The Possible Interstellar Anion CH$_2$CN$^-$: Spectroscopic Constants, Vibrational Frequencies, and Other Considerations

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ABSTRACT

The \( A^1B_1 \leftarrow \tilde{X}^1A' \) excitation into the dipole-bound state of the cyanomethyl anion (\( \text{CH}_2\text{CN}^- \)) has been hypothesized as the carrier for one diffuse interstellar band. However, this particular molecular system has not been detected in the interstellar medium even though the related cyanomethyl radical and the isoelectronic ketenimine molecule have been found. In this study we are employing the use of proven quartic force fields and second-order vibrational perturbation theory to compute accurate spectroscopic constants and fundamental vibrational frequencies for \( \tilde{X}^1A' \text{CH}_2\text{CN}^- \) in order to assist in laboratory studies and astronomical observations.

**Keywords:** Astrochemistry, ISM: molecular anions, Quartic force fields, Rotational constants, Vibrational frequencies

1. Introduction

It has been recently shown that anions are more prevalent in the interstellar medium (ISM) than previously thought. \( \text{C}_n\text{H}^- \) where \( n = 4, 6, 8 \) (McCarthy et al. 2006; Cernicharo et al. 2007; Brünken et al. 2007; Remijan et al. 2007; Cordiner et al. 2011) and the isoelectronic \( \text{C}_n\text{N}^- \) set where \( n = 1, 3, 5 \) (Thaddeus et al. 2008; Cernicharo et al. 2008; Agúndez et al. 2010) have been conclusively detected in the circumstellar envelope of the carbon-rich star IRC+10 216 and in a growing number of other interstellar regions, as well (Cordiner et al. 2011). It has also been proposed that anions (Sarre 2000; Cordiner & Sarre 2007) may play a role in explaining some features of the diffuse interstellar bands (DIBs), the unattributed interstellar spectrum nearly ubiquitously detected in interstellar sightlines for almost a century (Sarre 2006). For example, the \( \lambda 8037 \text{ Å} \) DIB observed towards the
star HD 183143 shows strong correlation to the $A ^1B_1 \leftarrow \tilde{X} ^1A' 0^0$ transition of CH$_2$CN$^-$, a ground valence state to dipole-bound excited state transition (Sarre 2000). A later study (Cordiner & Sarre 2007) compares the laboratory-observed 2.74 K CH$_2$CN$^-$ dipole-bound excited state transition (Lykke et al. 1987) convolved with HIRES data in the $\lambda$ 8035 Å to $\lambda$ 8040 Å range with astronomical observations towards HD 183143, HD 168112, and Cyg OB2 8a. The striking similarities reported between the laboratory/HIRES features and the interstellar observations make this molecule a reasonable DIB source.

In order for a more concrete correlation to be established between the $A ^1B_1 \leftarrow \tilde{X} ^1A'$ transition of CH$_2$CN$^-$ and the $\lambda$ 8037 Å DIB, radioastronomical detection of this anion is necessary. The corresponding CH$_2$CN radical form (Irvine et al. 1988) and the isoelectronic ketenimine (CH$_2$CNH) (Lovas et al. 2006) are known to exist in the ISM, and various interstellar processes could lead to the subsequent creation of CH$_2$CN$^-$ (Sailer et al. 2003; Andreazza et al. 2006; Cordiner & Sarre 2007; Romanskii 2008a,b; Yang et al. 2010; Larsson et al. 2012). However, no conclusive evidence for the interstellar presence of this anion has yet been reported in the literature, but this may only be the result of a lack of high-resolution spectroscopic data.

Dipole-bound states of anions represent a relatively new field of exploration for astrochemistry. In brief, an extra electron can be bound to the system by a simple monopole-dipole interaction in exactly one state if the dipole moment is large enough. The minimum dipole value is at least 1.625 D (Fermi & Teller 1947), but, in reality, it is probably closer to 2.5 D (Gutsev & Adamowicz 1995). For systems like CH$_2$CN$^-$, the ground state anion is closed-shell, and the additional electron is bound by valence forces and not dipolar forces. The resulting closed-shell anion is relatively stable (Simons 2008; Lykke et al. 1987; Gutsev & Adamowicz 1995). Additionally, the valence ground state allows for excitation into a single excited state of dipole-bound character as has been discussed for
CH$_2$CN$^-$ and similar anions (Fortenberry & Crawford 2011c,a,b, 2012). More studies have examined CH$_2$CN$^-$ than any other closed-shell anion known to possess a dipole-bound excited state except for possibly CH$_2$CHO$^-$ (Wetmore et al. 1980; Mullin et al. 1992, 1993; Simons 2008). Interstellar detection of CH$_2$CN$^-$ would give new insights into studies that correlate its electronic spectra with a particular DIB.

Even though the electronic spectrum of CH$_2$CN$^-$ motivates the astronomical interest in this molecule, the most reliable means of interstellar detection for a specific molecule remains rotational spectroscopy (McCarthy & Thaddeus 2001). Recent computational studies have been able to provide the necessary spectroscopic constants to aid laboratory microwave studies for the rotational spectrum of NCO$^-$ (Lattanzi et al. 2010). Other computational results have even been accurate enough to provide reference data for C$_5$N$^-$ (Aoki 2000; Botschwina 2005) that led to its interstellar detection (Cernicharo et al. 2008). Using established quantum chemical computational tools (Huang & Lee 2008) proven to provide rotational constants often as accurate as 20 MHz (especially for the $B$- and $C$-type constants) and also vibrational frequencies accurate to 5 cm$^{-1}$ or better (Huang & Lee 2008, 2009; Huang et al. 2011; Huang & Lee 2011; Inostroza et al. 2011; Fortenberry et al. 2011a,b, 2012c,b,a), we are computing the spectroscopic constants and also the fundamental vibrational frequencies to assist in the detection of $\tilde{X} \, ^1A'$ CH$_2$CN$^-$. The data provided here will inform experimental study in the laboratory and astronomical observation in the ISM of this anion.

2. Computational Details

Quartic force fields (QFFs) have been the primary low-cost means by which accurate computations of spectroscopic constants and vibrational frequencies have been determined. QFFs are fourth-order Taylor series approximations to the anharmonic potential for a given
system of interest:

\[
v = \frac{1}{2} \sum_{ij} F_{ij} \Delta_i \Delta_j + \frac{1}{6} \sum_{ijk} F_{ijk} \Delta_i \Delta_j \Delta_k + \frac{1}{24} \sum_{ijkl} F_{ijkl} \Delta_i \Delta_j \Delta_k \Delta_l \tag{1}
\]

for the force constants, \( F_{ij...} \), and displacements, \( \Delta_i \). Unlike the corresponding radical, \( \text{CH}_2\text{CN}^- \) is a non-planar \( C_s \) system. It has nine vibrational degrees of freedom. The symmetry-internal coordinates are defined from the atoms labeled in Fig. 1 as:

\[
S_1(A') = (C_1 - H_1) + (C_2 - H_2)
\]
\[
S_2(A') = C_1 - C_2
\]
\[
S_3(A') = C_2 - N
\]
\[
S_4(A') = (\angle C_2 - C_1 - H_1) + (\angle C_2 - C_1 - H_2)
\]
\[
S_5(A') = \angle H_1 - C_1 - H_2
\]
\[
S_6(A') = \angle C_1 - C_2 - N - X
\]
\[
S_7(A'') = (C_1 - H_1) - (C_2 - H_2)
\]
\[
S_8(A'') = (\angle C_2 - C_1 - H_1) - (\angle C_2 - C_1 - H_2)
\]
\[
S_9(A'') = \angle C_1 - C_2 - N - X
\]

where \( X \) is a dummy atom located in the \( \angle C_1-C_2-N \) plane directly above \( C_2 \). This point is necessary to define the in- and out-of-plane bending in \( S_6 \) and \( S_9 \) with linear coordinates LINX and LINY, respectively, available in the INTDER program (Allen & coworkers 2005). These coordinates are discussed in more detail in Fortenberry et al. (2012c). Due to the near-linearity in \( \angle C_1-C_2-N \), the dihedral angles \( \angle N-C_2-C_1-H_{1/2} \) are not well-defined in this system. However, linear combinations of coordinates \( S_4 - S_9 \) account for them in the coordinate system given.

The QFF is determined from points on the potential surface where up to a total of four displacements for each of the symmetry-internal coordinates are combined.
individual displacements are 0.005 Å for bond lengths and 0.005 radians for bond angles and linear bends. This produces 1814 symmetry-unique points. At each point, spin-restricted Hartree-Fock (RHF) (Scheiner et al. 1987) referenced coupled cluster (Lee & Scuseria 1995; Crawford & Schaefer 2000; Shavitt & Bartlett 2009) singles, doubles, and perturbative triples, CCSD(T) (Raghavachari et al. 1989), energies are computed with Dunning’s aug-cc-pVTZ and aug-cc-pVQZ basis sets (Kendall et al. 1992; Dunning et al. 2001). It has been shown that ground state computations of anions can be accurately undertaken with only adding a single set of functions to account for orbital diffuseness (Lee & Dateo 1997, 1999; Skurski et al. 2000). The triple- and quadruple-zeta energies at each point are then extrapolated to the complete one-particle basis set (CBS) limit using a two-point formula (Helgaker et al. 1997). To the extrapolated energies, further corrections are added for core-correlation (Martin & Taylor 1994) and scalar relativistic effects (Douglas & Kroll 1974). The use of these three terms in the composite energy gives the CcCR QFF, which is so named for CBS extrapolation (C), core-correlation (cC), and relativistic effects (R) included. This QFF differs from the CcCR QFF utilized effectively in previous studies (Huang & Lee 2008, 2009; Huang et al. 2011; Inostroza et al. 2011; Fortenberry et al. 2011a,b, 2012c,b,a) only in that aug-cc-pV5Z energies are not included in the basis set extrapolation.

The CcCR energies from the 2339 total symmetry-redundant points fit to a sum of residual squares on the order of $10^{-16}$ a.u.$^2$ yield the QFF. The symmetry-internal coordinate QFF is transformed into Cartesian coordinates with the INTDER program (Allen & coworkers 2005). The spectroscopic constants and vibrational frequencies are computed with second-order vibrational perturbation theory (VPT) (Mills 1972; Watson 1977) from a modified version of the SPECTRO (Gaw et al. 1996) program. The vibrationally-averaged rotational constants were determined using second-order perturbation theory (Papousek & Aliev 1982).
3. Discussion

The vibrationally-averaged $R_\alpha$ structure of the cyanomethyl anion (CH$_2$CN$^-$) is shown in Fig. 1. The $C_s$ anion geometry only differs slightly from the $C_{2v}$ radical. The singly-occupied $p$ orbital above and below the $sp^2$ methyl carbon in the radical allows for a planar $C_{2v}$ molecule, but the addition of the extra electron to create a closed-shell system leads to interference from the other already occupied orbitals. As a result, the bonds involving the methyl group bend the molecule into an $sp^3$ pyramidal structure reminiscent of ammonia with the extra lone-pair occupying the previously singly-occupied $p$ orbital. The off-axis dihedrals showcase this effect as they are $\pm 109.726^\circ$. The dihedrals and the other geometrical parameters are listed in Table 1 for both the vibrationally-averaged (zero-point) and equilibrium structures.

The fundamental vibrational frequencies of CH$_2$CN$^-$, given in Table 2, appear to be well-behaved and provide reference data for infrared studies. The lone exception is the $\nu_9$ C–C–N out-of-plane bend. When progressing from the harmonic approximation to the anharmonic, the frequency is reduced by 54.2% from 342.2 cm$^{-1}$ to 157.1 cm$^{-1}$. It is known that there is issue with VPT when describing modes of strong anharmonicity (Dateo et al. 1994; Martin & Taylor 1999; Torrent-Sucarrat et al. 2005; Yurchenko et al. 2009). Hence, the anharmonic VPT $\nu_9$ frequency is probably not as accurate as the other anharmonic fundamentals provided. In addition to the fundamentals, VPT also produces the zero-point and equilibrium spectroscopic constants for the system of study. These and most of the other spectroscopic constants for CH$_2$CN$^-$ are given in Table 1 with the vibration-rotation interaction constants listed in Table 3. Additionally, the symmetry-internal coordinate force constants computed are given in Tables 4 and 5.

The possible interstellar microwave detection of CH$_2$CN$^-$ could be referenced by related and potentially more abundant species. As mentioned previously, the ketenimine
(CH₂CNH) molecule, which is isoelectronic to the cyanomethyl anion, has been detected in the ISM. The extra out-of-plane hydrogen in ketenimine places the $A_0$ (201 445.279 MHz), $B_0$ (9 663.159 3 MHz), and $C_0$ (9 470.154 7 MHz) experimental rotational constants (Bane et al. 2011) below those of CH₂CN⁻ by 32 500 MHz, 1 160 MHz, and 939 MHz, respectively. The rotational constants discussed for CH₂CN⁻ are the vibrationally-averaged values.

Additionally, the known interstellar molecule propadienylidene (CH₂CC) (Cernicharo et al. 1991) has been proposed as another possible DIB carrier by Maier et al. (2011), and its geometry is very similar in structure to CH₂CN. The CH₂CC $A$-, $B$-, and $C$-type rotational constants are 288 783 MHz, 10 588.639 MHz, and 10 203.966 MHz, respectively, (Vrtilek et al. 1990), but the pyramidalization of the methyl carbon in the anion of interest consequently gives a smaller $A$-type rotational constant and larger $B$- and $C$-type constants relative to CH₂CC. The differences in the rotational spectra of ketenimine and propadienylidene may help to serve as markers for the microwave detection of CH₂CN⁻ in the ISM.

The structures of CH₂CC and the CH₂CN radical are very similar, and the relationship between their rotational constants and those of CH₂CN⁻ is also similar. For the CH₂CN radical, the $A_0$ rotational constant is 284 981 MHz, $B_0$ is 10 426.765 MHz, and $C_0$ is 9 876.035 MHz (Saito & Yamamoto 1997). Previously computed $A$-type CcCR rotational constants for other quasi-linear systems have not been as close to experimental values as were the other two rotational constants (Inostroza et al. 2011; Fortenberry et al. 2011a,b, 2012c,b), but the $A_0$ constant computed here should still be accurate to 500 MHz or better. This should be accurate enough to make comparison between the cyanomethyl radical and anion. From our results, we can conclude that $A_0$ for CH₂CN⁻ should be as much as 50 GHz less than that of the radical. Conversely, the anion $B_0$ and $C_0$ constants, where accuracies are more than an order of magnitude better, should be 400 and 500 MHz, respectively, greater than those of the radical. Later work by Ozeki et al. (2004) indicates
that $B - C$ for the radical should be 370.735 9 MHz whereas the earlier estimate by Saito & Yamamoto (1997) is 550.730 MHz. Our computations give $B - C$ of CH$_2$CN$^-$ to be 437.21 MHz. Hence $B - C$ is not a good means by which one should distinguish the radical from the anion. The microwave spectra of both the cyanomethyl radical and anion are closely related, but our data should allow the two to be distinguished in observation.

The dipole moment for the anion (0.90 D; see Table 1) indicates that a rotational spectrum should possess adequate intensities for detection provided the interstellar abundance is large enough. Additionally, the other spectroscopic constants provided here should aid in further studies of CH$_2$CN$^-$. If this anion can be detected radioastronomically in sightlines towards the stars HD 183143, HD 168112, and Cyg OB2 8a where the $\lambda$ 8037 Å band shows near-perfect overlap with the laboratory/HIRES data (Cordiner & Sarre 2007), CH$_2$CN$^-$ could be a viable DIB candidate carrier.

4. Acknowledgements

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Fig. 1.— Top-down and side-on views for the CcCR equilibrium geometry of $X^1A'$ CH$_2$CN$^−$. 
$\angle C-C-N$ is shown explicitly (units are degrees) in the lower side-on view.
Table 1: The Zero-Point ($R_\alpha$ vibrationally-averaged) and Equilibrium Structures, Rotational Constants, CCSD(T)/aug-cc-pVQZ Dipole Moment, and Other Spectroscopic Constants (including Watson $S$-Reduction terms) of CH$_2$CN$^-$ computed from the CcCR QFF.

<table>
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<tr>
<th></th>
<th>Value</th>
</tr>
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<td>$r_0$(C−N)</td>
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<tr>
<td>$r_0$(C−C)</td>
<td>1.394 316 Å</td>
</tr>
<tr>
<td>$r_0$(C−H)</td>
<td>1.089 964 Å</td>
</tr>
<tr>
<td>$\angle_0$(H−C−C)</td>
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<td>$\angle_0$(C−C−N)</td>
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<tr>
<td>$\angle_0$(H−C−H)</td>
<td>111.828°</td>
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<td>$\angle_0$N−C−C−H</td>
<td>± 109.726°</td>
</tr>
<tr>
<td>$A_0$</td>
<td>233 945.4 MHz</td>
</tr>
<tr>
<td>$B_0$</td>
<td>10 823.22 MHz</td>
</tr>
<tr>
<td>$C_0$</td>
<td>10 386.01 MHz</td>
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<tr>
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<td>$r_e$(C−H)</td>
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<td>$\angle_e$(H−C−C)</td>
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<td>$A_e$</td>
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<td>$B_e$</td>
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<tr>
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<td>$\tau^{\rho}_{acc}$</td>
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<tr>
<td>$\Phi_{bbb}$</td>
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<tr>
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<td>$\Phi_{abb}$</td>
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<tr>
<td>$D_JK$</td>
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</tr>
<tr>
<td>$d_2$</td>
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</tr>
<tr>
<td>$H_J$</td>
<td>-0.001 Hz</td>
</tr>
<tr>
<td>$H_JK$</td>
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</tr>
<tr>
<td>$H_KJ$</td>
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<td>$H_K$</td>
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<td>0.001 Hz</td>
</tr>
<tr>
<td>$h_3$</td>
<td>0.000 Hz</td>
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*The CH$_2$CN$^-$ coordinates (with the center-of-mass at the origin) utilized to generated the dipole moment components are:

C$_1$, 1.25313, 0.058510, 0.000000; C$_2$, -0.136782, -0.005295, 0.000000; N, -1.216834, -0.006267, 0.000000; H, 1.807100, -0.273271, ±0.995163.*
Table 2: The VPT CcCR QFF fundamental vibrational frequencies (in cm\(^{-1}\)) for CH\(_2\)CN\(^-\).

<table>
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<th>Mode</th>
<th>Description</th>
<th>Harmonic</th>
<th>Anharmonic</th>
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<tr>
<td>(\nu_1(A'))</td>
<td>symmetric C–H stretch</td>
<td>3122.3</td>
<td>2987.0</td>
</tr>
<tr>
<td>(\nu_2(A'))</td>
<td>C–N stretch</td>
<td>2115.7</td>
<td>2100.3</td>
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<tr>
<td>(\nu_3(A'))</td>
<td>H–C–H symmetric bend</td>
<td>1298.2</td>
<td>1262.2</td>
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<tr>
<td>(\nu_4(A'))</td>
<td>C–C stretch</td>
<td>991.5</td>
<td>956.1</td>
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<td>(\nu_5(A'))</td>
<td>C–C–N in-plane bend</td>
<td>585.5</td>
<td>556.9</td>
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<td>(\nu_6(A'))</td>
<td>symmetric torsion</td>
<td>434.5</td>
<td>433.1</td>
</tr>
<tr>
<td>(\nu_7(A''))</td>
<td>antisymmetric C–H stretch</td>
<td>3191.3</td>
<td>3045.1</td>
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<tr>
<td>(\nu_8(A''))</td>
<td>antisymmetric torsion</td>
<td>1045.5</td>
<td>1033.8</td>
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<td>(\nu_9(A''))</td>
<td>C–C–N out-of-plane bend</td>
<td>343.2</td>
<td>157.1</td>
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Table 3: The CcCR Vibration-Rotation Interaction Constants in MHz.

<table>
<thead>
<tr>
<th>mode</th>
<th>$\alpha^A$</th>
<th>$\alpha^B$</th>
<th>$\alpha^C$</th>
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<tbody>
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<td>1</td>
<td>6772.7</td>
<td>19.5</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>6907.5</td>
<td>14.0</td>
<td>4.3</td>
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<tr>
<td>3</td>
<td>-413.1</td>
<td>66.9</td>
<td>64.6</td>
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<tr>
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<td>-6.4</td>
<td>14.6</td>
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<td>5</td>
<td>1762.2</td>
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<td>9</td>
<td>-7495.6</td>
<td>-13.3</td>
<td>31.3</td>
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</tbody>
</table>
Table 4: The CcCR QFF Quadratic and Cubic Force Constants (in mdyn/Å²·radᵐ) for CH₂CN⁻ in the symmetry-internal coordinate system listed in Eqs. 2-10.

<table>
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