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Theoretical study on the excited states of HCN

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In the flash-photolysis of oxazole, iso-oxazole, and thiozole a transient band system was observed in the region 2500–3050 Å. This band system was attributed to a meta-stable form of HCN, i.e., either HNC or triplet HCN. Theoretical investigations have been carried out on the ground and excited states of HCN to characterize this and other experimentally observed transitions. The predicted geometries are compared with the experiment and earlier theoretical calculations. The present calculations show that the band system in the region 2500–3050 Å corresponds to the transition $4\,^3\text{-}A' \leftarrow 1\,^3\text{-}A'$ of HCN. © *2005 American Institute of Physics.*
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I. INTRODUCTION

The hydrogen cyanide (HCN) molecule has been the subject of several experimental and theoretical investigations over several years. Being a small polyatomic molecule, HCN is an ideal system for the development and testing models aimed to calculate its electronic and rovibrational states and other related properties. The possibility of intramolecular isomerization HCN–HNC has also made this an important system for the study of unimolecular reactions. In recent years, HCN has raised interest among astrophysicists due to its detection in the atmosphere of Titan[1] and Carbon stars.[2] HCN has also been identified via radiotechniques in both comets[3] and interstellar atmosphere.[4]

The excited singlet states of HCN were first experimentally studied by Herzberg and Innes,[5] who established the existence of three bent excited states of HCN. The lowest excited state lying 6.438 eV above the ground state was assigned as $\tilde{A}\,^1A''$ with bond angle 125° and electronic configuration $5a'^2 6a'^2 1a'' 7a'$. Herzberg and Innes assigned the electronic configuration of second $\tilde{B}\,^1A''(T_0=6.77\text{ eV})$ and third $\tilde{C}\,^1A'(T_0=8.14\text{ eV})$ excited singlet states of HCN to be $5a'^2 6a' 1a''^2 2a''$ with bond angle 114.5° and $5a' 6a'^2 1a''^2 7a'$ with bond angle 141°, respectively. While the assignment of the first excited singlet state is consistent with Walsh's[6] prediction, there are some serious discrepancies between the theoretical and experimental molecular structures for the $\tilde{B}\,^1A''$ and $\tilde{C}\,^1A'$ states of HCN. According to Walsh, there is only one significantly bent $^1A'$ state and the other two $^1A'$ states are either linear or nearly linear. Herzberg and Innes' assignment of $\tilde{C}\,^1A'$ state of HCN is also not in accord with Walsh's prediction. According to Walsh, this state should be strongly bent and not one with bond angle 141°. However, subsequent theoretical studies[7,8] clarified the breakdown of Walsh's rule which was based on one electron energy diagram.

Krishnamachari and Venkatsubrahmanian[9] have observed a transient (300 μs half life) absorption system with its origin at 32 844.1 cm^{-1} in the flash-photolysis of oxazole, iso-oxazole, and thiazole. The band system consists of a long progression involving CN stretching frequency of 1005 cm^{-1} in the upper electronic state. The spectrum was attributed to a meta-stable form of HCN, i.e., either HNC or triplet HCN. For HNC, Laidig and Schaefer[10] predicted the electronic transition to occur at 46 830 cm^{-1}, with a CN stretching frequency of 1100 cm^{-1} in the excited electronic state and a bent excited state compared to the linear ground state. The observed spectrum, though nearly agreeing with respect to CN stretching frequency, differs considerably with respect to transition energy by about 14 000 cm^{-1}. The absence of a progression involving the bending frequency is also not in agreement with the theoretical expectation. Thus the assignment of the HNC is not tenable and the alternative assignment, i.e., to triplet HCN, is to be preferred.

The main aim of the present work is to characterize the higher triplet states of HCN and assign the transient absorption spectrum. As shown in the following, the observed spectrum could be assigned to the transition $4\,^3A' \leftarrow 1\,^3A'$; the observed value of the transition energy and the CN stretching frequency agree well with the calculated value; the occurrence of a long progression of the CN stretching frequency and the absence of bands involving the bending frequency are in conformity with calculated change in the geometry in these two states.

We also report relevant spectroscopic data, such as ionization potentials, vibrational frequencies, dissociation energies, and dipole moments of HCN, some of which to our knowledge have not been reported before.

II. COMPUTATIONAL DETAILS

Two sets of basis functions are employed to compute the excitation energies, ionization potentials, and related molecu-

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TABLE I. Adiabatic excitation energies (in eV) of HCN.

State	Dominant configuration(s)	CASSCF	CC	Schwenzer *et al.*[a]	Expt.[b]
$X\,^1\Sigma^+$	$5\sigma^2 1\pi^4 (C_{\infty v})$	0.0	0.0	0.0	0.0
$1\,^1A''$	$7a'1a''$	6.48	6.48	6.48	6.48
$2\,^1A'$	$6a'7a'$ $1a''2a''$	6.70	6.93	6.78	6.77[c]
$2\,^1A''$	$6a'2a''$ $8a'1a''$ $6a'3a''$	7.66	7.79	7.52	
$3\,^1A'$	$1a''2a''$ $1a''3a''$ $6a'8a'$ $5a'8a'$	8.23	8.10	7.85	8.14
$3\,^1A''$	$7a'1a''$	8.99	8.64	8.97	8.88
$1\,^3A'$	$6a'8a'$	4.46	4.44	4.42	
$1\,^3A''$	$8a'1a''$	5.42	5.47	5.46	
$2\,^3A'$	$1a''2a''$	6.28	6.13	5.91	
$2\,^3A''$	$6a'2a''$	7.08	7.00	6.85	
$3\,^3A'$	$1a''2a''$ $6a'8a'$	7.11	6.81	6.98	
$3\,^3A''$	$5a'2a''$	7.61	7.47	7.41	
$4\,^3A'$	$6a'7a'1a''2a''$ $5a'7a'$	8.69			8.53[d]

[a] Reference 7.
[b] Reference 26.
[c] Estimated from the perturbation in the $\tilde{A}$ state (Ref. 5)
[d] Reference 9.

lar properties of HCN. The basis set chosen for the geometry optimization consists of $(4s,1p)/[2s,1p]$ contracted Dunning's basis[11] augmented with an $s(\zeta_s = 0.029740)$ and $p(\zeta_p = 0.141)$ function for H atom. For C and N, we employ Dunning's[11,12] $(9s,4p,1d)/[3s,2p,1d]$ contractions augmented with two s, two p, and one d functions. The exponents for the augmented s, p, and d functions for C (N) atom are 4.53 (6.233), 0.0469 (0.06124), 14.557 (19.977), 0.04041 (0.05611), and 0.151 (0.23), respectively. The transition energies, ionization potentials, dissociation energies and dipole moment (for the ground state) are computed with a basis comprised of $59a'$ and $28a''$ basis functions. Here, the H atom basis is constructed from Dunning's $(5s,2p)/[3s,2p]$ aug-cc-pVTZ contraction scheme. On the other hand, Dunning's $(11s,6p,3d,1f)/[5s,4p,3d,1f]$ aug-cc-pVTZ basis is used for C and N atoms. While the geometry optimization is performed at the complete active space self-consistent field (CASSCF) level,[13] transition energies, ionization potentials, and the related properties are computed using the coupled cluster based linear response theory[14–17] (also known as EOMCC).

A. Geometries and transition energies of HCN

The adiabatic transition energies (T_e) for the singlet and triplet states of HCN are compared with experiment and with other correlated calculations in Table I. The computed transition energies T_e of Schwenzer *et al.*[8] are actually 2.18 eV higher than their reported value. The motivation of this adjustment was based on the position of the $\tilde{A}\,^1A''$ state. In their calculations, this excited state was estimated to be 8.22 eV above the ground state, i.e., 2.18 eV higher than the experimental value. Therefore, all the T_e values reported by Schwenzer *et al.* were obtained by subtracting the 2.18 eV from the computed T_e values. This large error in the estimated energy is partly due to predisposition of the calculations in favor of closed shell ground state though the choice of basis function plays a significant role. We emphasize that the semiempirically adjusted T_e value of Schwenzer *et al.* agrees well with the experiment for $3\,^1A'(\tilde{A})$ and $3\,^1A''(\tilde{D})$ electronic states though their predicted T_e value for $3\,^1A'(\tilde{C})$ is slightly off from the experiment. We also adjust the position of $\tilde{A}\,^1A''$ state but in our calculation the $\tilde{A}\,^1A''$ excited singlet state is only off by 0.5 eV (for both CASSCF and CC) compared to 2.18 eV of Schwenzer *et al.*

Regarding the second excited state, Herzberg and Innes originally assigned a state at 6.78 eV as $\tilde{B}(^1A'')$.[5] However, it was later shown to be an extension of $1\,^1A'(\tilde{A})$ state.[18] The present as well as Schwenzer *et al.* calculations predict excited singlet state $1\,^1A'$ to be at 6.8 eV; though this state has not been directly observed, the existense of this state has been inferred through perturbation in the $\tilde{A}$ state.[5] The observed $\tilde{C}(3\,^1A')$ and $\tilde{D}(3\,^1A'')$ electronic state energies are well reproduced in the present calculations.

We now proceed to compare the theoretical and experimental predictions of the excited triplet states of HCN. Excited triplet states are of special interest to experimentalists as these metastable states can initiate/exhibit many interesting chemical phenomena.[19] To the best of our knowledge, nothing is known experimentally about triplet states of HCN except the one reported by Krishnamachari *et al.*[9] In their flash-photolysis experiments on oxazole, iso-oxazole, and thiozole, Krishnamachari *et al.* observed a transient spectrum in 2500–3050 Å region with a long progression involving CN stretching frequency of 1005 cm^{-1}. This band system was attributed to an excited metastable state of HCN, i.e., either triplet HCN or isomeric HNC. The present calculation estimates the T_e for $1\,^3A' \rightarrow 4\,^3A'$ to be 33308 cm^{-1}, which matches well with the observed value $32\,844^{-1}$. In addition, our predicted CN stretching frequency (1001 cm^{-1}) for the $4\,^3A'$ state is also in accord with the experiment.

The geometries and vibrational frequencies obtained from the CASSCF calculation for the ground and excited states of HCN are displayed in Tables II and III, respectively. To our knowledge, triplet state and high lying singlet geometries and the corresponding vibrational frequencies are not known experimentally. However, it is evident from Table II that our computed geometries are in agreement with those reported by Schwenzer *et al.* The slight difference in the estimated bond lengths and bond angle between these two theoretical works arises mainly because of the choice of basis functions and the procedure adopted in minimizing the energy with respect to its internal coordinates, i.e., with respect to r_{CH}, r_{CN}, and θ(HCN). Since our computed geometries and vibrational frequencies are reasonably close to the experiment, we feel that our predicted geometries and associated frequencies will also be reliable. While the calculated values for CN stretching and HCN bending frequencies are

TABLE II. Comparison of experimental and theoretically computed ground and excited state geometries of HCN. Bond distances are given in angstroms and bond angles in degrees.

	r_{CH}			r_{CN}			$\angle$HCN		
State	This work	Reference 7	Expt.[a]	This work	Reference 7	Expt.[a]	This work	Reference 7	Expt.[a]
$X\,^1\Sigma^+$	1.085	1.055	1.064	1.169	1.180	1.156	180.0	180.0	180.0
$1\,^1A''$	1.140	1.096	1.14	1.331	1.318	1.297	119.4	127.2	125.0
$2\,^1A'$	1.182	1.102		1.291	1.287		113.9	124.9	
$2\,^1A''$	1.105	1.076		1.332	1.316		143.6	164.4	
$3\,^1A'$	1.138	1.092	1.14	1.278	1.264		136.5	141.2	141.0
$3\,^1A''$	1.061	1.045		1.241	1.229		180.0	180.0	
$1\,^3A'$	1.125	1.081		1.313	1.294		121.9	128.6	
$1\,^3A''$	1.111	1.099		1.329	1.365		120.7	117.0	
$2\,^3A'$	1.098	1.063		1.331	1.320		147.4	160.0	
$3\,^3A'$	1.127	1.081		1.283	1.250		132.6	132.6	
$2\,^3A''$	1.107	1.061		1.329	1.314		143.7	157.4	
$3\,^3A''$	1.085	1.045		1.238	1.237		180.0	180.0	
$4\,^3A'$	1.109			1.571			121.0		
$4\,^3A''$	1.128			1.502			117.3		

[a] Reference 26.

in accord with the experiment, the computed CH stretching frequencies for the $1\,^1A''$ and $3\,^1A''$ states differ appreciably from the experimental values. The reason for this deviation may be due to the strong vibronic coupling of the CH stretching vibrations produced via intermediate $2\,^1A''$ state as has been pointed out by Bickel *et al.*,[20] Lee,[21] and Meenakhsi *et al.*[22]

B. Ionization potential of HCN

To our knowledge, only the first and second ionization potential of HCN are experimentally known so far. The electron impact experiment[23] estimates the first ionization potential of HCN to be 13.91 eV (89.1 nm). Later the vacuum ultraviolet (VUV) absorption spectrum of HCN between 62 and 148 nm was analyzed by Nuth and Glicker.[24] The VUV absorption spectra of HCN shows a weak vibrational structure that continues to the first adiabatic ionization potential (IP) at 89.1 nm. It was also pointed out by Nuth and Glicker that a complex Rydberg series starting at 122 nm converges to the first ionization potential and the series beginning at about 116 nm converges to the second ionization potential. The adiabatic IP for $^2\Pi$ (13.60 eV) estimated by Turner *et al.*[25] was also in agreement with Nuth.[24]

TABLE III. Comparison of experimental and theoretically computed vibrational frequencies (in cm^{-1}) of HCN. Entrees within parentheses are experimental (Refs. 9,24,26) vibrational frequencies.

State	ω_1 C–H Str.	ω_2 C–N Str.	ω_3 bend
$X\,^1\Sigma^+$	3351 (3312)	2101 (2098)	702 (714)
$2\,^1A'$	1987	1433	499
$3\,^1A'$	2524 (2273)	1595 (1530)	760 (869)
$1\,^1A''$	2606 (3160)	1413 (1495)	948 (941)
$2\,^1A''$	3095	1414	935
$3\,^1A''$	3602 (2367)	1762 (1626)	1011 (1038)
$1\,^3A'$	2818	1525	981
$2\,^3A'$	3121	1452	875
$3\,^3A'$	2764	1814	1032
$4\,^3A'$	3038	1001 (1005)	866
$1\,^3A''$	2605	1413	948
$2\,^3A''$	3072	1439	966
$3\,^3A''$	3356	1759	893
$4\,^3A''$	2782	1462	1003

Table IV reports the valence and satellite (shake-up) IPs of HCN obtained using the coupled cluster based linear response theory.[17] Both the first $[^2\Pi(1\pi^{-1})]$ and second ionization potentials $(^2\Sigma^+(5\sigma^{-1}))$ of HCN are in favorable agreement (off only by 0.1 eV or less) with the experiment. Since our computed IPs (the first and second) are in good agreement with the experiment, we strongly feel that our predicted third valence ionization potential $[^2\Sigma^+(4\sigma^{-1})]$ and satellite IPs will also be quite accurate.

C. Dissociation energy of HCN

The HCN molecule can dissociate either into CH and N or CN and H species. Energy required to break HCN into CH and N is much higher than that needed to dissociate HCN into CN and H. Here, we compute the dissociation energy only for

TABLE IV. Vertical ionization potentials (in eV) of HCN.

State	Peak type	Present work	Expt.[a]
$^2\Pi$	Valence $(1\pi^{-1})$	13.81	13.91
$^2\Sigma^+$	Valence $(5\sigma^{-1})$	13.94	14.01
$^2\Sigma^+$	Valence $(4\sigma^{-1})$	20.42	
$^2\Pi$	Satellite	24.66	
$^2\Sigma^+$	Satellite	26.56	
$^2\Sigma^+$	Valence $(3\sigma^{-1})$	29.24	

[a] References 24,25.

TABLE V. Spectroscopic constants of HCN($^1\Sigma^+$) and CN($^2\Sigma^+$).

System	Spectroscopic constants	Present work	Expt.[a]
HCN			
	μ (in D)	3.28	
	D_e (in eV)	5.70	5.62
	B_0 (in cm^{-1})	1.44	1.48
CN			
	IP (in eV)	14.08	14.10
	r_{CN} (in Å)	1.20	1.17

[a] References 26,27.

$$\mathrm{HCN}(^1\Sigma^+) \rightarrow \mathrm{CN}(^2\Sigma^+) + \mathrm{H}(^2S)$$

channel using CC method. The dissociation energy is calculated in two steps. First, the HCN($^1\Sigma^+$) ground state is computed using closed shell CC method. The ground state of CN($^2\Sigma^+$) is then calculated by adding an electron to the correlated closed shell ion CN$^+$ following the Fock-space scheme[16]

$$\mathrm{CN}^+(^1\Sigma^+) + e \rightarrow \mathrm{CN}(^2\Sigma^+).$$

Once the ground state energies of HCN($^1\Sigma^+$) and CN($^2\Sigma^+$) are known, the estimation of dissociation energy is trivial.

The dissociation energy (D_e) of HCN→CN($^2\Sigma^+$) +H(^2S), dipole moment (μ), and IP of CN are presented in Table V. The accuracy of our estimated D_e, IP of CN and other properties of HCN (discussed earlier) clearly indicates the reliability of the method.

D. Concluding remarks

The ground and excited state properties (including geometries) of HCN computed using the CASSCF and CC method of HCN are presented. The computed transition energy and CN stretching frequency strongly suggests that the transient band system in the region 2500–3050 Å arises from 4 $^3A' \leftarrow 1\ ^3A'$ transitions. The present study further suggests that the deviation of experimental bond angle from Walsh's prediction can be justified in terms of breakdown of single configuration picture. As could be seen from Table I, the first triplet–triplet transition of HCN, i.e., 1 $^3A'' \rightarrow 1\ ^3A'$ occurs at 1.29 μm, It would be possible to observe this transition in absorption in the photodecomposition of the oxazoles or thiozole.

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