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Potential energy curves of the lower states of CN^+

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Extended basis SCF CI potential curves for the low lying $^3\Pi$, $^1\Sigma^+$, $^1\Pi$ and $^3\Sigma^-$ states of CN^+ are reported. Equilibrium distances, with known experimental values in parentheses, are

$$r_e(^1\Sigma^+) = 1{\cdot}176\ (1{\cdot}173)\ \text{Å},\quad r_e(^1\Pi) = 1{\cdot}247\ (1{\cdot}248)\ \text{Å},$$
$$r_e(^3\Pi) = 1{\cdot}238\ \text{Å}\quad \text{and}\quad r_e(^3\Sigma^-) = 1{\cdot}346\ \text{Å}.$$

The nature of the ground state, whether $^3\Pi$ or $^1\Sigma^+$, is found to depend on the quality of the CI treatment undertaken. Our most extensive calculation makes these two states almost degenerate.

1. INTRODUCTION

For an investigation of the ground state potential energy surface of HCN^+ we required information about the potential energy curves of the lower states of CN^+. Whilst our study of this system was in progress two papers have been published [1, 2]. The first of these [1] reported a full valence CI calculation using a minimal STO basis and the second [2] reported a SCF treatment using a gaussian-lobe basis. Our own work is now complete and provides variationally better wavefunctions than either of these two papers and this short paper presents our results.

Of prime importance for this system is the question of the ground state. For the iso-electronic molecule C_2 the ground state is a singlet [3] although the lowest triplet state is thought to be only 0·1 eV higher in energy. Shimakura and co-workers [1] find the ground state of CN^+ to be a singlet (0·63 eV below the lowest triplet) but conclude that their calculations do not give a definite answer to the question. Wu [2] finds the ground state to be a triplet and by estimating correlation energy differences concludes that it is $0{\cdot}33 \pm 0{\cdot}2$ eV below the singlet.

Our initial supposition was that the ground state should be a triplet and we based this argument on the fact that the ground state dissociation products $C^+(^2P) + N(^4S)$ could give a triplet but not a singlet state. The lowest singlet must dissociate to $C^+(^2P) + N(^2D)$ which is 2·38 eV above the ground state

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products. We surmized that it would be unlikely that the strength of the bond in the singlet state could outweigh this disadvantage. Neither of the two previous calculations have treated the dissociation limit ; the SCF curves do not of course dissociate correctly and the CI calculations were taken only to 2·95 a_0 with no reported dissociation limits. In fact, as the exponents for the minimal basis STO calculations were optimized for the $^1\Sigma^+$ state at 2·215 a_0 it is almost certain that these calculations if continued to larger distances would give a poor result.

2. Calculations

Potential energy curves for the lowest $^3\Pi$, $^1\Pi$, $^3\Sigma^-$ and $^3\Sigma^+$ states have been calculated at points between 1 and 10 Å using the POL–CI (Polarization Configuration Interaction) method [4]. (All calculations reported in this paper were carried out in the ATMOL3 and SPLICE program systems documented by the Atlas Computing Division, Rutherford Laboratory.) The POL–CI method restricts the number of double excitations from a multi-term reference set by specifying a set of valence orbitals and permitting no more than one electron to occupy a virtual orbital outside this set. In the present study the reference set for each state was determined from preliminary calculations so as to include all configurations with a CI expansion coefficient $\geqslant 0{\cdot}15$ at any point on the associated potential curve. The valence orbital set in each case comprised the $1\sigma, \ldots, 5\sigma$ and 1π, 2π orbitals, with the carbon and nitrogen inner shell orbitals kept doubly occupied in all configurations. Experience with this method [4, 7] suggests that dissociation energies can be obtained to an accuracy of about 0·01 E_H with a good atomic basis.

SCF orbitals were first calculated using Dunning's [4*s*, 2*p*] contraction of the Huzinaga [9*s*, 5*p*] gaussian basis [5, 6]. The lowest energy molecular orbital configuration for the above states are $1\pi^4(^1\Sigma^+)$, $5\sigma 1\pi^3(^1\Pi, {}^3\Pi)$ and $5\sigma^2\ 1\pi^2(^3\Sigma^-)$. However, as has been pointed out before [1, 2] none of these states dissociates correctly in the single configuration SCF model. As it is economical to use the same SCF orbitals for CI calculations on all states, the compromise configuration $5\sigma^1\ 1\pi^3(^1\Pi)$ was chosen for this. The results of these calculations are shown in table 1 and figure 1. A few points were investigated with MO basis sets corresponding to the other SCF configurations but very little difference in the total energy found.

At $R=1$ Å the SCF configuration is dominant (coefficient greater than 0·95) except for the $^1\Sigma^+$ state for which four configuations, $4\sigma^2\ 1\pi^4$, $(4\sigma 5\sigma)1\pi^4$, $(5\sigma 1\pi_x)(4\sigma 2\pi_x)1\pi_y{}^2$ and $(5\sigma 1\pi_y)(4\sigma 2\pi_y)1\pi_x{}^2$ have coefficients greater than 0·15 ; the symbol $(4\sigma 5\sigma)$ indicates spin pairing in the two orbitals. At $R=2$Å there is strong configuration mixing for all four states. The $^3\Pi$ state, for example, has seven configurations with coefficients greater than 0·15. The $^1\Sigma^+$ state, which is the ground state in this calculation, has eight configurations with coefficients greater than 0·15.

The minimum energies of the $^1\Sigma^+$ and $^3\Pi$ states are $-91{\cdot}84746\ E_H$ and $-91{\cdot}83290\ E_H$ respectively. These values are approximately 0·15 E_H lower than those obtained by Shimakura and co-workers [1]. Dissociation limits were calculated as the energies at a bond length of 10 Å. The N(^2D)–N(^4S) separation was found to be 0·106 E_H compared with the experimental value of 0·088 E_H.

Table 1. POL–CI energies (hartrees) at different internuclear distances.

R(C–N)/Å	$^3\Sigma^-$	$^3\Pi$	$^1\Pi$	$^1\Sigma^+$
10·00	−91·725839	−91·723174	−91·622432	−91·617382
5·0	−91·726013	−91·723352	−91·622858	−91·617711
4·0	−91·726207	−91·723512	−91·623231	−91·619725
3·0	−91·731680	−91·729714	−91·640142	−91·638381
2·5	−91·740937	−91·739302		
2·0	−91·763403	−91·759818	−91·710266	−91·683967
1·75	−91·781503	−91·781429		
1·50	−91·788834	−91·816118	−91·776218	−91·780308
1·35	−91·777054	−91·832903	−91·789830	−91·824063
1·20	−91·729112	−91·821719	−91·773583	−91·847456
1·10	−91·642572	−91·767142	−91·715557	−91·821584
1·00	−91·470683	−91·634892	−91·580047	−91·724981

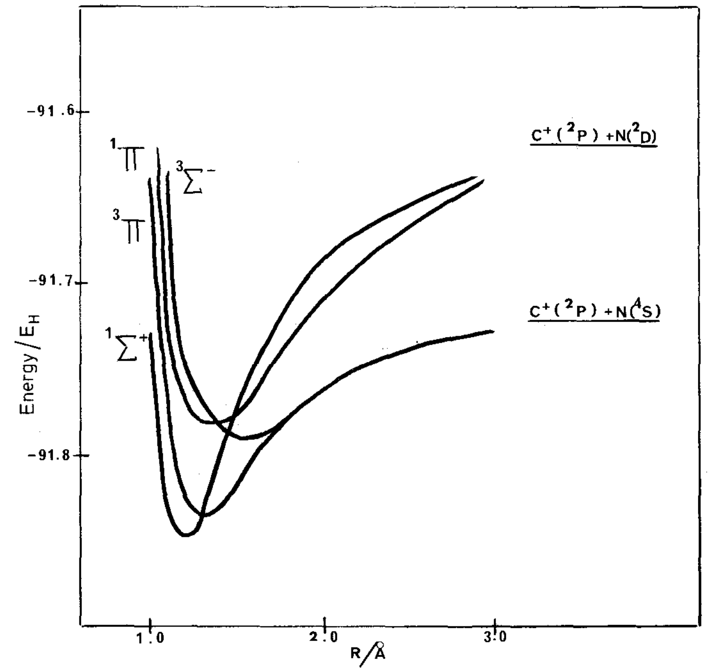

Figure 1. POL–CI potential energy curves for CN^+.

More accurate multi-reference double-excitation CI calculations were then performed for the four states in the region of their equilibrium bond lengths (between 1·0 and 1·4 Å). A larger basis was employed, Dunning's [5*s*, 3*p*] contraction of Huzinaga's [10*s*, 6*p*] gaussian basis [8] augmented by gaussian *d* polarization functions with optimized exponents $\zeta_d(C)=0{\cdot}7609$, $\zeta_d(N)=0{\cdot}8640$. Configuration interaction included all single and double excitations from the principal configurations listed in table 2 whose perturbation contribution was greater than $30\mu E_H$. Excitation from the atomic 1*s* orbitals and to their high energy compliments was excluded.

Table 2. Reference configurations used in the range $R = 1{\cdot}0$ to $1{\cdot}4$ Å. Both Π_x and Π_y components of the functions listed were included in the reference set.

$^3\Pi$	$^1\Pi$
$\ldots, 4\sigma^2\, 1\pi_y{}^2\, 5\sigma 1\pi_x$	$\ldots, 4\sigma^2\, 1\pi_y{}^2(5\sigma 1\pi_x)$
$\ldots, 4\sigma^2\, 2\pi_y{}^2\, 5\sigma 1\pi_x$	$\ldots, 4\sigma^2\, 2\pi y^2(5\sigma 1\pi_x)$
$\ldots, 4\sigma^2(2\pi_x 2\pi_y)5\sigma 1\pi_y$	$\ldots, 4\sigma^2(2\pi_x 2\pi_y)(5\sigma 1\pi_y)$
	$\ldots, 4\sigma^2(1\pi_x 1\pi_y)(5\sigma 2\pi_y)$
$^3\Sigma^-$	$^1\Sigma^+$
$\ldots, 4\sigma^2\, 5\sigma^2\, 1\pi^2$	$\ldots, 4\sigma^2\, 1\pi^4$
	$\ldots, 5\sigma^2\, 1\pi^4$
	$\ldots, 1\pi^4(4\sigma 5\sigma)$
	$\ldots, 1\pi_x{}^2(1\pi_y 2\pi_y)(4\sigma 5\sigma)$
	$\ldots, 1\pi_y{}^2(1\pi_x 2\pi_x)(4\sigma 5\sigma)$

The root functions for each state are specified in table 2. These functions were chosen from preliminary calculations at a 100 μE_H threshold and all configurations with coefficients greater than 0·1 at any point in the potential curve were included. Inspection of the final CI coefficients confirmed that no additional roots were required.

Table 3 and figure 2 show the results of these calculations. The ground state is now found to be the $^3\Pi$ but this is only slightly lower than $^1\Sigma^+$. Dissociation energies have been derived from a CI treatment of the $^3\Pi$ and $^1\Pi$ states at 10 Å utilizing the SCF MOs and reference sets comprising those terms required for correct dissociation. The energy difference is 0·088 E_H which agrees with the experimental N(^2D)–N(^4S) separation.

The $^3\Pi$ wavefunction is dominated by the SCF configuration in the region of the equilibrium bond length, the largest secondary coefficient being 0·15 for $4\sigma^2\, 2\pi_y{}^2\, 5\sigma 1\pi_x$ at 1·4 Å. For the competing $^1\Sigma^+$ state the SCF wavefunction $4\sigma^2\, 1\pi^4$ gives a poor description of the state even at its equilibrium distance. The final reference set employed reflects this fact. Configuration $5\sigma^2\, 1\pi^4$ has a coefficient of approximately 0·25 over the range studied whilst $(4\sigma\, 5\sigma)1\pi^4$ has a large coefficient, 0·43, at 1·0 Å which reduces rapidly with increasing bond length.

In order to determine the sensitivity of the ground state prediction to the CI expansion, a further study of the $^3\Pi$ and $^1\Sigma^+$ states was performed at the equilibrium bond distances of table 4, with explicit secular equations solved for

Table 3. Extended basis CI energies (hartrees) at different internuclear distances.

R(C–N)/Å	$^3\Pi$	$^1\Sigma^+$	$^3\Sigma^-$	$^1\Pi$
1·00	−91·84539	−91·88318	−91·71635	−91·80461
1·10	−91·94888	−91·96252	−91·86386	−91·91159
1·15		−91·97568		
1·20	−91·98235	−91·97613	−91·93246	−91·94926
1·25	−91·98428	−91·97159		−91·95240
1·30	−91·98028	−91·95323	−91·95602	−91·94918
1·35			−91·95773	
1·40	−91·96032	−91·91507	−91·95644	−91·93031

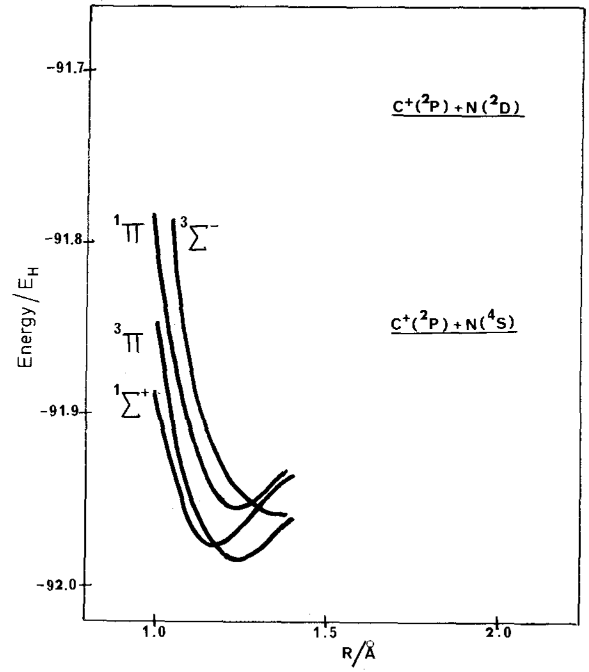

Figure 2. Extended basis CI calculations on CN^+ over a limited range of internuclear distance.

threshold values of $T=10$–$60\ \mu E_H$ in steps of $10\ \mu E_H$. A significant decrease in the $^3\Pi$–$^1\Sigma^+$ state separation was found on lowering the threshold, this energy gap decreasing from 0·28 eV at $60\ \mu E_H$ to 0·08 eV at $10\ \mu E_H$. Buenker and Peyerimhoff [9] have suggested a method for estimating the effect of the discarded configurations at each threshold and the resulting energy can then be extrapolated to zero threshold. This procedure led to an estimated $E(T=0)$ of 91·9970 E_H for the $^3\Pi$ state and $-91{\cdot}9975\ E_H$ for the $^1\Sigma^+$ state. Our conclusion is therefore that the $^3\Pi$ and $^1\Sigma^+$ states are almost degenerate.

Table 4. Calculated spectroscopic constants of CN^+. The numerical values in parentheses are the experimental values taken from [11, 12].

	$^3\Pi$	$^1\Sigma^+$	$^3\Sigma^-$	$^1\Pi$
r_e/Å	1·238	1·176 (1·173)	1·346	1·247 (1·248)
D_e/eV†	4·20	6·400	3·478	5·725
$K_e/10^3$ N m^{-1}	1·099	1·84	0·565	1·124
ω_e/cm^{-1}	1699	2200 (2033)	1218	1718 (1688)
$x_e\omega_e$/cm^{-1}	10·35	18·18 (16·14)	165·4	11·91 (15·12)
B_e/cm^{-1}	1·701	1·885	1·440	1·678

† Values for $^3\Pi$ and $^3\Sigma^-$ refer to dissociation to $N(^4S)+C^+(2p)$, values for the $^1\Sigma^+$ and $^1\Pi$ to dissociation to $N(^2D)+C^+(2p)$.

3. Spectroscopic parameters

Douglas and Routly [10] and Lutz [11] have observed some singlet–singlet emission spectra for CN^+. The experimental spectroscopic constants for the lowest $^1\Sigma^+$ and $^1\Pi$ states are compared with our calculated values in table 4. The calculated bond lengths for the two singlet states are in very good agreement with experiment. The calculated $^1\Pi$–$^1\Sigma^+$ separation is lower than that determined experimentally but the agreement between the two is considerably better than was obtained by Shimakura and co-workers.

There is a large difference in the equilibrium bond lengths of the $^1\Pi$ and $^1\Sigma^+$ states and likewise between the $^3\Sigma^-$ and $^3\Pi$. Thus the low energy emission bands between these pairs would be broad with their Franck–Condon maxima in the infra-red. For this reason both bands would be difficult to detect.

4. Comment on previous calculations

Finally, let us consider the calculations of Wu [2], who presented evidence in support of a $^3\Pi$ ground state lying $0{\cdot}33 \pm 0{\cdot}2$ eV below the $^1\Sigma^+$ state. This separation was based on a comparison of the calculated $b^1\Pi$–$^3\Pi$ separation and the experimentally determined $b^1\Pi$–$^1\Sigma^+$ separation. Wu assumes that the two Π states have the same correlation energy so that the difference in SCF energies can be used as an estimate of the true energy difference. By comparison with similar calculations on other diatomic molecules Wu concludes that his double zeta basis gives an SCF energy difference in error by only $\pm 0{\cdot}2$ eV. However, our own calculations show that the $b^1\Pi$–$^3\Pi$ spacing is lowered by the addition of polarization functions to the basis. Our calculated energy differences at 1·176 Å and 1·238 Å are 1·16 and 1·11 eV respectively, these correspond to energy lowerings of 0·26 and 0·23 eV with respect to the double zeta *sp* basis. Both values exceed Wu's estimate. To test the sensitivity of these results to a further increase in basis size an additional calculation was performed using a near Hartree–Fock [6] [11*s*7*p*2*d*] basis on each atom. This gave a $^3\Pi$–$^1\Pi$ separation of 1·13 eV at a bond length of 1·176 Å, to be compared with the [5*s*3*p*1*d*] estimate of 1·16 eV. In the light of these results the maximum possible separation of the $^3\Pi$ and $^1\Sigma^+$ state based on the analysis presented by Wu is 0·1 eV and it may well be even smaller than this.

References

[1] Shimakura, N., Inouye, H., Honjou, N., Sagara, M., and Ohno, K., 1978, *Chem. Phys. Lett.*, **55**, 221.
[2] Wu, A. A., 1978, *Chem. Phys. Lett.*, **59**, 457.
[3] Ballik, E. A., and Ramsay, D. A., 1959, *J. chem. Phys.*, **31**, 1128.
[4] Hay, P. J., and Dunning, T. H., 1976, *J. chem. Phys.*, **64**, 5077.
[5] Dunning, T. H., 1970, *J. chem. Phys.*, **53**, 2823.
[6] Huzinaga, S., 1965, *J. chem. Phys.*, **42**, 1293.
[7] Dunning, T. H., and Hay, P. J., 1977, *J. chem. Phys.*, **66**, 3767.
[8] Dunning, T. H., 1971, *J. chem. Phys.*, **55**, 716.
[9] Buenker, R. J., and Peyerimhoff, S. D., 1975, *Theor. chim. Acta*, **39**, 217.
[10] Douglas, A. E., and Routly, R. M., 1954, *Astrophys. J.*, **119**, 303.
[11] Lutz, B. L., 1971, *Astrophys. J.*, **163**, 131.
[12] Mizushima, M., 1975, *The Theory of Rotating Diatomic Molecules* (Wiley).