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Abstract

Simple molecular orbital theory predicts the existence of four low-lying, bound, quartet states of CN. *Ab initio* configuration interaction calculations have been carried out on these and other states of CN. The four states, $^4\Sigma^+$, $^4\Pi$, $^4\Delta$, and $^4\Sigma^-$ are calculated to lie at 4.02, 5.33, 5.91, and 6.67 eV. Only the X $^2\Sigma^+$, A $^2\Pi$, and B $^2\Sigma^+$ states of CN appear to lie below these four new states.

The CN radical is of considerable astrophysical and spectroscopic interest (see Herzberg 1950; Davis and Phillips 1963; and Gaydon 1968) and at least eight low-lying bound states have been identified (Douglas and Routly 1955; Carroll 1956; Lutz 1970). The lowest four states can be represented by the molecular orbital (MO) configurations

$$X\ {}^2\Sigma^+ \quad 1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma\ \ 1\pi^4 \tag{1}$$

$$A\ {}^2\Pi \quad 1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma^2\ \ 1\pi^3 \tag{2}$$

$$B\ {}^2\Sigma^+ \quad 1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma\ \ 5\sigma^2\ \ 1\pi^4 \tag{3}$$

$$D\ {}^2\Pi \quad 1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ \ 1\pi^4\ 2\pi \tag{4}$$

while the other four known states arise from the two configurations

$$E\ {}^2\Sigma^+,\ F\ {}^2\Delta,\ J\ {}^2\Delta \quad 1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma\ \ 1\pi^3\ 2\pi \tag{5}$$

$$H\ {}^2\Pi \quad 1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma^2\ \ 1\pi^2\ 2\pi \tag{6}$$

Although all the known states of CN are doublets, by simple symmetry arguments (see Herzberg 1950), we readily find that ${}^4\Sigma^+$, ${}^4\Sigma^-$, and ${}^4\Delta$ states can arise from MO configuration (5), and a ${}^4\Pi$ state can arise from MO configuration (6). Further, Hund's rules (see Herzberg 1950) indicate that these four quartet states should lie below the four known bound states of CN arising from configurations (5) and (6).

In order to test these simple empirical predictions of MO theory, we have carried out *ab initio* configuration interaction (CI) calculations on several states of CN. The calculations employ 1s Hartree-Fock atomic orbitals, plus 2s and 2p Slater-type orbitals for C and N, with orbital exponents optimized for the X ${}^2\Sigma^+$ ground state at its experimental internuclear separation. Holding the 1s atomic orbitals doubly occupied, full CI calculations were carried out for each state at ten internuclear separations. The number of configurations thus included were 320 ($^2\Sigma^+$), 164 ($^4\Sigma^+$), 196 ($^4\Sigma^-$), 292 ($^4\Pi$), and 152 ($^4\Delta$). The computational procedures used have been described elsewhere (Schaefer 1970 a, b).

The usefulness of the above theoretical approach has been demonstrated by studies on O_2 (Schaefer and Harris 1968), NH (Kouba and Ohrn 1970), SiO (Heil and Schaefer 1970), N_2 (Michels 1970), and CO (O'Neil and Schaefer 1970). The above studies all yielded potential curves in good qualitative agreement with experiment. In nearly every case the calculated ordering of states agreed with the avilable experimental data. Typically, 70% of the dissociation energy was obtained, and the spectroscopic constants r_e, ω_e, and B_e differed from experiment in a very consistent manner.

Figure 1 shows the calculated potential curves for the lowest three $^2\Sigma^+$ states and the lowest $^4\Sigma^+$, $^4\Sigma^-$, $^4\Pi$, and $^4\Delta$ states. Table 1 indicates the predicted spectroscopic constants.

Figure 1 indicates clearly that all four quartet states are bound and lie more than 1 eV below the E $^2\Sigma^+$ state. From the experimental data on doublet states (Douglas and Routly 1955; Carroll 1956; Lutz 1970) we conclude that the $^4\Sigma^+$, $^4\Pi$, $^4\Delta$, and $^4\Sigma^-$ are the 3rd, 4th, 5th, and 6th excited states of CN. And the $^4\Sigma^+$ state is seen to lie only slightly above the very well-characterized B $^2\Sigma^+$ state.

Although the B $^2\Sigma^+$ state dissociates to ^5S + ^4S in the present calculations, from the atomic dissociation limits and the non-crossing rule, the B $^2\Sigma^+$ must, in fact dissociate to ^3PC + ^2DN. This discrepancy arises from the inability of our small basis to adequately reproduce the splittings between the low-lying atomic states of C and N.

Figure 1 caption. Potential curves for the three lowest $^2\Sigma^+$ states and the lowest $^4\Sigma^+$, $^4\Pi$, $^4\Delta$, and $^4\Sigma^-$ states of CN. Arrows near the right margin indicate dissociation limits.

Table I. Spectroscopic constants for low lying quartet and three reference $^2\Sigma^+$ states of the 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})	minimum pt. (Hartrees)	dissoc. limit (Hartrees)
X $^2\Sigma^+$	Calc	0	6.178	1.236	1939.2	14.54	1.610	0.0151	-92.13438	-91.90734
	Exp	0	7.75±0.2^b	1.172^a	2068.7^a	13.14^a	1.900^a	0.0173^a		
B $^2\Sigma^+$	Calc	3.765	4.335	1.226	1765.2	32.53	1.636	0.0262	-91.99603	-91.83672
	Exp	3.193^a		1.151^a	2164.1^a	20.25^a	1.970^a	0.0222^a		
$^4\Sigma^+$	Calc	4.016	2.162	1.448	1249.4	14.82	1.174	0.0152	-91.98679	-91.90734
$^4\Pi$	Calc	5.326	0.853	1.629	873.0	13.15	0.927	0.0154	-91.93867	-91.90734
$^4\Delta$	Calc	5.913	2.187	1.441	1274.4	14.42	1.184	0.0147	-91.91709	-91.83672
$^4\Sigma^-$	Calc	6.666	∼1.85^c 1.434^c	1.446	1286.0	15.36	1.177	0.0138	-91.88942	-91.83672
E $^2\Sigma^+$	Calc	7.856	1.745	1.364	1717.1	30.57	1.322	0.0151	-91.84567	-91.78154
	Exp	7.334^d		1.320^d	1681.4^d	3.60^d	1.487^d	0.0064^d		

a) Herzberg (1950).

b) Gaydon (1968).

c) This state has a maximum. Upper figure is well depth from maximum. Lower figure is depth from dissociation limit .

d) Lutz (1970).

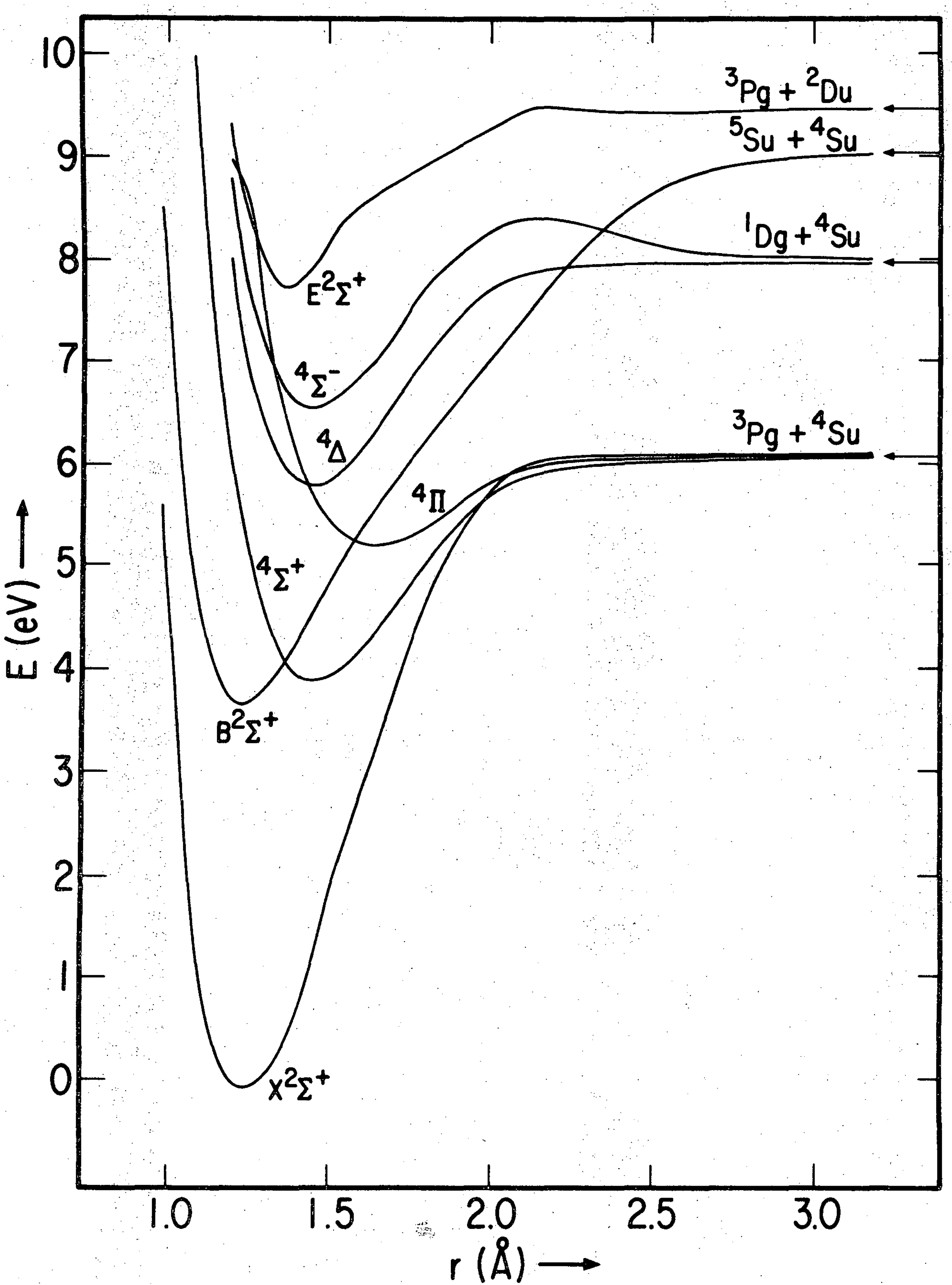
E (eV)
r (Å)
10
9
8
7
6
5
4
3
2
1
0
1.0
1.5
2.0
2.5
3.0
^{3}Pg + ^{2}Du
^{5}Su + ^{4}Su
^{1}Dg + ^{4}Su
^{3}Pg + ^{4}Su
$E^2\Sigma^+$
$^4\Sigma^-$
$^4\Delta$
$^4\Pi$
$^4\Sigma^+$
$B^2\Sigma^+$
$X^2\Sigma^+$

Fig. 1

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