Electronically Excited States of Interstellar Anions

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Abstract

In the search for carriers of the diffuse interstellar bands (DIBs), a nearly ubiquitous, as-of-yet unattributed interstellar absorption spectrum, new theories are being proffered to explain this astronomical phenomenon. One of these is that rarely occurring excited states of anions may be responsible for some of these features. Using state-of-the-art quantum chemical techniques we examine nearly twenty anions for their excited state properties. Using two known species as benchmarks, nine new molecules about which little is known are shown to possess dipole-bound excited states while three of these (CH$_2$SiN$^-$, SiCCN$^-$, and CCSiN$^-$) are predicted by our methods to possess both dipole-bound and potentially even valence-bound excited states, an incredibly rare circumstance. These anions may yet hold significance for the chemistry of the interstellar medium and for the DIBs.

Introduction

"The longest standing unsolved problem in spectroscopy"¹ is that of the carriers of diffuse interstellar bands (DIBs) — the series of as of yet unidentified absorption peaks known for over 90 years²–⁴ stretching from the UV to near-IR observed in multiple interstellar sight lines. Conclusive assignment of molecular carriers may only arise from the application of theoretical methods and computational tools to this problem⁵ since quantum chemical theory is tremendously flexible in its application to chemical problems and in the often necessary refinement of hypotheses. Theoretical methods have been applied to problems within astrochemistry for over thirty years,⁶–⁸ mainly for the microwave identification of molecules present in the interstellar medium (ISM). Quantum mechanical models provide accurate estimates of rotational constants for candidate species, laboratory experiments search for the corresponding fingerprints within high-resolution microwave spectra, and these are both compared to radioastronomical data.⁶–¹⁰ Unfortunately, a similar approach is problematic in the case of the diffuse interstellar bands, in part because, while modern quantum chemical methods can provide exceptionally accurate predictions of molecular structure necessary to derive rotational constants,¹¹,¹² electronic spectra are significantly more challenging. This is due to the greater sensitivity of electronic transition energies and oscillator strengths to the accuracy of the model, coupling of the electronic transitions to vibrational modes,¹³ etc. Nevertheless, ongoing efforts to identify the carriers of the DIBs may very well hinge on advances in the reliability of quantum chemical models⁵ and their ability to accurately predict the electronic absorption spectra for large numbers of proposed molecular carriers.

Figure 1: The DIBs¹⁴

Very recently, the Maier group and collaborators¹⁵ have offered a detailed argument for a molecular carrier of DIB features: propadienylidene, CCCH$_2$. Their earlier work¹⁶ had shown a near exact “coincidence” between the broad and shallow DIB feature at 5450 Å and a laboratory absorption band at that precise wavelength that had not been conclusively linked to a specific molecule. The group’s latest work¹⁵ clearly identified CCCH$_2$ as the carrier of the laboratory band at 5450 Å and a laboratory absorption band at that precise wavelength that had not been conclusively linked to a specific molecule. The group’s latest work¹⁵ clearly identified CCCH$_2$ as the carrier of the laboratory band at 5450 Å, assigned as the result of the $1\,^1B_1 \leftarrow 1\,^1A_1$ transition, and even showed very good agreement between the CCCH$_2$ band at 4887 Å and the DIB at this wavelength, as well. Additionally, there is the possibility for more correlation to be shown between the CCCH$_2$ spectrum beyond 6000 Å and other DIB features noted in this range, but more work must be done before absolute assignment can be made.¹⁷

The electronic states of CCCH$_2$ were studied first using quantum chemical methods as a means to help elucidate the various transitions observed in the labo-
ratory spectrum.\textsuperscript{18,19} These computations helped to inform the experimentalists of which excited states of CCCH\textsubscript{2} should be observable and at what frequencies they should be found.\textsuperscript{19} The uncertainty of the vibrational progressions present in the neon matrix experiments coupled with the uncertainty inherent in the computations made for an interesting but inconclusive spectral characterization of CCCH\textsubscript{2}. However, the general knowledge of where in the UV/Vis spectrum to expect the lowest-energy excited states of this molecule, perhaps relevant to the DIBs, was first established through the use of theory.

As with these initial examinations of CCCH\textsubscript{2}, theory is often employed for various reasons to help give a better understanding to the electronic transitions observed. For studies of interstellar spectra such as the DIBs, a molecule cannot be conclusively linked to an astronomical absorption feature until its spectrum has been recreated, often with much difficulty, in the laboratory where vacuum environments, molecule elucidation, and signal strengths can present serious challenges. Theoretical methods, on the other hand, suffer from no such restrictions, save for the often substantial computational costs associated with the most advanced models, which are essential for accurate simulations.

The recent conclusion that anions are more common in the ISM than originally thought\textsuperscript{20} has opened up another avenue for exploration in the excited states of interstellar molecules. Molecular anions have been thought to exist in the ISM since 1979 when Soifer and coworkers\textsuperscript{21} tentatively resolved OCN\textsuperscript{−} in the 4-8 \textmu m spectrum of protostar W33 A in the constellation Sagittarius, an assignment that is supported by recent laboratory studies by Bennett et al.\textsuperscript{22} Concerns remain that the ambient radiation field of background starlight might cause efficient ionization of such species, thus precluding their appearance as DIB carriers, though the recent work by McCarthy and coworkers has shown that anions are quite abundant and long-lived in the ISM.\textsuperscript{20} Other work has already proposed and cast doubt on excited states of CCCH\textsubscript{2} as a carrier of some DIBs.\textsuperscript{23,24} 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.\textsuperscript{20} 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 clear evidence for a what is called a dipole-bound state of CH\textsubscript{2}CHO\textsuperscript{−} was finally shown using configuration interaction wave functions.\textsuperscript{25}

According to various theoretical analyses starting with the earliest work by Fermi and Teller in 1947,\textsuperscript{26} a minimum electric dipole moment of 1.625 D is necessary to support a so-called dipole-bound state in an anion.\textsuperscript{27} Such states are observable in high-resolution spectra as “threshold resonances” very near the electron binding energy (\textit{eBE}) of the neutral molecule. Given that such binding energies are typically small — in the visible to near-infrared region of the spectrum — Sarre suggested\textsuperscript{28} more than a decade ago that dipole-bound states in small molecules could be carriers of interstellar spectroscopic features such as the DIBs. Such long wavelength transitions are not as common as they are for neutral or cationic molecular species, but, as explained by Simons,\textsuperscript{27} some anions do exhibit excited states below the deionization limit. In particular, Cornier and Sarre\textsuperscript{29} proposed a possible link between the CH\textsubscript{2}CN\textsuperscript{−} anion and the DIB at 8037Å. This intriguing idea led us to explore the possibility of singlet excited states in small closed-shell anions whose corresponding neutral radicals possess large dipole moments.\textsuperscript{30}

**Theoretical Considerations**

**Coupled Cluster Excited States**

The coupled cluster approach to electron correlation is based on an exponential expansion of the many-electron wave function,\textsuperscript{31–33}

$$|\Phi_{\text{CC}}\rangle = e^{\hat{T}}|\Phi_{0}\rangle,$$

(1)

where the cluster operator, $\hat{T} = \hat{T}_{1} + \hat{T}_{2} + \ldots$ generates linear combinations of substituted/excited Slater determinants from a reference function, $|\Phi_{0}\rangle$, typically the Hartree-Fock wave function. The advantage of the exponential form (as opposed to the linear expansions of configuration interaction or Møller-Plesset perturbation theory) can be seen from its power-series form:

$$e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2!}\hat{T}^{2} + \frac{1}{6!}\hat{T}^{3} + \ldots$$

(2)

Thus, if we choose to truncate the $\hat{T}$ operator at only singles and doubles (yielding the CCSD method), then the exponential produces products of $\hat{T}_{1}$ and $\hat{T}_{2}$ operators,

$$e^{\hat{T}_{1} + \hat{T}_{2}} = 1 + \hat{T}_{1} + \hat{T}_{2} + \frac{1}{2}\hat{T}_{1}^{2} + \hat{T}_{1}\hat{T}_{2} + \frac{1}{2}\hat{T}_{2}^{2}$$

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Therein lies one of the principal advantages of coupled cluster theory: even when the cluster operator is truncated, \( e.g. \), singles and doubles, the exponential wave function implicitly incorporates higher substitution levels. As a result, the coupled cluster expansion converges towards the full configuration interaction limit very quickly making it a highly accurate and reliable approach.

Excited states are accessible within coupled theory via the equation of motion (EOM-CC) approach,\(^{35,36}\) in which the exponential wave operator, \( e^{\hat{T}} \), is used to construct from the electronic Hamiltonian, \( \hat{H} \), an effective Hamiltonian,

\[
\hat{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}. \tag{4}
\]

When \( \hat{T} \) is limited to CCSD and \( \hat{H} \) is constructed as a matrix in a basis of all singly and doubly excited Slater determinants, thus defining the EOM-CCSD approach, the energies and wave functions of electronically excited states are obtained as the eigenvalues and eigenfunctions, respectively, of \( \hat{H} \), viz.,

\[
\hat{H} | \mathcal{R}_i \rangle = E_i | \mathcal{R}_i \rangle. \tag{5}
\]

However, the similarity transformation of Eq. (4) destroys the Hermitian character of the original electronic Hamiltonian (while leaving its energy spectrum formally unchanged), leading to distinct right- and left-hand eigenproblems:

\[
\langle \mathcal{L}_i | \hat{H} = E_i \langle \mathcal{L}_i |. \tag{6}
\]

While the excited-state energies, \( E_i \), are identical between Eqs. (5) and (6), the wave functions are related only by the biorthonormality condition,

\[
\langle \mathcal{L}_i | \mathcal{R}_j \rangle = \delta_{ij}. \tag{7}
\]

The left- and right-hand equations can be solved separately or simultaneously via a generalized Davidson-Liu algorithm\(^{37-39}\) for a small number of states. While excitation energies require solution of only Eq. (5) or (6), properties such as oscillator strengths or rotational strengths require solution of both.

An important advantage of coupled cluster methods is the high level of accuracy they provide for molecular systems near their equilibrium geometries. In an addition, they are formally extensible towards the exact limit: higher levels of electron correlation may be incorporated into the ground- and excited-state wave functions by extending the cluster operator, \( \hat{T} \), and the EOM-CC expansion space to include triples, quadruples, etc. However, each new complete excitation/substitution level increases the computational cost of the model by two orders of magnitude.\(^{31}\) While, CCSD scales nominally as the sixth power of the size of the molecule, the full singles, doubles, and triples (CCSDT) approach scales as the eighth power. Thus, more efficient approaches are used to offset these costs while (hopefully) maintaining the desired level of accuracy. For example, the most successful approximation to CCSDT for ground states is CCSD(T),\(^{40,41}\) in which the most important contributions from triples are included using perturbational expressions. For excited states, our work has focused on the approximation to CCSDT known as CC3, which was originally developed by the Aarhus group\(^{42,43}\) and which we extended in 2005 to excited states of open-shell molecules.\(^{44}\) Both CC3 and CCSD(T) scale as the seventh power of the size of the molecule, though CC3 is iterative and CCSD(T) is not.

**Computational Details**

Using the same computational approach and techniques as was done previously,\(^{36}\) the closed-shell anion computations involved the use of spin-restricted (RHF)\(^{45}\) reference wavefunctions while open-shell computations of the neutral radicals were based upon spin-unrestricted (UHF)\(^{46,47}\) wave functions. Coupled cluster theory at the singles, doubles, and perturbative triples level of theory [CCSD(T)]\(^{40}\) combined with the singly augmented form of Dunning’s correlation consistent triple-zeta basis set, aug-cc-pVTZ (Ref. 48,49) and aug-cc-pV(T+d)Z for the silicon atoms (Ref. 50), were used to compute ground state geometries. Coupled cluster at the singles and doubles level of theory with these same basis sets was used to predict dipole moments for the radicals.

Excited states were computed using equation of motion coupled cluster (EOM-CC) theory.\(^{35,51,52}\) Vertically excited states were computed at the CCSD and approximate triples (CC3)\(^{54-55}\) levels of theory, where the latter is known to better describe coupled cluster excited states.\(^{5,56}\) These computations employed Dunning’s double- and triple-zeta basis sets\(^{48-50}\) with increasing numbers of even-tempered diffuse functions where, again, extra \( d \) functions were placed on the silicon atoms. Adiabatic excited states are the result of the CCSD/d-aug-cc-pVDZ energy differences between optimized ground and excited states which was shown previously to be in good agreement with experiment.\(^{30}\) Vertical electron binding energies described as the removal of an electron out of the anion’s HOMO were also computed from the CCSD(T)/aug-cc-pVTZ geometries using equation of motion coupled cluster the-
tory for ionization potentials (EOMIP)$^{57}$ at the CCSD and CCSDT levels of theory with the CFOUR$^{58}$ quantum chemical program package. Core orbitals were frozen in all computations: $1s^2$ for carbon, oxygen, and nitrogen and $1s^22s^22p^6$ for silicon; all geometry optimizations are minima based on harmonic vibrational frequency computations; and, besides those using EOMIP, all computations utilized the PSI3 suite of computational chemistry programs.$^{59}$

**Results and Discussion**

CH$_2$CN$^−$ and CH$_2$CHO$^−$ are known to exhibit singlet dipole-bound excited states very near their electron binding limits.$^{60}$–$^{67}$ Thus, we chose these two molecules to calibrate our quantum chemical tools in the search for new candidates. We found that CCSD/aug-cc-pVTZ dipole moments based on CCSD(T)/aug-cc-pVTZ geometries match experiment to within 0.1 D for both molecules; CCSD(T)/aug-cc-pVTZ adiabatic eBEs differ from experiment by less than 0.06 eV; and adiabatic EOM-CCSD/d-aug-cc-pVDZ excitation energies are within 0.05 eV of experiment with negligible ZPE corrections. Additionally, it was shown through vertical excitation computations that exceptionally diffuse basis sets must be utilized in order to adequately treat the excited states of these weakly bound systems. This observation was also made by Skurski and coworkers$^{68}$ who recommend at least aug-cc-pVDZ or aug-cc-pVTZ basis sets$^{48}$ for the computation of ground state properties. Our own work indicates that one must go even further to triple or even quadruply augmented basis sets with even-tempered extrapolation in order to obtain convergence in vertical excitation energies.$^{30}$

Given the superb accuracy of coupled cluster methods for the excited states of the two known dipole-bound anions, we first explored twelve new anions whose singlet dipole bound excited nature had not been previously examined, including silicon analogues of our calibration molecules: CH$_2$SiN$^−$, SiH$_2$CN$^−$, CH$_2$SiHO$^−$, and SiH$_2$CHO$^−$; linear species: CN$^−$, C$_3$N$^−$, SiN$^−$, and C$_2$F$^−$; and others: CCOH$^−$, HCCO$^−$, CH$_2$NO$^−$, and CH$_2$OH$^−$. Structures for each of the anions are shown in Fig. 3 at the end of the document. Of these, six anions — CH$_2$SiN$^−$, SiH$_2$CN$^−$, CH$_2$SiHO$^−$, SiN$^−$, CCOH$^−$, and HCCO$^−$ — appear to possess a dipole-bound singlet excited state whose transition energy is below the eBE as shown in Table 1 also at the end of the document. Additionally, vertical excitation energies, reported in Table II of Ref. 30, suggest that the CH$_2$SiN$^−$ may possess several additional valence excited states.

However, the identification of such states is more difficult than for neutrals or cations because of both exquisite sensitivity to the quality of the basis sets used and the need for a careful balance between the method used to obtain the electron binding energy and that used to compute the excitation energy. Thus, we additionally carried out a series of combined EOM-CCSD calculations for both excitation energies and ionization energies. The latter is referred to as the EOMIP method,$^{57}$ and is analogous to the EOM-CC approach described in the previous section, except that the diagonalization of $H$ is carried out in a basis of ionized Slater determinants. However, since both the EOM-CCSD and EOMIP-CCSD approaches make use of the same similarity-transformed Hamiltonian, direct comparison between the anion binding energies and excitation energies can be made. Using basis sets up to q-aug-cc-pVĐZ, these EOM-CC computations reveal that only two of these states exist below or in at least close proximity to the vertical 2.341 eV eBE: the 1$^1B_1$ at 2.125 eV and the 2$^1B_1$ at 2.348 eV with the former being valence-bound and the latter dipole-bound.

Using the same vertical EOMIP and EOM techniques in addition to the adiabatic approaches, we were then able to explore five more anions of interstellar interest.$^{69}$ Since the silicon containing anions in our first examination show promise for the possession of excited states, we also examined silicon analogues of C$_3$N$^−$ with single silicon substitutions: SiCCN$^−$, CSiCN$^−$, and CCSiN$^−$. Additionally, the SiNC and SiCN radicals are known to exist in the ISM,$^{70}$–$^{71}$ and we also examined the excited states of the corresponding anions for these interstellar molecules in the same fashion. The adiabatic eBEs and first excited states for these anions are also listed in Table 1, as well. Information about the vertical states can be found in Table 2 of Ref. 69.

Like CH$_2$SiN$^−$, SiCCN$^−$, shown in Fig. 2a, appears to possess both a valence 2$^1Σ^+$ state and a dipole-bound 1$^1Π$ state. Our computations appear to indicate that CSiCN$^−$ is not stable as a molecular system, and, hence, will not possess excited states of any kind. CCSiN$^−$ appears to be the most interesting of all systems in that it possesses two valence states and one dipole-bound state just below the electron binding energy. Such a finding is not without precedent,$^{72}$–$^{73}$ but multiple excited states of anions are incredibly rare with our computations indicating that many such exist for CCSiN$^−$. Only one excited state of SiCN$^−$ is possible, but the difference between both the eBE computed vertically or adiabatically are at the edge (0.1 eV less than the excitation energy) of what appears to be too great for a dipole-bound state of SiCN$^−$ to exist. However, SiNC$^−$ is more likely to
Figure 2: CCSD(T)/aug-cc-pVTZ optimized structures for the closed-shell anions of: (a) SiCCN$^-$; (b) C$_2$SiCN radical as the anion is unstable; (c) CCSiN$^-$; (d) SiCN$^-$; and (e) SiNC$^-$. Possess a dipole-bound excited state since the vertical EOMIP eBE is around 0.05 eV less than the 1 $^1\Pi$ state.

Silicon containing species are known to exist in the ISM,$^{10}$ but little is known about CH$_2$SiN$^-$ and eight of the other nine anions reported here (SiN$^-$ being the exception). Hence, the excited states of these anions may be of interest to laboratory and observational astrochemists. Also, this theoretical approach is applicable to similar studies of other anions that may also be of significance for studies of the DIBs. These studies have thus far suggested that the excited state properties of other silicon containing anions are promising species for interstellar identification.

Conclusions and Prospectus

We have shown that ten new anions may possess dipole-bound excited states; these include the 2 $^1B_1$ state of CH$_2$SiN$^-;$ the 1 $^1A'$ states of CH$_2$SiHO$^-$, CCOH$^-$, and HCCO$^-$; the 1 $^1\Pi$ states of SiCCN$^-$ and SiNC$^-;$ the 2 $^1\Pi$ state of CCSI$^-$; and potentially the 2 $^1A'$ state of SiH$_2$CN$^-$; the 1 $^1\Pi$ state of SiCN$^-$, and the 2 $^1\Sigma^+$ state of SiN$^-$. In addition, we predict single valence-bound excited states of CH$_2$SiN$^-$ and SiCCN$^-$ below their respective eBEs and two valence-bound states (the 2 $^1\Sigma^+$ and 1 $^1\Pi$) of CCSI$^-$, an exciting and rare finding. Conclusive identification of threshold resonances associated with dipole-bound singlet excited states requires experimental analysis, of course, but the data we report 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.

We will continue to examine anions, especially those containing silicon atoms, for their excited state properties. Excited states of such anions have not been fully examined especially for application to interstellar spectroscopic problems like that of the carriers of the DIBs and are most easily studied using quantum chemical methods. Additionally, we will continue work on a promising family of cation species whose excited state features are in the 4429 Å range in line with one of the broadest DIB features.$^{74}$ Also, we have begun a collaboration with the Lee Group at NASA-Ames to examine rovibrational spectra of other interstellar species, specifically the HOCO radical as a first endeavor. As it can be seen there is still much to be studied in the way of interstellar spectroscopy whether it be UV, visible, or IR, and we will continue to find ways in which quantum chemical theory shows its worth as a valuable tool in this arena.

References


Figure 3: CCSD(T)/aug-cc-pVTZ optimized structures for the closed-shell anions of: (a) CH$_2$CN$^-$; (b) CH$_2$SiN$^-$; (c) SiH$_2$CN$^-$; (d) C$_3$N$^-$; (e) CN$^-$; (f) SiN$^-$; (g) C$_2$F$^-$; (h) HCCO$^-$; (i) CCOH$^-$; (j) CH$_2$CHO$^-$; (k) CH$_2$SiCHO$^-$; (l) SiH$_2$CHO$^-$; (m) CH$_2$NO$^-$; and (n) CH$_2$OH$^-$. 
Table 1: 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.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Radical Dipole Moment</th>
<th>Electron Binding Energy</th>
<th>Transition</th>
<th>Theory</th>
<th>Experiment</th>
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<tr>
<td>CH_2CN^-</td>
<td>3.599</td>
<td>1.48</td>
<td>1.543 ± 0.014</td>
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<td>1.49 (1.51)</td>
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<td>CH_2SiN^-</td>
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<td>-</td>
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<td>2.11</td>
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<td>3.524</td>
<td>2.31</td>
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<td>2.921</td>
<td>1.77 (1.79)</td>
<td>1.824g^8</td>
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<tr>
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^aHFP-CCSD/aug-cc-pVTZ values for the radicals at the HFP-CCSD(T)/aug-cc-pVTZ geometries.
^bThe differences between the RHF- (anion) and UHF- (radical) CCSD(T)/aug-cc-pVTZ energies.
^cAdiabatic EOM-CCSD/d-aug-cc-pVDZ values.
^dRCCSD(T)/aug-cc-pVQZ result from Ref. 64 where corroborating microwave spectroscopy reported in the same paper estimates this value at ca. 3.5 D.
^eReference 61.
^fReference 29.
^gCEPA-1/cc-pVQZ from Reference 77.
^hReference 80.
^iReference 82.
^jCEPA-1/cc-pVQZ from Reference 77.
^kReference 78.
^lReference 78.
^mReference 81.
^nReference 75.
^oReference 86.
^pReference 78.