Theoretical Study on the Ground and Excited States of Dicyanocarbene (C_3N_2) and Its Isomers: A Low-Temperature Matrix Emission Spectrum Attributable to 3-Cyano-2*H*-azirenylidene

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Ab initio calculations are used to characterize the ground and low lying excited electronic states of selected dicyanocarbene (C_3N_2 or $C(CN)_2$) isomers. Our calculated ground state geometries and the corresponding vibrational frequencies agree well with available experimental and theoretical data, thereby providing the reliability of the predicted quantities. The present calculations are used to identify the possible emitting species for some unidentified emission bands observed in certain low-temperature matrices. It is found that the $1^3A' \rightarrow X^1A'$ transition of 3-cyano-2*H*-azirenylidene, that is, cyclic C_2N-CN (Figure 1c) satisfactorily explains all of the observed spectral features of these bands.

I. Introduction

In recent years, the structure and properties of unsaturated molecules of the general formula C_nX, XC_nX, XC_nY, etc. have drawn considerable attention from astrophysicists because of their possible existence in the interstellar and circumstellar media. Thus, extensive studies have been carried out on heterocumelenes C_3X (X=H,N,O,S,P), XC_3X, and XC_3Y[1,2] to establish their presence in the interstellar and circumstellar clouds. Despite extensive investigations, none of these species (C_3X, XC_3Y, XC_3X) have been found in the interstellar and/or circumstellar clouds. Among these species, the ground state geometries of C_3N_2[3−8] and PC_3P[9] are predicted to be linear or slightly bent. The electron paramagnetic resonance (EPR) spectrum of C_3N_2 was recorded by Wasserman et al.[3] in flurolobe suspension and in hexaflurobenzene matrix. Although the EPR spectrum in flurolobe suspension suggests that the ground state of C_3N_2 is a linear triplet, the corresponding spectrum recorded in hexaflurobenzene matrix was found to be compatible with a slightly bent geometry. Thus, there exists an ambiguity concerning the geometry of the C_3N_2 species. This ambiguity is also present in theoretical calculations. On the basis of extended Hückel calculations, Hoffmann et al.[4] assigned a linear triplet for the ground state of C_3N_2, which has also been supported by several *ab intio* studies.[5,7,8] Similar trends have also been observed for the analogues NCN and HCH. However, two configuration, self-consistent field (SCF) calculations of Lucchese and Schaefer[6] suggest that the C_3N_2 triplet state is distinctly bent ($^3B_1$).

The formation, structural rearrangement, and decompositions of C_3N_2 have also received considerable attention from experimentalists. The synthesis of C_3N_2 and its ionic species from its precursors has been studied by Blanksby et al.,[7] who have also reported the geometrical parameters and relative stabilities of the linear ($D_{\infty}h$) and bent (C_{2v}) species. In 2003, Maier and coworkers[8] identified five stable isomers of C_3N_2 (dicyanocarbene, cyanoisocyanocarbene, 3-cyano-2*H*-azirenylidene, 3-isocyano-2*H*-azirenylidene, and diisocyanocarbene) in the photolysis and photoisomerization of matrix-isolated dicyanodiazomethane. They also presented the vibrational frequencies, geometrical parameters, and the relative energies of these isomers. It is pertinent to remark that their B3LYP/6-311+G* density functional calculations also predict a linear triplet state of $^3\Sigma_g^-$ symmetry for the ground state of dicyanocarbene.

The purpose of the present investigation is to identify the species responsible for the emission of an unidentified band system observed by Krishnamachari et al.[10,11] in the microwave discharge products of flowing mixtures of N_2 and CO/C_2H_2, condensed on a cold surface. Krishnamachari et al. have inferred (from ^{13}C isotope shift data) that the emitter contains *at least* two carbon atoms. They further conclude (from the energy transfer excitation mechanism) that the emission is most likely taking place from the low lying *stable* excited triplet state (T) to its *stable* singlet (S) ground state with ΔE_{S-T}(obs) ~4.5 eV. Our recent comprehensive calculations[12] strongly suggest that the isomers of C_2N_2 cannot be the possible emitter because none of its isomers have *stable* triplet excited states with ΔE_{S-T} ~4.5 eV, though one of its cyclic isomers possesses a ground state vibrational frequency close to the observed value. As explained in section IV, the C_3N_2 molecule could be considered a possible emitter of the bands. Because one of the ground state vibrational frequencies (677 cm^{-1}) of 3-cyano-2*H*-azirenylidene (henceforth abbreviated as cyclic C_3N_2 for convenience) is significantly close to the observed (670 cm^{-1}) value in the emission bands,[10,11] this isomer could be the possible *emitter* of the unexplained band system, provided its low lying triplet excited state is stable and is separated from its ground state singlet by ~4.5 eV.

This article describes calculations of the ground and low lying triplet state properties of linear and cyclic C_3N_2 isomers to identify the unknown emitter. Because the vibrational frequen-

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cies and the geometry of the ground and lowest excited triplet states are relevant to the identification of the emitter, our calculations are mainly confined to these two states of cyclic C_3N_2. Our calculations for the linear structures agree well with available experimental and theoretical data, thereby providing a benchmark for assessing the predictions. The present calculation further shows that all of the observed spectral features of the unidentified band system could be satisfactorily explained as being due to the $1^3A' \rightarrow X^1A'$ transition of cyclic C_3N_2.

The article is organized as follows. Section II describes the basis set used in the calculations for the ground and excited state properties of the C_3N_2 isomers. The results obtained from various correlated theories are discussed in section III, followed by the assignment of the emitter of the unidentified bands in section IV.

II. Computational Details

Two sets of basis functions are employed to compute the ground and excited state geometries, and state energies of C_3N_2. The structural parameters and vibrational frequencies of some selected C_3N_2 isomers (relevant to the present study) are calculated at the complete active space (CAS) self-consistent field (SCF) level using the DALTON[13] package with the [14s9p4d]/(6s4p2d) atomic natural (ANO) basis of Widmark et al.[14] The state energies, however, are estimated using the CCSD[15] (EOMCCSD[16] for the excited states of interest) method with the [14s9p4d3f]/(7s5p3d2f) ANO basis of Widmark et al.[14]

In addition to CCSD, we also report the transition energies (for the cyclic isomer) obtained from the multireference quasi-degenerate second-order perturbation theory(MCQDPT2),[17] multireference Möller−Plesset second-order perturbation theory (MRMP2),[18] and third-order effective valence Hamiltonian method (H^v_{3rd}).[19]

It is worth mentioning that the complete active space second-order perturbation theory (CASPT2)[20] is also capable of providing reliable and accurate ground and excited state properties for such systems. Because the CASPT2 code was not accessible to us, we employed the above-mentioned perturbative methods in which MCQDPT2 and MRPT2 are closely related to CASPT2, whereas the H^v_{3rd} method is also known to produce results of similar quality.[21]

III. Results and Discussions

The ground state structural parameters from the CASSCF and other correlated calculations[7,8] of dicyanocarbene and cyclic C_3N_2 are collected in Tables 1 and 2. The present calculation also predicts a linear $^3\Sigma_g^-$ ground state for dicyanaocarbene and is in accord with almost all previous theoretical calculations except the one reported by Lucchese and Schaefer.[6] As can be seen in Table 1, the CASSCF predicted CC (1.308 Å) and CN (1.197 Å) bond lengths are in excellent agreement with previous theoretical estimates of Maier et al.[8] and Blanksby et al.[7]

The vibrational frequencies for the ground state of dicyanocarbene determined from the CASSCF method are presented in Table 3. Recently, Maier and co-workers have calculated the vibrational frequencies of dicyanocarbene from the IR spectrum of dicyanodiazomethane irradiated with light of wavelength greater than 385 nm. They have also computed its vibrational frequencies using the B3LYP/6-311+G* method, which fits nicely with their observed values. Our predicted vibrational frequencies are also in accord with the observed and theoretical estimate of Maier et al.

TABLE 1: Ground State Geometrical Parameters of Dicyanocarbene Isomers (Figure 1a and b)[a]

	parameter	CASSCF	others
$X^3\Sigma_g^-$ (a)	r_{CC}	1.301	1.312[8]
			1.318[7]
	r_{CN}	1.197	1.186[8]
			1.194[7]
	∠CCC	180.0	180.0[8]
	∠NCC	180.0	180.0[8]
X^1A_1 (b)	r_{CC}	1.400	1.421[6]
			1.369[7]
	r_{CN}	1.153	1.160[6]
			1.181[7]
	∠CCC	113.2	114.9[6]
			123.6[7]
	∠NCC	175.1	174.0[6]
			171.9[7]

[a] Bond lengths and bond angles are given in Å and degrees, respectively.

TABLE 2: Ground and Excited State Geometrical Parameters of Cyclic C_3N_2 (Figure 1c and d)[a]

	parameter	CASSCF	Maier et al.[8]
X^1A' (c)	$r_{CC\ CC}(1)$	1.378	1.415
	$r_{CC}(2)$	1.417	1.393
	$r_{CN}(1)$	1.427	1.390
	$r_{CN}(2)$	1.301	1.304
	$r_{CN}(3)$	1.164	1.157
	CNC (α)	60.5	63.3
	CCN (β)	55.2	55.4
	NCC (γ)	179.1	180.0
$1^3A'$ (d)	$r_{CC}(1)$	1.386	
	$r_{CC}(2)$	1.441	
	$r_{CN}(1)$	1.414	
	$r_{CN}(2)$	1.306	
	$r_{CN}(3)$	1.318	
	∠CNC (α)	61.1	
	∠CCN (β)	55.6	
	∠NCC (γ)	123.4	

[a] Bond lengths and bond angles are given in Å and degrees, respectively.

TABLE 3: Ground and Excited State Vibrational Frequencies (in cm^{-1}) of Dicyanocarbenes (Figure 1a and b)

			Maier et al.[8]	
		CASSCF	calcd	obsd
$X^3\Sigma_g^-$ (a)	ν_1	1892.4	2023.4	1945.0
	ν_2	1648.4	1792.3	1747.6
	ν_3	1468.9	1585.4	1508.1
	ν_4	770.9	738.0	689.0
	ν_5	471.3	468.1	387.2
	ν_6	407.2	442.2	373.0
	ν_7	148.6	118.5	102.0
X^1A_1 (b)	ν_1	2348.9		
	ν_2	2273.3		
	ν_3	1170.9		
	ν_4	862.6		
	ν_5	593.7		
	ν_6	361.5		
	ν_7	345.4		
	ν_8	334.5		
	ν_9	139.0		

The bent singlet state dicyanocarbene with $^1A_1$ configuration was studied theoretically by Lucchese and Schaefer[6] using a two-configuration SCF method. Their two-configuration SCF geometry optimization predicts the CC and CN bond distances to be 1.421, and 1.16 Å, respectively, with ∠CCC = 114.9°, whereas the B3LYP/6-31+G(d) calculations[7] estimate these parameters to be 1.467 and 1.191 Å, and 125.0°, respectively. Unfortunately none of these studies provides any information on the vibrational frequencies and the stability the of $^1A_1$ state

TABLE 4: Ground and Excited State Vibrational Frequencies (in cm^{-1}) of Cyclic C_3N_2 Isomers (Figure 1c and d)

			Maier et al.[8]	
		CASSCF	calcd	obsd
X^1A' (c)	ν_1	2309.3	2314.5	2222.2
	ν_2	1758.6	1716.1	1628.8
	ν_3	1399.8	1286.8	1281.5
	ν_4	1004.8	1032.1	991.4
	ν_5	694.2	696.5	677.0
	ν_6	587.8	590.0	559.3
	ν_7	549.3	543.1	517.8
	ν_8	234.8	235.2	215.
	ν_9	218.5	217.9	193.
$1^3A'$ (d)	ν_1	1758.1		
	ν_2	1504.1		
	ν_3	1363.3		
	ν_4	1048.4		
	ν_5	790.1		
	ν_6	524.0		
	ν_7	474.9		
	ν_8	224.9		
	ν_9	118.9		

TABLE 5: Relative Energies (in kcal mol^{-1}) of the Neutral and Negative Ion States of C_3N_2 Isomers

state	this work	others
X^2B_1[a]	−68.87	−70.62[7]
$X^3\Sigma_g^-$	0.00	0.00
1^3B_1[b]	7.64	7.1[6]
1^1A_1	13.70	18.35[7] 18.20[8]
X^1A'	16.43	

[a] Computed at $^2B_1$ geometry. [b] Computed at $^1A_1$ geometry.

TABLE 6: Adiabatic Excitation Energies (in eV) of Cyclic C_3N_2[a]

state	CCSD	MCQDPT2	H^{v}_{3rd}
X^1A'	0.00	0.00	0.00
$1^3A''$	2.95 (2.89)	2.49	3.05
$1^3A'$	4.43 (5.16)	4.34	4.46
$2^3A'$	5.38 (6.35)	5.35	5.32

[a] Entries with parentheses are vertical excitation energies.

TABLE 7: Dissociation Energies ($C_3N_2 \rightarrow C_2N$+CN) of C_3N_2 Isomers[a]

state	CCSD
$X^3\Sigma_g^-$	3.93
X^1A'	4.80

[a] All entries are in eV.

of dicyanocarbene. It should be noted that the B3LYP/6-311+G* calculations of Maier et al.[8] exhibit numerical instability of the $^1A_1$ state wave function. However, no such numerical instability was found in the CASSCF calculation, which is evident from its positive vibrational frequencies (see Table 3). The CASSCF geometrical parameters for the $^1A_1$ state are also reasonably close to those in the earlier predictions.

The experimental vibrational frequencies for the ground $^1A'$ state of cyclic C_3N_2 were reported by Maier et al.[8] They have also computed the vibrational frequencies and structural parameters using B3LYP theory with a 6-311+G* basis. Because the ground state of cyclic C_3N_2 is a stable singlet and one of its vibrational frequencies is close to the observed value,[10,11] we investigated its ground and excited state properties to identify the unknown band system.[10,11] The CASSCF geometry optimization shows that cyclic C_3N_2 possesses stable $^1A'$ ground and $^3A'$ excited states. It is evident that geometry (Table 2) and vibrational wave numbers (Table 4) of the $^1A'$ ground state of cyclic C_3N_2 are in accord with the experimental and theoretical data.[8] Because our computed quantities for the ground state are reasonably close to experimental and other correlated calculations, we believe that our predicted geometry and vibrational frequencies for the excited state are likewise quite accurate. We also note that our computed singlet−triplet energy gap (see Table 6) for cyclic C_3N_2 agrees favorably well with experiment.[10,11]

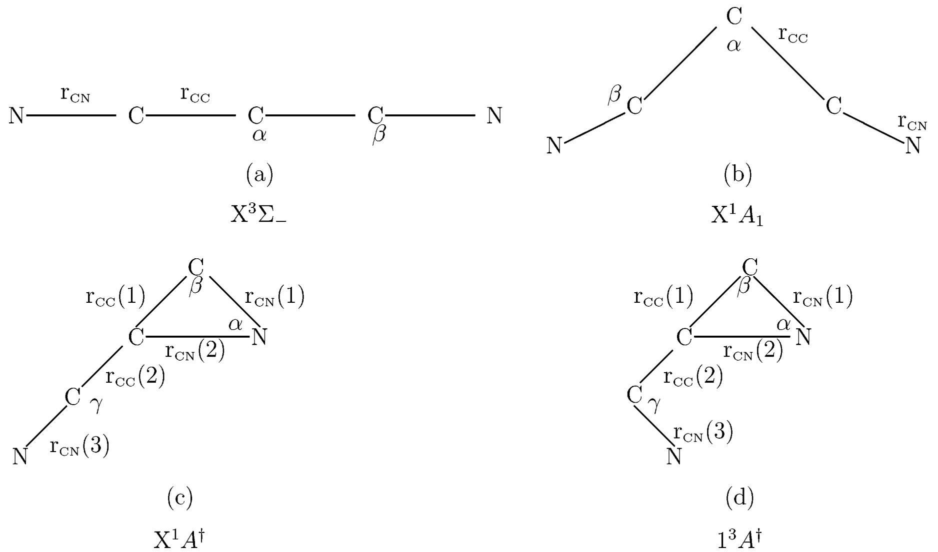
The CCSD state energies for the neutral and negative ions of C_3N_2 are summarized in Table 5. For simplicity, the CCSD state energies for the negative ions are computed at the *optimized geometry of the neutral species*. The present calculation shows that the dicyanocarbene anion is energetically more stable than its neutral counterpart. The cyclic C_3N_2 negative ion is unstable and, hence, not reported here. The relative state energies of dicyanocarbene and its negative ion and of cyclic C_3N_2 are in the following order: $X^2B_1 > X^3\Sigma_g^- > 1^3B_1 > X^1A_1 > X^1A'$.

The dissociation energy (D_e) of the ground state of dicyanocarbene and cyclic C_3N_2 are presented in Table 7. We report the $C_3N_2 \rightarrow C_2N + CN$ bond breaking energy because of its relevance to the assignment of the emission band. Because both C_2N and CN species are open shell doublets, CCSD state energies of these species are computed using open-shell coupled cluster theory for one-electron-attachment processes (OSCC-EA).[22] The dissociation energies of dicyanocarbene and cyclic C_3N_2 are helpful in explaining the stability of these molecules in a low-temperature deposit (discussed section IV).

The CCSD ground and low lying excited state energies of cyclic C_3N_2 are depicted in Figure 2 as a function of C_2N-CN bond distance, that is, rcc(2) of Figure 1c. As can be seen in Figure 2, the $2^3A''$ states of C_3N_2 exhibit an avoided crossing with the $1^3A''$ state near $R_{C_2N-CN} = 1.3$ Å. Perhaps because of this, the CASSCF geometry optimization procedure for the $2^3A''$ state fails to yield real frequencies for all of the vibrational degrees of freedom. The potential energy curves of cyclic C_3N_2 qualitatively show that the $1^3A'$ state joins the ground X^1A' state at the dissociation limit. We emphasize that although these curves explain several observed features of the *unidentified* band system (discussed below), they are not quantitatively correct, especially near the bond-breaking region. This arises mainly because of the multiconfiguration nature of the state(s) of interest. Multireference theories may be used to obtain more accurate and reliable potential energy curves, but this technically difficult problem is beyond the scope of the present work.

IV. Low-Temperature Matrix Emission Spectra

Krishnamachari et al.[10,11] observed two band systems in the 3000−4500 Å region that are emitted by the products of a microwave oscillator discharge through flowing mixtures of nitrogen and acetylene or nitrogen and carbon monoxide, which are then condensed on a surface that is cooled to liquid helium or liquid hydrogen temperatures. One of these systems (referred to here as system I) has its 0−0 band at 3013 Å and consists of a progression of six narrow and diffuse bands with an interval of 2300 cm^{-1}. The second system (referred to here as system II) has its 0−0 band at 2895 Å and consists of a long progression of 22 very broad (half-width at half-maximum intensity, 50 cm^{-1}) and diffuse bands with an interval of 668 ± 25 cm^{-1}. System I appears with good intensity as soon as the condensation of the discharge products begins, whereas system II emerges after a certain delay when a sufficient amount of deposit gets collected on the cold surface. In addition to the emission that occurs during the condensation of the discharge products through



(a)

$X^3\Sigma_-$

(b)

X^1A_1

(c)

$X^1A^\dagger$

(d)

$1^3A^\dagger$

Figure 1. CASSCF optimized ground (a−c) and excited state (d) geometries of dicyanocarbene and cyclic-C_3N_2.

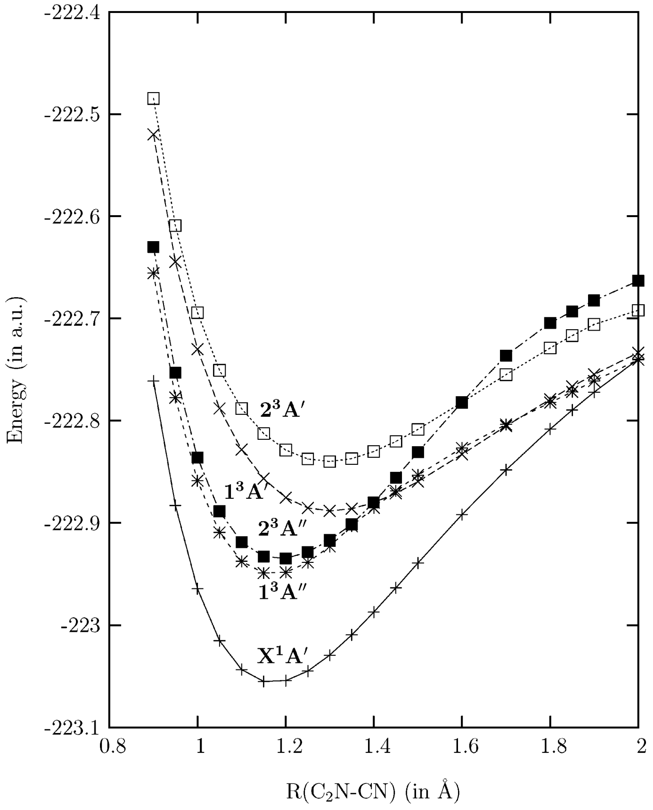


Figure 2. Ground and excited state potential energy curves of cyclic-C_3N_2 as a function C_2N-CN bond distance (rcc(2) of Figure 1c).

the gas mixtures, the two systems could also be excited from the initially formed deposit with the aid of the discharge products obtained from flowing nitrogen alone. These bands were initially assigned to CO_2^+ and NCO[10] but was later revised.[11] With the help of the ^{13}C isotope shifts observed in both systems, it was concluded that the emitting species contains at least two carbon atoms in each case.[11]

Valadier et al.[23] later produced these bands, using similar excitation conditions but with flowing mixtures of nitrogen and methane, methyl-chloride, dichloromethane, chloroform, or carbon tetrachloride. (Their band systems A and B correspond to our systems II and I, respectively.) They observed marked differences in the relative intensities of the two systems depending upon the nature of the gas mixture; thus, system I shows increasing intensity on passage from methane to carbon tetrachloride, whereas system II, which is very intense with methane, decreases in intensity on passing from methane to chloroform and is practically absent with carbon tetrachloride. These observations thus show that the two systems belong to different emitters. Valadier et al.[23] assigned the band system I to the $a^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transition of C_2N_2, corresponding to the absorption system in the gas phase observed by Calloman and Davey.[24] The emission in the low-temperature matrix arises as a result of the formation of C_2N_2 from the recombination CN radicals at the cold surface and the subsequent excitation of C_2N_2 through energy transfer from metastable N_2 $A^3\Sigma_u^+$ molecules, which are also formed in the discharge and reach the cold surface. This assignment was subsequently confirmed by Mayer et al.,[25] who observed this transition in emission in the gas phase by directly exciting C_2N_2 with N_2 $A^3\Sigma_u^+$ molecules. The emitter for the band system II, however, remains unidentified.

The band system II consists of a long progression of bands involving a ground state vibrational frequency of 668 ± 25 cm^{-1} and an electronic transition energy of 4.28 eV. In order to explain the observed vibrational structure of the band system, the emitter should have a ground-state vibrational frequency of 668 ± 25 cm^{-1}, and because the excitation takes place through energy transfer from N_2 $^3\Sigma_u^+$ molecules (6.22 eV), it should have a singlet ground state and a triplet excited state at the appropriate excitation energy. In an earlier communication,[12] we have considered the possibility of assigning this band system to cyanogen or one of its isomers, viz., isocyanogen, diisocyanogen, diazodicarbon, and cyclic cyanogens. Neither cyanogen nor any of these isomers was found to satisfy these requirements and hence could not be considered as the emitter.

Because the band system II could be generated with high intensity using N_2 and CH_4 or N_2 and C_2H_2 mixtures and because the discharges through CH_4 and C_2H_2 are known to produce the C_3 radical,[26] it is plausible that the emitter could be C_3N_2, which is formed by the recombination of C_3 and N_2 at the cold surface. In light of the theoretical calculations for the C_3N_2 isomers presented in section II, we analyzed the possibility of assigning the emitter to one of these isomers. The geometries of the stable C_3N_2 isomers (depicted in Figure 1) are shown in Tables 1 and 2. Because the excitation of the emission band arises by energy transfer from the metastable N_2 $A^3\Sigma_u^+$ molecule, in order to conserve spin, the emitter should have a singlet ground state and a triplet excited state. As in the case of C_2N_2 isomers, the triplet−singlet emission occurs because of relaxation of the spin selection rule due to the influence of the crystal field in the low-temperature matrix. In the solid matrix, the higher vibrational levels of the excited state relax very fast to the lowest vibrational level, and the emission essentially consists of progressions in the ground state.

The ground state of the linear C_3N_2 isomer (Figure 1a), which has the lowest energy of formation, is a triplet state ($^3\Sigma_g^-$) and hence could not be considered as the emitter. As shown in Table 5, the bent dicyanocarbene (Figure 1b) and the cyclic C_3N_2 (Figure 1c) have singlet ground states. However, none of the ground state vibrational frequencies of the bent dicyanocarbene are close to the observed value in the band system II, whereas the cyclic C_3N_2 isomer has a ground state frequency of 677 cm^{-1}, agreeing well with the observed value of 668 ± 25 cm^{-1} (Table 4) in band system II. The calculated energies for the excited electronic states of the cyclic C_3N_2 are given in Table 6. The CCSD estimate of adiabatic energy for the transition $1^3A' \rightarrow X^1A'$ is 4.43 eV, which, after correction for zero-point energies (ZPE) in the two states, comes to 4.36 eV, in quite good agreement with the observed value of 4.28 eV in band system II. It is pertinent to remark that the MCQDPT2 estimates of $1^3A' \rightarrow X^1A'$ transition energy (4.27 eV after ZPE correction) are in better agreement than CCSD. The CCSD vertical excitation energy (see Table 6) of the $1^3A'$ state is 5.16 eV, and thus, this state can be excited by energy transfer from $A^3\Sigma_u^+$ state N_2 molecules (6.22 eV). The geometrical parameters of the $1^3A'$ and X^1A' states are shown in Table 2. The NCC angle (γ in Figure 1d) displays a large change from 179.1° in the ground state to 123.4° in the excited state. This explains the occurrence of a long progression involving the bending frequency 668 ± 25 cm^{-1} in the ground state.

The recombination of C_3 and N_2 might directly lead to the formation of cyclic C_3N_2, or it might initially lead to the formation of the dicyanocarbene, which subsequently isomerizes to cyclic C_3N_2; the requisite isomerization energy of 16.43 kcal mol $^{-1}$ (5758 cm^{-1}) would be provided by vibrationally excited N_2 molecules (energy of the second vibrational level = 5809 cm^{-1}) that are present in the discharge products and that reach the cold surface without radiative loss. The latter possibility also explains the delay in the appearance of the band system II with respect to that of system I. The conversion of dicyanocarbene to cyclic C_3N_2 has also been observed in photoisomerization experiments in low-temperature matrices by Maier et al.[8] The cyclic C_3N_2 once formed, remains stable in the low-temperature matrix because the emission from the deposit persists for a long time from the discharge products of nitrogen alone; the emission may continue for more than an hour depending on the initial amount of deposit.[11] The calculated dissociation energy of the cyclic C_3N_2 of 4.80 eV (Table 7) is also in conformity with this observation and compares favorably than that of dicyanocarbene, which has a computed dissociation energy of 3.93 eV. (The cyclic C_3N_2 would be expected to be more stable in the low-temperature deposit.) The unusual width and diffuseness of the bands could be explained as follows: As mentioned in section III, the $1^3A'$ state joins the ground X^1A' state at the dissociation limit. The $v' = 0$ vibrational level of the $1^3A'$ state, which has an energy of 4.91 eV (adiabatic excitation energy + zero-point energy), lies in the dissociation continuum of the ground state, which begins at 4.80 eV. This causes predissociation of the $v' = 0$ level, resulting in the broadening and overlapping of its rotational levels. It is thus seen that the cyclic C_3N_2 satisfactorily explains all observed spectral features of band system II and can be considered as the possible emitter of this band system.

The dissociation of cyclic-C_3N_2 to C_2N + CN suggests the possibility of its formation through the recombination of C_2N and CN. However, although C_2N has been observed in the photolysis of diazomethane,[27] so far there is no report of its appearance in an electrical discharge through methane and nitrogen mixtures. Hence, this possibility is not considered here.

The present calculations for cyclic-C_3N_2 demonstrate the existence of a stable $1^3A''$ state with an adiabatic excitation energy of 2.95 eV (Table 6). In the experiments of Krishnamacahri and co-workers,[10,11] emission from this state could not be observed because of the mismatch of its vertical excitation energy (2.89 eV) with the energy of the N_2 $A^3\Sigma_u^+$ molecule (6.22 eV). However, it might be possible to produce this emission by exciting the deposit with radiation of the appropriate wavelength. It would also be possible to see the corresponding absorption spectrum in the deposit, though its intensity would be weak because of the spin forbidden nature of the transition. In view of the current astrophysical interest in cyano-molecules, it would be desirable to perform further studies on these spectra. While Maier et al.[8] have reported the formation of cyclic-C_3N_2 in the photolysis of dicyanodiazomethane, the present studies indicate the possibility of its formation by the recombination of C_3 and N_2, which would be of interest in the astrophysical context.

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