THE POSSIBLE INTERSTELLAR ANION CH$_2$CN$^-$: SPECTROSCOPIC CONSTANTS, VIBRATIONAL FREQUENCIES, AND OTHER CONSIDERATIONS

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ABSTRACT

The A $^1B_1$ ← $\tilde{X}$ $^1A'$ excitation into the dipole-bound state of the cyanomethyl anion (CH$_2$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 $\tilde{X}$ $^1A'$ CH$_2$CN$^-$ in order to assist in laboratory studies and astronomical observations.

Key words: astrochemistry – infrared: ISM – ISM: lines and bands – ISM: molecules – molecular data – radio lines: ISM

1. INTRODUCTION

It has been recently shown that anions are more prevalent in the interstellar medium (ISM) than previously thought. C$_n$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 C$_n$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 sight lines for almost a century (Sarre 2006). For example, the 8037 Å DIB observed toward the star HD 183143 shows strong correlation to the A $^1B_1$ ← $\tilde{X}$ $^1A'$ 0_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 8035–8040 Å range with astronomical observations toward 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 $^1B_1$ ← $\tilde{X}$ $^1A'$ transition of CH$_2$CN$^-$ and the 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, 2008b; 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 2011a, 2011b, 2011c; Fortenberry & Crawford 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, 2011; Huang et al. 2011; Inostroza et al. 2011; Fortenberry et al. 2011a, 2011b, 2012a, 2012b, 2012c), 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
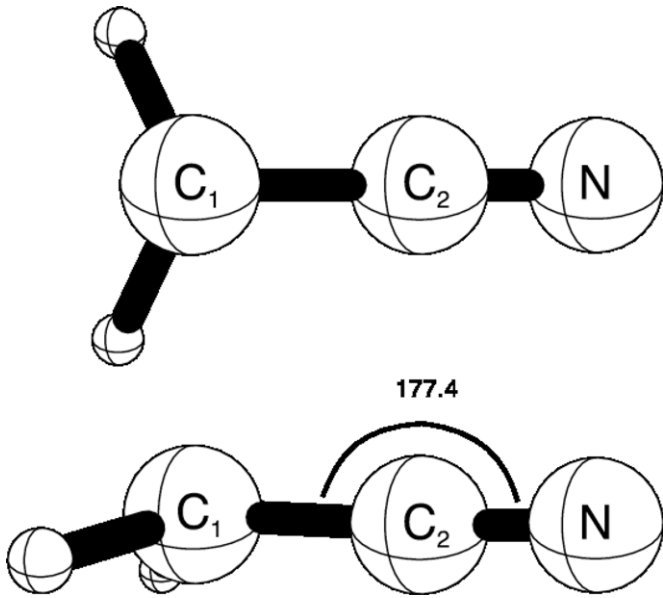
Figure 1. Top-down and side-on views for the CcCR equilibrium geometry of $\tilde{X}\,^1A'$ CH_2CN^-. $\angle C-C-N$ is shown explicitly (units are degrees) in the lower side-on view.

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:

$$V = \frac{1}{2}\sum_{ij} F_{ij}\Delta_i\Delta_j + \frac{1}{6}\sum_{ijk} F_{ikj}\Delta_i\Delta_j\Delta_k$$
$$+ \frac{1}{24}\sum_{ijkl} F_{ikjl}\Delta_i\Delta_j\Delta_k\Delta_l \qquad (1)$$

for the force constants, $F_{ij\ldots}$, and displacements, Δ_i. Unlike the corresponding radical, CH_2CN^- 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 Figure 1 as

$$S_1(A') = (C_1 - H_1) + (C_2 - H_2) \qquad (2)$$

$$S_2(A') = C_1 - C_2 \qquad (3)$$

$$S_3(A') = C_2 - N \qquad (4)$$

$$S_4(A') = (\angle C_2 - C_1 - H_1) + (\angle C_2 - C_1 - H_2) \qquad (5)$$

$$S_5(A') = \angle H_1 - C_1 - H_2 \qquad (6)$$

$$S_6(A') = \angle C_1 - C_2 - N - X \qquad (7)$$

$$S_7(A'') = (C_1 - H_1) - (C_2 - H_2) \qquad (8)$$

$$S_8(A'') = (\angle C_2 - C_1 - H_1) - (\angle C_2 - C_1 - H_2) \qquad (9)$$

$$S_9(A'') = \angle C_1 - C_2 - N - X, \qquad (10)$$

Table 1
The Zero Point (R_α 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_2CN^- Computed from the CcCR QFF

$r_0(C-N)$	1.184 912 Å
$r_0(C-C)$	1.394 316 Å
$r_0(C-H)$	1.089 964 Å
$\angle_0(H-C-C)$	118°378
$\angle_0(C-C-N)$	177°714
$\angle_0(H-C-H)$	111°828
$\angle_0 N-C-C-H$	±109°726
A_0	233 945.4 MHz
B_0	10 823.22 MHz
C_0	10 386.01 MHz
$r_e(C-N)$	1.186 272 Å
$r_e(C-C)$	1.391 438 Å
$r_e(C-H)$	1.080 053 Å
$\angle_e(H-C-C)$	116°976
$\angle_e(C-C-N)$	177°423
$\angle_e(H-C-H)$	114°048
$\angle_e H-C-C-N$	±109°726
A_e	230 904.9 MHz
B_e	10 849.79 MHz
C_e	10 445.37 MHz
μ	0.90 D
$\mu_x{}^a$	0.86 D
$\mu_y{}^a$	0.24 D
τ'_{aaaa}	−100.708 MHz
τ'_{bbbb}	−0.020 MHz
τ'_{cccc}	−0.017 MHz
τ'_{aabb}	−1.812 MHz
τ'_{aacc}	0.043 MHz
τ'_{bbcc}	−0.018 MHz
Φ_{aaa}	1.397×10^4 Hz
Φ_{bbb}	0.000 Hz
Φ_{ccc}	0.001 Hz
Φ_{aab}	21.402 Hz
Φ_{abb}	3.346 Hz
Φ_{aac}	−296.063 Hz
Φ_{bbc}	−0.002 Hz
Φ_{acc}	−0.016 Hz
Φ_{bcc}	0.001 Hz
Φ_{abc}	1.224 Hz
D_J	0.005 MHz
D_{JK}	0.434 MHz
D_K	24.739 MHz
d_1	0.000 MHz
d_2	0.000 MHz
H_J	−0.001 Hz
H_{JK}	2.297 Hz
H_{KJ}	−278.570 Hz
H_K	1.424×10^4 Hz
h_1	−0.001 Hz
h_2	0.001 Hz
h_3	0.000 Hz

Note. ^{a} The CH_2CN^- coordinates (with the center of mass at the origin) utilized to generate 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.

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

Table 2
The VPT CcCR QFF Fundamental Vibrational
Frequencies (in cm^{-1}) for CH_2CN^-

Mode	Description	Harmonic	Anharmonic
$\nu_1(A')$	Symmetric C−H stretch	3122.3	2987.0
$\nu_2(A')$	C−N stretch	2115.7	2100.3
$\nu_3(A')$	H−C−H symmetric bend	1298.2	1262.2
$\nu_4(A')$	C−C stretch	991.5	956.1
$\nu_5(A')$	C−C−N in-plane bend	585.5	556.9
$\nu_6(A')$	Symmetric torsion	434.5	433.1
$\nu_7(A'')$	Antisymmetric C−H stretch	3191.3	3045.1
$\nu_8(A'')$	Antisymmetric torsion	1045.5	1033.8
$\nu_9(A'')$	C−C−N out-of-plane bend	343.2	157.1

Table 3
The CcCR Vibration–Rotation Interaction Constants in MHz

Mode	α^A	α^B	α^C
1	6772.7	19.5	0.5
2	6907.5	14.0	4.3
3	−413.1	66.9	64.6
4	−2487.6	−6.4	14.6
5	1762.2	40.6	8.7
6	−10895.0	−13.4	35.6
7	−28597.9	−7.9	−23.2
8	28365.9	−47.6	−16.8
9	−7495.6	−13.3	31.3

and LINY, respectively, available in the INTDER program[3] (Allen et al. 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

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[3] *INTDER* 2005 is a general program written by W. D. Allen and coworkers, which performs vibrational analysis and higher-order nonlinear transformations.

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. The individual displacements are 0.005 Å for bond lengths and 0.005 rad for bond angles and linear bends. This produces 1814 symmetry-unique points. At each point, spin-restricted Hartree–Fock (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, 2011b, 2012a, 2012b, 2012c) 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 et al. 2005). The spectroscopic constants and vibrational frequencies are computed with second-order vibrational perturbation theory (VPT; Mills 1972; Watson 1977) from a modified

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Table 4
The CcCR QFF Quadratic and Cubic Force Constants (in mdyn/Å^n rad^m) for CH_2CN^- in the Symmetry-internal Coordinate System Listed in Equations (2)–(10)

F_{11}	5.530 104	F_{97}	0.023 263	F_{521}	0.2661	F_{651}	−0.0943	F_{882}	−0.1132
F_{21}	0.128 241	F_{98}	0.094 020	F_{522}	0.0458	F_{652}	−0.1221	F_{883}	−0.1145
F_{22}	6.555 883	F_{99}	0.488 664	F_{531}	−0.0496	F_{653}	−0.0071	F_{884}	−0.5701
F_{31}	−0.028 918	F_{111}	−22.6169	F_{532}	0.1555	F_{654}	−0.4512	F_{885}	−0.1370
F_{32}	0.828 276	F_{211}	0.1821	F_{533}	−0.0791	F_{655}	−0.2330	F_{886}	−0.0589
F_{33}	15.588 505	F_{221}	−0.4359	F_{541}	0.1369	F_{661}	−0.0476	F_{971}	0.0017
F_{41}	0.230 077	F_{222}	−38.2328	F_{542}	0.1713	F_{662}	−0.9049	F_{972}	−0.1306
F_{42}	0.656 729	F_{311}	−0.0215	F_{543}	−0.0559	F_{663}	−0.7569	F_{973}	−0.0740
F_{43}	−0.167 307	F_{321}	0.1660	F_{544}	0.4306	F_{664}	0.0573	F_{974}	−0.0367
F_{44}	0.429 388	F_{322}	−2.0024	F_{551}	−0.1351	F_{665}	0.0598	F_{975}	−0.0010
F_{51}	0.259 999	F_{331}	−0.1413	F_{552}	0.1132	F_{666}	−0.1294	F_{976}	−0.0421
F_{52}	0.140 187	F_{332}	−0.6860	F_{553}	−0.0258	F_{771}	−22.7980	F_{981}	−0.0507
F_{53}	−0.132 967	F_{333}	−105.9486	F_{554}	0.1846	F_{772}	0.2877	F_{982}	0.0218
F_{54}	−0.055 920	F_{411}	0.2890	F_{555}	−0.5143	F_{773}	−0.0386	F_{983}	−0.1650
F_{55}	0.410 435	F_{421}	0.0988	F_{611}	0.0250	F_{774}	0.0134	F_{984}	−0.1266
F_{61}	0.039 862	F_{422}	−0.0823	F_{621}	−0.0069	F_{775}	0.4085	F_{985}	−0.0393
F_{62}	0.091 750	F_{431}	−0.1456	F_{622}	−0.0968	F_{776}	0.0044	F_{986}	0.0626
F_{63}	0.039 511	F_{432}	0.2752	F_{631}	−0.0291	F_{871}	0.0772	F_{991}	−0.0303
F_{64}	−0.088 431	F_{433}	−0.2106	F_{632}	−0.0076	F_{872}	−0.3529	F_{992}	−0.5724
F_{65}	−0.098 023	F_{441}	−0.0189	F_{633}	−0.0404	F_{873}	−0.0494	F_{993}	−0.8348
F_{66}	0.669 124	F_{442}	0.0595	F_{641}	−0.1511	F_{874}	−0.1370	F_{994}	−0.0314
F_{77}	5.443 393	F_{443}	−0.2530	F_{642}	−0.1286	F_{875}	−0.0169	F_{995}	0.0054
F_{87}	0.177 131	F_{444}	−0.1887	F_{643}	−0.0403	F_{876}	−0.0009	F_{996}	−0.0664
F_{88}	0.528 308	F_{511}	0.0395	F_{644}	−0.8662	F_{881}	−0.1815		

Table 5
The Quartic Force Constants (in mdyn/Å^n rad^m) for CH_2CN^- in the Symmetry-internal Coordinate System for the CcCR QFF

F_{1111}	79.82	F_{5444}	5.15	F_{6631}	−0.49	F_{8755}	0.07	F_{9811}	−0.34
F_{2111}	−0.90	F_{5511}	0.40	F_{6632}	1.20	F_{8761}	−0.08	F_{9821}	0.19
F_{2211}	−1.61	F_{5521}	0.09	F_{6633}	−0.81	F_{8762}	0.17	F_{9822}	−0.62
F_{2221}	0.79	F_{5522}	−0.39	F_{6641}	0.01	F_{8763}	0.05	F_{9831}	−0.22
F_{2222}	181.08	F_{5531}	−0.52	F_{6642}	−0.05	F_{8764}	0.11	F_{9832}	0.17
F_{3111}	−0.55	F_{5532}	0.23	F_{6643}	−0.23	F_{8765}	0.14	F_{9833}	−0.20
F_{3211}	0.39	F_{5533}	−0.13	F_{6644}	−0.35	F_{8766}	−0.39	F_{9841}	0.03
F_{3221}	−1.13	F_{5541}	0.35	F_{6651}	0.35	F_{8777}	−0.87	F_{9842}	−0.05
F_{3222}	2.41	F_{5542}	0.23	F_{6652}	−0.28	F_{8811}	−0.39	F_{9843}	0.01
F_{3311}	−0.55	F_{5543}	0.02	F_{6653}	−0.23	F_{8821}	0.17	F_{9844}	−0.58
F_{3321}	0.31	F_{5544}	3.63	F_{6654}	−0.09	F_{8822}	−0.72	F_{9851}	0.13
F_{3322}	2.93	F_{5551}	0.94	F_{6655}	−0.07	F_{8831}	−0.20	F_{9852}	−0.24
F_{3331}	−0.27	F_{5552}	−0.37	F_{6661}	−0.10	F_{8832}	0.22	F_{9853}	−0.31
F_{3332}	−5.04	F_{5553}	−0.02	F_{6662}	0.33	F_{8833}	−0.25	F_{9854}	−0.25
F_{3333}	584.63	F_{5554}	2.44	F_{6663}	0.18	F_{8841}	0.22	F_{9855}	−0.09
F_{4111}	−0.05	F_{5555}	1.38	F_{6664}	−0.07	F_{8842}	−0.31	F_{9861}	−0.14
F_{4211}	0.31	F_{6111}	−0.15	F_{6665}	−0.07	F_{8843}	0.31	F_{9862}	−0.02
F_{4221}	−0.10	F_{6211}	0.13	F_{6666}	2.94	F_{8844}	−0.40	F_{9863}	0.03
F_{4222}	1.27	F_{6221}	−0.06	F_{7711}	82.01	F_{8851}	0.22	F_{9864}	0.14
F_{4311}	−0.35	F_{6222}	−0.04	F_{7721}	−0.45	F_{8852}	−0.41	F_{9865}	0.11
F_{4321}	0.12	F_{6311}	0.00	F_{7722}	−1.16	F_{8853}	0.06	F_{9866}	−0.18
F_{4322}	0.03	F_{6321}	0.04	F_{7731}	−0.37	F_{8854}	0.03	F_{9877}	−0.24
F_{4331}	−0.05	F_{6322}	0.16	F_{7732}	0.53	F_{8855}	0.22	F_{9887}	−0.30
F_{4332}	−0.83	F_{6331}	−0.18	F_{7733}	−0.31	F_{8861}	−0.07	F_{9888}	−0.23
F_{4333}	0.76	F_{6332}	0.04	F_{7741}	−0.18	F_{8862}	0.05	F_{9911}	−0.40
F_{4411}	−0.28	F_{6333}	−0.18	F_{7742}	0.22	F_{8863}	0.07	F_{9921}	0.13
F_{4421}	0.52	F_{6411}	−0.05	F_{7743}	−0.24	F_{8864}	−0.01	F_{9922}	0.07
F_{4422}	−0.14	F_{6421}	0.13	F_{7744}	0.04	F_{8865}	0.06	F_{9931}	−0.24
F_{4431}	−0.59	F_{6422}	0.31	F_{7751}	−0.12	F_{8866}	−0.39	F_{9932}	1.02
F_{4432}	0.35	F_{6431}	0.09	F_{7752}	−0.01	F_{8877}	−0.26	F_{9933}	−0.66
F_{4433}	−0.58	F_{6432}	−0.13	F_{7753}	−0.13	F_{8887}	−0.16	F_{9941}	0.01
F_{4441}	0.65	F_{6433}	0.22	F_{7754}	0.28	F_{8888}	−0.17	F_{9942}	0.42
F_{4442}	0.50	F_{6441}	−0.80	F_{7755}	−0.39	F_{9711}	−0.43	F_{9943}	−0.13
F_{4443}	0.29	F_{6442}	−1.41	F_{7761}	−0.11	F_{9721}	−0.02	F_{9944}	−0.00
F_{4444}	8.13	F_{6443}	0.18	F_{7762}	0.01	F_{9722}	−0.06	F_{9951}	0.28
F_{5111}	0.04	F_{6444}	−8.66	F_{7763}	0.01	F_{9731}	−0.29	F_{9952}	0.03
F_{5211}	−0.03	F_{6511}	−0.03	F_{7764}	0.06	F_{9732}	0.29	F_{9953}	−0.08
F_{5221}	0.24	F_{6521}	0.10	F_{7765}	0.08	F_{9733}	−0.23	F_{9954}	0.05
F_{5222}	0.29	F_{6522}	0.19	F_{7766}	−0.27	F_{9741}	0.10	F_{9955}	0.01
F_{5311}	−0.66	F_{6531}	0.09	F_{7777}	83.38	F_{9742}	0.12	F_{9961}	−0.12
F_{5321}	−0.01	F_{6532}	−0.07	F_{8711}	−0.79	F_{9743}	0.03	F_{9962}	0.09
F_{5322}	−0.06	F_{6533}	0.33	F_{8721}	0.02	F_{9744}	0.01	F_{9963}	0.02
F_{5331}	0.36	F_{6541}	−0.54	F_{8722}	−0.56	F_{9751}	0.16	F_{9964}	−0.11
F_{5332}	−0.72	F_{6542}	−0.90	F_{8731}	−0.29	F_{9752}	−0.10	F_{9965}	−0.08
F_{5333}	0.27	F_{6543}	0.02	F_{8732}	0.09	F_{9753}	−0.22	F_{9966}	0.64
F_{5411}	0.20	F_{6544}	−5.62	F_{8733}	−0.33	F_{9754}	0.15	F_{9977}	−0.23
F_{5421}	0.14	F_{6551}	−0.62	F_{8741}	0.13	F_{9755}	0.07	F_{9987}	−0.35
F_{5422}	−0.04	F_{6552}	−0.55	F_{8742}	0.31	F_{9761}	−0.16	F_{9988}	−0.05
F_{5431}	−0.17	F_{6553}	−0.08	F_{8743}	0.03	F_{9762}	0.07	F_{9997}	−0.30
F_{5432}	0.07	F_{6554}	−3.55	F_{8744}	−0.05	F_{9763}	−0.01	F_{9998}	−0.36
F_{5433}	−0.16	F_{6555}	−2.02	F_{8751}	0.31	F_{9764}	−0.07	F_{9999}	1.79
F_{5441}	0.70	F_{6611}	−0.53	F_{8752}	−0.03	F_{9765}	−0.01		
F_{5442}	0.18	F_{6621}	0.09	F_{8753}	−0.33	F_{9766}	−0.25		
F_{5443}	−0.30	F_{6622}	0.34	F_{8754}	0.06	F_{9777}	−0.45		

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_α structure of the cyanomethyl anion (CH$_2$CN$^-$) is shown in Figure 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 ±109°.726. 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_2CN^-, given in Table 2, appear to be well behaved and provide reference data for infrared studies. The lone exception is the ν_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 an 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 ν_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_2CN^- 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_2CN^- could be referenced by related and potentially more abundant species. As mentioned previously, the ketenimine (CH_2CNH) 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 CH_2CN^- by 32 500 MHz, 1 160 MHz, and 939 MHz, respectively. The rotational constants discussed for CH_2CN^- are the vibrationally averaged values. Additionally, the known interstellar molecule propadienylidene (CH_2CC) (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 CH_2CN. The CH_2CC 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 CH_2CC. The differences in the rotational spectra of ketenimine and propadienylidene may help to serve as markers for the microwave detection of CH_2CN^- in the ISM.

The structures of CH_2CC and the CH_2CN radical are very similar, and the relationship between their rotational constants and those of CH_2CN^- is also similar. For the CH_2CN 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, 2011b, 2012b, 2012c), but the A_0 constant computed here should still be accurate to 500 MHz or better. This should be accurate enough to make a comparison between the cyanomethyl radical and anion. From our results, we can conclude that A_0 for CH_2CN^- 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_2CN^- 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_2CN^-. If this anion can be detected radioastronomically in sight lines toward the stars HD 183143, HD 168112, and Cyg OB2 8a where the 8037 Å band shows near-perfect overlap with the laboratory/HIRES data (Cordiner & Sarre 2007), CH_2CN^- could be a viable DIB candidate carrier.

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