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Structure and Vibrational Modes of the Cyanovinyl Radical: A Study by Time-Resolved Fourier Transform IR Emission Spectroscopy†

Laura Letendre and Hai-Lung Dai*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

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The structure and vibrational modes of the cyanovinyl radical have been characterized by using time-resolved Fourier transform IR emission spectroscopy. The cyanovinyl radical was generated with internal excitation through photodissociation of acrylonitrile. IR emission, detected with submicrosecond time resolution, from reaction products following photodissociation revealed the vibrational modes. The two vibrational modes of the cyanovinyl radical with the strongest transition strength have been identified at their fundamental transition frequencies: the CN stretch mode at 2563 cm^{-1} and the CH_2 out-of-plane wag at 965 cm^{-1}. The assignments were supported by experiments with deuterated acrylonitrile and ab initio calculations. Rotational contour analysis of the CN emission band indicates that the equilibrium structure is bent at the CCC angle.

I. Introduction

A complete understanding of the chemistry of the atmosphere requires extensive knowledge of many highly reactive radicals and transient species which most appear as reaction intermediates. One important class of radicals is cyano-substituted unsaturated hydrocarbons that are prevalent in planetary atmospheres such as Titan, the largest moon of Saturn. Titan has the only atmosphere aside from Earth that has substantial quantities of N_2. Reactions initiated by the photolysis of methane produce the minor constituents in Titan's atmosphere: C_2H_6, C_3H_8, C_2H_2, HCN, CH_3C_2H, C_4H_2, HC_3N, and C_2N_2 in addition to vinyl cyanide.[1] The radicals related to these species are also important reaction intermediates in Earth's atmosphere. Knowledge of the structure and vibrational frequencies of the cyano-containing radicals is essential for probing the reactivity of these intermediates as well as for quantitative analysis of astronomical data of planetary systems.

The cyano-containing radicals would also unavoidably exist in hydrocarbon combustion systems where nitrogen exists. Again, to fully characterize these combustion or materials systems, knowledge of the structure, reactivity, and spectroscopy of the CN-containing radicals is indispensable.

Fundamentally, cyano radicals are interesting because the unpaired electron may be either localized or π-delocalized leading to significant changes in the structure and reactivity of the molecule. Reactivity is greatly affected by the electron densities at the carbon and nitrogen atoms. For example, the cyanovinyl (CH_2CCN) radical has two resonance structures, $H_2C{=}\dot{C}{-}C{\equiv}N \leftrightarrow H_2C{=}C{=}C{=}N^{\bullet}$, each with a different reactive site.

Because these radicals are difficult to produce in a laboratory setting, there have been few experimental studies performed to uncover their structural and vibrational information. The smallest cyanoalkyl radical, cyanomethyl, has been studied by using IR diode laser absorption spectroscopy.[2] A single vibrational band, ν_5, in the infrared spectrum was determined. Large changes in the A rotational constant upon vibrational excitation were observed. Other studies of this radical included an investigation of the microwave rotational spectrum[3] and an infrared argon matrix study.[4]

Larger cyano radicals have been even less well characterized. There has been only one experimental study using electron spin resonance on the cyanovinyl radical, which suggested that the structure of the radical changes with energy from a bent structure to the linear CCCN configuration.[5] Several theoretical studies have been performed to determine the electronic structure[6] and the minimum energy geometry of the cyanovinyl radical,[7,8] although none have reported information concerning the vibrational modes.

Because radicals are generally produced in small quantities with short lifetimes and because vibrational transitions are relatively weak, vibrational spectroscopy of radical species has been experimentally challenging. Transient absorption techniques have been effective particularly if it is known a priori where to search for the vibrational transitions.[9] For radicals with stable electronic states, vibrational levels can be detected through techniques such as resonance Raman,[10] time-resolved dispersed fluorescence,[11] or stimulated emission spectroscopy.[12]

In the experiments described here a newly developed approach was employed for determining the structure and vibrational modes of the cyanovinyl radical. This approach has been described in detail in ref 13 and will be reviewed briefly here with application to cyanovinyl. The cyanovinyl radical was produced with excess vibrational energy by 193 nm photodissociation of the precursor molecule vinyl cyanide, also known as acrylonitrile (CH_2CHCN). Using time-resolved Fourier transform emission spectroscopy (TR-FTES), the IR emission spectrum from the excited cyanovinyl as well as other excited species generated in the photodissociation reactions was recorded. Two features in the IR emission spectrum can be assigned, primarily based on isotope substitution experiments and ab initio calculations, to cyanovinyl. Time-resolved spectra show a blue shift of these features with time, indicating relaxation of the excited species through collisions. The spectral features at longer times after dissociation therefore represent the fundamental transitions of the emitting modes. Rotational analyses of the emission bands allow determination of the structure of the radical.

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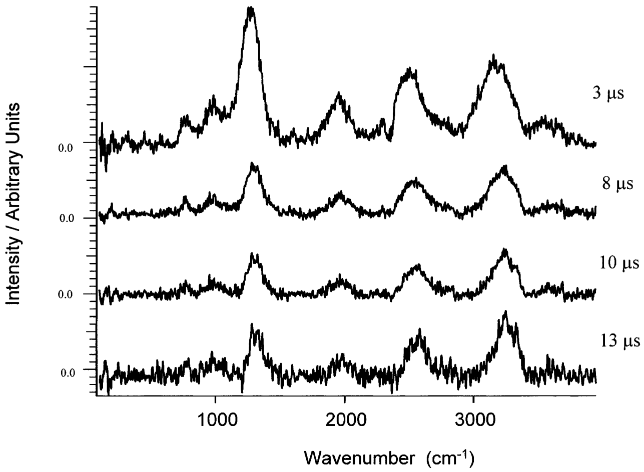

Figure 1. Selected time slices from the emission spectra collected at 3, 8, 10, and 13 μs after photodissociation of acrylonitrile induced by 193 nm excitation.

TABLE 1: IR Emission Features Observed in the Time-Resolved Spectra and Their Assignment

obsd freq[a] (cm^{-1})	species	vibration	reaction channel
3652	HNC	HN stretch	1
2023	HNC	NC stretch	1
748	acetylene	CH bend	1
3289	acetylene	CH antisym stretch	1
1300	acetylene	CH bend combination	1
3320	cyanoacetylene	CH stretch	2
1300	cyanoacetylene	CH bend combination	2
2563 ± 26	cyanovinyl	CN stretch	4
965 ± 23	cyanovinyl	CH_2 oop wag	4

[a] The frequencies are reported as the center value of the emission band contour. The uncertainties are reported as a quarter of the fwhm of the band.

II. Experimental Section

The experimental procedure used here for probing IR emission from excited photofragments following photodissociation of the precursor molecule has been described in detail previously.[13,14] Briefly, in the current experiments between 10 and 70 mTorr of acrylonitrile was flowed through a gas cell at a flow rate of 4.3 sccm that was measured by a mass flow meter (Tylan FM-360). As the background gas 4 Torr of argon was used to promote vibrational relaxation. Argon was introduced into the cell in a manner that prevented deposition of products on the cell window.[15] Acrylonitrile was excited with 193 nm pulses from an ArF excimer laser (Lambda Physik EMG 201 MSC) run at 20 Hz. The laser pulse energy measured right before the cell was ≤30 mJ/pulse. The UV laser beam was lightly focused into the cell with a 1-m focusing lens to a beam size of 1.44 cm^2. The laser pulses had a nominal width of 30 ns.

IR emission from the photoproducts following the photolysis laser pulse was collected using a White cell mirror configuration inside the gas cell and focused through a 12 mm aperture into the Fourier transform spectrometer (Bruker IFS-88) and detected by an MCT detector (EG&G J15D14, rise time 500 ns). Only the IR fluorescence signal in the region between 700 and 4000 cm^{-1} was recorded. A long pass cutoff filter was used to allow transmission of emission below 4000 cm^{-1}. The detector sensitivity cut off below 700 cm^{-1}. The signals were corrected for detector sensitivity over this range. Spectra were taken with 3−16 cm^{-1} resolution.

Fifty laser shots were averaged for each mirror position of the interferogram. The signal was amplified (×10) by a fast amplifier (SRS SR445) before reaching the transient digitizer (Bruker PAD82A internal board, 200 MHz sampling) for signal processing.

Acrylonitrile (>99% purity, inhibited by 35−45 ppm monomethyl ether hydroquinone, Sigma Aldrich), acrylonitrile-d_3, and acrylonitrile-*2*-d_1 (Isotec, >99% purity) were used directly without further purification. The acrylonitrile-*2*-d_1 molecule is deuterated on the same carbon as the cyano group.

III. Results and Analysis

A. Time-Resolved Emission Spectra. Figure 1 shows selected time slices of IR emission spectra recorded at 3, 8, 10, and 13 μs following acrylonitrile photodissociation at 193 nm. The emission spectral peaks are due to vibrationally excited products from reactions 1−4. All four reactions have been detected in the molecular-beam mass-spectrometry photolysis experiment with the exception that HCN was reported as the product.[16]

$$H_2C{=}CHCN \rightarrow HC{\equiv}CH + HNC \text{ (and HCN)} \qquad (1)$$

$$H_2C{=}CHCN \rightarrow HC{\equiv}CCN + H_2 \qquad (2)$$

$$H_2C{=}CHCN \rightarrow H_2C{=}CH + CN \qquad (3)$$

$$H_2C{=}CHCN \rightarrow H_2C{=}CCN + H \qquad (4)$$

Since the photon energy is much higher (about 100 kcal/mol) than the dissociation energy, it is expected that photoexcited acrylonitrile has a unity dissociation quantum yield on the time scale of the laser pulse[16] and does not contribute to IR emission.

The excited products generated immediately following the dissociation contain the maximum amount of vibrational energy and would irradiate to the red of the fundamental frequency of the emitting modes due to anharmonicity. As time proceeds, collisions with ambient gases relax the vibrational excitation toward the ground state and the emission features gradually shift to the blue. The longer time spectra in which spectral peak positions no longer shift, i.e., when the molecule is vibrationally relaxed, can be used for determining the fundamental frequencies. For example, the peak at 2455 cm^{-1} at early times moves to 2563 cm^{-1} at 13 μs. Similarly, the 881 cm^{-1} peak shifts to 965 cm^{-1}.

The center frequencies of the emission features, determined from a Gaussian profile fit of the band contour, are reported in Table 1. A comparison with known frequencies of the products of reactions 1−4 shows that all of the emission peaks aside from those at 2563 and 965 cm^{-1} can be assigned to the photoproducts acetylene, cyanoacetylene, and HNC from reactions 1 and 2. (See Table 1.) Reaction 1 should result in HNC and/or HCN. The bands assignable to HNC are clear throughout the time-resolved spectra. Comparatively, emission bands from HCN are not as evident. The strongest HCN emission band should situate at 711 cm^{-1}. This band is immediately below the acetylene bending mode emission at 730 cm^{-1}. An emission band is observed from 750 cm^{-1} to the detector cutoff at 700 cm^{-1}. The detected intensity, however, may be primarily due to acetylene, as its intensity approximately agrees with the amount of acetylene predicted from the other observed acetylene emission bands listed in Table 1. The H−CN stretching band is in overlap with the cyanoacetylene C−H stretch band and cannot be independently identified. The weaker HCN 2097 cm^{-1}

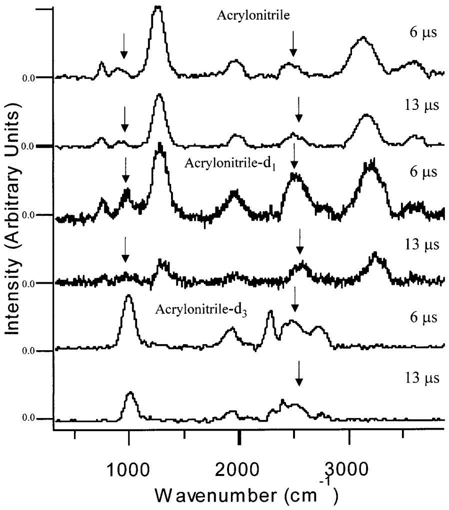

Figure 2. IR emission spectra detected at 6 and 13 μs following 193 nm photodissociation of acrylonitrile, acrylonitrile-d_1, and acrylonitrile-*2*-d_3, respectively. The assignments of all the apparent peaks have been made and stated in section IIIB. The arrows indicate the emission from the CN stretch normal mode and the CH_2 out-of-plane wag of the cyanovinyl radical.

band, the only one that is not in overlap with other emission bands, does not appear to be evident in the spectra. Reaction 1 may have resulted in HCN, as suggested previously,[16] but the emission spectra at present support HNC as the primary product. Similarly in the experiments involving deuterated acrylonitrile, bands associated with DCN cannot be clearly identified. More details can be found elsewhere and will be discussed in the future.[15]

Reaction 3 results in the production of the vinyl and CN radicals. Emission from the vinyl radical has been amply observed with intensities comparable to those for acetylene in previous experiments of photodissociation of vinyl halides.[13] In those experiments, vinyl was produced in amounts comparable to acetylene. Here, vinyl was not observed upon photodissociation of acrylonitrile, indicating that reaction 3 is a minor photodissociation channel.

Reaction 4, which involves the dissociation of a CH bond, is a major channel in the 193 nm photodissociation of acrylonitrile.[16,17] The excess energy of this channel is 40 kcal/mol, which will result in vibrationally excited cyanovinyl as a product. All frequencies of this radical were previously unknown. By reason of elimination, the emission features at 2563 and 965 cm^{-1} are assigned to the cyanovinyl radical. This conclusion and further assignment of these bands to specific vibrational modes can be elucidated with isotope substitution experiments and ab initio calculations discussed below.

B. Results from Deuterated Acrylonitrile Photodissociation. To confirm the spectral assignments of the photoproducts, experiments were also performed using fully and partially deuterated precursor molecules, acrylonitrile-d_3 and acrylonitrile-*2*-d_1. Figure 2 shows three sets of spectra. The upper two traces are from the photofragments of acrylonitrile, the middle traces show the emission from the acrylonitrile-*2*-d_1 precursor, and the lowest traces are from the fully deuterated precursor. The spectra shown are recorded at 6 and 13 μs respectively after the photolysis and reflect emission from initial as well as vibrationally relaxed products. In the later time spectra the peak positions are no longer red shifted from their fundamental positions. The earlier time spectra are shown so that the correlation of the peaks in different-time spectra can be identified. Some of the emission bands in the early time spectra have stronger intensities and can be more clearly identified.

The peak at 2563 cm^{-1} does not shift in spectra from deuterated precursors and can be attributed to the CN stretch of the cyanovinyl radical. The 965 cm^{-1} band apparently has shifted to frequencies below the 700 cm^{-1} detector cutoff and cannot be observed, suggesting that this mode is related to a low-frequency motion associated with the C−H bonds.

The assignment of the remaining spectral peaks in Table 1 to products of reactions 1 and 2 is consistent with observations made in the experiments with deuterated precursors. In the spectrum obtained from acrylonitrile-*2*-d_1, the following peaks are observed: 3652 (NH stretch) and 2023 cm^{-1} (NC stretch) from HNC, and 2757 (ND stretch) and 1927 cm^{-1} (NC stretch) from DNC produced via reaction 1; 3289 (CH stretch), 1342 (CH bend combination), 3336 (CH stretch), 2583 (CD stretch), and 1853 cm^{-1} (CC stretch) from C_2HD;[18] both are presumably from isomerization of vinylidene produced from reaction 1; and 3322 (CH stretch) and 1350 cm^{-1} (CH bend combination) from cyanoacetylene from reaction 2.

In the spectrum obtained from photodissociation of acrylonitrile-d_3, DNC peaks are observed at 2757 and 1927 cm^{-1}. Peaks corresponding to acetylene-d_2 are observed at 2439 (CD stretch) and 1046 cm^{-1} (CD combination band). The cyanoacetylene-*d* higher frequency IR active normal modes are at 2608, 2252, and 1968 cm^{-1}.[19] The peak at 2252 cm^{-1} is due to the CC stretching mode and is the only cyanoacetylene peak not completely obscured by emission from other photoproducts.

In the emission spectra from dissociation of both deuterated acrylonitrile molecules, no clear indication of the strong CD stretch band at 2630 cm^{-1} and the weaker CN stretch at 1925 cm^{-1} [18] of DCN from reaction 1 can be clearly identified.

C. Anharmonic Shift and Band Contour. The 108 cm^{-1} blue shift of the 2563 cm^{-1} peak recorded in the time-resolved spectra from the initial emission position to the longer time position indicates that the emitting species is vibrationally excited immediately after photodissociation, and as time proceeds collisions relax its vibrational excitation. Concomitantly the band contour is also changing with time. The band contour of the 2563 cm^{-1} emission feature has a distinctly asymmetric and broad shape at early times after acrylonitrile photodissociation. A band contour, recorded at 1.65 μs and with 16 cm^{-1} resolution, is shown in Figure 3a. Over time the band contour becomes narrower and more symmetrical. The contour of the emission band without any blue shift at longer time is shown in Figure 3b. The broad bandwidth and asymmetric shape of the early time spectra of this feature may be due to several contributions. The initial rotational temperature of the emitting molecules is high. The high vibrational energy content of the emitting molecules will result in energy shift in the emitting mode through anharmonic coupling. At high vibrational energies, the barrier of transition from the bent structure to its mirror image may be overcome and the excited radical may appear to assume a linear geometry through large amplitude motion. A more quantitative discussion on the origins for the width and shape of the CN stretch emission feature in both early and later time spectra is presented below in the Discussion section.

IV. Ab Initio Calculations

Since no prior information, experimental or theoretical, can aid us in the assignment of the observed IR emission features attributed to cyanovinyl, ab initio calculations of the vibrational frequencies and intensities were performed as a guide. The calculations were performed with the GAUSSIAN 94 compu-

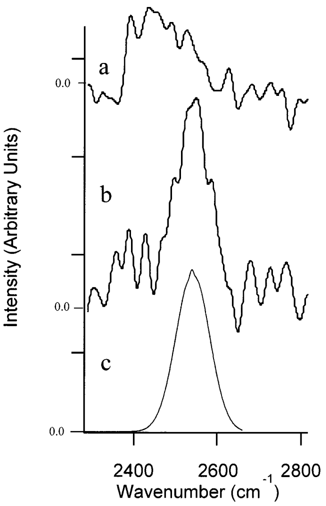

Figure 3. Band contour of the CN stretching mode of cyanovinyl. (a) From spectra collected 1.65 μs after the photodissociation pulse. (b) From spectra collected 20 μs after the photodissociation pulse. (c) Band contour simulation using rotational constants listed in Table 5 for the bent configuration for both the upper and lower states.

TABLE 2: Vibrational Modes of Acrylonitrile[a]

theoretical, MP2/6-311++G**		experimental			
ν (cm^{-1})	IR intensity (km/mol)	ν (cm^{-1})	IR intensity (km/mol)	correction factor	mode
3415	7.17	3125	strong	0.92	CH stretch
3366	6.71	3078	strong	0.91	CH stretch
3323	6.36	3042	strong	0.92	CH stretch
2590	1.60	2239	weak	0.86	CN stretch
1832	5.04	1615	medium	0.88	CC stretch
1565	4.23	1416	medium	0.90	CH$_2$ deformation
1429	0.25	1282	weak	0.90	CH rock
1199	2.38	1096	weak	0.91	CH$_2$ rock
1119	32.74	972	very strong	0.87	HRCC wag
1099	33.76	954	very strong	0.87	H$_2$CC wag
926	0.92	869	medium	0.94	C−C stretch
779	8.53	679	strong	0.87	C═C torsion

[a] The experimentally observed and assigned normal modes from refs 18 and 21 are listed. Theoretical values are from ab initio calculations. The correction factor listed is calculated as the experimental frequency divided by the theoretical frequency.

tational package.[20] Unrestricted open-shell wave functions, UMP2, and the frozen-core approximation were employed. The molecular geometry was optimized using the 6-311++G** basis set and harmonic vibrational frequencies were determined for this geometry.

As a test of the effectiveness of this calculation on frequencies and IR intensities for a molecule with a cyano group, an MP2/6-311++G** calculation was first run for the precursor acrylonitrile molecule. The acrylonitrile frequencies and IR intensities obtained from the calculation are compared to experimentally determined frequencies and intensities from refs 18 and 21 in Table 2. The intensity of the three lowest bending modes of acrylonitrile was not reported in the literature. Since these frequencies are also outside the detection range in our experiments, the comparison of theory to experiment for these modes was not made. This comparison shows that the frequencies obtained from the calculation should be corrected by a factor of on average 0.9 to match the experimental values. The calculated CN stretching frequency is especially high and needs a 0.86 correction factor. The relative intensities of the normal modes, with the exception of the CC stretch, of acrylonitrile are well predicted by the MP2 calculation. For instance, the two peaks predicted to be the strongest, the HRCC wag and the H$_2$CC wag, are listed as the only two "very strong" features in the experimental report.[18]

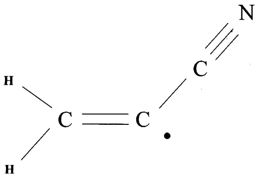

Figure 4. Structure of cyanovinyl from the ab initio calculation.

TABLE 3: Optimized Geometry of the Cyanovinyl Radical from ab Initio Calculation

bond	bond length/Å	angle	bond angle/deg
C1−C2	1.28	H1−C1−C2	121.45
C2−C3	1.43	C1−C2−C3	135.88
C3−N1	1.13	C2−C3−N1	178.60
H1−C1	1.09	H1−C1−H2	117.54
H2−C1	1.08		

TABLE 4: Vibrational Modes of the Cyanovinyl Radical from ab Initio Calculation

freq (cm^{-1})	IR intensity (km/mol)	sym	mode
216	2.13	A′	CCN bend
376	2.11	A″	oop bend
607	5.40	A′	in-plane bend
745	12.49	A″	oop bend
844	3.84	A′	in-plane bend
1031	2.87	A′	in-plane bend
1093	47.51	A″	oop CH$_2$ wag
1432	13.72	A′	CH$_2$ scissor
1862	2.82	A′	CC stretch
3091	505.6	A′	CN stretch
3156	3.67	A′	CH sym stretch
3267	2.04	A′	CH asym stretch

The same program and procedure were then used to calculate an optimized structure and vibrational frequencies of the cyanovinyl radical. The frequencies calculated for the cyanovinyl radical, after a scaling factor, can be used as a guide for assignment. The optimized angles and bond lengths obtained from the calculation are listed in Table 3 and the geometry is shown in Figure 4. Previously published calculations by Mayer et al.[8] reported a similar C_s symmetry optimized structure when UHF, UMP2, RMP2, QCISD, and QCISD(T) levels of theory were employed. The calculated bond angles for the CC−CN angle were between 135° and 137° for all the UMP2 basis sets used. In contrast, DFT calculations produced a collinear CC−CN bond angle with the cyanovinyl radical having C_{2v} symmetry.[8] The calculated frequencies, IR transition strengths, mode symmetries, and assignments from the present calculation are listed in Table 4.

Unlike the acrylonitrile molecule where the CN stretch mode is weak, for cyanovinyl by far the most intense feature is the CN stretch. Its calculated wavenumber, 3091 cm^{-1}, requires a correction factor 0.83 to agree with the observed value of 2563 cm^{-1}. This is quite reasonable, considering that the correction factor is 0.86 for acrylonitrile. The next most intense feature would be the CH$_2$ out-of-plane wag, predicted to be over 10 times weaker than the CN stretch. This mode is calculated to be at 1093 cm^{-1}. It is suggested that the 965 cm^{-1} band observed in our spectra should be assigned to this mode, using the correction factor of 0.88. Although the calculation shows that the transition strength of the CN stretch is stronger than that of the CH$_2$ out-of-plane wag mode, it does not correctly reproduce the observed intensity ratio of 1.6. All of the other normal modes are expected to be over 100 times weaker than the CN stretch. Considering these transition strengths, it is expected that only the CN stretch and CH_2 out-of-plane wag modes would be observed in the emission spectra.

V. Discussion

A. Emission from Other Reaction Products. While we make assignments of the bands attributed to the cyanovinyl radical, we must ascertain that there is no other possible molecule in the reaction systems that may be responsible for these bands. For the emission at 2563 cm^{-1} it is necessary to consider cyanovinylidene, produced by the loss of H_2 from acrylonitrile photodissociation. This reaction channel is predicted to be minor,[16] and cyanovinylidene would be short-lived due to the small potential barrier of 2 kcal/mol for isomerization to cyanoacetylene.[22,23] Nevertheless we will consider the possibility of both cyanovinylidene and cyanoacetylene as a source for the emission at 2563 cm^{-1}.

Little is known about the ground state of cyanovinylidene experimentally; however the $^3A_1$ excited state has been identified in a neutralization−reionization mass spectrometry study.[22] Ab initio calculations by Hu and Schaefer have proposed the equilibrium structure, vibrational frequencies, and energies of the ground state and the first two excited triplet states.[23] The calculated CN stretching frequency, at 2595 cm^{-1} without a correction factor, is close to the observed strong emission band observed at 2563 cm^{-1}. Were this band from cyanovinylidene, however, at least four additional modes with comparable or stronger IR intensity should have appeared in our experimental spectra. For example, all levels of theoretical calculations predict the most intense band to be the CC stretching band at 1842 cm^{-1}, yet there is no equivalent peak observed in the emission spectra. Emission from the triplet cyanovinylidene can also be ruled out. Ab initio calculations predict a CN stretch frequency in this region (2582 cm^{-1} without correction) for the triplets.[23] Here, all other modes have 10 times less IR transition strength and may not be observed. The energetics of the reaction generating triplet cyanovinylidene, however, would leave only 2800 cm^{-1} of energy for all internal degrees of freedom. This allows only a single quantum of CN stretch as the maximum possible cyanovinylidene excitation. If the observed band is from the low vibrational level of triplet cyanovinylidene, there would be no blue shift in the emission spectra, which is contradictory to the large frequency shift (108 cm^{-1}) observed in the time-resolved emission spectra.

The IR spectrum of cyanoacetylene has been recorded[24] and no IR active modes can be found in the 2400−2600 cm^{-1} region, thus eliminating cyanoacetylene as a candidate for the emission feature observed at 2563 cm^{-1}.

B. The Structure of Cyanovinyl. Although the spectral resolution is not good enough to resolve single rotational lines, it is sufficient for determining the band type of the transition, thus allowing the determination of the symmetry of the band. The band contour analysis may even allow the examination of the structure of the emitting molecule.

A rotational contour calculation of the 2563 cm^{-1} band was performed using rotational constants listed in Table 5, which correspond to the geometry obtained from the MP2/6-311++G** optimization. The rotational contour calculation was performed using the ASYTOP program designed to calculate the rotational spectra of asymmetric top molecules.[25] The contour of the fully relaxed, later time spectral feature agrees reasonably well with the one calculated with a temperature set at 298 K with a type b transition. With the current resolution the c-type transition can be distinguished by the strong Q-branch in the contour that is absent in the a- and b-type transitions. The a-type transition is similar to that of the b-type except that the contour is very narrow. Increasing the temperature increases the width of each band type. Even at rotational temperatures up to 9000 K the a-type transition has only a width of 75 cm^{-1} whereas the width of the emission feature is 200 cm^{-1} and can be well fit by the 300 K, predominantly b-type transition. Under the experimental conditions, by 20 μs (the spectrum in Figure 3b) the excited molecules have suffered on average 1000 collisions with Ar and it is reasonable to assume an ambient rotational temperature for the molecules. The rotational constants used indicate that the radical is in the bent CCCN configuration as shown in Figure 4.

TABLE 5: Calculated Rotational Constants of Cyanovinyl Radical

	rotational constant (cm^{-1})	
sym axis	CCCN angle of 135.88°	CCCN angle of 180°
A	3.36	10.7
B	0.16	0.14
C	0.15	0.14

Both the transition type and the width of the feature are not inconsistent with the assignment that this emission is due to the CN stretch of the cyanovinyl radical at 298 K. According to symmetry considerations, the CN stretch mode has an in-plane transition dipole, resulting in a mixture of a and b band types. Spectral simulation shows that type b dominates for this emission band. Intuitively based on molecular symmetry, one expects type a transition to contribute more as the *A* rotation axis lies closer to the CN bond. On the other hand, if the strongest bond dipole is not at the CN bond, but instead, as in many other similar molecules, is at the CC and CH bonds, it is then understandable that the transition dipole may have a strong type b component. The bond dipoles estimated from the charge distribution generated from the ab initio calculation indeed show that the CC bond dipoles are the largest, followed by the CH bonds and then the CN bond. This point, along with other structural and energetics questions illustrated below, would be of interests for higher level theoretical and experimental investigations.

One possible reason for the asymmetry of the emission band shape in early time spectra is that at early times the radical possesses sufficient internal energy to exist in a linear CCCN geometry. This configuration has been calculated by several groups to exist either as a second minimum on the potential surface or as a saddle point depending on the ab initio method used for geometry optimization.[7,8] The linear geometry is predicted to be approximately 0.8 eV higher in energy than the bent structure. Using MP2, QCISD, and HF methods, the energy was minimized when the molecule was in the bent configuration and the linear geometry appeared as a saddle point.

To fit the vibrationally hot, asymmetric features in the observed spectra, it is necessary to use rotational constants that change significantly from the upper to lower vibrational states of the transition. This implies that the radical undergoes a geometry change as it vibrationally relaxes. Indeed, rotational contour simulation of the CN stretching feature using rotational constants determined for a linear configuration of the molecule reproduced the asymmetric shape of the emission feature at early times.[15]

It is also possible that the asymmetric shape and broader bandwidth at early times are due to vibrational excitation: the wide energy distribution in the emitting mode may create a broader emission feature because of anharmonic shift, and the excitation of the other vibrational modes may affect the energy of the emitting levels through anharmonic coupling. Comparing the two band contours in Figure 3, we found a narrowing of the bandwidth by more than 80 cm^{-1} with the concomitant change of the shape from early time to later time spectra. While this vibrational broadening is expected to make some contribution to the observation, it is not clear if it can account for the entire bandwidth and shape change. The detected anharmonic shift from the early time position, when the product molecules have in excess of ~100 kcal/mol, to the later time position, when the radicals are vibrationally relaxed, is 108 cm^{-1} for this band. If the 80 cm^{-1} broadening is from anharmonic shift, it implies a very wide vibrational energy distribution in the initial product molecules. The interpretation of the band contour change based on vibrational excitation induced structural change, on the other hand, is consistent with the observations made in the only prior experimental study of the structure of this radical. Fenistein et al.[5] used electron spin resonance to determine the structure of the cyanovinyl radical preadsorbed in zeolite at several temperatures. In that study the structure of cyanovinyl was assumed to have a bent CCN angle at lower temperatures but to become a linear configuration at higher temperatures.

VI. Conclusion

Using the time-resolved Fourier transform spectroscopy technique to monitor the IR emission spectra from species generated from 193 nm photodissociation of acrylonitrile, we have observed IR emission bands assignable to the cyanovinyl radical, of which no normal-mode frequencies have previously been experimentally reported. Based on results from isotope substitution experiments and ab initio calculations, the two normal modes with the strongest fundamental transitions have been identified for this radical: the CH_2 out-of-plane wag at 965 cm^{-1} and the CN stretch mode at 2563 cm^{-1}. Rotational contour analysis of the CN emission band suggests that the equilibrium structure of the radical is bent, consistent with the calculation result of a CCC angle of 136°. Early time slices of the emission spectra reveal a very anharmonic CN stretching emission peak with an asymmetric and broadened shape. The large frequency shift of this peak position with time indicates cyanovinyl is generated with ample vibrational excitation from acrylonitrile dissociation by 193 nm light. The high internal excitation of the cyanovinyl radicals also results in the asymmetric and broadened emission band shape as well as a linear geometry due to large amplitude motions, consistent with previous experimental reports.

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