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Electronic Spectrum of Dicyanoacetylene. 1. Calculations of the Geometries and Vibrations of Ground and Excited States of Diacetylene, Cyanoacetylene, Cyanogen, Triacetylene, Cyanodiacetylene, and Dicyanoacetylene[†]

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The predictive reliability of calculations of the excitation energies, geometries, and vibration frequencies for the lower singlet states of NCCCCN is tested by similar calculations on well-characterized states of HCCCCH, HCCCN, NCCN, HCCCCCCH, and HCCCCCN. Their performance encourages confidence in the predictions for the so far unanalyzed first singlet transition of NCCCCN.

Introduction

The purpose of this work is to assist the interpretation of the hitherto unexplained first singlet electronic transition of the linear molecule dicyanoacetylene, N≡C−C≡C−C≡N.[1] We do this by computational prediction of the shape, rotational constant(s), and vibration frequencies of the excited molecule.

To establish the credentials of these predictions, we carried out similar calculations on five related molecules for which there is a good deal of reliable experimental data drawn from analyzed spectra. These molecules are diacetylene (butadiyne) HC≡C−C≡CH,[2−6] cyanoacetylene HC≡C−C≡N,[7,8] cyanogen N≡C−C≡N,[9] triacetylene (hexatriyne) HC≡C−C≡C−C≡CH,[3,5] and cyanodiacetylene (cyanobutadiyne) HC≡C−C≡C−C≡N. A special feature of these triple-bonded molecules is, as was first recognized in acetylene HC≡CH[10] and hydrogen cyanide HC≡N,[11] that they may become (trans-)bent in certain excited states, especially in the first excited state. We find we are able to predict such changes in full agreement with the available spectroscopic evidence, giving us confidence in the predictions for the target molecule NCCCCN.

Expected Excited States

The lower electronic excitations of all six molecules (and of HCCH and HCN) are of the same kind. In molecular orbital terms, the relevant electron configurations (in point group $D_{\infty h}$) are

$$\text{ground state } ...(\pi_u)^4(\pi_g)^4 \rightarrow {}^1\Sigma_g^+$$

$$\text{excited states } ...(\pi_u)^4(\pi_g)^3(\pi_u) \rightarrow {}^1\Sigma_u^-,\ {}^1\Delta_u,\ {}^1\Sigma_u^+$$

plus the corresponding triplets, The excited states are listed in the order predicted at virtually all levels of approximation in MO (molecular orbital) methods (the triplets differ: see NCCN and NCCCCN in Table 1). For HCCCN and HCCCCCN the point group is $C_{\infty v}$, and the g, u subscripts do not apply. If the molecule becomes trans-bent, the Σ_u^- state transforms as A_u, and $\Delta_u \rightarrow A_u + B_u$ (for bent HCCCN, point group C_s, $\Sigma_u^- \rightarrow A''$, $\Delta \rightarrow A' + A''$). In the cyanides, $\pi^* \leftarrow$ n transitions from the nitrogen lone pairs are also possible, but have not been seen in molecules of this class and must lie unobserved among strong $\pi^* \leftarrow \pi$ absorptions at higher energy.

Calculations

Methods. Molecular orbital calculations were carried out using the GAUSSIAN 98 [12] and MOLPRO 2000 [13,14] suites of programs to determine the electronic state energies, molecular structures, and vibration frequencies of the lowest excited states of the six molecules. Several different procedures were used. In the configuration interaction with single excitations (CIS) method[12,15] geometry optimizations and harmonic frequency calculations were undertaken for all the excited states of interest. In terms of electronic state energies CIS has been found to be qualitatively accurate. Its quantitative predictions for both energies and molecular structural parameters are in general less reliable than computational methods that include configuration interactions higher than singles, such as CASSCF and CASPT2 discussed below. It is comparable to Hartree−Fock (HF) theory for ground electronic states. However, with respect to the accuracy of vibrational frequency predictions, the CIS scaled harmonic frequencies, in a number of instances, have been found to be more reliable than the more comprehensive methods.[16] Multiplication of the CIS calculated harmonic frequencies by an appropriate scaling factor takes into account the neglected electron correlation. The scaling factor used is that recommended for the HF predicted frequencies,[17] 0.895, and is one that has been found to work satisfactorily for a number of molecules.

The excited states were also investigated using the complete active space multiconfiguration self-consistent field (CASSCF) method.[13] This method takes some account of the electron correlation by combining a self-consistent field (SCF) computation with a full configuration interaction involving a subset of the orbitals. The CASSCF method neglects some important additional electron correlation effects. To incorporate these, it is possible to use the CASSCF wave functions as reference for further calculations. This was achieved by implementation of a second-order perturbation method (CASPT2, multireference Rayleigh−Schrödinger perturbation theory).[14] In so far as the reliability of the different methods is concerned, it should be noted that in some recent studies on the transition energies of

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TABLE 1: Adiabatic Transition Energies (eV) and Geometries of Lower Excited States[a]

state	obs	CIS	CAS	CASPT2	geometry	
			(12/12)	(8/8)	obs	calc
Diacetylene (HCCCCH)						
^1A_u	4.33[b]	4.06	5.03	4.12	bent[b]	bent
$^1\Delta_u$	5.06[c]	4.73			linear[d]	linear
$^1\Sigma_u^+$	7.54[e]	$<$10.3[f]				$<D_{\infty h}$
Cyanoacetylene (HCCCN)						
$^1A''$	4.77[g]	4.29	5.30	4.64	bent[g]	bent
$^1\Delta$	5.48[h]	5.12	6.11	4.99	linear[h]	linear
$^1\Sigma^+$	8.55[i]	$<$11.0[f]				bent
Cyanogen (NCCN)						
$^3\Sigma_u^+$	4.13[j]	3.48	4.55	3.49	linear[j]	linear
$^1\Sigma_u^-$	5.63[k]	5.19	6.67	5.35	linear[k]	linear
$^1\Sigma_u^+$	9.17[i]	$<$11.8[f]				$<D_{\infty h}$
Triacetylene (HCCCCCCH)						
$^1\Sigma_u^-$		3.76	4.72	3.38		linear
$^1\Delta_u$	4.19[l]	4.01	5.14	3.67	linear[l]	linear
$^1\Sigma_u^+$	6.82[m]	8.52				linear
Cyanodiacetylene (HCCCCCN)						
$^1\Sigma^-$		3.95	4.94	3.51		linear
$^1\Delta$		4.22	5.38	3.81		linear
$^1\Sigma^+$		8.98				linear
Dicyanoacetylene (NCCCCN)						
$^3\Sigma_u^+$	3.18[n]	2.75	3.61	2.02	linear[n]	linear
$^1\Sigma_u^-$	4.40[o]	4.20	5.26	3.68	linear[o]	linear
$^1\Delta_u$	4.62[p]	4.49			linear[p]	linear
$^1\Pi_u$		$<$9.7[f]				$<D_{\infty h}$
$^1\Sigma_u^+$	7.69[i]	$<$9.0[f]				$<D_{\infty h}$

[a] Calculated values all include corrections for zero-point vibrations. [b] From ref 2. [c] From refs 3 and 19. [d] From ref 19. [e] From ref 5. [f] A global minimum could not be found for this state. [g] From ref 7. [h] From ref 8. [i] From ref 20. [j] From ref 9. [k] From ref 21. [l] From ref 3. [m] From ref 5. [n] From ref 22. [o] From refs 1,23. [p] From ref 1.

the diazines it was found that the most reliable results were given by CASPT2, coupled cluster, and density functional procedures.[16,18]

Ground-state calculations were carried out at the HF, CASSCF, and CASPT2 theoretical levels, Additional ground-state calculations were carried out at the MP2 (second-order Moller−Plesset perturbation theory) and B3LYP (Becke-style three-parameter density functional theory) levels, but since the results did not show significant differences from our HF and CASSCF calculations, they have not been included in the tables.

All calculations used the 6-31G(d) basis. This is a polarized basis set with d functions on the C and N atoms. It is an adequate basis set for the ground and valence excited states studied in this work where the inclusion of diffuse functions is not necessary. For the higher-lying $^1\Sigma_u^+$ and $^1\Pi_u$ states, larger basis sets would have been more appropriate, but with the existence of only very limited experimental information this was not done. Calculated results for these states only appear in Table 1 and are restricted to excitation energies and geometries.

The CASSCF active space has been limited to 12 electrons in 12 orbitals. For the linear structures of cyanogen, cyanoacetylene, and diacetylene this consisted of all four π and two σ for the occupied orbitals and a similar choice for the vacant orbitals. For the nonlinear structures the corresponding orbitals were chosen. For triacetylene, cyanodiacetylene, and dicyanoacetylene the CASSCF space consisted of all six π for the occupied orbitals and six π^* for the vacant orbitals. Because of memory and time limitations, the CASPT2 computations could not be carried out at the same 12/12 level at which the CASSCF calculations were undertaken. The CASPT2 space was limited to 8 electrons in 8 orbitals and consisted of four π and four π^* for the occupied and vacant orbitals, respectively. The corresponding orbitals were used for the nonlinear structures.

Geometry optimizations and frequency determinations were carried out at the CASSCF level, but not at the CASPT2 level. The CASPT2 transition energies were calculated for the CASSCF optimized structures. Harmonic vibrational frequencies were determined analytically in the CASSCF method, and the frequencies were not scaled.

For all six molecules geometry optimizations were allowed to proceed from both linear and nonlinear initial geometries. This ensured that true global minima were obtained. Despite this approach some initial confusion was encountered in the calculations for diacetylene. For optimizations started from a linear structure the global minimum for the lowest singlet excited state, obtained at both CIS and CASSCF levels, corresponded to the linear molecule. However, when optimization proceeded from the trans structure determined for the lowest triplet state, the molecule adopted a trans structure for the lowest singlet, ^1A_u (corresponds to Σ_u^- for the linear molecule). In the trans geometry one component of the near-lying $^1\Delta_u$ state is ^1A_u. We surmise that upon distortion of the molecule to the trans geometry this state dropped in energy to experience an avoided crossing with the other ^1A_u state whose energy increased upon departure from the linear geometry. Such a pattern of behavior was not encountered for cyanoacetylene, which is also bent in its lowest excited singlet state.

Results. Successive tables give, for all the molecules and for selected electronic states, the adiabatic transition energies for optimized geometries, the geometries themselves, and the vibration frequencies. The states chosen for inclusion are those for which there are experimental data or which exhibit features

TABLE 2: Bond Lengths (Å), Angles (deg), and Rotational Constants[a] (cm^{-1}) in Selected States

	ground state			excited state			excited state		
	obs	HF	CAS[b]	obs	CIS	CAS[b]	obs	CIS	CAS[b]
Diacetylene									
		$^1\Sigma_g^+$			^1A_u			$^1\Delta_u$	
CH	*1.094*[c]	1.057	1.077		1.078	1.097		1.055	
CC	*1.218*	1.187	1.212		1.281	1.303		1.256	
CC	*1.384*	1.389	1.383		1.300	1.295		1.305	
HCC					132.6	129.9			
CCC					172.0	163.9			
A				*16.38*[d]	16.43	13.70			
B	*0.1464*[d]	0.1479	0.1449	*0.14715*	0.1486	0.1471		0.1461	
C				*0.14583*	0.1472	0.1455			
Cyanoacetylene									
		$^1\Sigma^+$			^1A			$^1\Delta$	
NC	*1.1585*[e]	1.136	1.175	*(1.16)*[f]	1.145	1.191		1.187	
CC	*1.3786*	1.391	1.387	*1.40*	1.392	1.377		1.311	
CC	*1.2033*	1.185	1.210	*1.25*	1.347	1.388		1.273	
CH	*1.0690*	1.058	1.078	*(1.08)*	1.079	1.081		1.056	
NCC				*(180)*	174.5	173			
CCC				*143*	132.6	129.7			
CCH				*164*	124.7	121.0			
A				*7.005*	4.821	3.084			
B	*0.1517*[g]	0.1536	0.1494	*0.1594*[h]	0.1603	0.1623		0.1512	
C				*0.1559*[h]	0.1576	0.1580			
Cyanogen									
		$^1\Sigma_g^+$			$^3\Sigma_u^+$			$^1\Sigma_u^-$	
NC	*1.1578*[i]	1.134	1.173		1.207	1.264		1.208	1.255
CC	*1.3839*	1.397	1.395		1.320	1.300		1.310	1.296
B	*0.1571*[j]	0.1595	0.1537	*0.1532*[k]	0.1560	0.1496	*0.1538*[j]	0.1568	0.1513
Triacetylene									
		$^1\Sigma_g^+$			$^1\Sigma_u^-$			$^1\Delta_u$	
CH		1.057	1.056		1.056	1.055		1.056	
CC		1.188	1.212		1.224	1.252		1.223	
CC		1.385	1.380		1.318	1.303		1.317	
CC		1.191	1.215		1.272	1.293		1.268	
B	*0.0442*[l]	0.0444	0.0437		0.0444	0.0439		0.0445	
Cyanodiacetylene									
		$^1\Sigma^+$			$^1\Sigma^-$			$^1\Delta$	
NC	*1.161*[m]	1.137	1.162		1.158	1.190		1.159	
CC	*1.364*	1.388	1.382		1.336	1.320		1.335	
CC	*1.222*	1.189	1.213		1.271	1.292		1.268	
CC	*1.362*	1.348	1.379		1.308	1.296		1.309	
CC	*1.209*	1.187	1.211		1.233	1.260		1.232	
CH	*1.057*	1.058	1.057		1.057	1.056		1.057	
B	*0.04441*	0.04471	0.04396		0.04460	0.04410		0.04467	
Dicyanoacetylene									
		$^1\Sigma_g^+$			$^1\Sigma_u^-$			$^1\Delta_u$	
NC	*1.161*[n]	1.136	1.161		1.164	1.196		1.164	
CC	*1.367*	1.390	1.383		1.327	1.312		1.327	
CC	*1.198*	1.186	1.210		1.277	1.295		1.273	
N···N	*6.254*	6.238	6.298		6.259	6.311		6.255	
B_0	*0.04459*[o]			*0.04524*[p]			$<B(^1\Sigma_g^+)$[q]		
B_e	*0.04452*[o]	0.04495	0.04417	*>0.0424*[p]	0.04473	0.04425		0.04482	

[a] Observed (italicized) and calculated rotational constants are B_0 and B_e and refer to the vibrationless level and equilibrium structure, respectively. [b] CAS results are for 12/12. [c] From ref 24. [d] From ref 2. [e] From ref 25. [f] From ref 7. Values in parentheses are assumed. [g] From ref 26. [h] From ref 7. The measured quantity was $\bar{B}_0 = (B_0 + C_0)/2$, the individual values were inferred. [i] From ref 27. [j] From refs 21 and 28. [k] From ref 9. [l] From ref 29. [m] From ref 30. [n] From ref 31. [o] From ref 32. [p] From ref 23. [q] Red-degraded bands, ref 1.

of consequence, e.g. nonlinearity, to the discussion of this and the following paper in this issue. The calculations on unstudied HCCCCCN are included for completeness.

Table 1 gives the energies. Zero-point corrections to the calculated energies were derived from the respective HF- and CIS-calculated ground- and upper-state frequencies (Table 3). They are small (~-0.1 to -0.2 eV). The same corrections were applied to the CAS (CASSCF) and CASPT2 results and are included in the listed values of Table 1. The data cited as "observed" we deem to be well-established. The CIS and CAS(12/12) calculations tend to bracket the observed values, the CIS results being the closer. The CASPT2 method is a considerable improvement on CAS(12/12). The performance of all calculations leaves little doubt that the order of the states is correctly predicted. The observed gross geometry—linear or bent—is predicted correctly throughout. There is a simple way of looking at such geometry changes in HCCH and HCN: namely, that the promotion from a π-bonding to a π-antibonding orbital in the triple bond effectively converts it to a double bond and so should induce the bent geometry of ethylene. With two conjugated triple bonds this tendency has to compete with an alternative, namely, that the C−C single bond joining them

TABLE 3: Vibrational Frequencies (cm^{-1}) in Selected Electronic States

vibn	obs	HF	CAS[a]	vibn	obs	CIS	CAS[a]	vibn	obs	CIS
Diacetylene										
		$^1\Sigma_g^+$				^1A_u			$^1\Delta_u$	
$\sigma_g^+(1)$	3332[b]	3280	3409	$a_g(1)$		3071		$\sigma_g^+(1)$		3283
(2)	2189	2244	2329	(2)		2006		(2)	2105[c]	2096
(3)	872	844	921	(3)		898		(3)	964	912
$\sigma_u^+(4)$	3333	3280	3408	(4)		712		$\sigma_u^+(4)$		3264
(5)	2019	2070	2136	(5)		398		(5)		1421
$\pi_g(6)$	626	795	650	$a_u(6)$		1107		$\pi_g(6)$	428	518
(7)	483	610	545	(7)		208		(7)	288	287
$\pi_u(8)$	628	737	586	$b_g(8)$		482		$\pi_u(8)$		335
(9)	220	251	235	$b_u(9)$		3070		(9)		237
				(10)		1441				
				(11)		439				
				(12)		223				
Cyanoacetylene										
		$^1\Sigma^+$				$^1A''$			$^1\Delta$	
$\sigma^+(1)$	3327[d]	3272	3408	a(1)		2996		$\sigma^+(1)$		3270
(2)	2271	2377	2374	(2)		2197		(2)	2120[f]	2124
(3)	2077	2137	2165	(3)		1547		(3)		1454
(4)	876	838	905	(4)		921		(4)	953	890
$\pi(5)$	663	762	617	(5)	884[d]	806[e]		$\pi(5)$	414	451
(6)	500	552	500	(6)		520		(6)	290	284
(7)	224	245	227	a(7)	160	199		(7)	226	231
				(8)		798				
				(9)		333				
Cyanogen										
		$^1\Sigma_g^+$				$^3\Sigma_u^+$			$^1\Sigma_u^-$	
$\sigma_g^+(1)$	2330[g]	2451	2413		2049[h]	2175	2138		2140[i]	2190
(2)	845	830	885		899	875	918		915	895
$\sigma_u^+(3)$	2158	2276	2193			663[e]	857[e]			1028[e]
$\pi_g(4)$	503	547	521		264	292	310		276	356
$\pi_u(5)$	233	250	241		211	221	223			238
Triacetylene										
		$^1\Sigma_g^+$				$^1\Sigma_u^-$			$^1\Delta_u$	
$\sigma_g^+(1)$	3313[j]	3277	3648			3274				3276
(2)	2201	2307	2390			2120			2163[k]	2133
(3)	2019	2082	2155			1692				1724
(4)	625	584	635			603				607
$\sigma_u^+(5)$	3329	3278	3648			3262				3264
(6)	2129	2173	2263			1604				1669
(7)	1115	1096	1200			1199				1204
$\pi_g(8)$	622	849	700			541			549[e]	564
(9)	491	705	556			431				464
(10)	258	285	259			250			327[e]	265
$\pi_u(11)$	621	773	590			552				575
(12)	443	552	490			448				462
(13)	105	113	107			99				101
Cyanodiacetylene										
		$^1\Sigma^+$				$^1\Sigma^-$			$^1\Delta$	
$\sigma^+(1)$		3273	3645			3261				3263
(2)	2256[l]	2379	2445			2167				2177
(3)		2270	2342			1898				1918
(4)		2119	2191			1543				1606
(5)		1097	1200			1191				1196
(6)		579	630			593				597
$\pi(7)$	642[m]	796	620			560				595
(8)		643	543			469				497
(9)		506	425			428				445
(10)		285	253			247				265
(11)		113	106			91				97
Dicyanoacetylene										
		$^1\Sigma_g^+$				$^1\Sigma_u^-$			$^1\Delta_u$	
$\sigma_g^+(1)$	2297[n]	2413	2493		2115[o]	2211			2192[p]	2224
(2)	2123	2216	2266			1759				1789
(3)	620	572	623		551	577			591	583
$\sigma_u^+(4)$	2245	2359	2409			1754				1798
(5)	1155	1092	1196			1179				1187
$\pi_g(6)$	505	553	437		422	415			458	455
(7)	261	282	246		223	236			260	265
$\pi_u(8)$	472	500	422			424			443	441
(9)	107	114	106		87	91			99	98

[a] CAS results are for 12/12. [b] From ref 33. [c] From ref 19. [d] From ref 7. [e] See text. [f] From ref 8. [g] From refs 21,28. [h] From ref 9. [i] From ref 21. [j] From refs 29 and 34. [k] From ref 3. [m] From ref 35. [n] From ref 36. [p] From ref 32. [q] From ref 23. [r] From ref 1. The 591 and 443 cm^{-1} frequencies, considered uncertain in the reference, are considered to be confirmed.

acquires double bond character, which would tend to favor the linear structure of the cumulenes, e.g. $H_2C{=}C{=}C{=}CH_2$. Thus we do not expect to find any simple intuitive way of rationalizing the pattern of the geometry effects.

The results for the ${}^1\Sigma_u^+$ states are also included in the table. These states are electric-dipole-allowed and long-axis-polarized and are associated with large transition intensities. Their transition energies have been experimentally determined but not their geometries. Only for triacetylene and cyanodiacetylene could global minima be determined for the linear $D_{\infty h}$ structure with the CIS calculations. The other molecules, including dicyanoacetylene, have reduced symmetry in this state, and no global minima nor optimized structures could be obtained. In the reduced point group, there are states of the same symmetry at lower energies and the search for a minimum experiences a cascade through lower states. This applies also to the ${}^1\Pi_u$ state of dicyanoacetylene. These results have important implications for possible vibronic coupling activity. Because of the reduced symmetries of the ${}^1\Sigma_u^+$ and ${}^1\Pi_u$ states of dicyanoacetylene, and as a consequence of the relaxed selection rules governing the vibronic coupling, additional vibrations may be active in inducing intensity from these states. It is this reasoning that will be put forward to account for the presence and intensities of bands that are nominally electric-dipole-forbidden in the 2800 Å system of dicyanoacetylene (see the following paper[23]).

The data given for diacetylene require comment. The origin of the transition to a bent first excited state is confidently placed[2] among a group of weak rotationally resolved bands around 34 912 cm^{-1} (4.33 eV), but there is a further pattern of hot and cold bands, diffuse but more intense, centered around 4.85 eV and attributed speculatively to a linear form of the ${}^1\Sigma_u^-$ molecule.[3] These bands, which were not found in solid Ar,[4] deserve further investigation. For the location of the second excited state there are alternative proposals[3,4,6,19] which are not far apart; we follow the most recent study (Bandy et al.[19]): 40 855 cm^{-1} (5.06 eV). The geometry of this higher state (${}^1\Delta_u$ if linear) is uncertain—indeed Chang and Graham[4] favor marginally a slightly bent state but the arguments are finely balanced, and we give more weight to the absence of the progressions in bending modes that are prominent in the spectrum of cyanoacetylene.[7] Also it is stated by Bandy et al.[19] that their results support the arguments for a linear structure.

Table 2 lists molecular geometries. Insofar as observed data allow, there are no obvious anomalies. Listed too are the rotational constants B (and A, C when applicable), which are inversely proportional to the principal moments of inertia. There are several opportunities to compare these equilibrium constants B_e with observed constants applicable to the zero-point level, B_0, or to some excited vibrational level. The corrections to be applied in comparing the predicted and observed values are small: of the order of 1%, $B_0 - B_e$ being negative for short molecules and positive for longer ones where the contributions of degenerate bending vibrations prevail. It seems that the predicted changes in the B values are in the right direction, and for the molecules that bend, the sensitive value of A, dependent on the moment of inertia about the long molecular axis, is well-handled. For our target molecule, dicyanoacetylene, for which from rotational analyses[23] we find ΔB_0 to be positive, but ΔB_e almost certainly negative, we include the overall molecular lengths (N···N) which increase as expected, and then calculations of B_e which predict little change.

Table 3 gives the vibration frequencies. For the ground states, as with the excitation energies in Table 1, the HF and CAS-(12/12) calculations almost consistently bracket the observed values. There are no exceptions to this statement that we see as being of any consequence. For much more testing comparisons with excited states, there are fewer available, but such as can be made are singularly close, indeed, with respect to the second excited state of NCCCCN, correct to within 2%. A less good comparison is with ν_5 of ${}^1A''$ HCCCN (884 obs, 806 calc), but for DCCCN the comparison is better (682 obs, 688 calc).

We have imposed our own interpretations of two spectra: The ${}^1\Delta_u \leftarrow {}^1\Sigma_g^+$ transition of diacetylene has been measured in the vapor and trapped in argon at 9 K.[3,4,6,19] The most recent study[19] places the forbidden origin at 40 845 cm^{-1}, and bands at +288 and +428 cm^{-1} have been assigned as 6_0^1 and a bending mode or overtone/combination band. We propose that a more appropriate assignment has these bands as 7_0^1 and 6_0^1, respectively. The revised assignment is in much better agreement with the CIS calculated values of 287 and 518 cm^{-1} (Table 3) and compares well with similar assignments for HCCCN.[8] For triacetylene, the ${}^1\Delta_u$ state, the analysis proposed[3] uses $\nu_8' = 324$ cm^{-1} and $2\nu_8' = 546$ cm^{-1}. The spectrum is similar to that of the corresponding transition of NCCCCN which has two vibronic origins. We consider that this spectrum, the features in which are broad, is more reasonably assigned (on an unchanged forbidden origin) in terms of $\nu_8' = 549$ cm^{-1} and $\nu_{10}' = 327$ cm^{-1}, which are the numbers in Table 3.

However, the most plainly anomalous results occur with the so far unobserved antisymmetric CN stretching mode $\sigma_u^+(3)$ of excited cyanogen, for which in two states the predicted values appear to be far too low. By analogy with all the other molecules, one would expect ~1500 cm^{-1}. The predicted values are, for the triplet, 663 (CIS) and 857 cm^{-1} (CAS) and, for the first singlet, 1028 cm^{-1} (CIS). Vibronic coupling, not necessarily otherwise manifest (e.g. by stolen intensity), can be responsible for large changes in specific frequencies.[37,38] To restrict the vibronic interaction matrix elements to acceptable magnitudes[39] (<1500 cm^{-1}), such an explanation would require the ${}^3\Sigma_g^+$ and ${}^1\Sigma_g^-$ states, which we suggest are responsible for the anomalous predicted frequencies, to lie energetically close (within 1 eV) to the states for which the vibration calculations were performed. Preliminary calculations on the energies of higher excited states put the separations at less than 2 eV.

Dicyanoacetylene: Further Vibrational Calculations

We employ the normal coordinates generated in the course of the calculations to make two predictions relating to the electronic spectrum of NCCCCN.

The first relates to the three symmetric stretching modes ν_1, ν_2, ν_3. The predicted changes of bond length on excitation (Table 2) are much the same for the ${}^1\Sigma_u^-$ and ${}^1\Delta_u$ states. The stretching coordinates q_1', q_2', q_3' can be expressed similarly, and when the shift in geometry is projected onto them, it is found that q_1' predominates in the (normalized) result; e.g., geometry shift $= 0.94q_1' + 0.34q_2' + 0.04q_3'$ (${}^1\Sigma_u^-$). Franck–Condon intensities of the first ($\Delta v = 1$) progression members should be approximately proportional to the squares of the above coefficients. Thus ν_1' should be dominant in both transitions and ν_2', ν_3' only marginally detectable, as is the case.[1,23]

Second, we can calculate the realignment of the normal coordinates (Duschinsky rotation) on excitation to ${}^1\Sigma_u^-$. We find seven of the nine coordinates to be little changed, but the coordinates of ν_6 and ν_7 (π_g) undergo a rotation of 22° (i.e. $q_{6/7}' = 0.93q_{6/7}'' \pm 0.38q_{7/6}''$). This rotation explains, via a simple vectorial argument, a marked difference in the intensities of bands 6_0^1, 7_0^1 and (Boltzmann corrected) 6_1^0, 7_1^0 observed in the ${}^1\Sigma_u^- \leftarrow {}^1\Sigma_g^+$ spectrum.[23]

Conclusion

The calculations of geometries and vibration frequencies, whether by the HF/CIS or the CAS method, pass exacting tests of their applicability to the ground and excited states of HCCCCH, HCCCN, and NCCN, and the ground states of HCCCCCCH, HCCCCCN, and NCCCCN. They also fit extraordinarily well six known frequencies of the second excited singlet state of the last molecule. We conclude that they also have strong predictive value in relation to the linear geometry and, especially the bending vibration frequencies of NCCCCN's first excited singlet state, $^1\Sigma_u^-$. Their application to the spectrum is described in the subsequent paper.[23]

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References and Notes

(1) Miller, F. A.; Hannan, R. B. *Spectrochim. Acta* **1958**, *12*, 321.
(2) Hardwick, J. L.; Ramsay, D. A. *Chem. Phys. Lett.* **1977**, *48*, 399.
(3) Haink, H.-J.; Jungen, M. *Chem. Phys. Lett.* **1979**, *61*, 319.
(4) Chang, K. W.; Graham, W. R. M. *J. Mol. Spectrosc.* **1982**, *94*, 69.
(5) Kloster-Jensen, E.; Haink, H.-J.; Christen, H. *Helv. Chim. Acta* **1974**, *57*, 1731.
(6) Lamotte, J.; Binet, C.; Romanet, R. *J. Chim. Phys*. **1977**, *74*, 577.
(7) Job, V. A.; King, G. W. *J. Mol. Spectrosc.* **1966**, *19*, 155.
(8) Job, V. A.; King, G. W. *J. Mol. Spectrosc.* **1966**, *19*, 178.
(9) Callomon, J. H.; Davey, A. B. *Proc. Phys. Soc.* **1963**, *82*, 335.
(10) Ingold, C. K.; King, G. W. *J. Chem. Soc.* **1953**, 2702, 2725.
(11) Herzberg, G.; Innes, K. K. *Can. J. Phys.* **1957**, *35*, 842.
(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98*, Revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
(13) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1985**, *82*, 5053. Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1985**, *115*, 259.
(14) Werner, H.-J. *Mol. Phys*. **1996**, *89*, 645.
(15) Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 135.
(16) Weber, P.; Reimers, J. R. *J. Phys. Chem. A* **1999**, *103*, 9830.
(17) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.
(18) Fischer, G.; Wormell, P. *Chem. Phys.* **2000**, *257*, 1.
(19) Bandy, R. E.; Lakshminarayan, C.; Zwier, T. S. *J. Phys. Chem.* **1992**, *96*, 5337.
(20) Connors, R. E.; Roebber, J. L.; Weiss, K. *J. Chem. Phys.* **1974**, *60*, 5011.
(21) Fish, G. B.; Cartwright, G. D.; Walsh, A, D.; Warsop, P. A. *J. Mol. Spectrosc.* **1972**, *41*, 20.
(22) Smith, A. M.; Schallmoser, G.; Thoma, A.; Bondybey, V. E. *J. Chem. Phys.* **1993**, *98*, 1776.
(23) Fischer, G.; Johnson, G. D.; Ramsay, D. A.; Ross, I. G. *J. Phys. Chem*., the following paper in this issue.
(24) Tanimoto, H.; Kuchitsu, K.; Morino, Y. *Bull. Chem. Soc. Jpn*. **1971**, *44*, 386.
(25) Watson, J. K. G.; Roytburg, A.; Ulrich, W. *J. Mol. Spectrosc*. **1999**, *196*, 102.
(26) Mallinson, P. D.; de Zafra, R. L. *Mol. Phys*. **1978**, *36*, 827.
(27) Botschwina, P.; Flugge, J. *Chem. Phys. Lett*. **1991**, *180*, 589.
(28) Craine, G. D.; Thompson, H. W. *Trans. Faraday Soc*. **1953**, *49*, 1273.
(29) McNaughton, D.; Bruget, D. N. *J. Mol. Spectrosc*. **1991**, *150*, 620.
(30) Alexander, A. J.; Kroto, H. W.; Walton, D. R. M. *J. Mol. Spectrosc*. **1976**, *62*, 175.
(31) Brown, K. W.; Nibler, J. W.; Hedberg, K.; Hedberg, L. *J. Phys. Chem*. **1989**, *93*, 5679.
(32) Winther, F.; Schönhoff, M. *J. Mol. Spectrosc*. **1997**, *186*, 54.
(33) Owen, N. L.; Smith, C. H.; Williams, G. A. *J. Mol. Struct*. **1987**, *161*, 33.
(34) Bjarnov, E.; Christensen, D. H.; Nielsen, O. F.; Augdahl, E.; Kloster-Jensen, E.; Rogstad, A. *Spectrochim. Acta A* **1974**, *30*, 1255.
(35) Yamada, K. M. T.; Winnewisser, G. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1985**, *40*, 476.
(36) Haas, S.; Winnewisser, G.; Yamada, K. M. T. *Can. J. Phys.* **1994**, *72*, 1165.
(37) Fischer, G. *Vibronic Coupling*; Academic Press: London, 1984.
(38) Innes, K. K.; Ross, I. G.; Moomaw, W. R. *J. Mol. Spectrosc.* **1988**, *132*, 492.
(39) Hochstrasser, R. M.; Marzzacco, C. *J. Chem. Phys.* **1968**, *49*, 971.