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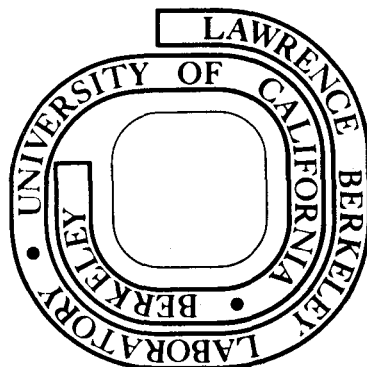1975-04-01

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CONFIRMATION OF THE DISCREPANCY BETWEEN THEORY AND EXPERIMENT FOR THE B̃ ^{1}A$''$ STATE OF HCN

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ABSTRACT

Ab initio calculations have been carried out on the first and second ^{1}A$''$ states of HCN using relatively large and flexible basis sets. The predicted geometries have been compared with the experimental results of Herzberg and Innes and with earlier calculations on HCN. These calculations concur with earlier theoretical results and the Walsh diagram prediction that Herzberg and Innes' assignment of the B̃ ^{1}A$''$ state with bond angle 114.5° is incorrect.

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In a recent publication[1] we reported a new theoretical

approach for the treatment of excited electronic states and

used this method to study the geometries of the ground state

and twelve excited states of HCN. The results were generally

consistent with qualitative predictions based on Walsh's

orbital binding energy diagram for HAB molecules.[2] Herzberg

and Innes[3,4] have experimentally studied three of the excited

states of HCN, providing geometry determinations and assigning

electron configurations. However, there appears to be a

serious discrepancy between the theoretical[1,2] and experimental[3,4]

molecular structures for the second $^1A''$ state of HCN. Herzberg

and Innes identified this state as the $\tilde{B}$ $^1A''$ state, with a bond

angle of 114.5° and assigned the configuration $5a'^2 6a' 1a''^2 2a''$.

However Walsh's rules[2] predict a linear or slightly bent state

for this configuration; and the ab initio study[1] concurred, giving

a bond angle of 164.4° for the second $^1A''$ state.

The primary goal of the present research was to perform a

more exhaustive study of the second $^1A''$ state in order to help

clarify this inconsistency. In particular, the most serious

weakness of our earlier study[1] was the use of a double zeta basis

set. Here the importance of both polarization functions and

diffuse (or Rydberg) functions has been carefully explored.

The first two $^1A''$ states are known from our previous study

to have the predominant configurations $5a'^2 6a'^2 1a'' 7a'$ and

$5a'^2 6a' 1a''^2 2a''$ respectively. Separate SCF calculations

should be meaningful for both of these configurations (although

they are of the same symmetry) because their orbital symmetries
are different. The virtual orbital to be occupied in the first
configuration is $7a'$ while it is $2a''$ in the second. A flexible
double zeta plus polarization basis set was initially adopted.
Aside from the polarization functions, this is Dunning's[5]
contraction of Huzinaga's[6] primitive gaussian basis set. The
final basis set is shown in Table A, contained in our complete
report[7] of this research.

The geometries of the two excited states were obtained by
minimizing the total energy with respect to the two bond
distances r(HC) and R(CN) and the bond angle θ(HCN). A guess
was made at (r_g, R_g, θ_g) and calculations were carried out at
this point and six others

$$(r_g + 0.05\overset{o}{A}, R_g, \theta_g)$$

$$(r_g - 0.05\overset{o}{A}, R_g, \theta_g)$$

$$(r_g, R_g + 0.05\overset{o}{A}, \theta_g)$$

$$(r_g, R_g - 0.05\overset{o}{A}, \theta_g)$$

$$(r_g, R_g, \theta_g + 5°)$$

$$(r_g, R_g, \theta_g - 5°)$$

If (r_g, R_g, θ_g) yielded an energy lower than the other six then
the equilibrium geometry was obtained by fitting these seven
points to the simple analytic form $E = a + b(r-r_e)^2 + c(R-R_e)^2 +
d(\theta-\theta_e)^2$. Otherwise, the lowest computed energy was used to
define a new geometry (r_g, R_g, θ_g) and the process repeated.

Table I gives the optimized parameters for the ground
state[8] and the first two $^1A''$ states of HCN with this basis

set, as well as the experimental geometries of Herzberg and

Innes. The ground state and the first excited state are in

good agreement with Herzberg's determinations, as was the case

in our previous study, for which a summary is given in Table C.

The SCF results show slightly shorter bond lengths than experi-

ment; this is typical[9] of SCF calculations. The second $^1A''$

state however is predicted to be linear, which is essentially

in agreement with Walsh's rules, which predict it to be a

slightly bent state.[1] Our previous calculations showed a

slight mixing of the two configurations for this state. It

was the mixing of the $5a'^2 6a'^2 1a'' 7a'$ configuration with

the $5a'^2 6a' 1a''^2 2a''$ configuration to which we attributed

the slightly bent 164° character of this state. Thus it seems

likely that configuration interaction (CI) calculations with

this large basis would yield a bond angle near 164° for the

$2\ ^1A''$ state.

The observed $\tilde{B}\ ^1A''$ state is sufficiently high (6.8 eV)

in energy, that one cannot completely rule out the possibility

of a significant amount of Rydberg character. Were this the

case, of course, both the Walsh and ab initio theoretical pre-

dictions would be inappropriate, since they assume a valence-like

description of the second $^1A''$ state. For this reason a further

extension of the basis set was carried out to include Rydberg

functions on carbon and nitrogen. The Rydberg functions, shown

in Table B, were obtained by adding diffuse even tempered[10]

functions to Dunning's basis set. This final larger basis set

was employed (a) at the optimized geometry for the double zeta plus polarization basis set and (b) at the experimental geometry[4] for the $\tilde{B}\ ^1A''$ state. The results are summarized in Table II. There is an energy lowering of approximately 0.003 hartrees for both the first and second $^1A''$ states upon extension of the basis set. Approximately the same change in the energy is observed for the calculation at Herzberg's geometry. It seems clear that no further extension of the basis set will cause the dramatic shift in energy needed in order to obtain a 2 $^1A''$ state of lesser bond angle. An examination of the coefficients of the different gaussian functions in the orbitals shows that the second $^1A''$ state is not a Rydberg state.

The energy separation between the ground state and the first $^1A''$ state is 6.48 eV experimentally and 5.50 eV in the present study. Errors of this magnitude are to be expected[9] from the Hartree-Fock level of theory: The separation between the 1 $^1A''$ and the 2 $^1A''$ states is 0.94 eV, in comparison with 1.04 eV from our previous calculations and 0.29 eV from Herzberg and Innes. Hence the two theoretical treatments are in essential agreement concerning both the structure of the 2 $^1A''$ state and its position relative to the $\tilde{A}\ ^1A''$ state.

In conclusion, it seems very difficult to reconcile the present theoretical predictions with Herzberg and Innes' assignment of a 114.5° bond angle to the $\tilde{B}\ ^1A''$ state of HCN.

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TABLE I. Geometries predicted by SCF calculations with a double zeta plus

polarization basis set. Experimental quantities in parentheses

refer to the lowest vibrational level ($v_1 = v_2 = v_3 = 0$) and

are taken from Herzberg.[4]

	r_e(HC) Å	R_e(CN) Å	θ_e(HCN) deg.	Configuration
$^1\Sigma^+ \; ^1A'$	1.062 (1.064)	1.136 (1.156)	180 (180)	$5a'^2 \, 6a'^2 \, 1a''^2$
$^1A''$	1.104 (1.14)	1.285 (1.297)	124.5 (125.0)	$5a'^2 \, 6a'^2 \, 1a'' \, 7a'$
$2\,^1A''$	1.060 (1.14)	1.290 (1.334)	180 (114.5)	$5a'^2 \, 6a' \, 1a''^2 \, 2a''$

TABLE II. Results of single configuration SCF calculations for HCN. For the $2\ ^1A''$ state, the total energy calculated at the theoretical equilibrium geometry is followed (in parentheses) by the energy calculated at the Herzberg-Innes experimental geometry.[4] Energies are given in hartrees.

Configuration		Double zeta plus polarization	Double zeta plus polarization plus Rydberg functions
$^1\Sigma^+$ $^1A'$	$5a'^2\ 6a'^2\ 1a''^2$	-92.88972[a]	
$^1A''$	$5a'^2\ 6a'^2\ 1a''\ 7a'$	-92.68754	-92.69068
$2\ ^1A''$	$5a'^2\ 6a'\ 1a''^2\ 2a''$	$-92.65310\ (-92.59231)$	$-93.65662\ (-92.59529)$

[a] Reference 8.

TABLE A. Double zeta plus polarization basis set for HCN

Center	Type	Exponent	Coefficient
H	s	19.2406	0.032828
		2.8992	0.231208
		0.6534	0.817238
	s	0.1776	1.0
	p	1.0	1.0
C	s	4232.61	0.002029
		634.882	0.015535
		146.097	0.075411
		42.4974	0.257121
		14.1892	0.596555
		1.9666	0.242517
	s	5.1477	1.0
	s	0.4962	1.0
	s	0.1533	1.0
	p	18.1557	0.018534
		3.9864	0.115442
		1.1429	0.386206
		0.3594	0.640089
	p	0.1146	1.0
	d	0.75	1.0
N	s	5909.44	0.002004
		887.451	0.015310
		204.749	0.074293
		59.8376	0.253364
		19.9981	0.600576
		2.6860	0.245111

TABLE A. Continued

	s	7.1927	1.0
	s	0.7000	1.0
	s	0.2133	1.0
	p	26.786	0.018257
		5.9564	0.116407
		1.7074	0.390111
		0.5314	0.637221
	p	0.1654	1.0
	d	0.8	1.0

TABLE B. Rydberg functions

C	s	0.0470	1.0
	p	0.0370	1.0
N	s	0.0650	1.0
	p	0.0510	1.0

TABLE C. Summary of previous HCN data[a]

Symmetry	T_e(eV)	r_e(HC) Å	R_e(CN) Å	θ_e(HCN)	Most important configuration	Coefficient
$^1\Sigma^+$ $^1A'$	0.00	1.055	1.180	180	$5a'^2\ 6a'^2\ 1a''^2$	0.9684
$^1A''$	6.48	1.096	1.318	127.2	$5a'^2\ 6a'^2\ 1a''\ 7a'$	0.9714
$2\ ^1A'$	7.52	1.076	1.316	164.4	$5a'^2\ 6a'\ 1a''^2\ 2a''$	0.8209
					$5a'^2\ 6a'^2\ 1a''\ 7a'$	0.5372

[a] Reference 1.