²A); (m) CH₂NO⁻ (1¹A' & 1²A'); and (n) CH₂OH⁻ (1¹A & 1²A).

The CCSD/aug-cc-pVTZ//CCSD(T)/aug-cc-pVTZ level of theory yields a dipole moment for the CH₂CN neutral radical in close agreement with the experimental and computational results of Ozeki and co-workers⁶⁰ at around 3.5 D.

The CCSD(T)/aug-cc-pVTZ adiabatic eBE of 1.49 eV including a small zero-point vibrational energy (ZPE) correction matches previous autodetachment¹⁵ and photoelectron⁷¹ spectroscopy results to within 0.06 eV. The first excited state



FIG. 2. CCSD/d-aug-cc-pVDZ optimized structures of the ground (top values) and first excited states (bottom values) of: (a) CH₂CN⁻ (1¹A' & 1¹B₁, respectively)(The geometry shown is the C_s 1¹A' ground state and that the excited 1¹B₁ is $C_{2\nu}$.); (b) CH₂SiN⁻ (1¹A₁ & 1¹B₁); (c) SiH₂CN⁻ (1¹A' & 2¹A'); (d) C₃N⁻ (1¹\Sigma⁺ & 2¹\Sigma⁺); (e) CN⁻ (1¹D⁺ & 1¹\Pi); (f) SiN⁻ (1¹D⁺ & 2¹D⁺); (g) C₂F⁻ (1¹D⁺ & 2¹A')(The ground state of C₂F⁻ is $C_{\infty\nu}$, and the first excited state is C_s .); (h) CCOH⁻ (1¹A' & 1¹A''); (i) HCCO⁻ (1¹A' & 2¹A'); (j) CH₂CHO⁻ (1¹A' & 1¹A''); (k) CH₂SiCHO⁻ (1¹A' & 1¹A''); (l) SiH₂CHO⁻ (1¹A' & 2¹A'); (j) CH₂CHO⁻ (1¹A' & 1¹A''); (k) CH₂SiCHO⁻ (1¹A' & 1¹A''); (l) SiH₂CHO⁻ (1¹A' & 2¹A'); (l) SiH₂CHO⁻ (1¹A' & 2¹A'); (l) SiH₂CHO⁻ (1¹A' & 1¹A''); (l) SiH₂CHO⁻ (1¹A' & 2¹A'); (l) SiH₂CHO⁻ (

TABLE I. Experimental and theoretical dipole moments (in Debye of the corresponding neutral radical), electron binding energies (in eV), and first adiabatic excited state transition energies (in eV) and wavelengths (in nm) for several anions. ZPE-corrected values are in parentheses.

	Radical dipole moment		Electron binding energy			Theory ^a		Experiment	
Molecule	This Work ^b	Previous	Theory ^c	Experiment	Transition	Energy	Wavelength	Energy	Wavelength
CH ₂ CN ⁻	3.509	3.508 ^d	1.48 (1.49)	$1.543 \pm 0.014^{\rm e}$	$1 {}^{1}B_1 \leftarrow 1 {}^{1}A'$	1.49 (1.51)	832 (822)	1.543	803.778 ^f
CH ₂ SiN ⁻	4.110		2.49		$1 {}^{1}B_1 \leftarrow 1 {}^{1}A_1$	2.11	589		
SiH ₂ CN ⁻	3.524		2.31		$2 {}^{1}A' \leftarrow 1 {}^{1}A'$	2.39	519		
CH ₂ CHO ⁻	2.921	3.191 ^g	1.77 (1.79)	1.8249 ^h	$1 {}^{1}A'' \leftarrow 1 {}^{1}A'$	1.77 (1.80)	700 (688)	1.759	704.9 ⁱ
CH ₂ SiHO ⁻	4.452		2.45		$1 {}^{1}A'' \leftarrow 1 {}^{1}A'$	2.46	504		
SiH ₂ CHO ⁻	2.391		1.93		$2^{1}A \leftarrow 1^{1}A$	2.03	612		
C_3N^-	2.889	2.785 ^j	4.38	4.305 ^k	$2^{1}\Sigma^{+} \leftarrow 1^{1}\Sigma^{+}$	4.68	265		
CN ⁻	1.471	1.45 ¹	3.82	3.862 ^m	$1^{1}\Pi \leftarrow 1^{1}\Sigma^{+}$	4.42	281		
C_2F^-	1.075		3.17		$2^{1}A' \leftarrow 1^{1}\Sigma^{+}$	3.51	353		
SiN ⁻	2.585	2.558 ⁿ	2.97	2.949°	$2^{1}\Sigma^{+} \leftarrow 1^{1}\Sigma^{+}$	3.24	383		
CCOH-	4.401	4.410 ^p	2.52		$1 {}^1A'' \leftarrow 1 {}^1A'$	2.43	511		
HCCO-	2.170		2.39	2.338 ^q	$1 {}^1A'' \leftarrow 1 {}^1A'$	2.38	521		
CH_2NO^-	2.317		1.42		$2 {}^{1}A' \leftarrow 1 {}^{1}A'$	1.55	799		
CH_2OH^-	1.474		-0.25						

^aAdiabatic EOM-CCSD/d-aug-cc-pVDZ values.

^bUHF-CCSD/aug-cc-pVTZ values for the radicals at the UHF-CCSD(T)/aug-cc-pVTZ geomtries.

^cThe differences between the RHF- (anion) and UHF- (radical) CCSD(T)/aug-cc-pVTZ energies.

^dRCCSD(T)/aug-cc-pVQZ result from Ref. 60 where corroborating microwave spectroscopy reported in the same paper estimates this value at ~3.5 D.

^eReference 15.

^fReference 23.

^gCISD/SVP result from Reference 61.

^hReference 62.

ⁱReference 17.

^jCEPA-1/cc-pVQZ from Ref. 63. ^kReference 64

¹Experimental result from Reference 65.

^mReference 66.

ⁿCCSD(T)/aug-cc-pV6Z result from Ref. 67.

^oReference 68.

PCISD/TZ3P(2f,2d) result from Reference 69.

^qReference 70.

of the CH₂CN⁻ anion reverts back to the $C_{2\nu}$ symmetry upon optimization giving the 1¹B₁ excited state, yielding a 1.51 eV EOM-CCSD/d-aug-cc-pVDZ adiabatic excitation energy, which matches experiment^{15,23} to within 0.05 eV. Even though the excitation energy of CH₂CN⁻ is predicted to lie 0.01 eV (0.02 with ZPE) higher in energy than the eBE, these two computed values fall well within the accepted level of computational accuracy for these theoretical methods (~0.1 eV, Ref. 72). Hence, within the error bars of our theoretical models, the computations agree with the experimental data that CH₂CN⁻ can exhibit a dipole-bound excited state.

As shown in Figs. 1(j) and 2(j), the CH₂CHO class of molecules all possess a C_s symmetry, and the ground state Hartree-Fock configuration for the anion is $(\text{core})9a'^21a''^210a'^22a''^2$. Table I reports that the 2.921 D dipole moment we computed for the ground ${}^2A''$ state of the radical agrees with the CISD/saturated vapor pressure (SVP) theoretical result of 3.191 D computed by Huyser and co-workers⁶¹ used in the experiments done by Mead, Lykke, and Lineberger.⁷³ As for CH₂CN⁻, we predict the eBE of CH₂CHO⁻ (1.77 eV) to lie within 0.06 eV of experiment,⁶² and the ZPE correction affects this only slightly. The 1.77 eV excitation energy of the $1 {}^{1}A'' \leftarrow 1 {}^{1}A'$ transition is predicted to be within 0.02 eV of the measured transition energy.¹⁷ Our methods predict the CH₂CHO⁻ anion to have an exci-

tation energy and eBE that are nearly identical, as expected for a dipole-bound state. However, the excitation energy rises above the eBE when the ZPE is considered, but only by 0.02 eV. Again, this anion is known to possess a dipole-bound excited state, and our methods can corroborate this within the expected error bars of the coupled cluster approach.

The vertical excitation energies reported in Table II also demonstrate the need for robust basis sets. For CH₂CN⁻, the 5.218 eV EOM-CCSD/cc-pVDZ excitation energy for the $2^{1}A'$ state (which correlates to the $1^{1}B_{1}$ state in a $C_{2\nu}$ symmetry⁷⁴) compares poorly to the experimental value of 1.54 eV due to the lack of diffuse functions in the basis set. Augmentation of the basis set to the t-aug-cc-pVDZ level coincidentally brings the EOM-CCSD vertical excitation into perfect agreement with experiment, with the largest contribution to the excited-state wave function arising from the Rydberg-like 3s orbital. Use of triple-zeta basis sets in conjunction with diffuse orbitals tends to shift the excitation energies upward relative to their double-zeta counterparts, and inclusion of the EOM-CCSD/d-aug-cc-pVDZ adiabatic shift of -0.14 eV with the EOM-CCSD/d-aug-cc-pVTZ vertical transition energies yields a small 0.1 eV error compared to experiment. The oscillator strength of this transition, as requested by Cordiner and Sarre,²³ at the EOM-CCSD/d-augcc-pVTZ level of theory is found to be 0.014.

TABLE II. Comparison of methods and basis sets^a for vertically excited state energies (in eV) based upon each anion's CCSD(T)/aug-cc-pVTZ ground state geometry.

Molecule	Transition	Method	pVDZ	apVDZ	dapVDZ	tapVDZ	pVTZ	apVTZ	dapVTZ	f^{b}	Experiment
CH ₂ CN ⁻	$2 {}^{1}A' \leftarrow 1 {}^{1}A'$	CCSD	5.22	2.17	1.63	1.54	4.56	2.20	1.79	0.01	1.543 ^c
		CC3	4.68	2.09	1.54	1.46	4.56	2.09	1.68		
		B3LYP	4.78	1.91	0.79	0.11	4.18	1.75	0.77		
		PBE	4.64	1.64	0.31		4.05	1.46	0.28		
CH₂SiN [−]	$1 {}^{1}B_1 \leftarrow 1 {}^{1}A_1$	CCSD	2.90	2.24	2.13	2.13	2.69	2.29	2.23	0.003	
		CC3	2.76	2.11	2.00	2.00	2.54	2.14	2.08		
	$2^1B_1 \leftarrow 1^1A_1$	CCSD	6.44	3.38	2.60	2.39	5.87	3.33	2.73	0.004	
		CC3	6.19	3.24	2.47	2.27	5.61	3.17	2.58		
	$2^{1}A_{1} \leftarrow 1^{1}A_{1}$	CCSD	5.18	3.92	2.69	2.43	4.89	3.92	2.84	0.23	
		CC3	5.11	3.80	2.57	2.31	4.93	3.77	2.69		
	$3^1B_1 \leftarrow 1^1A_1$	CCSD	5.22	4.27	2.74	2.46	4.80	4.12	2.94	0.02	
		CC3	4.96	4.00	2.62	2.33	4.54	3.97	2.79		
	$4^1B_1 \leftarrow 1^1A_1$	CCSD	7.35	4.33	3.04	2.55	7.16	4.30	3.17	0.007	
		CC3	7.21	4.18	2.91	2.42	6.97	3.99	3.02		
SiH2CN-	$2^{1}A' \leftarrow 1^{1}A'$	CCSD	7.20	3.92	3.15	2.85	6.53	3.93	3.27	0.003	
		CC3	7.02	3.85	3.08	2.77	6.43	3.85	3.19		
CH2CHO-	$1 {}^{1}A'' \leftarrow 1 {}^{1}A'$	CCSD	5.62	2.52	1.89	1.78	5.06	2.50	2.03	0.009	
		CC3	5.55	2.48	1.85	1.75	4.97	2.43	1.96		1.76 ^d
		B3LYP	5.10	2.19	0.93	0.27	4.58	1.99	0.88		
CH2SiHO-	$1 {}^{1}A'' \leftarrow 1 {}^{1}A'$	CCSD	5.23	3.12	2.59	2.62	4.94	3.10	2.73	0.02	
		CC3	5.03	3.04	2.52	2.46	4.74	2.99	2.63		
SiN ⁻	$2^{1}\Sigma^{+} \leftarrow 1^{1}\Sigma^{+}$	CCSD	6.61	4.25	3.24	3.01	6.07	4.20	3.32	0.02	
		CC3	6.41	4.01	2.98	2.77	5.85	3.93	3.03		
CCOH-	$1 {}^{1}A'' \leftarrow 1 {}^{1}A'$	CCSD	4.85	2.92	2.68	2.66	4.47	2.99	2.82	0.003	
		CC3	4.63	2.73	2.49	2.47	4.24	2.77	2.60		
HCCO-	$1 {}^1A'' \leftarrow 1 {}^1A'$	CCSD	5.35	3.07	2.48	2.37	5.20	3.09	2.64	0.007	
		CC3	5.32	2.92	2.33	2.21	5.15	2.89	2.44		

^aDunning's correlation consistent basis sets are abbreviated, e.g., d-aug-cc-pVDZ is dapVDZ.

^bOscillator strengths computed at the EOM-CCSD/d-aug-cc-pVTZ level of theory.

^cReference 23.

^dReference 17.

Inclusion of triples via CC3 for the $2^{1}A'$ state of CH₂CN⁻ and the *n*-aug-cc-pVTZ series of basis sets converges closely to the experimental value, though adiabatic shifts would push the final excitation energy lower. As observed at the CCSD level, the character of this state is primarily s-type Rydberg, with a largest contribution of 0.4 for the 3s orbital. On the other hand, the B3LYP and PBE density functionals fail dramatically for this state, as expected,⁷⁵ yielding excitation energies up to a factor of ten too small with large basis sets. For the vertically excited computations of the $1^{-1}A''$ state of CH₂CHO⁻ shown in Table II, the *n*-augcc-pVDZ computations for both CCSD and CC3 converge to within 0.05 eV of the experimental value for this state's transition energy at 1.76 eV.¹⁷ The triple-zeta basis set results do not converge as neatly for the inclusion of more highly diffuse functions, but these values are still more well behaved than density functional theory with either series of basis sets.

It can thus be seen from the calibration of our methods using CH_2CN^- and CH_2CHO^- that predictions can be made

as to whether or not a given anion may possess a dipole-bound excited state and where this transition may be found, based on both vertical and adiabatic excitation energies and on eBEs, all computed using basis sets that include adequate diffuse functions. In subsequent sections, we employ this approach for various closed-shell anions whose neutral radicals possess a sufficiently large dipole moment. While the optimized structures reported below are minima, we do not include ZPE corrections to the energies as these were found to have no appreciable affect on the predicted excitation energies and eBEs of CH_2CN^- and CH_2CHO^- .

B. Potential anions with dipole-bound excited states

1. Silicon analogues of CH₂CN⁻

The logical place to begin the search for new anions possessing dipole-bound excited states is with isovalent systems closely related to the original calibration molecules. Single replacement of silicon for each of the carbon atoms in CH_2CN^- and CH_2CHO^- leads to molecular systems about which little has been reported in the literature, including the existence of dipole-bound excited states. The fact that Si–C bonds are longer than C–C bonds as well as the electronegativity difference between the two elements will have an affect on the dipole moments of the Si-substituted molecules. Silicon containing molecules have been known to exist in the ISM since the initial discovery of SiO in 1971 (Ref. 76) and the first evidence of an interstellar Si–C bond came in 1984 (Ref. 77). Additionally, SiN (Ref. 78) and SiNC (Ref. 79) have been found in the ISM. SiH₂SiN⁻ will not be studied since no Si–Si bond has previously been detected in the ISM.⁸⁰

As shown in Table I, CH_2SiN^- is predicted to have a very large dipole moment (4.110 D, one of the largest of all the species considered in this study) and an eBE 0.38 eV higher in energy than its first excitation energy of 2.11 eV (adiabatic EOM-CCSD/d-aug-cc-pVDZ level of theory), suggesting that this silicon analogue of CH_2CN^- possesses at least one excited state. CH_2SiN^- has a ground state electronic configuration of (core) $9a_1^2 2b_1^2 3b_2^2 3b_1^2$ and is a $C_{2\nu}$ molecule in both its ground and $1^{-1}B_1$ (first excited) states. The point group symmetry for the ground state of CH_2SiN^- differs from the original CH_2CN^- anion, but the terms of the first excited state of each anion correlate directly. All of these structures are shown in Figs. 1(b) and 2(b).

Surprisingly, CC3/t-aug-cc-pVDZ predicts that five vertically excited states of CH_2SiN^- lie below the 2.49 eV eBE: $1^{1}B_{1}$, $2^{1}B_{1}$, $2^{1}A_{1}$, $3^{1}B_{1}$, and $4^{1}B_{1}$. The $1^{1}B_{1}$ state is a transition out of the $3b_1$ HOMO and, as can be seen in Table II, the inclusion of higher angular momentum functions in the basis set does lower the energy of the transition but the effect is much smaller than in the calibration anions. Analysis of the virtual orbitals involved in the excitation with the t-aug-cc-pVDZ basis set shows that the excitation character of the wave function is comprised of transitions into diffuse s-type orbitals. However, the impact of such functions is much smaller for the $1^{1}B_{1}$ state than for the higher states, suggesting that its diffuse character is less than its cohort. The character of the $2^{1}B_{1}$ state is dominated by a $3b_{1} \rightarrow s$ transition, and the inclusion of the more diffuse functions in the basis set is absolutely necessary for this state given that the vertical excitation energy decreases by over 4 eV for EOM-CCSD over the course of the *n*-aug-cc-pVDZ series. The 2¹A₁ state is predominantly composed of a $3b_1 \rightarrow p_x$ excitation as predicted by both CCSD and CC3 with the t-aug-cc-pVDZ basis set. The $3^{1}B_{1}$ and $4^{-1}B_{1}$ states exhibit mixed diffuse s- and p-type character.

Needless to say, the appearance of multiple states below the eBE of a small anion, such as CH₂SiN⁻ would be a surprising and perhaps an unprecedented finding. The variation in the excitation energies reported in Table II reveals their exquisite sensitivity to the adequate inclusion of diffuse functions. In addition, the comparison between CCSD(T)/ aug-cc-pVTZ adiabatic eBE values to adiabatic and vertical EOM-CCSD/ or CC3/n-aug-cc-pVXZ excitation energies is not completely balanced, given the differences in geometries and wave function parametrizations. To correct for these prob-

TABLE III. EOMIP-CCSD electron binding energies and lowest EOM-CCSD ${}^{1}A_{1}$ and ${}^{1}B_{1}$ vertical excitation energies (in eV) of CH₂SiN⁻ with diffuse basis sets.

	VD7	1 VD7	4VD7	VD7				
	apvDZ	dapvDZ	tapvDZ	qapvDZ				
	EOMIP-CCSD							
eBE	2.30	2.34	2.34	[2.34] ^a				
State	EOM-CCSD							
$2 {}^{1}A_{1}$	3.92	2.69	2.43	2.37				
$3 {}^{1}A_{1}$	4.51	3.16	2.56	2.39				
$1 {}^{1}B_{1}$	2.24	2.13	2.13	2.13				
$2^{1}B_{1}$	3.38	2.60	2.39	2.35				
$3 {}^{1}B_{1}$	4.27	2.74	2.46	2.37				
$4^{1}B_{1}$	4.33	3.04	2.55	2.39				

^aDue to SCF convergence difficulties with the q-aug-cc-pVDZ basis set, the EOMIP-CCSD/t-aug-cc-pVDZ eBE value is reported.

lems, we have further analyzed the eBE and the lowest excited states of CH₂SiN⁻ using EOMIP-CC and EOM-CC methods, respectively, at the same CCSD(T)/aug-cc-pVTZ optimized structure and with the same basis sets. These methods make use of the same CCSD ground-state wave function, but the subsequent diagonalization of the similarity-transformed Hamiltonian is carried out in different determinantal spaces: EOM-CCSD uses all singles (hp) and doubles (2h2p) in the *N*-electron space of the anion, while EOMIP-CCSD uses the *h* and 2hp determinants in the *N* – 1-electron space of the neutral radical.

Table III summarizes the EOMIP-CCSD and EOM-CCSD results for CH_2SiN^- using basis sets up to q-aug-ccpVDZ. The EOMIP-CCSD results were obtained using the CFOUR package,⁵³ while the EOM-CCSD data were computed using PSI.⁵¹ The eBE of the anion converges rapidly to a value of 2.34 eV, which is 0.15 eV lower than the adiabatic CCSD(T)/aug-cc-pVTZ result of 2.49 eV. While the latter should be considered more accurate for eventual comparison to experiment, the purpose of the EOMIP-CCSD/ EOM-CCSD data is to provide a balanced comparison of the eBE and corresponding excitation energies for the characterization of the excited states.

As noted earlier, the 1 ${}^{1}B_{1}$ excited state converges rapidly to a value of 2.13 eV with respect to the number of diffuse functions in the basis set, suggesting that its character is valence rather than dipole-bound. This interpretation is further supported by the fact that its EOM-CCSD energy is 0.21 eV lower than the EOMIP-CCSD eBE of 2.34 eV. Further computations at the EOMIP-CCSDT and EOM-CCSDT levels of theory also support this conclusion, with the former yielding an aug-cc-pVDZ eBE of 2.24 eV and the latter an excitation energy of 2.01 eV.

The next lowest state is $2^{1}B_{1}$, whose energy is much more sensitive to the diffuse-function space: the difference between the t-aug-cc-pVDZ and q-aug-cc-pVDZ excitation energies is still 0.041 eV. While the EOM-CCSD/q-aug-ccpVDZ excitation energy is 2.35 eV, it is reasonable to conclude that this value would fall below the eBE if the basis-set were augmented even further, and thus the $2^{1}B_{1}$ state is indeed dipole-bound. The remaining states reported in Table III still do not appear to be converged even with the q-aug-ccpVDZ basis set, and thus strong conclusions regarding their character are not possible. Nevertheless, we can predict with some confidence not only the existence of a dipole-bound state for CH_2SiN^- near the CCSD(T)/aug-cc-pVTZ adiabatic value of 2.49 eV, but also a rare valence excited state roughly 0.4 eV lower in energy at the EOM-CCSD/d-aug-cc-pVDZ adabatic excitation energy of 2.11 eV. These results clearly make the CH_2SiN^- anion an interesting molecule for subsequent experimental study.

The excited state chemistry of SiH₂CN⁻ does not appear to be quite as rich as the other silicon analogue of CH_2CN^- , but this anion may also possess one dipole-bound excited state. As shown in Fig. 1(c), the ground state of SiH₂CN⁻, like the ground state of CH₂CN⁻, drops to the lower symmetry C_s point group as the hydrogens in the silvlene group are more stable in a nonplanar configuration. However, for SiH_2CN^- , this is also true of the radical [also Fig. 1(c)] and the 2 ${}^{1}A'$ state [Fig. 2(c)]. The ground state electronic configuration is: (core) $2a''^2 11a'^2 3a''^2 12a'^2$ where the $12a'^2$ HOMO has a majority of its electron density directly above the silylene group with the corresponding out of phase lobe contained in the space between the two downward-bent hydrogens and the Si-C bond. The two other small lobes of the 12a' orbital are above and below the cyano group like in the 9a' HOMO of CH_2CN^- .

Our methods predict a dipole moment for SiH₂CN⁻ of 3.52 D and a 2.31 eV eBE with an adiabatic first excited $(2^{-1}A')$ state at 2.39 eV, close to the limit of what can be considered a dipole-bound excited state. The next item to note for this excited state is that there is a fairly large adiabatic affect. The adiabatic EOM-CCSD/d-aug-cc-pVDZ 2 ${}^{1}A'$ state of SiH₂CN⁻ is predicted to be 2.39 eV above the ground state, but the vertical value for the same level of theory and basis set is 3.15 eV, a difference of 0.76 eV. This is mainly due to an even larger decrease of the H-Si-H bond angle from the ground state to the excited state. Similar but more subtle effects on the H-C-H bond in the methylene group change the point group symmetry between the CH₂CN radical and the anion. The vertical CC3/t-aug-cc-pVDZ $2^{-1}A'$ excited state has a strong Rydberg character, as evidenced by the diffuse s-type nature of its wave function and the large dependence of the excitation energy on the presence of diffuse functions in the basis set (cf. Table II).

2. Silicon analogues of CH₂CHO⁻

The dipole-bound excited states of the silicon analogues of CH₂CHO⁻ are not as numerous as the silicon analogues of CH₂CN⁻, but the CH₂SiHO⁻ anion [see Fig. 1(k)] does appear to exhibit an excited state. CH₂SiHO⁻ has a ground state configuration of (core) $12a'^22a''^213a'^23a''^2$, and the 3a''HOMO is an out-of-plane orbital which has most of its density above and below the methylene group in the radical. Our methods predict this radical also to have a very large dipole moment (4.445 D) and the anion to have a 2.45 eV eBE. The adiabatic excitation energy for the $1 \, {}^{1}A''$ state is predicted to be 2.46 eV, slightly higher than the eBE, but, again as with CH₂CHO⁻, this does not rule out the possibility of its existence, given the error bars of the coupled cluster approach. Additionally, this molecule does not exhibit a very large adiabatic effect, 0.13 eV. CC3/t-aug-cc-pVDZ indicates that the wave function describing this state has a strong Rydberg *s*-type character. This excitation is directly analogous to that seen in the $1^{-1}A''$ state of the CH₂CHO⁻ anion. The $1^{-1}A''$ state of CH₂SiHO⁻ exhibits slightly less change in the vertical excitation energy resulting from an increase in the n value for the *n*-aug-cc-pVXZ basis set series than the $1^{-1}A''$ state of CH₂CHO⁻, but diffuse basis sets are still imperative.

The excitation energy for the 2 ${}^{1}A$ state of the other analogue, SiH₂CHO⁻, is 2.03 eV, 0.10 eV higher than the eBE. This is just at the limit for what we are considering to be potential dipole-bound excited states. As can been seen in Figs. 1(1) and 2(1), the hydrogens in the silylene group bend out-of-the-plane of the molecule, such as SiH₂CN⁻, but the structure of the formyl group leaves SiH₂CHO⁻ with no symmetry, and we expect no excited state to be observable experimentally.

3. Linear anions

One of the simplest molecules known to exist in the ISM is the cyano radical.⁸¹ CN [Fig. 1(e)] has a relatively small dipole moment of 1.471 D at the CCSD/aug-cc-pVTZ level of theory (in agreement with previous work⁶⁵) and is less than the 1.625 D limit (Ref. 3). Additionally, from Table I, the excitation energy of the corresponding anion found recently in the ISM⁸² [Fig. 2(e)] is predicted to be right at 0.6 eV higher in energy than the eBE, indicating that CN^- does not possess a dipole-bound singlet excited state.

SiN shown in Fig. 1(f), which has been known to exist in the ISM for nearly 20 years now⁷⁸ and whose anion has been suspected to possess dipole-bound states for some time,⁸³ is reported to have a much larger dipole moment at 2.558 D (Ref. 67), and our computations agree. The CCSD(T)/augcc-pVTZ eBE of 2.97 eV for SiN⁻ [Fig. 2(f)], which improves upon previous computations for this value at 2.86 eV (Ref. 83), is in close agreement with the experimental value of 2.95 eV (Ref. 68). However, our methods predict the $2^{1}\Sigma^{+}$ excited state to lie adiabatically at 3.24 eV (the corresponding vertical transition is 3.24 eV), well above the eBE. However, the convergence of the vertical excitation energy with increasing numbers of diffuse functions in the basis set suggests that the excitation energy for this state is less than 3 eV. At the CC3 level of theory, the excitation energy decreases by 0.21 eV between the d-aug-cc-pVDZ and t-aug-cc-pVTZ basis sets (cf. Table II). If this shift was applied to the d-aug-ccpVTZ basis set result, the CC3 method would yield a vertical excitation energy of ~ 2.82 eV, well within the eBE limit. Hence, a dipole-bound $2^{1}\Sigma^{+}$ state of SiN⁻ may exist near the eBE. While a ${}^{3}\Sigma^{+}$ state is known,⁶⁸ this work provides the first indication of a singlet state in the same energetic region.

Extending the carbon chain in CN^- to C_3N^- [both of which have been identified in the ISM (Refs. 84 and 85)] allows for greater charge-density separation and nearly doubles the dipole moment of C_3N (2.889 D) versus CN. Even so, the adiabatic excitation energy for the $2^{1}\Sigma^+$ excited state

of C_3N^- [see Fig. 2(d)], 4.68 eV, is 0.30 eV higher in energy than the predicted 4.38 eV eBE which agrees well with previous experiment.⁶⁴ We therefore conclude that no dipolebound singlet excited state of C_3N^- exists. While C_2F^- is linear, the C_2F neutral radical^{86,87} [see Fig. 1(g)] is bent at 154.9°, yielding an eBE of 3.17 eV at the CCSD(T)/aug-cc-pVTZ level of theory and a relatively small dipole moment of 1.075 D. However, the linear radical (which is not a minimum on the potential surface) has a much larger dipole moment of 2.403 D. This is not enough, however, to stabilize the lowest singlet excited state, as the EOM-CCSD/d-aug-cc-pVDZ adiabatic transition energy is 3.51 eV, well above the required threshold.

4. Other anions

The last four entries of Table I give the data of four other anions in our search for new species potentially possessing dipole-bound excited states. The first two molecules, CCOH⁻ and HCCO⁻ [see Figs. 1(h)/2(h) and 1(i)/2(i), respectively] have been previously examined. Our coupled cluster data are in close agreement with the CISD prediction for the 4.4 D dipole moment of the CCOH radical⁶⁹ and are within 0.05 eV of the 2.338 eV eBE for HCCO⁻ obtained from photoelectron spectroscopy.⁷⁰

The C_s CCOH⁻ anion has a Hartree-Fock configuration of (core)1 $a''^2 8a'^2 9a''^2 a''^2$ and is predicted to have an adiabatic 1 ¹A'' excited state state at 2.43 eV, below the predicted 2.52 eV eBE. The vertical excitation energies differ by 0.26 eV from their adiabatic counterparts at the EOM-CCSD/ d-aug-cc-pVDZ level of theory. A small 0.02 eV difference in the excitation energy of the 1 ¹A'' state appears between the d-aug-cc-pVDZ and the t-aug-cc-pVDZ basis sets, indicating that no additional diffuse orbitals are necessary. CC3 also exhibits this small excitation energy difference between the most diffuse basis functions of this excited state, but, additionally, CC3/t-aug-cc-pVDZ lowers the excitation energy by about 0.2 eV as compared to EOM-CCSD/t-aug-cc-pVDZ. Based on these results, we predict that CCOH⁻ exhibits a dipole-bound singlet excited state near 2.5 eV.

The HCCO⁻ isomer also exhibits the same Hartree-Fock configuration as CCOH⁻, but the singly occupied orbital of the neutral radical is the 9a' orbital, which has a carbene-like lone pair on C₁ [cf. Fig. 1(i)]. However, the lowest-energy excitation still occurs from the $2a'' \pi$ -type orbital into diffuse *s*-type orbitals similar to CCOH⁻. The computed adiabatic excitation energy of 2.38 eV is just below the eBE of 2.39 eV (see Table I), and the adiabatic shift is ~0.1 eV (cf. Tables I and II). This energy decreases a bit more for HCCO⁻ from the d-aug-c-pVDZ to the t-aug-cc-pVDZ than with CCOH⁻, but we still predict that the $1^{1}A''$ state is a dipole-bound excited state occurring in HCCO⁻.

The bottom two lines of Table I list the final two anions examined in this study, CH_2NO^- and CH_2OH^- [Figs. 1(m)/2(m) and 1(n)/2(n)]. These two anions have methylene groups and, hence, similar HOMOs to those of CH_2CN^- and CH_2CHO^- . CH_2NO^- can be viewed as the result of nitrogen replacement in the second carbon position of CH_2CHO^- . Our methods indicate that this molecule has a large enough dipole moment (2.317 D) for it to potentially possess a dipole-bound excited state, but the excitation energy to the 2 ${}^{1}A'$ state is 0.14 eV above the eBE. Basis set extension does not appear to shift the excitation energy below the eBE. Hence, we conclude that CH₂NO⁻ is not likely to possess a dipole-bound excited state. Last, CH₂OH⁻, a molecule with no symmetry, has a dipole moment for the corresponding radical below 1.625 D. Additionally, our methods demonstrate that this anion is actually less stable than the neutral radical since a negative eBE is reported. This necessarily shows that CH₂OH⁻ cannot exhibit a dipole-bound excited state.

IV. CONCLUSIONS

We have shown that six new anions may possess dipole-bound excited states; these include the $2^{1}B_{1}$ state of CH₂SiN⁻; the $1^{1}A''$ states of CH₂SiHO⁻, CCOH⁻, and HCCO⁻; and potentially the $2^{1}A'$ state of SiH₂CN⁻ and the $2^{1}\Sigma^{+}$ state of SiN⁻. In addition, we predict a valence-bound excited state of CH₂SiN⁻ near 2.11 eV, roughly 0.4 eV below its eBE of 2.49 eV. Conclusive identification of threshold resonances associated with dipole-bound singlet excited states requires experimental analysis, of course, but the data reported here should provide the requisite starting point for further study. Clearly, there are still many molecules whose properties have not been fully explored computationally or experimentally that may yet hold the key for a better understanding of the chemistry present in the ISM.

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