Submitted to Journal of Chemical Physics

LBL-1983
Preprint c.2

GEOMETRIES OF THE EXCITED ELECTRONIC STATES OF HCN

RECEIVED
LAWRENCE
RADIATION LABORATORY

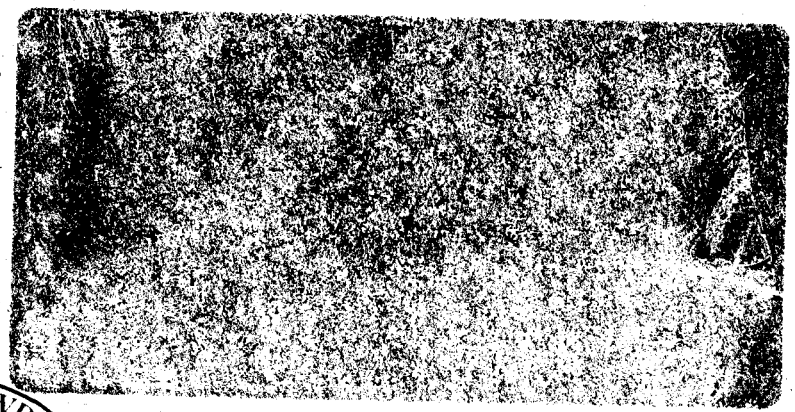
NOV 16 1973

LIBRARY AND
DOCUMENTS SECTION

Gretchen M. Schwenzer, Stephen V. O'Neil,
Henry F. Schaefer III, Craig P. Baskin
and Charles F. Bender

September 1973

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48



LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

LBL-1983
c.2

3ta.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

GEOMETRIES OF THE EXCITED ELECTRONIC STATES OF HCN*

Gretchen M. Schwenzer, Stephen V. O'Neil†, and Henry F. Schaefer III††

Department of Chemistry and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

and

Craig P. Baskin‡ and Charles F. Bender‡‡

Lawrence Livermore Laboratory
University of California
Livermore, California 94550

ABSTRACT

Ab initio quantum mechanical electronic structure calculations have been carried out for the ground state and 12 low-lying (< 10 eV) excited states of HCN. A contracted gaussian basis set of essentially double zeta quality was employed. A new theoretical approach, which should be widely applicable, was applied to the excited electronic states. First one selects a physically meaningful set of orbitals, which, hopefully, will be about equally suitable for all the electronic states of interest. After selecting a single configuration to described each electronic state, configuration interaction is performed including all configurations differing by one orbital from any of the selected reference configurations. The method appears to be one of the simplest capable of treating several states of the same symmetry. The predicted geometries have been compared with the experimental results of Herzberg and Innes, as well as the appropriate Walsh diagram. The *ab initio* calculations and the Walsh diagram concur that Herzberg and Innes's assignment of the $\tilde{B}\,^1A''$ state, with bond

angle 114.5°, is incorrect. Although the theoretical predictions are in several cases at variance with the Walsh diagram, these differences can in most cases be justified in terms of a breakdown of the single configuration picture of electronic structure. One modification of Walsh's diagram is suggested, a change in the shape of the 5a' orbital binding energy. Without this modification, the Walsh prediction is in serious disagreement with Herzberg and Innes's 141° bond angle for the $\tilde{C}\ ^1A'$ state. The present theoretical study predicts a bond angle of 141.2° for the third $^1A'$ electronic state of HCN.

THEORETICAL MOTIVATION AND APPROACH

It is now well established[1,2] that non-empirical self-consistent-field theory is capable of yielding reliable predictions of the geometries of molecules in their electronic ground states. In principle, these same methods should yield accurate geometry predictions for most excited states. An obvious exception would be any excited electronic state which is not well described by a single electron configuration.

Unfortunately, single configuration self-consistent-field (SCF) procedures are not as well defined for the first and higher excited states of a particular symmetry. This is because such excited state single configuration SCF wave functions do not, in general,[3] yield variational energies. In general, multiconfiguration wave functions are required to provide a variational description of excited states of a single symmetry.[4]

In recent years we have used a somewhat unconventional method for obtaining SCF wave functions for the lowest state of a particular symmetry.[5] The method exploits Brillouin's Theorem,[6] which states that for a closed shell system, the SCF wave function has zero matrix elements with all configurations ("single excitations") differing by one orbital from the SCF configuration. The procedure is as follows: one makes any plausible guess for the SCF orbitals and then carries out a configuration interaction (CI) calculation including the SCF configuration plus all single excitations. The first-order density matrix from this wave function is then diagonalized to yield a new set of orbitals, the natural orbitals.[7] Using the new set of orbitals, the CI calculation is repeated. Continued use of the iterative natural orbital procedure[8] on this particular type of wave function results in a CI wave function in which the

coefficient of the SCF configuration is 1.0 and the coefficients of all other configurations are 0.0. By satisfying Brillouin's theorem, one has obtained the true SCF wave function within the chosen basis set.

It is important to point out that the above procedure is equally applicable to open shell SCF wave functions, even though it is often stated that Brillouin's theorem holds only for closed shell SCF wave functions. In fact, Brillouin's theorem is applicable in a restricted sense[1] to open shell systems. Specifically, an open-shell SCF wave function will have zero matrix elements with all singly-excited configurations which retain the open shell structure (e.g. the spin coupling) of the SCF wave function. Consider, for example, the SCF wave function for the lowest $^3\Pi$ state of CO

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^4\ (5\sigma\ 2\pi\ {}^3\Pi) \tag{1}$$

where the triplet coupling of the unfilled 5σ and 2π orbitals has been indicated. If one has obtained the correct SCF wave function for the $^3\Pi$ state then the following single excitations will have vanishing matrix elements with ψ_{SCF}:

$$(1\sigma\ n\sigma\ {}^1\Sigma^+)\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^4\ (5\sigma\ 2\pi\ {}^3\Pi) \tag{2}$$

$$1\sigma^2\ (2\sigma\ n\sigma\ {}^1\Sigma^+)\ 3\sigma^2\ 4\sigma^2\ 1\pi^4\ (5\sigma\ 2\pi\ {}^3\Pi) \tag{3}$$

$$1\sigma^2\ 2\sigma^2\ (3\sigma\ n\sigma\ {}^1\Sigma^+)\ 4\sigma^2\ 1\pi^4\ (5\sigma\ 2\pi\ {}^3\Pi) \tag{4}$$

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ (4\sigma\ n\sigma\ {}^1\Sigma^+)\ 1\pi^4\ (5\sigma\ 2\pi\ {}^3\Pi) \tag{5}$$

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ (1\pi^3\ m\pi\ {}^1\Sigma^+)\ (5\sigma\ 2\pi\ {}^3\Pi) \tag{6}$$

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^4\ (n\sigma\ 2\pi\ {}^3\Pi) \tag{7}$$

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^4\ (5\sigma\ m\pi\ {}^3\Pi) \tag{8}$$

where $n\sigma$ represents 6σ, 7σ, 8σ, 9σ, ..., and $m\pi$ represents 3π, 4π, 5π, 6π, ... Note that the ${}^3\Pi$ coupling of the last two orbitals is retained in all the above configurations. By analogy with the closed-shell case, then, the iterative natural orbital procedure applied to a wave function consisting of all configurations (1) through (8) will yield the true SCF wave function for the lowest ${}^3\Pi$ state of CO.

With the above discussion in mind, let us return to the problem of obtaining SCF wave functions for more than one electronic state of a particular symmetry. Assume that from simple molecular orbital theory one has a good idea of the electron configurations which correspond to each state of interest. Then, a reasonable course of action might be to construct a CI wave function including all appropriate (as indicated in the previous paragraph) single excitations with respect to all the electron configurations we desire to describe properly. This wave function should be of single configuration SCF quality for all the electronic states we wish to describe. Actually, the wave functions obtained should be of better than SCF quality, since all single excitations have been included with respect to several reference configurations. Therefore, some double excitations will be included with respect to any one particular SCF configuration.

The procedure described would appear to be a relatively simple but presumably reliable method for the prediction of the geometries of the excited states of molecules. In the present research we have applied this method to the valence excited states of HCN.

QUALITATIVE VIEW OF THE LOW-LYING EXCITED STATES OF HCN

HCN is isoelectronic with two simpler diatomic molecules, N_2 and CO, from which we begin our qualitative discussion. It is somewhat easier to make analogy between HCN and CO, since both molecules (unlike N_2) lack a center of inversion. In addition, somewhat more information, both theoretical[9] and experimental,[10] is available for CO than for N_2.

The electronic ground state of CO is well described near its equilibrium geometry by the electron configuration

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma^2\ 1\pi^4 \qquad {}^1\Sigma^+ \tag{9}$$

The only low-lying unoccupied valence orbital is 2π and the molecular excited states arise from the electron configurations

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma\ 1\pi^4\ 2\pi \qquad {}^3\Pi,\ {}^1\Pi \tag{10}$$

and

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma^2\ 1\pi^3\ 2\pi$$

$$ {}^3\Delta,\ {}^1\Delta,\ {}^3\Sigma^-,\ {}^1\Sigma^-,\ {}^3\Sigma^+,\ {}^1\Sigma^+ \tag{11}$$

Except for ${}^1\Sigma^+$, all eight of these excited states have been predicted theoretically[9] and observed experimentally.[10] If isoelectronic arguments are appropriate, then one would expect all of these states to have counterparts in the HCN molecule.

For general geometry, the HCN molecule has only a plane of symmetry and therefore belongs to the C_s point group. The relation between the $C_{\infty v}$ and C_s

orbitals is: $1\sigma \longrightarrow 1a'$, $2\sigma \longrightarrow 2a'$, $3\sigma \longrightarrow 3a'$, $4\sigma \longrightarrow 4a'$, $5\sigma \longrightarrow 5a'$, $1\pi \longrightarrow 6a'$ and $1a''$, $2\pi \longrightarrow 7a'$ and $2a''$. Thus, the C_s configurations corresponding to (10) are

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'\ 6a'^2\ 1a''^2\ 7a' \qquad {}^3A',\ {}^1A' \tag{12}$$

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'\ 6a'^2\ 1a''^2\ 2a'' \qquad {}^3A'',\ {}^1A'' \tag{13}$$

In the same way the $C_{\infty v}$ electron configuration (11) becomes, for C_s symmetry, four distinct electron configurations.

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'^2\ 1a''\ 7a' \qquad {}^3A'',\ {}^1A'' \tag{14}$$

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'^2\ 1a''\ 2a'' \qquad {}^3A',\ {}^1A' \tag{15}$$

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'\ 1a''^2\ 7a' \qquad {}^3A',\ {}^1A' \tag{16}$$

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'\ 1a''^2\ 2a'' \qquad {}^3A'',\ {}^1A'' \tag{17}$$

In this way one can combine the available information about CO with simple molecular orbital theory to predict the low-lying excited states of HCN: ${}^1A'$ (3, or 2 excluding the repulsive[9] ${}^1\Sigma^+$ state of CO), ${}^3A'$ (3), ${}^1A''$ (3), and ${}^3A''$ (3).

BOND ANGLE PREDICTIONS FROM WALSH'S RULES; COMPARISON WITH EXPERIMENT

Perhaps the earliest attempt to predict the bond angles of the excited states of HCN was that of Walsh[11] in 1953. The one-electron energy diagram he constructed is reproduced in Fig. 1. By assuming that the total energy of any electronic state is just the sum of the one-electron energies, one can qualitatively predict the ordering and bond angles of the HCN excited states. For the electron configurations discussed earlier, these predictions are summarized in Table I.

The predictions of Table I are based in part on Walsh's belief[11] that "HAB molecules containing 10 or less valency electrons will be linear in their ground states". Thus, replacing any ground state orbital by the 2a" orbital will yield a linear excited state. In this regard, note that the 1a" ⟶ 2a" states should have essentially the same bending force constant as the HCN ground state, since the 1a" and 2a" one-electron energies are parallel as a function of bond angle in Fig. 1.

It is important to point out that Walsh's predictions were made in 1953, prior to the availability of any information concerning the HCN excited state bond angles. In 1957, the spectroscopic work of Herzberg and Innes[12] established the existence of three bent excited states of HCN. The lowest (T_o = 6.48 eV) of these is the $\tilde{A}\ ^1A''$ state, with bond angle 125°, and Herzberg and Innes assign this state to electron configuration (14), $5a'^2\ 6a'^2\ 1a''\ 7a'$. The $\tilde{B}\ ^1A''$ lies at 6.77 eV with bond angle 114.5 and is assigned to electron configuration (17), $5a'^2\ 6a'\ 1a''^2\ 2a''$. Finally Herzberg and Innes observed the $\tilde{C}\ ^1A'$ state at 8.14 eV and bond angle 141°, and assigned it to electron configuration (12), $5a'\ 6a'^2\ 1a''^2\ 7a'$.

For the $\tilde{A}$ state of Herzberg and Innes, their findings are completely consistent with Walsh's diagram, Fig. 1, and the corresponding prediction in Table I. For the $\tilde{B}$ state (bond angle 114.5°), however, there is a serious and inescapable conflict between the experimental assignment ($^1A''$) and the Walsh diagram. As Table I indicates, the Walsh argument states that there is only a single significantly bent $^1A''$ state of HCN, and that the other two $^1A''$ valence states are nearly linear and linear. In addition, the assignment of the $5a'\ 6a'^2\ 1a''^2\ 7a'$ configuration to the $\tilde{C}\ ^1A'$ state is not completely consistent with Walsh's diagram. From the Walsh diagram, this configuration should yield a strongly bent state, not one with bond angle 141°.

One of the primary goals of the present research then, is to attempt to resolve and understand the discrepancies between Walsh's diagram and experiment for the bond angles of the $\tilde{B}$ and $\tilde{C}$ states. In this regard we note that Absar and McEwen[13] have attempted to rationalize the experimental results by constructing a new Walsh-like diagram for HCN. In addition, we would hope to predict the bond angles of the eight expected excited states of HCN which have not been observed experimentally.

Finally, there is considerable interest in the HNC isomer, which has been isolated in a noble gas matrix,[14] and perhaps observed in intersteller space.[15] This brings to mind the possibility of the existence of excited electronic states of HNC. In addition, an electronic state with equilibrium geometry intermediate between that of HCN and that of HNC might provide a mechanism for isomerization. At present we can state only that preliminary results imply many similarities between HNC and HCN, but no apparent electronic pathway for facile interconversion. A later paper will deal with the excited states of HNC in detail.

DETAILS OF THE THEORETICAL APPROACH

The basis set chosen for the present work consisted of contracted gaussian functions centered on each nucleus. For hydrogen, a 3s contraction of Huzinaga's 5s primitive gaussian basis[16] was used. For C and N, Dunning's 4s 2p contractions[17] of Huzinaga's 9s 5p basis sets were used. For general geometry, then, the basis consists of 19a' and 4a" basis functions.

Perhaps the most serious difficulty in calculations of the present type concerns the choice of procedure for obtaining the molecular orbitals. Since the use of the iterative natural orbital procedure for each electronic state would remove the calculations from the "simple" classification, we desired a set of molecular orbitals that would be about equally appropriate for each electronic state. Note that the type of CI we have in mind depends only on the form of the 1a' - 7a' and 1a" - 2a" orbitals, which are occupied in the single configuration wave functions (12) - (17), which we expect will provide a good qualitative description of the electronic states of interest.

The first approach taken was to obtain the molecular orbitals from SCF calculations on the $^5A'$ state

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'\ 1a''\ 7a'\ 2a'' \qquad (18)$$

This procedure is analogous to that used successfully by Fougere and Nesbet[18] for the excited electronic states of C_2 at large internuclear separation. Unfortunately, this method did not work outstandingly well for HCN. Specifically, using these valence orbitals, some of the states we expected to be well described by a single configuration were in fact described as linear combinations of several configurations.

A more adequate procedure involved the use of the SCF orbitals 1a' - 6a' and 1a" from the ground $^1A'$ state SCF wave function. The additional orbitals 7a' - 19a' and 2a" - 4a" were required (by a previously described method[19]) to describe the single particle states of the HCN^+ ion. This was brought about by doing a CI including the configurations

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 1a''^2\ na' \qquad n = 7 - 19 \tag{19}$$

and a second CI including

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'^2\ ma'' \qquad m = 2 - 4 \tag{20}$$

By transforming the virtual orbital space according to the eigenvectors of the above two CI problems, one obtains orbitals optimum to HCN^+, and reasonable for HCN. These orbitals yielded improved total energies for the pertinent excited states of HCN, and, in addition, allowed a much simplified (fewer important configurations) picture of the electronic structures.

As outlined in the theoretical introduction, for each of the four symmetries, a CI was performed including all single excitations (retaining the open-shell spin coupling) with respect to each reference configuration expected to describe one of the excited states. For $^1A'$, in addition to the three reference configurations given in Table I, all single excitations were included with respect to the ground state configuration $5a'^2\ 6a'^2\ 1a''^2$. Following this approach, we find 322 configurations for $^1A'$, 270 for $^3A'$, and 266 for both $^1A''$ and $^3A''$.

GEOMETRY SEARCH PROCEDURE

The predicted geometry of each electronic state was obtained by minimizing the total energy with respect to the two bond distances r (HC) and R (CN) and the bond angle θ (HCN). After some preliminary calculations designed to roughly determine the location of the minima, the following procedure was used. First a guess (r_g, R_g, θ_g) was made of the equilibrium geometry. Then calculations were carried out for that point plus the six others

(r_g + 0.1 bohr, R_g, θ_g)

(r_g - 0.1 bohr, R_g, θ_g)

(r_g, R_g + 0.1 bohr, θ_g)

(r_g, R_g - 0.1 bohr, θ_g)

(r_g, R_g, θ_g + 5°)

(r_g, R_g, θ_g - 5°)

If the initial geometry yields a total energy lower than the other six (which form an octahedral structure about the guessed geometry), then the true equilibrium geometry must be quite close to (r_g, R_g, θ_g). The seven energies are fit to the simple analytic form

$$E = a + b(r - r_e)^2 + c(R - R_e)^2 + d(\theta - \theta_e)^2$$

which determines the equilibrium geometry (r_e, R_e, θ_e). As a check, a final calculation was run at the predicted equilibrium and a least squares fit of

all eight energies made to the seven-parameter form. In most cases the check geometry agreed with that obtained from the seven-point fit to within 0.001 Å for each bond distance and 0.1° for the bond angle. The geometries reported here are those obtained the (exact) seven-point fit to the seven parameter form.

In most cases the first seven geometries chosen did not bracket a minimum. In that case the geometry corresponding to the lowest calculated energy was taken as the new guessed geometry (r_g, R_g, θ_g) and the entire procedure repeated. Although this procedure is certainly not the most efficient one imaginable, it is essentially foolproof, allowing all three geometrical parameters to adjust simultaneously.

RESULTS

Our results for the singlet and triplet electronic states of HCN are summarized in Table II and III, respectively. As noted in the caption, however, the excitation energies T_e have been semi-empirically adjusted. The motivation for this adjustment may be seen by comparing the $X\ ^1\Sigma^+$ minimum energy, -92.9580 hartrees, with that for the $\tilde{A}\ ^1A''$ state, -92.6397 hartrees. The difference, 0.3183 hartrees = 8.66 eV, is more than 2 eV greater than the experimental[20] value, T_o = 6.48. This large error is due to the calculations being predisposed in favor of the ground state. The most obvious reason for this predisposition is the fact that for <u>all</u> electronic states the 1σ - 5σ and 1π orbitals are the SCF orbitals for the $X\ ^1\Sigma^+$ state. Therefore, all the T_e values have been obtained by subtracting the difference (8.66 - 6.48) = 2.18 eV from the <u>ab initio</u> T_e values.

We now proceed to a comparison of the theoretical, experimental,[20] and Walsh predictions of the excited state HCN geometries. For the first excited singlet state ($\tilde{A}\ ^1A''$), the three bond angles are in essential agreement, the <u>ab initio</u> result differing by 2.2° from experiment. A somewhat similar, but less complete, CI calculation by Ditchfield, Del Bene, and Pople[21] yielded a bond angle of 127.8°. The CI wave function is dominated by the $5a'^2\ 6a'^2\ 1a''\ 7a'$ configuration (coefficient 0.9714), and Walsh's diagram may be used to predict this state as the lowest excited singlet, with a distinctly bent structure. The CH and CN bond distances differ from experiment by 0.044 and 0.021 Å, the former discrepancy being somewhat larger than expected. Note that for the ground state the CH and CN bond distance errors are 0.009 and 0.024 Å.

According to Herzberg and Innes,[12] the second excited singlet state of HCN is the $\tilde{B}\ ^1A''$ state, with bond angle 114.5°. As noted earlier, this result

is not consistent with Walsh's diagram. Nor is the result of Herzberg and Innes consistent with the present theoretical study. We predict the second $^1A''$ state to have bond angle 164.4° and the third to be linear. And these two states are fairly well described by exactly the configurations deduced from Walsh's diagram, $5a'^2\ 6a'\ 1a''^2\ 2a''$ and $5a'\ 6a'^2\ 1a''^2\ 2a''$. We conclude that the assignment of the second excited singlet state of HCN as a $^1A''$ state is incorrect. Note, in this regard, that Johns, Shurvell, and Tyler[22] found no analogue of the $\tilde{B}\ ^1A''$ state in their study of the related HCP molecule.

It is curious that our calculations predict to first excited $^1A'$ state to lie at 6.78 eV, while the state Herzberg and Innes refer to as $\tilde{B}\ ^1A''$ lies at 6.77 eV. The angle of the calculated $2\ ^1A'$ state is 124.9°, the smallest of any of the singlet states of HCN. Note, however, that there is still a 10.4° discrepancy between our $2\ ^1A'$ state and the state labeled $\tilde{B}\ ^1A''$ by Herzberg and Innes. Our result is consistent with the conclusion drawn from Walsh's diagram (see Table I) that the $2\ ^1A'$ state should have a smaller bond angle than the lowest $^1A''$ state. However, Walsh's diagram would also be consistent with a bond angle of 114.5° for the $2\ ^1A'$ state.

Actually, Table II seems to suggest that Walsh's rules cannot be applied in a simple manner to the $2\ ^1A'$ state. This is because the single configuration $5a'^2\ 6a'\ 1a''^2\ 7a'$ does not dominate the computed wave function at the equilibrium geometry. In fact, this configuration amounts to only $(0.7024)^2 \sim 49.3\%$ of the CI wave function. It is particularly worth noting that the other two configurations with coefficient greater than 1/3, $5a'\ 6a'^2\ 1a''^2\ 7a'$ and $5a'^2\ 6a'^2\ 1a''\ 2a''$, would have opposite effects on the predicted bond angle. However, we must be rather cautious here in our criticism of the single

configuration approximation, since our remarks pertain only to calculations carried out with a set of molecular orbitals suited to the ground electronic state. A set of orbitals expressly tailored for the 2 $^1A'$ state might yield a simpler description of the CI wave function. This intuitive feeling is strengthened by the fact (see Table III) that the 1 $^3A'$ state is very well described by the $5a'^2\ 6a'\ 1a''^2\ 7a'$ configuration.

In order to test this intuitive feeling, additional analysis of the 2 $^1A'$ state wave function was performed. Specifically, the natural orbitals were obtained by diagonalizing the first order density matrix.[7] Then the CI was repeated using the 2 $^1A'$ natural orbitals. The coefficient of the $6a' \longrightarrow 7a'$ configuration was 0.8794, or 77.3% of the wave function. Thus, the 2 $^1A'$ state is rather well described by a single configuration in terms of its own natural orbitals. The other major effect of the natural orbital transformation is to lessen the coefficient of the $5a' \longrightarrow 7a'$ configuration from 0.5123 to 0.0323. The $1a'' \longrightarrow 2a''$ configuration does remain important, with coefficient 0.3807. Finally, the natural orbital occupation numbers for the 2 $^1A'$ state were ... $4a'^{1.995}\ 5a'^{1.966}\ 6a'^{1.178}\ 7a'^{0.849}\ 1a''^{1.839}\ 2a''^{0.160}$.

Our discrepancy with Herzberg and Innes over their $\tilde{B}\ ^1A''$ state (and the resulting uncertainty as to whether this state is in fact the 2 $^1A'$ state) makes it difficult to compare our results with their third HCN excited state, $\tilde{C}\ ^1A'$. The fact that this state lies at 8.13 eV and has a 141° bond angle inclines us to believe that the $\tilde{C}\ ^1A'$ is our 3 $^1A'$ state, which has T_e = 7.85 eV and bond angle 141.2°. This is another case where there is no dominant configuration in our wave function, although $5a'\ 6a'^2\ 1a''^2\ 7a'$ corresponds to 55.4% of the wave function. Note that this configuration is the one assigned

by Herzberg.[20] However, from Walsh's diagram, this configuration should yield a strongly bent electronic state. The second most important configuration, however, tends to make the state linear in a Walsh picture. Our general feeling is that Walsh's rules are not invalid, but rather inapplicable, in situations of this kind.

The three remaining excited singlet states are all either linear or nearly linear, the 2 $^1A''$ state having bond angle 164.4°. The latter result agrees very nicely with our Walsh diagram prediction (Table I) that this state should be slightly bent. In addition, the 3 $^1A''$ and 4 $^1A'$ states are correctly predicted by the Walsh diagram to be linear.

To our knowledge, nothing is known experimentally about the geometries of the triplet states of HCN. However, in the sense that each state is reasonably well-described (coefficient $\geqslant 0.8$) by a single configuration, the triplets provide a much more clearcut test of the validity of Walsh's ideas. The lowest triplet, the $^3A'$ (6a' $\longrightarrow$ 7a' in simplified notation) is indeed bent (128.6°) as predicted by Walsh but is less bent than the 1 $^3A''$ (1a" $\longrightarrow$ 7a') state (117.0°). According to Walsh's diagram, the 6a' $\longrightarrow$ 7a' configuration should be slightly more bent than the 1a" $\longrightarrow$ 7a' configuration.

The 2 $^3A'$ state is predicted by the <u>ab initio</u> calculations to be slightly bent (160.0°), while the Walsh diagram suggests that its dominant configuration (1a" $\longrightarrow$ 2a") should yield a bond angle identical to that of the ground $^1\Sigma^+$ state. However, this slightly bent state can be easily rationalized by noting that the strongly bent configuration 6a' $\longrightarrow$ 7a' contributes about 25% of the wave function at equilibrium. The 2 $^3A''$ (6a' $\longrightarrow$ 2a") state is also calculated to be slightly bent (157.4°), and this prediction is completely consistent with the Walsh diagram.

A 132.6° bond angle was computed for the 3 $^3A'$ (5a' ⟶ 7a') state. Since Walsh's diagram suggests that this triplet state should be the most bent, there is a significant discrepancy here. Again the discrepancy can be rationalized in terms of the significant amount of mixing with the linear (1a" ⟶ 2a") configuration. In this sense this state is analogous to its isoconfigurational signlet, the 3 $^1A'$ state. However, both results can be rationalized in a single configuration picture by changing the shape of the 5a' binding energy. Rather than increasing with decreasing bond angle, <u>we suggest that the 5a' binding energy should decrease very slightly with bending</u>. This will predict the singlet and triplet states arising from the 5a' ⟶ 7a' excitation to have slightly larger bond angles than the 125.0° found experimentally for the (1a" ⟶ 7a') $\tilde{A}$ $^1A''$ state. It is important to note that this adjustment does not affect the many other correct predictions made from Walsh's diagram. This is because the 5a' orbital is doubly occupied in all the other electron configurations except 5a' ⟶ 2a". And, since X $^1\Sigma^+$ HCN has a substantial bending frequency (713 cm^{-1}), it can easily be argued that the 5a' ⟶ 2a" configuration will remain linear. Thus, the 180° bond angles of the 3 $^1A''$ and 3 $^3A''$ are understood in terms of both the original and the modified Walsh diagrams.

CONCLUDING REMARKS

For the most part, the present theoretical study of the excited states of HCN provides a broad confirmation of the validity of Walsh's orbital binding energy vs. bond angle diagram.

A crucial test concerns the state with 114.5° bond angle assigned as $\tilde{B}\ ^1A''$ by Herzberg and Innes. Our *ab initio* calculations support the qualitative conclusion to be drawn from the Walsh diagram, that this assignment is incorrect. A more plausible assignment (from a theoretical point of view) is that this state is the second state of $^1A'$ symmetry.

There are several discrepancies with Walsh's diagram, the two most serious of which can be eliminated by changing the shape of the 5a' orbital binding energy curve. Perhaps more important, this modification eliminates the discrepancy with the 141° bond angle of Herzberg and Innes for the $\tilde{C}\ ^1A'$ state. Alternatively, in most cases the results may be justified in terms of a breakdown of the single configuration picture, and a resultant mixing of configurations with different characteristic bond angles.

ACKNOWLEDGEMENTS

We thank Dr. N. W. Winter for helpful discussions. This work was supported in part by the National Science Foundation, Grant GP-31974.

FOOTNOTES AND REFERENCES

*Work performed under the auspices of the U. S. Atomic Energy Commission.

†Neshan Zovick Fellow.

††Alfred P. Sloan Fellow.

‡Present address: Department of Chemistry, University of California, Berkeley, California 94720.

‡‡M. H. Fellow.

1. H. F. Schaefer, The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results, (Addison-Wesley, Reading, Massachusetts, 1972).

2. W. A. Lathan, W. J. Hehre, and J. A. Pople, J. Am. Chem. Soc. 93, 808 (1971); L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, J. Am. Chem. Soc. 93, 5339 (1971).

3. There are classes of exceptions, however. See J. F. Perkins, J. Chem. Phys. 42, 3927 (1965).

4. J. K. L. Macdonald, Phys. Rev. 43, 830 (1933).

5. This method was first used in our work on methylene, C. F. Bender and H. F. Schaefer, J. Am. Chem. Soc. 92, 4984 (1970).

6. L. Brillouin, Actualites Sci. Ind. No. 71 (1933); No. 159 (1934).

7. R. McWeeny and B. T. Sutcliffe, Methods of Molecular Quantum Mechanics, (Academic Press, New York, 1969).

8. C. F. Bender and E. R. Davidson, J. Phys. Chem. 70, 2675 (1966).

9. S. V. O'Neil and H. F. Schaefer, J. Chem. Phys. 53, 3994 (1970).

10. P. H. Krupenie, The Band Spectrum of Carbon Monoxide, Natl. Std. Ref. Data Ser., Natl. Bur. Std. (U.S.) 5 (1966); S. G. Tilford and J. D. Simmons, J. Phys. Chem. Ref. Data 1, 147 (1972).

11. A. D. Walsh, J. Chem. Soc. 1953, 2288.

12. G. Herzberg and K. K. Innes, Can. J. Phys. 35, 842 (1957); and further unpublished work referred to in Ref. 20 below.

13. I. Absar and K. L. McEwen, Can. J. Chem. 50, 653 (1972).

14. D. E. Milligan and M. E. Jacox, J. Chem. Phys. 39, 712 (1963).

15. D. Buhl and L. Snyder, Bull. Am. Astr. Soc. 3, 388 (1971); P. K. Pearson, G. L. Blackman, H. F. Schaefer, B. Roos, and U. Wahlgren, Astrophys. J. Letters 184, L19 (1973).

16. S. Huzinaga, J. Chem. Phys. 42, 1293 (1965).

17. T. H. Dunning, J. Chem. Phys. 53, 2823 (1970).

18. P. F. Fougere and R. K. Nesbet, J. Chem. Phys. 44, 285 (1966).

19. C. F. Bender and H. F. Schaefer, J. Chem. Phys. 55, 4798 (1971).

20. G. Herzberg, Electronic Spectra of Polyatomic Molecules, (Van Nostrand Reinhold, New York, 1966).

21. R. Ditchfield, J. Del Bene, and J. A. Pople, J. Am. Chem. Soc. 94, 4806 (1972).

22. J. W. C. Johns, H. F. Shurvell, and J. K. Tyler, Can. J. Phys. 47, 893 (1969).

Table I. Predictions of the bond angles of HCN excited states based on Walsh's diagram, Fig. 1.

Symmetry	Electron Configuration	Bond Angle
$^1A'$ and $^3A'$	$5a'^2\ 6a'\ 1a''^2\ 7a'$	more bent
	$5a'^2\ 6a'^2\ 1a''\ 2a''$	180°
	$5a'\ 6a'^2\ 1a''^2\ 7a'$	most bent
$^1A''$ and $^3A''$	$5a'^2\ 6a'^2\ 1a''\ 7a'$	bent
	$5a'^2\ 6a'\ 1a''^2\ 2a''$	slightly bent
	$5a'\ 6a'^2\ 1a''^2\ 2a''$	180°

Table II. Summary of theoretical predictions for the singlet states of HCN. T_e values were obtained semi-empirically as described in the text. Bond distances are given in Å and bond angles in degrees. Experimental quantities (in parentheses) refer to the lowest vibrational level ($v_1 = v_2 = v_3 = 0$) and are taken from Herzberg.[20] All configurations with coefficient greater than 1/3 are indicated.

Symmetry	T_e (eV)	r_e (HC)	R_e (CN)	θ_e(HCN)	Most Important Configurations	Coefficients
$X\ ^1\Sigma^+\ ^1A'$	0.00(0.00)	1.055(1.064)	1.180(1.156)	180(180)	$5a'^2\ 6a'^2\ 1a''^2$	0.9684
$\tilde{A}\ ^1A''$	6.48(6.48)	1.096(1.14)	1.318(1.297)	127.2(125.0)	$5a'^2\ 6a'^2\ 1a''\ 7a'$	0.9714
$2\ ^1A'$	6.78	1.102	1.287	124.9	$5a'^2\ 6a'\ 1a''^2\ 7a'$	0.7024[a]
					$5a'\ 6a'^2\ 1a''^2\ 7a'$	0.5123
					$5a'^2\ 6a'^2\ 1a''\ 2a''$	0.3852
$2\ ^1A''$	7.52	1.076	1.316	164.4	$5a'^2\ 6a'\ 1a''^2\ 2a''$	0.8209
					$5a'^2\ 6a'^2\ 1a''\ 7a'$	0.5372
$3\ ^1A'$	7.85	1.092	1.264	141.2	$5a'\ 6a'^2\ 1a''^2\ 7a'$	0.7442
					$5a'^2\ 6a'^2\ 1a''\ 2a''$	0.4879
					$5a'^2\ 6a'\ 1a''^2\ 7a'$	0.3264
$3\ ^1A''$	8.97	1.045	1.229	180	$5a'\ 6a'^2\ 1a''^2\ 2a''$	0.9392
$4\ ^1A'$	9.54	1.313	1.254	180	$5a'^2\ 6a'\ 1a''^2\ 8a'$	0.8639

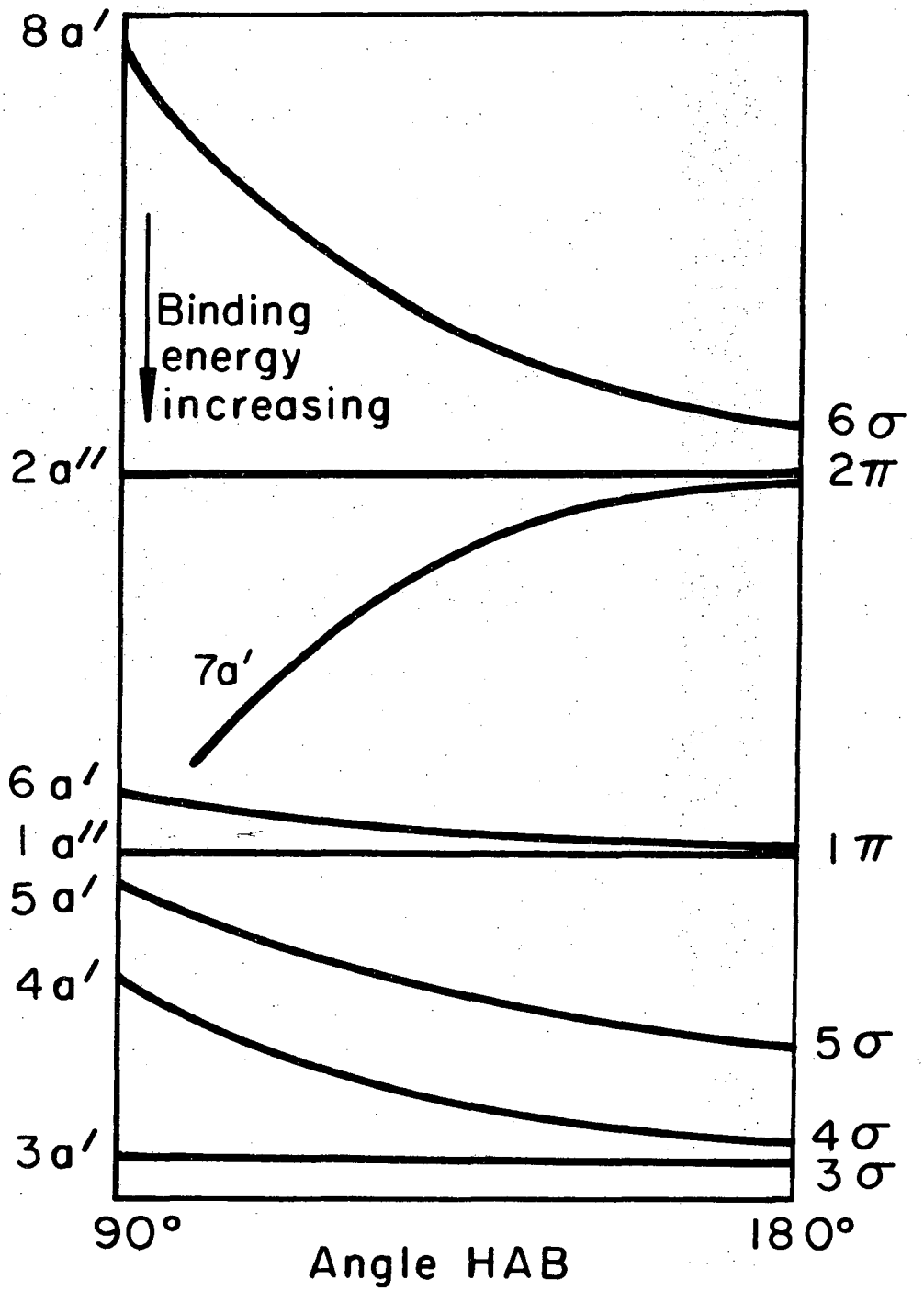
[a]This coefficient becomes 0.8794 when the wave function is obtained in terms of the $2\ ^1A'$ natural orbitals. See text for a discussion.

Table III. Summary of *ab initio* predictions for the triplet states of HCN. The format is identical to that of Table II.

Symmetry	T_e (eV)	r_e (HC)	R_e (CN)	θ_e(HCN)	Most Important Configurations	Coefficients
1 $^3A'$	4.42	1.081	1.294	128.6	$5a'^2\ 6a'\ 1a''^2\ 7a'$	0.9548
1 $^3A''$	5.46	1.099	1.365	117.0	$5a'^2\ 6a'^2\ 1a''\ 7a'$	0.9673
2 $^3A'$	5.91	1.063	1.320	160.0	$5a'^2\ 6a'^2\ 1a''\ 2a''$	0.8400
					$5a'^2\ 6a'\ 1a''^2\ 7a'$	0.5200
2 $^3A''$	6.85	1.061	1.314	157.4	$5a'^2\ 6a'\ 1a''^2\ 2a''$	0.8285
					$5a'^2\ 6a'^2\ 1a''\ 7a'$	0.4951
3 $^3A'$	6.98	1.081	1.250	132.6	$5a'\ 6a'^2\ 1a''^2\ 7a'$	0.8794
					$5a'^2\ 6a'^2\ 1a''\ 2a''$	0.3689
3 $^3A''$	7.41	1.045	1.237	180	$5a'\ 6a'^2\ 1a''^2\ 2a''$	0.9537

FIGURE CAPTION

Fig. 1. Original Walsh diagram[11] for HAB molecules. The labeling of the orbitals has been changed to reflect current notation.



XBL734-2652

Fig. 1

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720