Carbanion Spectroscopy: CH$_2$CN$^-$

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Abstract: We have measured the photoelectron spectra of CH$_2$CN$^-$ and CD$_2$CN$^-$ and report the following electron affinities: EA(CH$_2$CN) = 1.543 ± 0.014 eV and EA(CD$_2$CN) = 1.538 ± 0.012 eV. From an analysis of the peak splittings and intensities, we extract potential-energy curves for the umbrella mode of the CH$_2$CN$^-$ negative ion and the CH$_2$CN radical. The radical is found to be a planar, C_{2v} species. The structure of the cyanomethide ion is almost described as CH$_2$=C=N$^-$, but the hydrogens are bent slightly out of the molecular plane. A Franck-Condon analysis leads to a value of the out-of-plane deformation angle as 30 ± 5° with a very small inversion barrier of 100 ± 50 cm^{-1}. Our structural conclusions are reinforced by a series of ab initio Hartree-Fock and Møller-Plesset perturbation calculations on both the cyanomethyl radical and cyanomethide ion. Using the gas-phase acidity of CH$_3$CN, we obtain the following bond-dissociation energy for acetonitrile: DH$°_{298}$(H-CH$_2$CN) = 94.2 ± 2.0 kcal/mol.
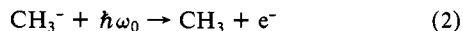
I. Introduction

We have measured the photoelectron spectrum of a simple carbanion, the cyanomethide ion. Our experiment consists of irradiating a mass-selected ion beam of CH$_2$CN$^-$ with an intense light source ($\hbar\omega_0$) and measuring the kinetic energy of the scattered electrons. This technique affords a direct measure of the electron affinity (EA) of the cyanomethyl radical, CH$_2$CN, as well as insights into the molecular structure of both the negative ion and the radical. To aid in the analysis of our photoelectron spectra, we have carried out a series of ab initio calculations on both the radical and the anion.

A naive view of the molecular structures involved in this experiment might be as follows. We irradiate a resonance stabilized carbanion to detach an electron and produce a conjugated radical.

$$[^-CH_2-CN \leftrightarrow CH_2=C=N^-] + \hbar\omega_0 \rightarrow$$
$$[^\bullet CH_2-CN \leftrightarrow CH_2=C=N^\bullet] + e^- \quad (1)$$
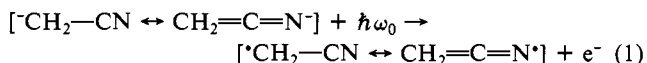
This type of expression (eq 1) leads one to expect that both reactive intermediates will be flat, C_{2v} molecules. In earlier studies of the photodetachment threshold of CH$_2$CN$^-$ in an ICR cavity, the cyanomethide ion was assigned a symmetric, planar structure.[1] This original interpretation has been sharpened in recent high-resolution spectroscopic studies of the dipole-bound states of the cyanomethide ion.[2]

One might question the validity of eq 1 in light of what is known about simple methyl radicals. Detachment studies[3] of CH$_3$$^-$ clearly indicate that while the anion is a classical pyramid, the final methyl radical is certainly[4] planar.

$$CH_3^- + \hbar\omega_0 \rightarrow CH_3 + e^- \quad (2)$$

Recent precision microwave studies of substituted methyl radicals have yielded structures[5,6] for the pyramidal CF$_3$ radical and the planar CH$_2$F and CH$_2$Cl radicals.[7,8] In view of the planarity of the chloromethyl and fluoromethyl radicals, it seems quite likely that the cyanomethyl radical is likewise a symmetric, C_{2v} species. All ab initio calculations of the geometry of CH$_2$CN report a planar geometry (see Table I) for the ground state of the radical, $\tilde{X}$ $^2B_1$.

Although CH$_3$$^-$ is a pyramidal carbanion, the enolate anion of acetaldehyde (CH$_2$CHO$^-$) is powerfully stabilized by conjugation with a carbonyl group[15] and is a planar ion, CH$_2$=CH-O$^-$. So one could argue that the cyanomethide ion is pyramidal (since it is a methide ion) or planar (on account of conjugation with the nitrile group). The neutral species isoelectronic to CH$_2$CN$^-$ is

the cyanamide molecule, NH$_2$CN. Infrared and microwave studies have clearly demonstrated that cyanamide is nonplanar. Many ab initio calculations have been reported for the cyanomethide ion and several of the most recent computed structures find that the CH$_2$CN$^-$ ion is slightly nonplanar with a $\tilde{X}$ $^1A_1$ ground state.

From an analysis of the photoelectron spectrum of CH$_2$CN$^-$ we will conclude that the cyanomethyl radical is completely planar and is a symmetric C_{2v} species while the cyanomethide anion is slightly nonplanar. Our structure for the anion is bent from the molecular plane by about 30° but the inversion barrier is only roughly 100 cm^{-1}. With the aid of ab initio Hartree-Fock and Møller-Plesset perturbation calculations on both the negative ion and radical, we are able to quantitatively model the Franck-Condon profile for both CH$_2$CN$^-$ and CD$_2$CN$^-$. The results can be rationalized by a set of simple generalized valence bond (GVB) diagrams.[26,27]

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Table I. Experimental and ab Initio Geometrical Constants[a]

species	r(CN)	r(CC)	r(CH)	α(HCH)	α(HCC)	α(CCN)	ξ	b[b]	ref
CH_2CN	1.221	1.399	1.084	118.8	120.6	180	≈ 0	≈ 0	9
CH_2CN	1.23	1.35	1.11	115	123	180	0	0	10
CH_2CN	1.21	1.44	1.105	120	120	180	0	0	11
CH_2CN	1.179	1.388	1.07	119.8	120.4	180			12
CH_2CN	1.159	1.392	1.072	120.4	119.8	180	0	0	13
CH_2CN	1.139	1.401	1.066	119.7	120.2	180			14
CH_2CN	1.173	1.377	1.070	120	120	180			16
CH_3CN	1.157	1.458	1.104	109.5	109.5	180			17
NH_2CN	1.160	1.346	1.001	113.5	115.6	180	43.0	467	18, 19
NH_2CN	1.138	1.343	0.999	113.0	114.6	177.9	40.0	343	13
CH_2CN^-	1.171	1.361	1.073	118.3	120.9	180	0	0	78
CH_2CN^-	1.174	1.366	1.073	118.3	120.9	180	0	0	20
CH_2CN^-	1.169	1.401	1.083	111.0	113.5	180	≈ 0	≈ 0	21
CH_2CN^-	1.168	1.413	1.086	109.9	111.3	180			22
CH_2CN^-	1.170	1.365	1.073	118.3	119.6	180			14
CH_2CN^-	1.186	1.387	1.085	119.2	120.4	180	0	0	23
CH_2CN^-	1.197	1.366	1.073	119.6	120.9	180			24
CH_2CN^-	1.162	1.393	1.077	117.5	118.0	178.3	25.0	105	25
CH_2CN^-	1.162	1.395	1.078	116.9	117.4	178.0	28.3	39	13

[a] Bond lengths in Å. α and ξ in deg. [b] The inversion barrier in cm⁻¹.

II. Experimental Section

We have used the technique of photoelectron spectroscopy to study the cyanomethide ion. The essence of the experiment is to prepare ion beams of M⁻ and to irradiate them with a fixed-frequency, continuous laser. One measures the kinetic energy (KE) of the scattered electrons.

$$M^- + \hbar\omega_0 \rightarrow M + e^-(KE) \qquad (3)$$
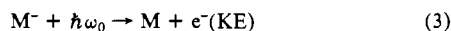
This technique has recently been reviewed[28,29] and a complete description of our spectrometer has been published.[30,31] A short discussion of our experimental procedure is as follows.

We prepare the ions in a high-pressure (roughly 0.2 Torr), magnetically confined plasma. For these spectra we use ammonia and acetonitrile to produce CH₂CN⁻; employment of a 0.015 in. Ta filament and a 10-mA emission current produces intense (approximately 1 nA) negative ion beams. All of the negative ions are extracted from our source, velocity selected by a Wien filter, and delivered to an ultra-high-vacuum (10⁻⁹ Torr) chamber for detachment.

The ion beam is crossed with the output of an Ar II laser operating CW on a single line (λ_0 = 488 nm or $\hbar\omega_0$ = 2.540 eV); the laser maintains about 75 W of intracavity power. Detached electrons are collected and analyzed by a pair of hemispherical analyzers; these electrostatic analyzers operate with a resolution of roughly 20 meV (fwhm) as measured with a beam of O⁻ ions. The photoelectron spectrum must be calibrated with a reference ion and transformed to the center of mass (CM) frame. We employ OH⁻ as a calibration ion[32] with EA_{cal}(OH) = 1.827670 ± 0.000021 eV and M_{cal} = 17 amu. We use the following expression to calculate the KE in the CM frame.

$$KE = KE_{cal} + \gamma(V_{cal} - V) + mW[M^{-1} - M_{cal}^{-1}] \qquad (4)$$

In (4) KE is the CM energy (eV) of an electron detached from an ion of mass M (amu); V is the slit voltage of the energy analyzer. The CM kinetic energy of the calibration ion is KE_{cal} (=$\hbar\omega_0 - EA_{cal}$). The slit voltage at the center of the calibration ion's peak is V_{cal} while γ is a dimensionless scale compression factor (typically 1.00 ± 0.01) measured from the Cr⁻ photoelectron spectrum.[33] The ion beam kinetic energy is W (eV) while m is the mass of an electron (amu).

III. Results

Figure 1 is a survey photoelectron spectrum of the m/z 40 ion produced from a discharge of NH₃ and CH₃CN in the ion source. We assign this ion as the cyanomethide ion, CH₂CN⁻. Each data point in this spectrum is separated by about 10 meV, and we have scanned our analyzer out to the laser photon energy, $\hbar\omega_0$ = 2.540 eV. Figure 1 indicates that the electron affinity of the cyanomethyl

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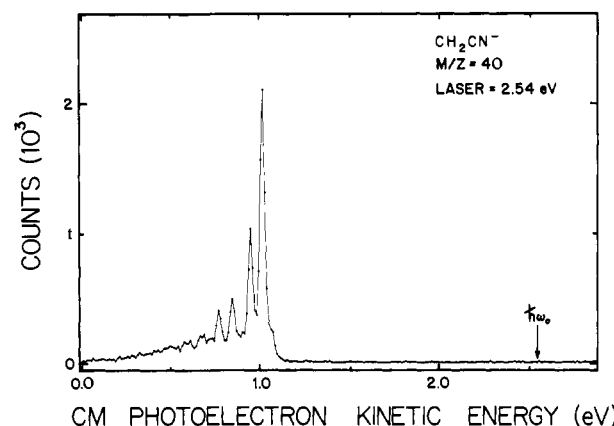

Figure 1. A fast scan of the photoelectron spectrum of CH₂CN⁻. The data points are separated by roughly 10 meV; the energy of our laser is 2.540 eV and is marked by $\hbar\omega_0$.
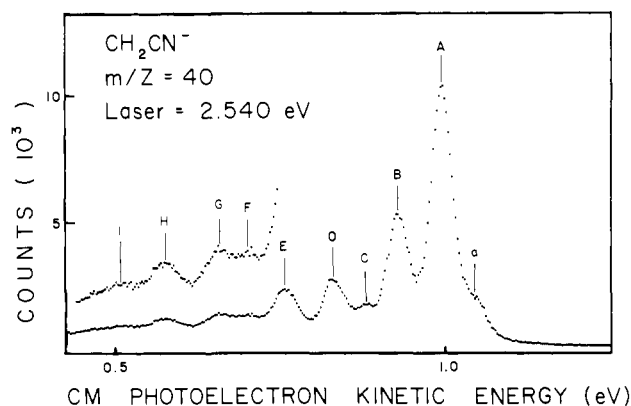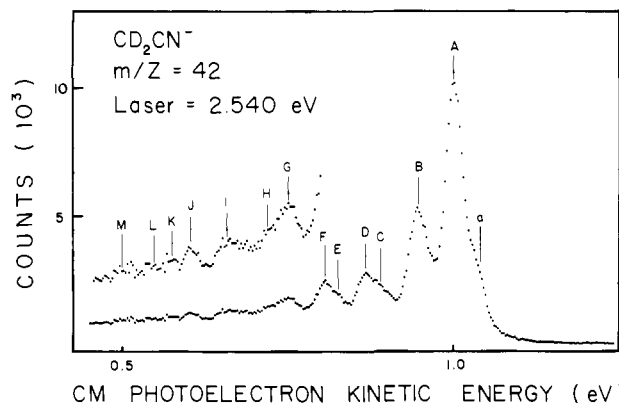

Figure 2. A slow scan of the photoelectron spectrum of CH₂CN⁻. The data points are separated by roughly 2.8 meV. Values of the peak positions (a–I) are collected together in Table II.

radical is about 1.5 eV. Earlier ICR photodetachment threshold studies[1] reported a value for EA(CH₂CN) of 1.507 ± 0.018 eV. This further strengthens our assignment of CH₂CN⁻ as the carrier of the signal in Figure 1. It is also evident that there are numerous vibrational modes excited in the final CH₂CN radical upon detachment of the ion. This suggests that there is a significant geometry change between the cyanomethide ion and the cyanomethyl radical.

Figures 2 and 3 are higher signal-to-noise spectra of the CH₂CN⁻ and CD₂CN⁻ ions; the data points are about 2.8 meV apart. Several transitions can be resolved and are labeled (a, A,

Figure 3. A slow scan of the photoelectron spectrum of CD_2CN^-. The data points are separated by roughly 2.8 meV. Values of the peak positions (a–M) are collected together in Table II.

Table II. Measured CM Kinetic Energy (eV) for Cyanomethide Ions (Laser λ_0 = 488.0 nm (2.540 eV))

peak	CH_2CN^-	CD_2CN^-
a	1.046 ± 0.022	1.040 ± 0.017
A	0.996 ± 0.014	1.001 ± 0.012
B	0.930 ± 0.015	0.947 ± 0.015
C	0.882 ± 0.015	0.889 ± 0.016
D	0.828 ± 0.012	0.867 ± 0.014
E	0.756 ± 0.016	0.825 ± 0.012
F	0.700 ± 0.019	0.806 ± 0.014
G	0.658 ± 0.016	0.751 ± 0.024
H	0.576 ± 0.022	0.720 ± 0.017
I	0.510 ± 0.020	0.659 ± 0.023
J		0.604 ± 0.022
K		0.576 ± 0.017
L		0.549 ± 0.020
M		0.501 ± 0.023

B, ..., I). These features result from detachment from vibrational levels of the CH_2CN^- ion to several final vibrational states of the CH_2CN radical. We ignore rotational effects since we cannot resolve them; recall that the fwhm of our electrostatic analyzer is 20 meV or 160 cm^{-1}.

The feature labeled a originates from a vibrationally excited CH_2CN^- ion (a "hot band"). We are certain of this because the presence of the shoulder depends dramatically upon our ion source conditions and upon the ion precursor; by appropriate variations of the pressure in the source, one can cause peak a nearly to vanish. Most other features (A, B, ..., I) are invariant to source conditions for both the CH_2CN^- and CD_2CN^- ions. Our conclusion that peak A is the origin is strengthened by comparing the d_0 ion (Figure 2) with the d_2 ion (Figure 3). The proper (0,0) transition will shift very little upon isotopic substitution; transitions to excited vibrational states in the cyanomethyl radical (features B, ..., I) will collapse to higher KE toward the origin while the hot band (a) will also shift toward the (0,0) band and lower KE. This is exactly the situation in Figures 2 and 3. The apparent or raw electron affinities are then extracted from the CM KE of peak A: raw EA(CH_2CN) = 1.544 ± 0.014 eV and raw EA(CD_2CN) = 1.539 ± 0.012 eV. All of the peak locations from Figures 2 and 3 are collected together in Table II.

IV. Discussion

A. Identity of the Active Modes. To discuss the structured spectra in Figures 2 and 3, we must consider the vibrational modes of CH_2CN and CH_2CN^-. All of the computational (see Table I) and experimental evidence available for CH_2CN suggests that the ground state is a symmetric, C_{2v} radical, $\tilde{X}\,^2B_1$. A large number of electron spin resonance studies have detected the cyanomethyl radical in a cryogenic matrix subsequent to γ-irradiation.[34-43] These ESR studies show clear evidence for spin

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Table III. $H_2C–CN$ Vibrational Modes

mode	symmetry	approximate description
ω_1	a_1	CH s-stretch
ω_2	a_1	C≡N stretch
ω_3	a_1	CH_2 scissors
ω_4	a_1	C—C stretch
ω_5	b_1	CH_2 deformation (umbrella)
ω_6	b_1	C—C—N out-of-plane bend
ω_7	b_2	CH a-stretch
ω_8	b_2	CH_2 rock
ω_9	b_2	C—C—N in-plane bend

delocalization: [$^\bullet CH_2$—C≡N ↔ CH_2=C=N$^\bullet$]. This suggests that cyanomethyl is a flat molecule. Infrared and ultraviolet bands have been attributed to CH_2CN following co-deposition of acetonitrile and argon metastables in an Ar matrix.[44]

We will consider CH_2CN to have C_{2v} symmetry and use local modes to approximate the vibrational degrees of freedom (Table III); these assignments were based upon the ab initio frequencies and normal modes described below. Suppose that the cyanomethide ion is also a planar, C_{2v} species. Detachment of ground-state CH_2CN^- ions [$\tilde{X}\,^1A_1$ ($v'' = 0$)] will have an extreme propensity to produce cyanomethyl radicals excited in the a_1 modes. That is to say that C_{2v} ions and radicals will only have ω_1, ω_2, ω_3, or ω_4 (and combinations) as active vibrations. We can estimate these symmetric frequencies by considering related molecules. Values for symmetric C–H stretches (ω_1) are generally in the range 2900–3100 cm^{-1} and nitriles have a characteristic band (ω_2) at about 2300 cm^{-1}. The CH_3–CN stretch in acetonitrile is 920 cm^{-1} and this is a reasonable conjecture for ω_4. We can estimate the CH_2 scissoring motion in cyanomethyl by considering the experimental values[45-49] for the halomethyl radicals: $\omega_{sciss}(CH_2Cl)$ = 1356 cm^{-1}, $\omega_{sciss}(CH_2Br)$ = 1355.7 cm^{-1}, and $\omega_{sciss}(CH_2I)$ = 1331.5 cm^{-1}. We conjecture that ω_3 will be roughly 1200–1400 cm^{-1} for cyanomethyl radical.

Consider the photoelectron spectrum of CH_2CN^- in Figure 2. Since peak A is the (0,0) band, most of the structure in the spectrum belongs to the CH_2CN radical. One of the more intense features is peak B, which is split by 532 cm^{-1} from the origin (Table II). Since all of the a_1 frequencies of cyanomethyl (ω_1–ω_4) are expected to be around 950 cm^{-1} or higher, the presence of this prominent band B seems to imply that either the CH_2CN^- ion or the CH_2CN radical (or both) does not have C_{2v} symmetry. From the CD_2CN^- spectrum, we can say that this low-frequency mode strongly involves hydrogen motions on account of the large isotope effect.

The most plausible way to interpret the photoelectron spectra is to consider the CH_2CN^- ion to be a nonplanar, pyramidal molecule and that detachment takes place to a planar CH_2CN radical. With this supposition, Figure 4 shows that the cyanomethide ion is deformed from planarity by an angle ξ. If this is the case we can use the C_s point group to classify both the ion and the radical. Under C_s all of the a_1 and b_1 modes in Table III now become a' while the three b_2 vibrations transform like a'' modes. Under C_s symmetry, detachment of the cyanomethide

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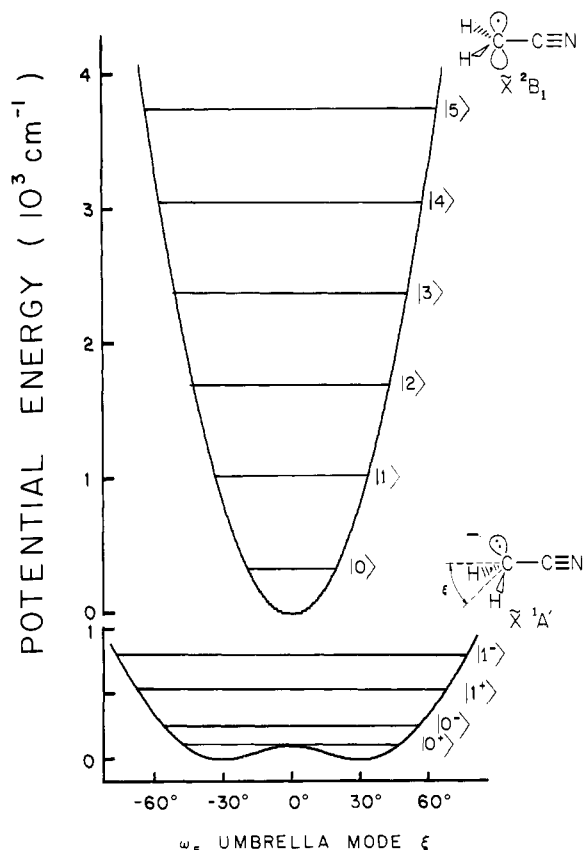
Figure 4. Curves used to model the asymmetric umbrella potential (ω_5) of CH_2CN^- and CH_2CN. The vibrational energy levels are calculated by variationally solving a model hamiltonian (Table V). The inversion barrier is only 100 cm^{-1} in the carbanion so each of the vibrational level is split into a pair of levels; these are labeled $|0°\rangle$, $|0-\rangle$, $|1+\rangle$, $|1-\rangle$, etc. The CH_2CN radical is a planar species with little or no inversion barrier.

ion can have any of the a' modes as active vibrations. In particular ω_5 (the unbrella mode) now becomes an allowed mode.

Qualitatively everything begins to fit. All ESR and ab initio studies of the cyanomethyl radical find that the molecule is a planar, symmetric species. Cyanamide (NH_2CN), a species isoelectronic to CH_2CN^-, is known experimentally to be pyramidal and this finding has been reached by recent ab initio studies. An infrared study of the alkali metal salts ($M^+CH_2CN^-$ where M^+ = Li$^+$, Na$^+$, and K$^+$) in a variety of solutions could not be analyzed to yield a structure for CH_2CN^- itself.[50] Our detachment spectra show activity in a low-frequency mode that is quite sensitive to deuteriation.

We should not ignore other possibilities, however. These include the case of a planar cyanomethide ion and a nonplanar cyanomethyl radical or the likelihood that there are several active modes in addition to ω_5. Our photoelectron spectra in Figures 2 and 3 are quite irregular and we must attempt to model them in a quantitative fashion. In order to proceed, we need to estimate the molecular geometries and vibrational frequencies for both the CH_2CN^- ion and the CH_2CN radical.

B. Computational Results. The results of our ab initio molecular orbital calculations on the cyanomethyl radical and the cyanomethide ion are shown in Table IV. Geometries were optimized at the Hartree-Fock (HF), self-consistent-field (SCF) level with the 6-31+G(d) basis set; the optimized geometries and HF energies are in Table IV. This is a polarized, split-valence basis set[51] augmented with a set of diffuse functions on the non-hydrogen atoms.[52] The diffuse functions are needed to describe the negative

Table IV. Ab Initio Calculated Properties

I. Energies

CH_2CN (C_{2v})

A. Total Energy:
[UHF/6-31+G(d)] = -131.310 74 hartrees
[UCISD/6-31++G(d,p)] = -131.683 26 hartrees
[UMP2/6-311++G(d,p)] = -131.736 12 hartrees
["UMP4/6-311++G(d,p)"] = -131.779 55 hartrees

B. Scaled [UHF/6-31+G(d)] Harmonic Vibrational Frequencies (cm^{-1}):
ω_7 = 3085, ω_1 = 29848 ω_2 = 1848, ω_3 = 1402, ω_8 = 1004, ω_4 = 965, ω_5 = 580, ω_6 = 383, ω_9 = 359

C. Rotational Constants [UHF/6-31+G(d)]
A = 9.663 cm^{-1}, B = 0.344 cm^{-1}, C = 0.332 cm^{-1}

CH_2CN^- (C_s)

A. Total Energy:
[RHF/6-31+G(d)] = -131.311 85 hartrees
[RCISD/6-31++G(d,p)] = -131.715 42 hartrees
[RMP2/6-311++G(d,p)] = -131.796 76 hartrees
["RMP4/6-311++G(d,p)"] = -131.832 92 hartrees

B. Harmonic Vibrational Frequencies (cm^{-1}) from a Scaled [RHF/6-31+G(d)] Calculation:
ω_7 = 2983, ω_1 = 2992, ω_2 = 2077, ω_3 = 1396, ω_8 = 1032, ω_4 = 987, ω_5 = 550, ω_9 = 425, and ω_6 = 276

C. Rotational Constants [UHF/6-31+G(d)]
(A = 9.320 cm^{-1}, B = 0.343 cm^{-1}, C = 0.332 cm^{-1}

II. Geometrical Constants [UHF/6-31+G(d)][a]

species	r(CN)	r(CC)	r(CH)
CH_2CN	1.159	1.392	1.072
CH_2CN^-	1.162	1.395	1.078

species	α(HCH)	α(HCC)	α(CCN)	ξ	b
CH_2CN	120.4	119.8	180	0	
CH_2CN^-	116.9	117.4	178.0	28.3	39

[a] Bond lengths in Å; b is the inversion barrier in cm^{-1}. α and ξ in deg. The correlated MP2/6-31+G(d) values for xi and b for the anion are in much better accord with experiment than the Hartree-Fock values, see sections IV.B and IV.C.

ion, and they have little or no effect on the computed geometry of the radical. At this level of calculation bond lengths are generally accurate[53] to ± 0.02 Å and bond angles are correct to ±2°. However, contamination of the spin unrestricted, UHF, wave function used for the radical can lead to larger errors.[54] Such wave functions, in general, are not eigenfunctions of the spin-squared operator, (S^2), and can be contaminated by quartets, sextets, etc. In the case of CH_2CN $\langle S^2 \rangle$ is 0.92 whereas for a doublet it would be 0.75. For diatomic molecules[54] with a comparable amount of spin contamination, bond lengths differ from the optimized RHF values by 0.01–0.02 Å. Table IV also gives the rotational constants computed from the UHF/6-31+G(d) geometries; they can be expected to be accurate[55] to about ±5%.

The harmonic vibrational frequencies computed at the UHF/6-31+G(d) level and then scaled[56] by 0.89 are listed in Table IV; the absence of imaginary frequencies confirms that the optimized geometries are minima on the theoretical potential-energy surface. This scaling procedure applied to a collection of closed-shell, neutral molecules with the 6-31G(d) basis set resulted in frequencies with a mean error of 49 cm^{-1}; 92% of them agreed with experiment to better than 100 cm^{-1} and the frequencies were as likely to be too high as too low.[56] The diffuse-function augmented basis, 6-31+G(d), used with the scale factor of 0.89 gave equally accurate frequencies for the anions[57-59] OH$^-$ and NH$_2^-$(ω_1).

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The cyanomethyl radical frequencies can be expected to be less accurate because of the spin contamination.

The inversion barrier, b, for the anion was computed by optimizing the geometry of CH_2CN^- in a planar, C_{2v} configuration; vibrational frequencies computed for this structure show a single, out-of-plane imaginary frequency, correct for a transition state. Cyanamide, NH_2CN, is isoelectronic with the cyanomethide anion; theoretical (HF/6-31+G(d)) and experimental values for the inversion barrier are compared in Table I. The error of 124 cm^{-1} (0.4 kcal mol^{-1}) is consistent with calculations at this level for other compounds.[60] Because of the much smaller barrier computed for CH_2CN^-, 39 cm^{-1}, we examined the effect of increasing the size of the basis set to the triple-split, polarized, diffuse-function-augmented level (6-311++G(d,p))[52,61] and the effect of electron correlation at the level of second-order Møller–Plesset perturbation theory (MP2).[62] Thus, at the UHF/6-311++G(d,p) level of theory we obtained $\xi = 29.9°$ and $b = 43$ cm^{-1}; and at the UMP2/6-31+G(d) level $\xi = 33.0°$ and $b = 145$ cm^{-1}. The prediction of nonplanarity for the cyanomethide ion is thus verified as is the very small barrier to inversion.

Single-point calculations were performed to estimate the gas-phase acidity or proton affinity (see eq 7 of section V) of CH_2CN^- and the electron affinity of CH_2CN. The relevant total energies, shown in Table IV, were computed at the UHF/6-31+G(d) geometries. We calculated the proton affinity (PA) at the MP2/6-311++G(d,p) level using scaled 6-31+G(d) vibrational frequencies for the vibrational energies.[63] In a study of the proton affinities of small neutral and anionic bases this level of calculation was shown to be particularly accurate[57] with a mean error of about 3 kcal mol^{-1}. For the cyanomethide anion the computed PA of 375 kcal mol^{-1} is consistent with the measured value of 372.2 ± 2.0 kcal/mol[64] and is larger than that computed with a smaller basis set at the MP2/6-31+G(d) level, 371 kcal/mol.[25]

The calculation of accurate electron affinities requires both large basis sets and wave functions that include high-order terms (triples and quadruples). EAs for first-row atoms and diatomic hydrides have been computed[65] to within ±0.2 eV with use of complete fourth-order perturbation theory (MP4)[66] and very large basis sets (6-311++G(3df,3pd), for example).[67] With the smaller 6-311++G(d,p) basis set, errors at the MP4 level are as large as 0.6 eV for the diatomic hydrides.[65] Additional errors arise when larger, spin-contaminated, molecules are considered with the UHF formalism.[68] These errors are inconsistent, with some electron affinities being too large and others too small at the same level of approximation. While a configuration interaction wave function including all single and double substitutions (CISD) leads to larger errors they are more predictable. Thus, with the 6-31++G(d,p) basis set, the UCISD electron affinities of a sequence of open-shell species are in error by from −0.12 to −1.02 eV (the calculation always underestimating the EA) while the UMP4 errors with the same basis range from −0.76 to +0.37 eV.[68] These results suggest that accurate electron affinities for open-shell molecules with

significant spin contamination cannot be computed with the modest basis sets that are practical for molecules the size of CH_2CN and that neither UCISD nor UMP4 wave functions are likely to give reliable results even were such basis sets practical. Nonetheless, it is useful to compare electron affinities computed with these theoretical models to the experimental value. We have done so at two levels; at each the agreement with the photoelectron value of $\simeq 1.5$ eV is surprisingly good, though the results discussed above indicate that this must be fortuitous. The EA at the UCISD/6-31++G(d,p) level is 0.9 eV while at the "MP4/6-311++G(d,p)" level it is 1.5 eV. (The quotations show that this calculation was approximated with use of a technique that has been shown to lead to small errors.[69])

C. Quantitative Modeling of the Franck–Condon Profile. The change in the molecular geometry between the cyanomethyl radical and the cyanomethide anion is reflected in the photoelectron spectra in Figures 2 and 3. Accurate modeling of such spectra is generally an intractable problem. If either the radical or ion is totally asymmetric, then the Franck–Condon problems of Figures 2 and 3 will be quite severe, on the order of (9 modes × 9 modes) or 81 dimensional. This assumes that the vibrational, rotational, spin, and orbital angular momentum are uncoupled.

We have modeled the spectra in Figures 2 and 3 by assuming that only 3 or fewer vibrations are active. We ignore all other degrees of freedom. The idea of our calculation is to compute separately the vibrational states of the CH_2CN^- ion and the CH_2CN radical and then use these vibrational wave functions to generate numerically the Franck–Condon profile of Figure 2. One varies the nature of the active vibrational modes until a best fit of Figure 2 can be attained. If our answer is to make any sense, we must then be able to predict the CD_2CN^- spectrum in Figure 3.

The calculation of the vibrational frequencies and wave functions for the ion and radical means that we must set up and solve a vibrational Schrödinger equation for each species. We will assume that each of the vibrational modes is independent and can be solved for separately. We will approximate the active modes as local modes (Ω_{vib}) and attempt to calculate them from the following vibrational Schrödinger equation.[70]

$$[\tfrac{1}{2}g_{vv}\hbar^2 \, \partial^2/\partial Q_v^2 + V(Q_v)]\Omega_{vib}(Q_v) = E_v\Omega_{vib}(Q_v) \qquad (5)$$

Equation 5 describes the v-th vibrational mode, $\Omega_{vib}(Q_v)$. The effective mass of the oscillator is given by the reciprocal of the Wilson **g**-matrix element, g_{vv}, and $V(Q_v)$ is the vibrational potential function. The potential $V(Q_v)$ depends directly upon molecular geometry through force constants, equilibrium bond angles and bond lengths, anharmonicity constants, and the like.

Our program is straightforward. We must separately guess the molecular parameters for the ion and radical to construct the respective potentials, $V(Q_v)$. For example, we could use $V(Q_{st}) = \tfrac{1}{2}k_{st}(R - R_e)^2$ as a simple potential for a stretching vibration. We would have to estimate the force constant (k_{st}) and the equilibrium bond length (R_e) for the oscillator. In this simple case we would know the vibrational frequencies and harmonic wave functions without having to solve (5). For more complicated anharmonic vibrational motions such as torsions, rocking, umbrella motions, and the like, we must find vibrational wave functions by solution of the appropriate Schrödinger equation (eq 5). The differential equation is solved numerically in a variationally correct manner in a basis set of cubic B-splines.[71]

We have tried three different approaches to unraveling Figures 2 and 3. (a) The first is motivated by CH_3^- and NH_2-CN which suggests a very pyramidal CH_2CN^- carbanion and a symmetric, planar CH_2CN radical. (b) The second case treated the cyanomethide anion as a flat, resonance-stabilized carbanion which is detached to a pyramidal cyanomethyl radical. (c) The final model

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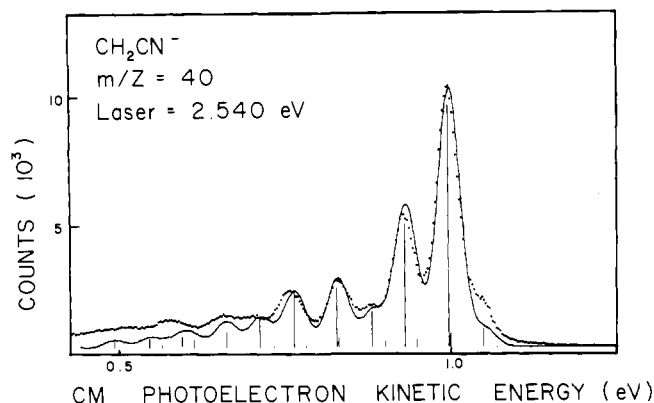(71) ONeil, S. V.; Reinhardt, W. P. *J. Chem. Phys.* **1978**, *69*, 2126.

Carbanion Spectroscopy: CH₂CN⁻

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Figure 5. The photoelectron spectrum of CH_2CN^-. The points are the experimental spectrum from Figure 2 while the solid line is a calculated spectrum for comparison. The modeled spectrum results from a Franck–Condon calculation with use of the potential curves in Figure 4.

used a planar CH_2CN radical and a very weakly pyramidal CH_2CN^- ion. We find that case (c) fits all of our experimental data.

Since the CH_3^- ion is pyramidal,[3] our first attempts used a nonplanar CH_2CN^- ion which would be detached to a flat cyanomethyl radical. Figure 4 shows a structure of the cyanomethide ion deformed from planarity by an angle ξ. Since cyanamide is such a nonplanar species (see Table I), we initially used an angle $\xi \simeq 45°$ with an inversion barrier of roughly 500 cm⁻¹. To represent the umbrella mode (ω_5) we used a potential consisting of a harmonic oscillator perturbed by a Gaussian barrier together with the appropriate Wilson g-matrix element.[72] This approach fails to describe the spectra in Figures 2 and 3. We next tried to use a planar cyanomethide ion and a nonplanar cyanomethyl radical. To begin to fit our spectra, we must use at least three different active modes: ω_3 (CH_2 scissors), ω_4 (C–C stretch), and ω_5 (CH_2 umbrella mode). We were able to construct a Franck–Condon profile which resembles those in Figures 2 and 3.

We have finally considered the possibility of a slightly bent anion being detached to yield a flat, planar radical. The ab initio results of Table IV predict that the major differences between the cyanomethyl radical and the cyanomethide ion are $\Delta\alpha$(H–C–H) and $\Delta\xi$. The inversion barrier (b) is calculated to be only 39 cm⁻¹. We have considered only a single mode to be active and that is ω_5, the umbrella mode, Figure 4 depicts the potentials that we have employed. The CH_2CN^- ion is represented by a linear oscillator perturbed by a Gaussian barrier.[72]

To model Figure 2, we select parameters for the anion [$V''(Q_5)$] and the radical [$V'(Q_5)$] and then solve separately for the vibrational states. In doing so we must also supply parameters [r(CH), r(CC), and α(H₂C)] for the effective mass of each oscillator, $1/g_{55}$. These values are chosen in light of the ab initio results in Table IV and from the experimental findings[7,8] for CH_2F and CH_2Cl; they are constrained throughout the fitting procedure. Since Table IV suggests that the ion is only slightly nonplanar, we have systematically varied $V''(Q_5)$ and $V'(Q_5)$ over a wide range of k_5, C, and β. Our search covered angles such that $0° < \xi < +60°$ and inversion barriers $0 < b < 500$ cm⁻¹.

The result of our calculations is plotted in Figure 5 where the points are the experimental data (from Figure 2) and the solid line is the calculated Franck–Condon factors (sticks) folded with an experimental line width. The precise values of all of the molecular constants are collected together in Table V. We can now test the potentials (Table V) which we used to generate Figure 5. In a Born–Oppenheimer world, we should be able to predict the photoelectron spectrum of CD_2CN^- by simply changing the M_H in Table V to M_D, recalculating the vibrational states, and forming the Franck–Condon factors for the transition $CD_2CN \leftarrow CD_2CN^-$. The results of this exercise are shown in Figure 6

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Table V. Vibrational Schrödinger Equation (H_2C–CN Umbrella Mode (ω_5))

A. Formulae
$V(Q_5) = (1/2)k_5Q_5^2 + C \exp(-\beta Q_5^2)$
$g_{55} = (M_C + M_N)^{-1} + (M_C)^{-1} + (M_C/2)(X/Z) + [(2M_H + M_C)/(2M_HM_C)](X/Z)^2$
where:
$Q_5(\xi) = [\pi/180]X\xi$; $X = r_{CC}$; $\alpha_0 = H$–C–H angle
$Z = r_{CH} \cos (\alpha_0/2)$; $\rho = \ln [2C\beta/k_5]$
$\xi_{min} = (180/\pi X)[\rho/\beta]^{1/2}$; barrier = $b = C(e^\rho - \rho - 1)e^{-\rho}$

B. Fitting Parameters

radical	anion
$r_{CH}' = 1.07$ Å	$r_{CH}'' = 1.08$ Å
$r_{CC}' = 1.39$ Å	$r_{CC}'' = 1.39$ Å
$\alpha_0' = 120°$	$\alpha_0'' = 117°$
$k_5' = 3039$ cm⁻¹ Å⁻¹	$k_5'' = 655$ cm⁻¹ Å⁻²
$C' = 0$ cm⁻¹	$C'' = 481$ cm⁻¹
$\beta' = 0$ Å⁻²	$\beta'' = 1.593$ Å⁻²
$\xi_{min}' = 0° \pm 5°$	$\xi_{min}'' = 30° \pm 5°$
$b' = 0 \pm 50$ cm⁻¹	$b'' = 100 \pm 50$ cm⁻¹

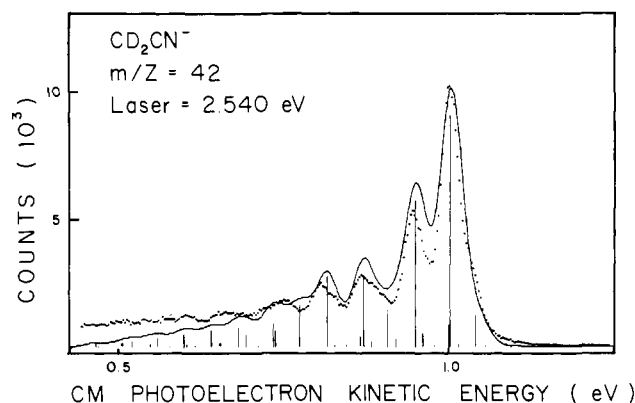*a* The parameters r_{CH}, r_{CC}, and α_0 are constrained during the fit of $V(Q_5)$.

Figure 6. The photoelectron spectrum of CD_2CN^-. The points are the experimental spectrum from Figure 3 while the solid line is a calculated spectrum for comparison. The modeled spectrum results from a Franck–Condon calculation with use of the potential curves in Figure 4.

where the points are the experimental data from Figure 3 and the solid line is the synthesized spectrum.

From a comparison of the calculated photoelectron spectra and the observed data (Figures 5 and 6), we conclude that the potentials in Figure 4 and Table V provide a plausible set of structures for the cyanomethyl radical and the cyanomethide ion. We find that the CH_2CN^- ion is slightly nonplanar with $\xi = 30 \pm 5°$ and an inversion barrier of $b = 100 \pm 50$ cm⁻¹. The CH_2CN radical is a strictly symmetric, planar radical.

The agreement between the experimental results in Table VI and the theoretical results in Table IV is generally satisfactory. Of the several methods used to compute the inversion barrier b and the angle ξ, agreement is best with the correlated UMP2/6-31+G(d) results where $b = 145$ cm⁻¹ and ξ is 33°; the SCF results are in poor agreement with the empirically derived barrier height. The experimental value of ω_5 for CH_2CN^- of 424 cm⁻¹ is in remarkable accord with the ab initio value of the "in-plane" C=C=N bend, ω_9, 425 cm⁻¹. (The usage of "in-plane" and "out-of-plane" refers to the molecular plane in the radical and the analogous pseudoplane in the anion, not the symmetry plane in the anion.) Examination of the computed normal coordinates indicates that the local-mode descriptions in Table III are appropriate for the radical but not for two of the modes in the anion: the umbrella mode which is ω_5 (b₁) in the radical is ω_6 (a') in the anion and the out-of-plane CCN bend which is ω_6 (b₁) in the radical is ω_5 (a') in the anion. The harmonic scaled HF/6-31+G(d) value for the umbrella frequency is 276 cm⁻¹; since the photoelectron spectra show that the umbrella mode in the anion is significantly anharmonic, it is difficult to compare the calculated

Table VI. Experimental Molecular Properties

	radical[a]		anion[b]	
	CH_2CN	CD_2CN	CH_2CN^-	CD_2CN^-
$\omega_5{}^c$	680	538	424	308
$0^{\pm}$ inversion splitting[a]	0	0	152	101
inversion barrier[a]		0 ± 50		100 ± 50
$\xi_{min}{}^d$		0 ± 5		30 ± 5
A^c	9.74 ± 0.15	4.87 ± 0.10	9.16 ± 0.32	4.63 ± 0.16
B^c	0.344 ± 0.010	0.304 ± 0.010	0.343 ± 0.010	0.305 ± 0.010
C^c	0.332 ± 0.010	0.286 ± 0.010	0.333 ± 0.010	0.288 ± 0.010
asymmetry constant	-0.997	-0.992	-0.998	-0.992
$\Delta H_f^{\circ}{}_{298}{}^e$	59.7 ± 2.0		24.1 ± 2.0 kcal/mol	

[a] $EA(CH_2CN) = 1.543 \pm 0.014$ eV. $\Delta H^{\circ}{}_{acid}(H-CH_2CN) = 372.2 \pm 2.0$ kcal/mol. [b] $EA(CD_2CN) = 1.538 \pm 0.012$ eV. $DH^{\circ}{}_{298}(H-CH_2CN) = 94.2 \pm 2.0$ kcal/mol. [c] cm⁻¹. [d] deg. [e] kcal/mol.

harmonic frequency with the experimentally determined splittings (ω_5 and $0^{\pm}$ inversion splitting for CH_2CN^- in Table VI). In the radical the discrepancy is also large, 680 cm⁻¹ experimentally versus 580 cm⁻¹ theoretically. This difference may be attributable in part to spin contamination of the UHF wave function used to compute the frequencies of CH_2CN, and thus an RHF calculation of these frequencies would be very useful.

The rotational constants associated with our model in Table VI are imperfectly determined. The one-dimensional fits in Figure 5 and 6 are quite sensitive to the angle ξ and the barrier height, b. The geometrical constants r_{CH}, r_{CC}, and α_0 only enter into the reduced mass of the Q_5 oscillator; the bond length r_{CN} is completely ignored. We have chosen reasonable values for these parameters, but of course the rotational constants are strongly dependant upon these values. Apart from employing 1.16 Å for the CN bond length (see CH_3CN and NH_2CN in Table I), our model for the CH_2CN radical (Table V) uses $r_{CH} = 1.07$ Å, $r_{CC} = 1.39$ Å, $\alpha_0 = 120°$, and $\xi = 0°$; this leads to $A = 9.740$ cm⁻¹, $B = 0.344$ cm⁻¹, and $C = 0.332$ cm⁻¹. In contrast the theoretical geometry from Table IV ($r_{CH} = 1.072$ Å, $r_{CC} = 1.392$ Å, $\alpha_0 = 120.4°$, and $\xi = 0°$) points toward a different set of constants: $A = 9.663$ cm⁻¹, $B = 0.344$ cm⁻¹, and $C = 0.332$ cm⁻¹. Consequently we cannot be sure that the A rotational constant is fixed to any better than 0.2 or 0.3 cm⁻¹; the B and C constants are probably determined to within 0.01 cm⁻¹.

The parameters resulting from our study (Table V) are plausible. An umbrella frequency of 680 cm⁻¹ for the cyanomethyl radical is certainly higher than might be expected; recall[7,8] that $\omega_4(CH_2F) = 300 \pm 30$ cm⁻¹ and $\omega_4(CH_2Cl) = 400$ cm⁻¹. Conjugative stabilization by the nitrile may be at work here. From a study of the dipole bound states of CH_2CN^-, values of the rotational constant A were estimated.[2] It was concluded that $A(CH_2CN) \simeq 9.45 \pm 0.05$ cm⁻¹ and $A(CH_2CN^-) = 9.19 \pm 0.05$ cm⁻¹.

So what is our understanding of the CH_2CN radical and the CH_2CN^- ion? How can we most easily view the spectra in Figures 2 and 3? We are inclined to favor our simple model of a bent carbanion being detached to a flat radical with excitation of a single active vibration, the umbrella mode. This one-dimensional picture does quite a good job of reproducing the complicated Franck–Condon envelopes in Figures 2 and 3. It is in accord with the best ab initio findings and earlier ESR and diode laser studies of the cyanomethyl radicals and related species such as the halomethyl radicals, CH_2X. Thus we constantly write the cyanomethide anion like CH_2CN^- and not as $^-CH_2CN$. Nevertheless we cannot absolutely exclude a different interpretation which is based on a strictly planar anion and pyramidal radical. This latter picture necessitates at least three distinct active modes, does not fit our experimental data (Figures 2 and 3) quite as well as the potentials in Figure 4, and conflicts with the ab initio results.

D. GVB Models. Our findings support the notions of a planar, symmetric cyanomethyl radical and a mildly pyramidal carbanion, CH_2CN^-. These conclusions are consistent with earlier experimental results for CH_2F, CH_2Cl, and $CH_2=CH-O^-$ and with the findings of ab initio calculations (Table I).

We can try to rationalize these molecular structures in terms of some GVB ideas.[27] Reference to Figure 7 depicts the com-
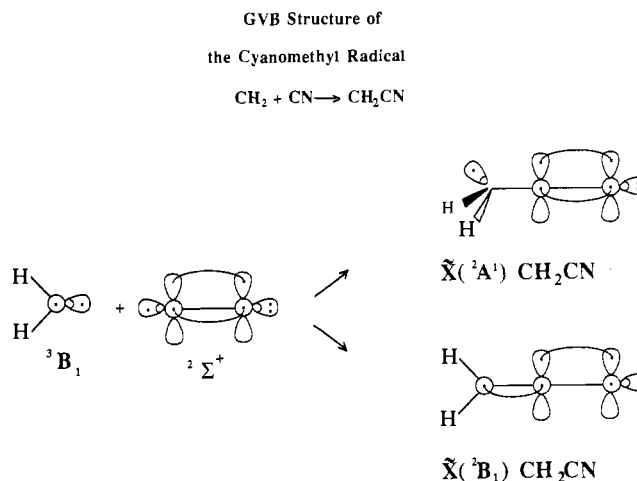
GVB Structure of

the Cyanomethyl Radical

$CH_2 + CN \longrightarrow CH_2CN$

Figure 7. GVB diagrams showing the formation of the cyanomethyl radical, CH_2CN, from ground-state CH_2 and CN. Bonding of the CN radical to the out-of-plane π-like orbital of $\tilde{X}\,^3B_1$ methylene would lead to a nonplanar radical, CH_2CN ($\tilde{X}\,^2A'$). Alternatively, CN could combine with the in-plane lobe orbital of CH_2 to produce a planar radical, CH_2CN ($\tilde{X}\,^2B_1$).

bination of the CH_2 and CN radicals to yield cyanomethyl. The cyano radical can couple to CH_2 $\tilde{X}\,^3B_1$ in two distinct ways. (a) Bonding to the methylene out-of-plane π-like b_1 orbital would produce a nonplanar CH_2CN $\tilde{X}\,^2A'$. (b) Alternatively the CN radical could combine with the in-plane a_1 CH_2 lobe orbital to form a planar radical, CH_2CN $\tilde{X}\,^2B_1$. GVB calculations on methyl radicals find that combination (b) is favored rather than (a) on account of the reduced bond–bond repulsions; in case (a) each of the bonding pairs would be roughly 90° apart while case (b) has them 120° apart. One might argue that bonding of a very electronegative ligand such as CN would be favored to the b_1 orbital rather than the a_1 lobe orbital. However, recent microwave studies of the fluoromethyl radical[7] and chloromethyl radical[8] find both of these molecules to be planar species. All arguments then suggest that scheme (b) is the favored bonding pattern in the CH_2CN radical. The added ability of the CN group to conjugate with the radical center reinforces the preference (b) for a planar molecule. The ground state of the CH_2CN radical is $\tilde{X}\,^2B_1$.

Figure 8 suggests the manner in which CH_2^- and CN could combine to afford the cyanomethide ion. Since CH_2^- has the a_1 lobe orbital doubly occupied and the b_1 orbital singly occupied, the only way that the CH_2^- radical anion and the CN radical can couple is to produce a closed-shell ion, CH_2CN^- $\tilde{X}\,^1A_1$. Bonding of $C\equiv N$ to the b_1 orbital favors the formation of a bent CH_2CN^- ion; delocalization of the negative charge over the nitrile group onto the N atom strongly favors a planar ion. The final structure for the cyanomethide ion is a compromise between these two effects.

V. Thermochemistry

The EA properly corresponds to the $|CH_2CN(v' = 0, J'K' = 0)\rangle \leftarrow |CH_2CN^-(v'' = 0, J''K'' = 0)\rangle$ transition. In order to obtain

GVB Structure of
the Cyanomethide Ion

$$CH_2^- + CN \rightarrow CH_2CN^-$$

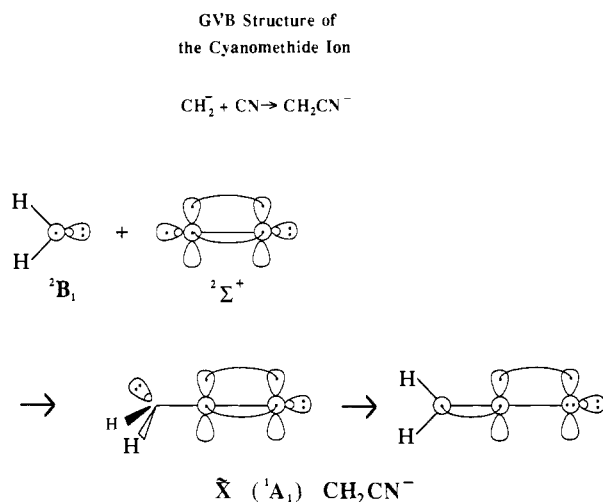

$\tilde{X}$ ($^1A_1$) CH_2CN^-

Figure 8. GVB diagrams showing the formation of the cyanomethide anion, CH_2CN^-, from ground-state CH_2^- and CN. Bonding of the CN radical to the out-of-plane π-like orbital of $\tilde{X}\,^2B_1$ CH_2^- is now the only coupling likely. This suggests the formation of a nonplanar ion, CH_2CN^- ($\tilde{X}\,^1A'$). Stabilization of the negative ion by interaction with the π-system of CN will favor a flat, C_{2v} ion.

the adiabatic EA, we must make a rotational adjustment to the uncorrected or raw EA. These corrections have been discussed earlier[73] and will be applied here. Our final results are collected in Table VI.

We make the rotational correction[74] by treating both the ion and radical as simple prolate tops and by estimating the rotational constants (A and B) with the help of the molecular geometries in Table VI. Our working expression for the rotational correction is

$$\Delta_{rot} = k_B T_{rot}[(B'/B'') + (A'/2A'') - (3/2)] \qquad (6)$$

The Boltzmann constant is written as k_B and we use a rotational temperature, T_{rot}, of 500 K. The final resulting corrections turn out to be quite small; $\Delta_{rot}(CH_2CN^-) = 0.0015 \pm 0.0006$ eV and $\Delta_{rot}(CD_2CN^-) = 0.0010 \pm 0.0005$ eV. Thus we finally arrive at the corrected values for the electron affinities: $EA(CH_2CN) = 1.543 \pm 0.014$ eV and $EA(CD_2CN) = 1.538 \pm 0.012$ eV. These values are slightly different from those reported by threshold photodetachment experiments in an ICR. Initial experiments[1] reported $EA(CH_2CN) = 1.507 \pm 0.018$ eV but more recent reports[2] find $EA(CH_2CN) = 1.560 \pm 0.006$ eV and $EA(CD_2CN) = 1.549 \pm 0.006$ eV.

The gas-phase acidity of acetonitrile has been measured[64] earlier in an ICR spectrometer to be 372.2 ± 2.0 kcal/mol. The gas-phase acidity is defined to be the room temperature free energy change of the heterolytic bond dissociation.[75]

$$H-CH_2CN \rightarrow CH_2CN^- + H^+ \qquad (7)$$

We can use the $EA(CH_2CN)$ and the acidity to calculate the bond strength of acetonitrile.

$DH°_{298}(H-CH_2CN) =$
$$\Delta H°_{acid}(H-CH_2CN) + EA(CH_2CN) - IP(H) \quad (8)$$

We find a $DH°_{298}(H-CH_2CN) = 94.2 \pm 2.0$ kcal/mol. If we employ the most recent version[76] of the heat of formation of acetonitrile $[\Delta H_f°_{298}(CH_3CN) = 17.62 \pm 0.19$ kcal/mol], this corresponds to a heat of formation of the cyanomethyl radical of $\Delta H°_{f298}(CH_2CN) = 59.7 \pm 2.0$ kcal/mol in excellent agreement with earlier determinations[77] which reported a value of $\Delta H°_{f298}(CH_2CN) = 58.5 \pm 2.2$ kcal/mol. Using our experimental value for the electron affinity, and assuming that the heat capacity of a free electron is 0.0, we find a value for the heat of formation of the cyanomethide ion of $\Delta H_f°_{298}(CH_2CN^-) = 24.1 \pm 2.0$ kcal/mol.

VI. Conclusions

We have used photoelectron spectroscopy to measure a variety of molecular properties of CH_2CN^- and CH_2CN. Analysis of our spectra aided with a set of ab initio calculations concludes that cyanomethyl is a planar, symmetric radical while the CH_2CN^- is slightly pyramidal. We can understand our results by consideration of some simple GVB diagrams.

(73) (a) Nimlos, M. R.; Ellison, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 6522. (b) Nimlos, M. R. Ph.D. Thesis, University of Colorado, 1986, Appendix 1.
(74) Engelking, P. C. *J. Phys. Chem.* **1986**, *90*, 4544.

(75) A complete discussion of gaseous acid–base chemistry is set forth by Moylan and Brauman (Moylan, C. R.; Brauman, J. I. *Annu. Rev. Phys. Chem.* **1983**, *34*, 187). The gas-phase acidity is a free-energy change and is related to the equilibrium constant of (7), $\Delta G_{acid} = -RT \ln K_7$. To measure the enthalpy change of (7), one needs to determine the slope of the van't Hoff plot corresponding to K_7. The enthalpy change is defined to be the proton affinity (PA) or (as Moylan and Brauman prefer) the heat of deprotonation (HD). The entropy change in (7) is approximated quite well by the rotational entropy change; this is a small value so $\Delta G_{acid}(H-CH_2CN) \simeq \Delta H_{acid}(H-CH_2CN) = HD(H-CH_2CN)$. In order to use (8) to relate $HD(H-CH_2CN)$ which is measured at 298 K to the IP(H) and the $EA(CH_2CN)$ which are constants at 0 K, we must strictly have

$$IP_{298}(H) - EA_{298}(CH_2CN) = IP_0(H) - EA_0(CH_2CN) \qquad (9)$$

Equation 9 is generally true to about ± 0.2 kcal/mol.
(76) Baghal-Vayjooee, M. H.; Collister, J. L.; Pritchard, H. O. *Can. J. Chem.* **1977**, *55*, 2634.
(77) King, K. D.; Goddard, R. D. *Int. J. Chem. Kinet.* **1975**, *7*, 837.
(78) Hopkinson, A. C.; Lien, M. H.; Yates, K.; Mezey, P. G.; Csizmadia, I. G. *J. Chem. Phys.* **1977**, *67*, 517. Hopkinson, A. C.; Lien, M. H. *Int. J. Quantum Chem.* **1980**, *18*, 1371.