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Electronic Structures and Potential Energy Curves for the Low-Lying States of the CN Radical*

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At 11 internuclear separations *ab initio* calculations have been carried out on those 59 molecular states of CN which dissociate to atomic limits up to ${}^1DC+{}^2DN$. Four electrons are held frozen in carbon and nitrogen $1s$ Hartree-Fock atomic orbitals, and a full configuration interaction is carried out for the remaining nine electrons using optimized $2s$ and $2p$ Slater-type orbitals on each atom. The ${}^2\Pi$ calculations, which include 486 configurations, are the most complicated. Eighteen significantly bound states ($D_e \geq 0.84$ eV) were obtained, nine of which have been observed spectroscopically. With the exception of the third ${}^2\Pi$ state, the theoretical ordering of states agrees with experiment. Three of the states never observed experimentally (${}^4\Sigma^+$, ${}^4\Pi$, and ${}^4\Delta$) lie below all but three of the known states of CN. Calculated spectroscopic constants are compared with experiment. The potential curves show many interesting features, including potential maxima in the ${}^4\Sigma^-$, ${}^2\Sigma^-$, $J^2\Delta$, and ${}^2\Pi$ IV bound states. By performing natural orbital analyses, dominant molecular orbital configurations have been unambiguously assigned to the lowest 18 bound states. The second, third, and fourth ${}^2\Pi$ states experience numerous avoided crossings among themselves, and natural orbitals have been used to follow the changes in electron configuration as a function of internuclear separation. The question of the approximate validity of the quantum numbers g and u is discussed.

I. INTRODUCTION

The fact that there are four low-lying states of the carbon atom (3P , 1D , 1S , 5S) and three low-lying states (4S , 2D , 2P) of the nitrogen atom guarantees the existence of a substantial number of low-lying (less than 10 eV) states of the CN molecule. Combined with the experimental interest,¹⁻¹¹ particularly astrophysical, in CN, there would appear to be a great deal of motivation for *ab initio* calculations on the low-lying states of CN. Nevertheless, we have been able to find only one such study in the literature, by Guerin.¹² He carried out calculations based on SCF orbitals and including no more than three configurations for the $A^2\Pi$, $D^2\Pi$, $F^2\Delta$, and $J^2\Delta$ states of CN. Although such calculations can be useful¹³ in the study of excitation energies, it is well known¹⁴ that diatomic molecular formation and dissociation cannot be properly described within the single configuration approximation unless one of the atoms is a closed shell species.

Over a wide range of internuclear separations, we have carried out *ab initio* configuration interaction (CI) calculations on all the states of CN which dissociate to atomic limits up to 1D carbon plus 2D nitrogen. Perhaps the most important aspect of the present work is the prediction of the existence of nine new bound states of CN.¹⁵ A second area of emphasis in the present work involves the use of natural orbitals¹⁶ to discuss the electronic structure of the valence-excited states of CN.

II. BASIS SET

Hartree-Fock atomic orbitals¹⁷ for the ground states of C and N were used to describe the inner shell electrons. $2s$ and $2p$ Slater-type orbitals on each atom complete the basis set. The orbital exponents for the latter functions were optimized in repeated calculations on the $X^2\Sigma^+$ ground state at the experimental internuclear separation. The resulting exponents for carbon were

$\zeta(2s) = \zeta(2p) = 1.674$ and for nitrogen $\zeta(2s) = \zeta(2p) = 1.988$.

With the exception that the 1σ and 2σ molecular orbitals (MO's) are always doubly occupied, full CI calculations were carried out for all symmetries of interest. The calculated atomic energies for C and N are combined to give molecular dissociation limits in Table I. The comparison with experiment in Table I

TABLE I. Calculated and experimental dissociation limits for CN radical.

Atomic states	Calculated total energy (hartree)	Energy relative to ${}^3P\text{C}+{}^4S\text{N}$ (in eV)	
		Calculated	Experimental ^a
C N			
${}^3P_g+{}^4S_u$	-91.90734	0	0
${}^1D_g+{}^4S_u$	-91.83672	1.92	1.26
${}^5S_u+{}^4S_u$	-91.79773	2.98	4.17
${}^1S_g+{}^4S_u$	-91.78503	3.33	2.68
${}^3P_g+{}^2D_u$	-91.78154	3.42	2.38
${}^3P_g+{}^2P_u$	-91.73809	4.61	3.58
${}^1D_g+{}^2D_u$	-91.71092	5.34	3.65
Rydberg ^b + 4S	7.48

^a C. E. Moore, Natl. Bur. Std. (U. S.), Circ. 467 (1949).

^b First Rydberg state of the carbon atom, $1s^22s^22p^3s^2P$ state.

indicates that the primary deficiency in the atomic calculations is due to the fact that the 5S state of carbon lies too low relative to the 1D and 1S states.

The basis set outlined above is the smallest with which one can reasonably expect to get meaningful results for potential surfaces. And in fact CI calculations of the same type (with molecule-optimized exponents) yielded good qualitative agreement with experiment for CO,¹⁸ with seven of the eight known

TABLE II. Spectroscopic parameters for bound states of CN molecule.

State	T_e (eV)	D_e (eV)	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	α_e (cm ⁻¹)
$X^2\Sigma^+ I$ calc.	0	6.178	1.236	1939.2	14.54	1.610	0.0151
exptl	0	7.75 ± 0.2^b	1.172^a	2068.7^a	13.14^a	1.900^a	0.0173^a
$A^2\Pi I$ calc.	1.883	4.295	1.324	1621.4	16.74	1.403	0.0149
exptl	1.146^a		1.233^a	1814.4^a	12.88^a	1.717^a	0.0175^a
$B^2\Sigma^+ II$ calc.	3.765	4.335	1.226	1765.2	32.53	1.636	0.0262
exptl	3.193		1.151^a	2164.1^a	20.25^a	1.970^a	0.0222^a
$4\Sigma^+ I$ calc.	4.016	2.162	1.448	1249.4	14.82	1.174	0.0152
$4\Pi I$ calc.	5.326	0.853	1.629	873.0	13.15	0.927	0.0154
$4\Delta I$ calc.	5.913	2.187	1.441	1274.4	14.42	1.184	0.0147
$D^2\Pi II$ calc.	~ 6.593	3.008	1.590	1041.6	6.38	0.972	0.010
exptl	6.755^c		1.499^c	1004.7^c	8.78^c	1.162^c	$0.013^c (= \alpha_0)$
$4\Sigma^- I$ calc.	6.666	~ 1.42	1.446	1286.0	15.36	1.177	0.0138
$3\Phi I$ calc.	7.742	1.860	1.621	950.7	12.63	0.936	0.0123
$H^2\Pi III$ calc.	7.807	1.794	1.414	1651.3	43.84	1.229	0.0021
exptl	$7.556^c (= T_0)$		$1.310^c (= r_0)$			$1.520^c (= B_0)$	
$E^2\Sigma^+ III$ calc.	7.856	1.745	1.364	1717.1	30.57	1.322	0.0151
exptl	7.334^d		1.320^d	1681.4^d	3.60^d	1.487^d	0.0064^d
$F^2\Delta I$ calc.	7.879	1.722	1.461	1253.7	15.35	1.152	0.0138
exptl	$7.400^c (= T_0)$		$1.378^c (= r_0)$			$1.374^c (= B_0)$	
$4\Sigma^+ II$ calc.	7.898	1.263	1.749
$2\Sigma^- I$ calc.	7.988	1.613	1.453	1225.5	14.92	1.165	0.0155
$J^2\Delta II$ calc.	8.432	1.169	1.457	1211.7	17.58	1.159	0.0159
exptl	8.090^c		1.414^c	1121.6^c	13.93^c	1.305^c	$0.0207^c (= \alpha_0)$
$4\Delta II$ calc.	8.619	0.982	1.787	651.5	2.75	0.770	0.0057
$2\Sigma^- II$ calc.	8.704	2.080	1.468	1183.2	14.04	1.142	0.0157
$3\Pi IV$ calc.	~ 8.76	~ 0.84	1.532	1446.4	15.60	1.047	0.0005

^a Reference 1.^b Reference 6.^c Reference 3.^d Reference 11.

valence (i.e., non-Rydberg) states lying in the experimental order. Calculations of this type with atom-optimized exponents have also yielded qualitatively correct potential curves for O_2 ,¹⁹ NH ,²⁰ N_2 ,²¹ and SiO .²² Although much more accurate total energies than those reported here can be obtained using extended basis sets, the problem of treating molecular formation and dissociation is a difficult one within larger basis sets, and accurate potential curves of this type have only been reported for a few states of a few diatomic molecules.²³ Perhaps the primary virtue of CI treatments of the type used here is that all molecular states dissociate smoothly to their exact atomic limits.

Since our all-numerical methods²⁴ for the computation of molecular integrals allow for the use of arbitrary orbitals, the present calculations could equally well have been done entirely in terms of accurate Hartree-Fock orbitals.¹⁷ This would have yielded much lower total energies and still retained the correct dissociation behavior for all states. However, as we have shown for F_2 ²⁴ and Cl_2 ,²⁵ such a basis is optimum for the separated atoms but far from optimum for the molecule, and this results in very poor calculated dissociation energies. The basis set adopted here, HFAO's for the core and

STO's for the valence region, is about equally good (or bad) for both the molecule and the separated atoms and thus yields reasonable potential curves.

The methods used in the present study for the evaluation of integrals and construction of symmetry-adapted linear combinations of determinants are described elsewhere.^{24,26} Fifty-nine molecular states dissociate to the first seven atomic limits (see Table I) of CN. The resulting full valence CI calculations include the largest computations of this type reported to date.¹⁸⁻²² The calculations are summarized in our complete report²⁷ where it is seen that the largest calculation, of 2Π symmetry, requires the ten lowest eigenvalues of a 486×486 matrix. Total CDC 6600 time used for all calculations was about seven hours.

The calculated total energies for 59 states at 11 internuclear separations (1.85, 2.0, 2.25, 2.5, 2.75, 3.0, 3.25, 3.5, 4.0, 5.0, 6.0) are not included here but can be obtained from the authors.²⁷

III. SPECTROSCOPIC CONSTANTS: COMPARISON WITH EXPERIMENT

In Table II the *ab initio* spectroscopic constants are compared with available experimental data. Eight

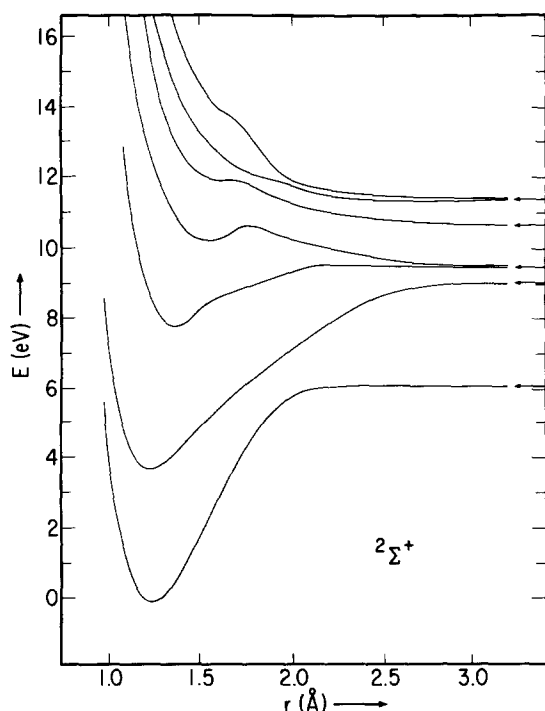


FIG. 1. Calculated potential energy curves for $2\Sigma^+$ states of CN. The arrows near the right margin indicate dissociation limits.

states of CN have been fairly unambiguously identified and a ninth, designated $G^2\Pi$, has been tentatively assigned by Lutz.¹¹ For the eight known states our predicted ordering agrees with experiment except for the $H^2\Pi$ state. The H state is calculated to lie 0.049 eV below the $E^2\Sigma^+$ state and 0.072 eV below the $F^2\Delta$ state, but Douglas and Routly's measurements² indicate that the $H^2\Pi$ state in fact lies 0.156 eV above the

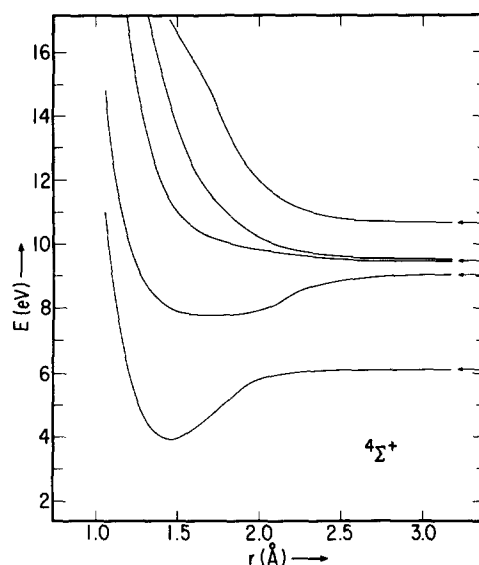


FIG. 3. $4\Sigma^+$ states.

$F^2\Delta$ state. Thus if our calculated $H^2\Pi$ state were to lie 0.073 eV higher the *ab initio* order would be in complete agreement with experiment for CN.

Our calculations predict a fourth 2Π bound state which lies 0.95 eV above the 2Π III state. Lutz¹¹ however tentatively assigns a fourth 2Π state lying 0.04 eV below the $H^2\Pi$ state. However, inspection of Lutz's potential curves¹¹ shows that, if his analysis is correct, the G and H states at 60 624 cm^{-1} and 60 939 cm^{-1} are not two states but two different minima in a single 2Π III state.

The theoretical r_e values are in all eight cases larger than experiment, the differences ranging from 0.064

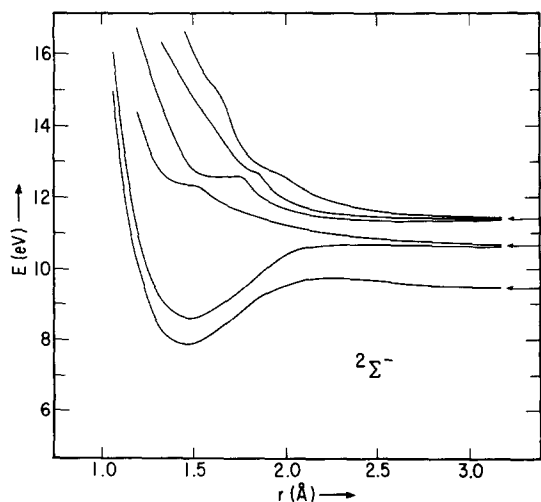


FIG. 2. $2\Sigma^-$ states.

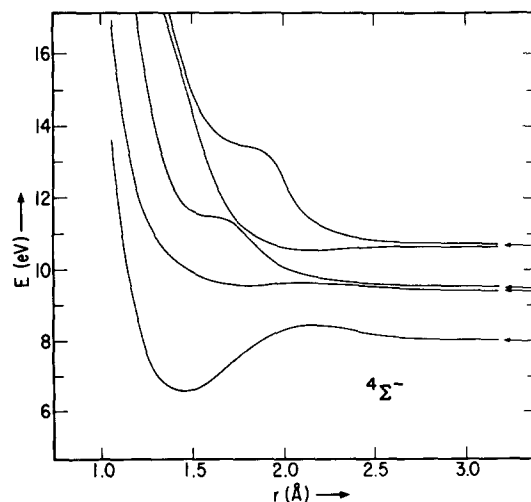
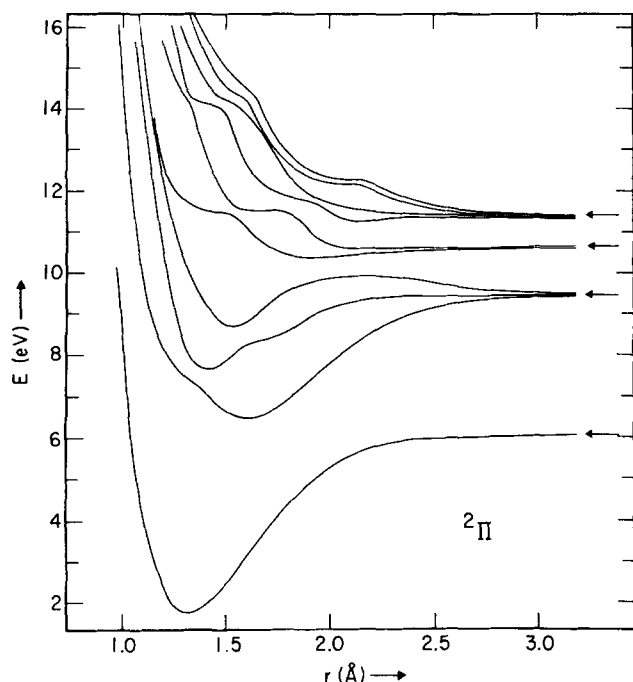


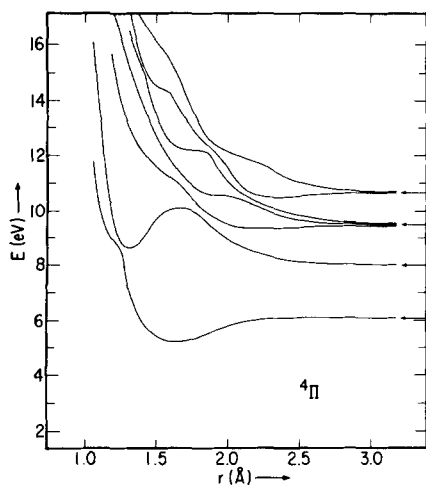
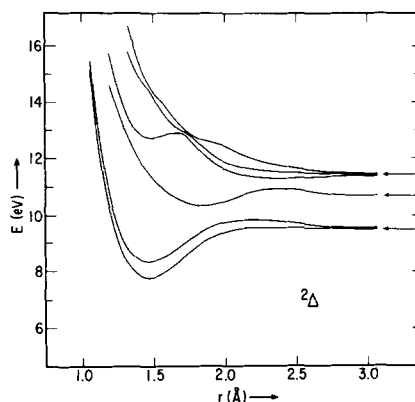
FIG. 4. $4\Sigma^-$ states.

FIG. 5. $^2\Pi$ states.

to 0.104 Å. The relative differences are even better and the calculated ordering of r_e agrees with experiment except, again, for the $H^2\Pi$ state. The predicted rotational constants B_e follow the same pattern with respect to experiment, since B_e is proportional to $(1/r_e)^2$.

The calculated values of ω_e are the following percentages of experiment $X^2\Sigma^+$ 94%, $A^2\Pi$ 89%, $B^2\Sigma^+$ 82%, $D^2\Pi$ 104%, $E^2\Sigma^+$ 102%, $J^2\Delta$ 108%. Except for the $B^2\Sigma^+$ value; the theoretical ω_e 's fall in the experimentally observed order.

The higher spectroscopic constants $\omega_e x_e$ and α_e are

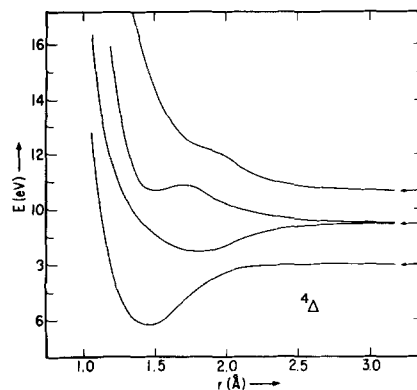
FIG. 6. $^4\Pi$ states.FIG. 7. $^2\Delta$ states.

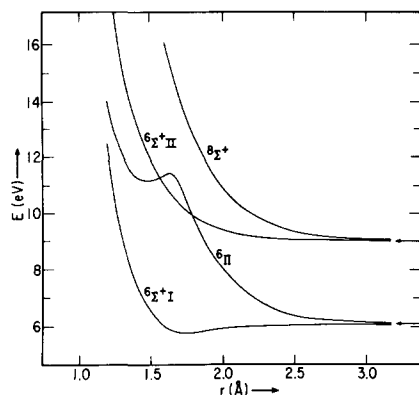
usually qualitatively similar to the experimental values. As can be seen from Table II, however, for the $E^2\Sigma^+$ state, the agreement for $\omega_e x_e$ is particularly poor.

IV. NEW BOUND STATES OF CN

Since qualitatively correct spectroscopic constants were obtained for the known bound states of CN, it is to be expected that useful predictions can be made concerning states not yet observed experimentally. Table II predicts the existence of nine new states of CN. It is not surprising that none of these states have been observed, since six are quartet states, two are $^2\Sigma^-$, and the last is a $^2\Phi$ state. Transitions from these nine states to the ground $X^2\Sigma^+$ state are electronically forbidden.

It is perhaps surprising how low-lying some of the quartet states are. For example the $^4\Sigma^+$ state is predicted to lie only 0.251 eV above the very well characterized $B^2\Sigma^+$ state. And both the $^4\Pi$ and $^4\Delta$ states lie below the fourth known state of CN, $D^2\Pi$. Since all nine of these new states are observably bound ($D_e > 0.85$ eV), we hope that the present theoretical predictions will spur new experimental interest in the CN spectrum.

FIG. 8. $^4\Delta$ states.

FIG. 9. $6\Sigma^+$, 6Π , and $8\Sigma^+$ states.

V. POTENTIAL CURVES

Figures 1–10 contain the calculated potential curves for 59 states of CN. In Fig. 11 the lowest bound states are seen. Several attempts were made to plot the higher bound states but the number of curve crossings makes the resulting figure virtually inscrutable. So, in Fig. 12 we indicate the energy of each of these bound states and the r_e value. This group of CN potential curves is the most interesting we have studied^{18,19,22} to date since there are a large number of significantly bound states and many more potential maxima than previously encountered.

Among the eighteen lowest bound states the $4\Sigma^-$, $2\Sigma^-$, $J^2\Delta$, and 2Π IV all have potential maxima at about four bohrs. The heights of these maxima are, respectively, 0.43, 0.24, 0.43, and 0.32 eV. All four maxima appear to be due to avoided crossings with higher states. The curves for the two lowest $2\Sigma^-$ and 2Δ states are particularly interesting, since for both of these symmetries there are two nearly parallel bound states. Figure 6 shows that the 4Π II state is quasibound. This state has a potential well of depth 1.41 eV, but the minimum nevertheless lies 0.67 eV above the dissocia-

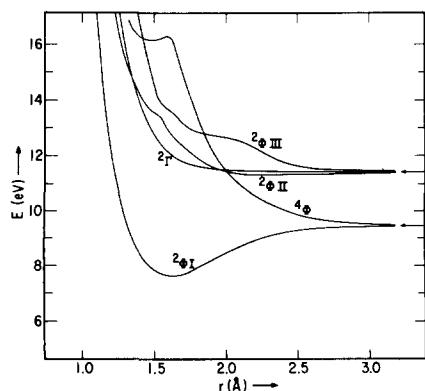
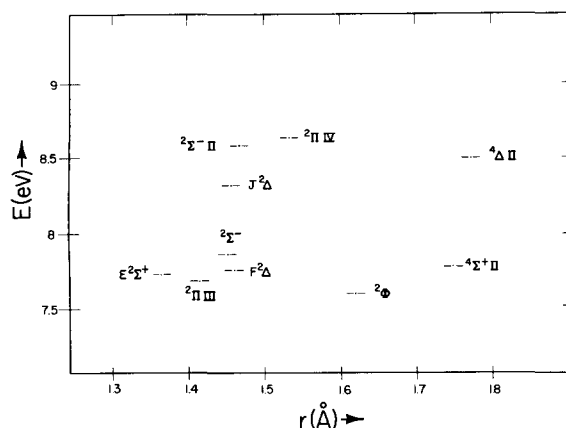
FIG. 10. 2Φ , 2Γ , and 4Φ states.

FIG. 11. Potential curves for the eight lowest bound states of CN.

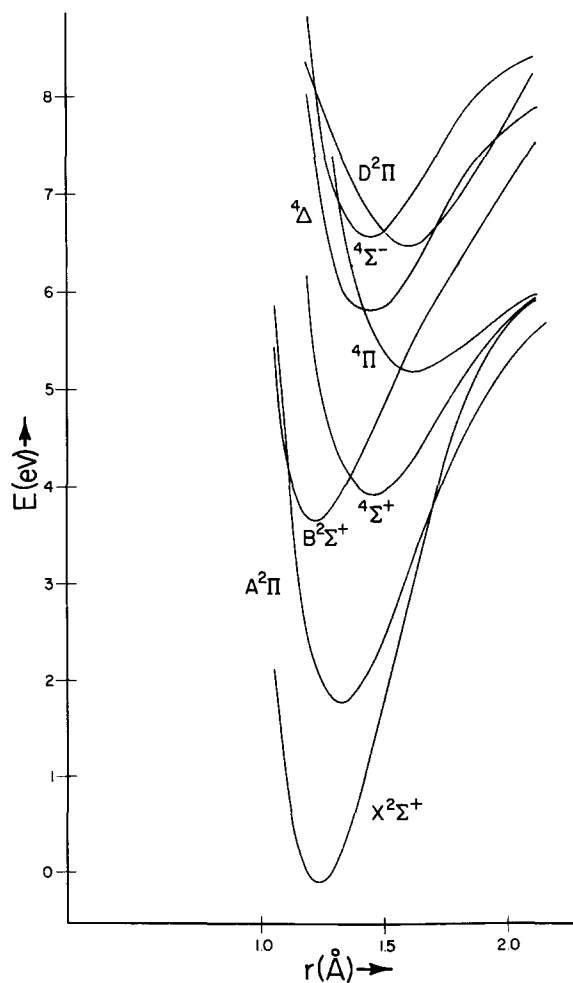


FIG. 12. Positions of the ninth through 18th lowest bound states of CN.

tion limit. Two higher states having potential maxima are ${}^2\Delta$ III and ${}^4\Delta$ III.

The fact that, in our calculations, the 5S state of carbon lies too low is reflected in our ${}^2\Sigma^+$ results. Figure 1 implies that the B state dissociates to 5S carbon plus 4S nitrogen, whereas in fact, it must dissociate to ${}^3PC+{}^2DN$. The ${}^2\Sigma^+$ IV curve is also affected, the maximum in its potential curve being a result of the ${}^5S+{}^4S$ atomic limit lying too low. If we realize this limitation of the present results, one can more sensibly predict that the ${}^2\Sigma^+$ IV state should dissociate smoothly to ${}^3PC+{}^2PN$. Thus the ${}^2\Sigma^+$ IV state is predicted to be bound with a dissociation energy of ~ 0.5 eV. Lutz¹¹ has mentioned the possibility of the existence of a fourth ${}^2\Sigma^+$ state.

Several other points of interest can be seen in Figs. 1–12. The second ${}^4\Sigma^+$ state has a very unusual shape, much like that of a bathtub. The lowest ${}^6\Sigma^+$ state is slightly bound ($D_e \approx 0.3$ eV) with a minimum at $r = 3.25$ bohr. Furthermore, since this state dissociates to ground state carbon and nitrogen atoms, it is very low lying ($T_e < 6.0$ eV).

A particularly interesting series of crossing occurs for the ${}^2\Sigma^-$ states, where the third, fourth, fifth, and sixth potential curves avoid crossing a curve which dissociates to a higher atomic limit than those considered here.

Mention should be made concerning the possibility of molecular Rydberg states causing serious deviations from the predictions given here, since our basis set is incapable of describing such Rydberg states. Table I shows that the lowest Rydberg dissociation limit occurs 3.31 eV above the highest dissociation limit we have considered. However, since some of the CN Rydberg states are no doubt more bound than our higher predicted states, there is still a possibility of some interaction. The dissociation energies of these Rydberg states should be close to those of the lowest states of CN^+ . However the ground state dissociation energy of CN^+ is only 4.7 ± 0.4 eV⁶ which implies (see Table I) that the lowest Rydberg state of CN lies ~ 2.7 eV above ground state carbon plus ground state nitrogen. Our highest reported bound state, ${}^2\Pi$ IV, lies ~ 2.6 eV above the ground state atoms, so if Rydberg states affect our predicted bound states at all, it is likely that only the very highest potential curves are altered.

VI. ELECTRONIC STRUCTURES

Molecular orbital configurations for the low-lying states of CN have been discussed in several experimental papers.^{2,3,11} In this work, we have directly investigated this problem by computing natural orbitals (NO's)¹⁶ for the lowest state of each symmetry. The natural orbitals have a highly desirable nonarbitrary form in these calculations, since our full CI calculations assume no foreknowledge of the form of the orbitals.

A. Molecular Orbital Configurations

For the lowest state of each symmetry except ${}^2\Pi$ which yielded at least one of the 18 significantly bound states, natural orbital occupation numbers are given in our complete report.²⁷ The fact that almost all the occupation numbers are nearly integral implies that most of these states are well represented by a single configuration. For the ground state, NO analyses have been carried out at five different internuclear separations. It is seen²⁷ that as r becomes larger the 2π NO becomes more important. This is a manifestation of the fact¹⁴ that for diatomic molecules made up of two open-shell atoms, as $r \rightarrow \infty$, the single configuration MO approximation becomes increasingly poorer.

Using the natural orbitals thus obtained for each symmetry, the full CI wavefunctions were recomputed to determine the dominant configurations in each wavefunction. These dominant configurations are reported in Table III and give quantitative information on the electronic structure of CN. For eight of the 14 bound states in Table III, there is only one configuration with coefficient greater than 0.25, corresponding to $\sim 6.25\%$ of the total wavefunction. For only one state, ${}^4\Sigma^+$ II, is it not possible to clearly identify a single dominant configuration. Table III shows that for all eight doublet states excluding ${}^2\Pi$, the predicted electron configurations of Douglas and Routly² and

TABLE III. Dominant configurations for bound states of CN. The coefficients given arise from a recomputation of each wavefunction in terms of the natural orbitals for the lowest state of that symmetry. Each coefficient incorporates the effects of all diatomic symmetry eigenfunctions arising from the given orbital occupancy. Only configurations with coefficient greater than 0.25 are included here.

State	R (bohr)	Configurations	Coefficient
$X {}^2\Sigma^+$	2.25	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^4$	0.9304
$B {}^2\Sigma^+$	2.25	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 5\sigma^2 1\pi^4$	0.8587
		2. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3 2\pi$	0.3682
$B' {}^2\Sigma^+$	2.25	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^2 2\pi$	0.8976
		2. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 5\sigma^2 1\pi^4$	0.2803
${}^2\Sigma^-$	2.75	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3 2\pi$	0.9528
${}^2\Sigma^- \Pi$	2.75	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^2 2\pi$	0.9324
${}^4\Sigma^+$	2.75	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3 2\pi$	0.9173
		2. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^2 2\pi^3$	0.2819
${}^4\Sigma^+ \Pi$	2.75	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 5\sigma^2 1\pi^3 2\pi$	0.7365
		2. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^2 2\pi^2$	0.5168
${}^4\Sigma^-$	2.75	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3 2\pi$	0.9348
${}^4\Pi$	3.0	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2 2\pi$	0.9624
$F {}^2\Delta$	2.75	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3 2\pi$	0.9320
$J {}^2\Delta$	2.75	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3 2\pi$	0.9378
${}^4\Delta$	3.0	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^2 2\pi$	0.9292
${}^4\Delta \Pi$	3.0	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^2 2\pi^2$	0.9142
		2. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2 2\pi$	0.2879
${}^2\Phi$	3.0	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2 2\pi$	0.9680

Lutz¹¹ are correct. For the quartet states, electron configurations have not been predicted.

B. Avoided Crossings Among the $^2\Pi$ States

The $^2\Pi$ wavefunctions were recomputed at five r values using $X^2\Sigma^+$ natural orbitals. This was done in order to "follow", in terms of MO configurations, the avoided crossings which occur among the second, third, and fourth $^2\Pi$ states. As can be seen in Table IV, three configurations— $5\sigma^21\pi^3$, $5\sigma^21\pi^22\pi$, and $1\pi^42\pi$ —dominate these four states. By simultaneously looking at Fig. 5 and Table IV it can be seen that each avoiding crossing is accompanied by a change in the dominant electron configuration.

At its minimum, the $D^2\Pi$ state is dominated by the $5\sigma^21\pi^22\pi$ configuration (actually two $^2\Pi$ configurations arise from this orbital occupancy²⁶). However, between $r=2.75$ and $r=2.50$, the $D^2\Pi$ states shifts to the $1\pi^42\pi$ configuration.

The third calculated $^2\Pi$ state (which we assume is the H state) experiences two avoided crossings. At $r=2.25$ and $r=2.50$, $^2\Pi$ III is dominated by $5\sigma^21\pi^22\pi$. However, at the lowest calculated energy, $r=2.75$, the H state is dominated by the $1\pi^42\pi$ configuration. At $r=3$ bohr both the $5\sigma^21\pi^22\pi$ and $1\pi^42\pi$ orbital occupancies are important, indicating that this is near another avoided crossing. Finally, at $R=3.25$, the $5\sigma^21\pi^22\pi$ configuration again becomes dominant.

TABLE IV. Dominant configurations for the 4 lowest $^2\Pi$ state of CN. These results arise from 486 configuration calculations carried out using the $X^2\Sigma^+$ ground state natural orbitals.

		$5\sigma^21\pi^3$	$5\sigma^21\pi^22\pi$	$1\pi^42\pi$
$A^2\Pi$	$R=2.25$	0.9475	0.1395	0.0555
	$R=2.50$	0.9320	0.1530	0.0485
	$R=2.75$	0.9083	0.1826	0.0421
	$R=3.00$	0.8704	0.2360	0.0360
	$R=3.25$	0.8083	0.3122	0.0286
$D^2\Pi$	$R=2.25$	0.0280	0.0608	0.8198
	$R=2.50$	0.0425	0.1810	0.8255
	$R=2.75$	0.1595	0.9107	0.1050
	$R=3.00$	0.2354	0.8831	0.0489
	$R=3.25$	0.3372	0.8346	0.0347
$^2\Pi$ III	$R=2.25$	0.0727	0.9450	0.0197
	$R=2.50$	0.1001	0.9247	0.1128
	$R=2.75$	0.0114	0.2664	0.8052
	$R=3.00$	0.0480	0.7175	0.5249
	$R=3.25$	0.0804	0.8435	0.2575
$^2\Pi$ IV	$R=2.25$	0.0162	0.1208	0.1001
	$R=2.50$	0.0339	0.9091	0.0071
	$R=2.75$	0.0427	0.8790	0.1659
	$R=3.00$	0.0407	0.5458	0.6111
	$R=3.25$	0.0419	0.2704	0.7082

The lowest calculated energy for the fourth $^2\Pi$ state is found at $R=3.0$ bohrs, but the calculated energy is less than 0.1 eV higher at $R=2.75$. Thus the minimum of the $^2\Pi$ IV state occurs very near an avoided crossing between the third and fourth $^2\Pi$ states. For smaller r than 3.0, $^2\Pi$ IV is dominated by $5\sigma^21\pi^22\pi$, and for larger r , $1\pi^42\pi$ is the dominant configuration.

Our MO configuration assignments for the four $^2\Pi$ states at their equilibrium internuclear separations are the same as those of Lutz,¹¹ except for the $^2\Pi$ IV state (which he calls G), for which we cannot specify a single configuration. A final interesting point is that at different r values the $1\pi^42\pi$ configuration dominates the second, third, and fourth $^2\Pi$ states.

C. The Question of g and u Symmetry

Douglas and Routly,² on the basis of the observance and nonobservance of certain transitions, have suggested that the CN radical is nearly enough homonuclear that the symbols g and u have some meaning. Carroll³ and Lutz¹¹ have also discussed this matter. In particular, both Douglas and Routly² and Lutz¹¹ state that the ground state can be approximately labeled as $^1\Sigma_g^+$, and thus that the 5σ orbital is more appropriately termed $3\sigma_g$, as in the N_2 molecule.

Our 5σ natural orbital from the $X^2\Sigma^+r=2.25$ calculation has the form

$$5\sigma = 0.6092\ 2s(C) + 0.1888\ 2s(N) \\ - 0.6375\ 2p(C) - 0.4958\ 2p(N)$$

in terms of the normalized STO's used to describe the valence region. This orbital does not appear to approximate g character. However, the 1π natural orbital from the same calculation has the form

$$1\pi = 0.5935\ 2p(C) + 0.6617\ 2p(N)$$

and thus approximates a $1\pi_u$ orbital rather closely. Similar results to the above were also found for $r=2.5$ bohr, and we conclude that the g and u labels are more appropriate for the π than the σ orbitals.

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Transfer-State Population in Liquid Scintillators

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A parameter, n_e , which represents the number of primary excited solvent molecules from which energy can be transferred to the scintillator, may be determined by studying fluorescence under high-energy and ultraviolet excitations. The temperature variation of n_e was measured over a range of 200°C and was found to be considerable for high-energy excitation. This variation is attributed to changes in intermolecular coupling. Following ideas of Magee and Platzman, we assume the (bulk modulus)^{1/3} as a measure of this coupling. The experimental results show good agreement with the theory. Study of different solutes reveals that n_e is made up of two factors only one of which is temperature dependent.

The primary excited states of molecules in a scintillator solution excited by charged particles are assumed¹⁻⁴ to be those with large values of the oscillator strength. This has led to the idea² that the great majority of initial excitations may be into "superexcited" states, in which the energy exceeds the molecular ionization energy. Of the molecules so excited, only that fraction which ends up in lower excited states may transfer electronic excitation energy to other unexcited molecules. The remainder dissociate or, following ionization, the electrons recombine preferentially into triplet states which are usually nontransferring. The rapid intra- and intermolecular redistribution of initial excitation energy, according to this picture, strongly affects the amount of energy available for solvent-solute transfer, hence the scintillation yield of the solution.

It has been theorized by Magee⁵ that the intermolecular coupling strength strongly affects the ability of a highly excited molecule to share energy with neighbors rather than dissociate; weakly coupled molecules, in contrast, will tend to dissociate. Strongly coupled mole-

cules, rapidly sharing excess energy with neighbors, have a higher efficiency for internal degradation to lower excited states.

Fluorescence experiments at different temperatures tend to corroborate Magee's hypothesis. The fluorescence intensities of degassed organic liquid solutions, excited by ultraviolet light and gamma radiation, were measured at temperatures ranging from 20 to above 200°C. Under irradiation by (radium) gamma rays, electrons released in Compton and secondary scattering processes are responsible for the primary excitation of the solvent molecules whereas uv irradiation excitation does not involve charged particles. For those molecules which energetically degrade to a transferring electronic state (generally S_1), energy migration leading to solute excitation competes with further degradation to the ground solvent state.

The steady-state solute fluorescence intensity (I_{su}) is proportional to⁶

$$I_{su} \sim n_e c (Q + c)^{-1} F_{su}, \quad (1)$$