

The complexes featuring the H of HF bound to the carbon of the hydrocarbons prove to be nonbinding for acetylene and ethylene, while for benzene a binding energy of 3.04 kcal/mol is shown. The benzene-HF complex similar to the structures in Figures 1a and 2a shows a binding energy of only 1.53 kcal/mol.

Table I shows no significant changes in the geometries of the subsystems upon the different types of complexation.

The binding energies shown in Table II fall into the range of other complexes of nonpolar molecules with HF;^{2e} that is, they feature values up to 5 kcal/mol. The values are very close for the three systems studied and as such they do not show the strong dependence on polarizability exhibited by the molecules examined in ref 2e. Neither do the quadrupole moment differences seem to have an effect on the binding energies. The ethylene and acetylene complexes with Li⁺ show the same lack of dependence of their binding energies on both polarizabilities and quadrupole moments. This might be due to the compensation of the trend in polarizability by the reverse trend in quadrupole moment which leads to an equalization of the binding energies.

The benzene-HF complex features a binding energy below the value expected by its polarizability and quadrupole moment. The fact that C_{6v} complex proves more stable seems to conflict with a HOMO-LUMO type of interaction. The strong positive charge on the HF hydrogen (0.529 eu) points to it being electrostatically attracted to the π -electron cloud of benzene. However, in addition to this attraction, an examination of the molecular orbital composition shows the hydrogen is to participate mostly in the 14th and 15th MO's. In these MO's, the carbons also feature a p_z atomic orbital participation leading to an overlap with the 1s of the hydrogen. This type of bonding resembles somewhat a very weak multicenter type of bonding, as present in bridged inorganic

compounds. The same effect is also present in the ethylene and acetylene complexes. The CH₃CN shows a stronger binding energy than the other complexes, of 7.91 kcal/mol. To assert the fact that the increase is due to the total dipole moment of the molecule (which is 4 D) and not simply to the presence of the lone pair on the nitrogen, we calculated the binding energy of cyanogen to HF and found it to be 3.98 kcal/mol, that is, in the range of values of the other complexes. As such, we might conclude that the dipole moment of the CH₃CN molecule plays an important role in the binding.

An examination of the Mulliken overlap population shown in Table III reveals a consistently low but nonzero electron density in the binding region. The charge transfer which takes place upon complexation features values from -0.034 to +0.017 eu. It can be seen that the HF molecule acquires negative charge in complexes where the hydrogen binds to the π -electron cloud of the hydrocarbons and donates it in the others.

In conclusion, the most stable complexes of the π -bonded systems with HF exhibit a T geometry for ethylene and acetylene and a C_{6v} symmetry for benzene. The binding is electrostatic with, in addition, some overlap between the 1s orbital of the HF hydrogen and the p_z atomic orbitals of the carbons. The linear CH₃CN complex exhibits a higher binding energy, due to its dipole moment, while the C₂N₂ linear complex's energy falls in the range of the other complexes examined.

Acknowledgment. This work was supported by grant no. 13908 from the City University of New York, for which we extend our thanks.

Registry No. C₂H₂-HF, 73787-82-3; C₂H₄-HF, 73787-89-0; C₂H₆-HF, 91281-76-4; C₆H₆-HF, 32001-54-0; CH₃CN-HF, 78971-71-8.

Electronic Structure of CNa and CNa₂ in Their Electronic Ground States

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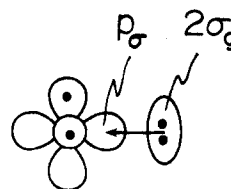
(Received: April 23, 1984)

We have studied the electronic structure of the carbyne CNa and the carbene Na₂C using ab-initio SCF, MCSCF, and CI techniques. We find that CNa has a ⁴ Σ^- ground state with the companion ² Π state being, at best, slightly bound. The carbene Na₂C has a highly bent ³A₂ ground state ($\theta = 86^\circ$) with the linear ³ Σ_g^- state approximately 8 kcal/mol higher. The similarity of the bonding in both CNa and Na₂C to that found for CLi and Li₂C is discussed.

Introduction

Recent work in this laboratory^{2,3} suggested that CLi has a ⁴ Σ^- ground state with a ² Π state some 33 kcal mol⁻¹ higher. This is to be contrasted with CH which has a ² Π ground state^{4,5} and a ⁴ Σ^- excited state approximately 17 kcal mol⁻¹ higher. In addition we predicted² that CLi₂ would have two low-lying triplet states: one of ³ Σ_g^- symmetry, the other of ³A₂ symmetry. The ³ Σ_g^- state is a typical "carbene state" having two unpaired electrons in the p _{π} orbitals of carbon while the ³A₂ is a highly bent ($\theta = 88.1^\circ$) state in which there is substantial Li₂ bonding and for which the

orbital structure admits the representation



i.e., donation of electrons from the Li₂ 2 σ_g bonding MO into a formally empty p σ orbital on C. The ³ Σ_g^- and ³A₂ states are within a few kilocalories of one another and our calculations are not accurate enough to say which is the ground state.

The purpose of this report is to determine to what extent CNa and CNa₂ behave like CLi and CLi₂. Our results indicate that CNa also has a ⁴ Σ^- ground state with the companion ² Π being unbound or at best very slightly bound. Similarly CNa₂ resembles CLi₂ in that the ³ Σ_g^- and ³A₂ are the two lowest triplet states with the highly bent ³A₂ state being the lower.

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TABLE I: Energies (E), Equilibrium Bond Lengths (R_e), Dissociation Energies (D_e), and Spectroscopic Constants of Na_2 and Na_2^+ Molecules

method	E , hartree	R_e , bohr	D_e , kcal mol $^{-1}$	ω_e , cm $^{-1}$	$\omega_e x_e$, cm $^{-1}$	B_e , cm $^{-1}$	α_e , cm $^{-1}$	$10^7 \bar{D}_e$, cm $^{-1}$
$\text{Na}_2^+(\chi^1\Sigma_g^+)$								
ab initio ^a	-323.741 80	5.944	16.37	158.48	0.7024	0.1482	0.001 02	5.19
ab initio ^b	-323.743 04	5.998	16.87	151.64	0.6889	0.1455	0.000 83	5.36
ab initio, this work	-323.729 80 ^c	6.041	13.70	142.73	0.7369	0.1435	0.000 96	5.80
experimental		5.878 ^d	17.12 ^d	159.124 ^e	0.7254 ^e		0.000 874 ^e	5.81 ^e
$\text{Na}_2^+(\chi^2\Sigma_g^+)$								
ab initio, this work ^f	-323.559 17	7.00	20.75	110	0.1925	0.105	0.000 3	3.82
pseudopotential ^g		6.70	~23	126				
experimental		~6.80 ^h	22.83 ⁱ	~105 ^h	~-0.50 ^h			

^aReference 12; R_e and the spectroscopic constants were calculated by us from values in ref 18. ^bReference 13; spectroscopic constants calculated by us from values in ref 19. ^c $E_{\text{SCF}}(R = 6.00 \text{ bohrs}) = -323.70683$ hartrees. ^dKusch, P.; Hessel, M. M. *J. Chem. Phys.* **1978**, *68*, 2591. ^eReference 5. ^fThe only ab initio, all electron, calculation we are aware of is the unpublished one by Wahl and Bertoncini; for the parameters R_e , D_e , and ω_e they predict 6.97 bohrs, 23.0 kcal mol $^{-1}$, and 116 cm $^{-1}$, respectively. ^gReference 15. ^hBarrow, R. F.; Travis, N.; Wright, C. V. *Nature (London)* **1960**, *187*, 141. Robertson, E. W.; Barrow, R. F. *Proc. Chem. Soc.* **1961**; p 329. ⁱHerrman, A.; Schumacher, E.; Wöste, L. *J. Chem. Phys.* **1978**, *68*, 2327. In ref 5 a value of 21.68 kcal mol $^{-1}$ is given.

Basis Sets, Computational Details, Fragment Energies

For the carbon atom the Gaussian (11s,6p) basis set was obtained from the van Duijneveldt compilation⁶ and it was contracted to [5s,3p] according to Raffanetti.⁷ This gives an energy $E(^3\text{P}) = -37.68802$ hartrees, 0.00060 hartree higher than the corresponding Hartree-Fock energy. For the sodium atom the Gaussian basis of McLean-Chandler⁸ was employed; the (12s,9p) primitive set was contracted following Raffanetti⁷ to [6s,4p]. With this basis, the SCF energies for the ^2S and ^2P states of Na are -161.853 98 and -161.781 33 hartrees, respectively. The HF energy is $E(^2\text{S}) = -161.858 89$ hartrees. The excitation energy $^2\text{S} \rightarrow ^2\text{P}$ computed above is 0.07265 hartree or 1.977 eV which compares fairly well with the experimental 2.103 eV.⁹ The MCSCF function which takes into account the near degeneracy of the carbon 2s,2p orbitals has the form

$$1s^2(2s^2 - \lambda 2p_x^2)2p_x 2p_y \alpha \alpha$$

and results in the energy $E(^3\text{P}) = -37.706892$ hartrees with $\lambda = 0.1504$. Na_2 has a $^1\Sigma_g^+$ ground state with an SCF description

$$|^1\Sigma_g^+\rangle = \mathcal{A}\{1\sigma_g^2 2\sigma_g^2 3\sigma_g^2 4\sigma_g^2 1\sigma_u^2 2\sigma_u^2 3\sigma_u^2 1\pi_u^4 1\pi_u^4\} = \mathcal{A}\{(\text{core})4\sigma_g^2\}$$

At the SCF level an equilibrium bond distance of $^1\Sigma_g^+$ is obtained at $R_e = 6.00$ bohrs but the state is unbound with respect to two ^2S Na atoms by ~ 0.001 hartree.¹¹ Following the paper of Stevens et al.¹² a four-configurational MCSCF wave function was constructed

$$|^1\Sigma_g^+\rangle = \mathcal{A}\{(\text{core})[C_{\text{SCF}}4\sigma_g^2 + C_1 4\sigma_u^2 + C_2 5\sigma_g^2 + C_3 2\pi_u^2]\}$$

where the three configurations included in addition to the SCF take into account left-right, in-out, and angular correlations respectively. At infinite internuclear separation the CI coefficients have the values $C_{\text{SCF}} = C_1 = 2^{1/2}$, $C_2 = C_3 = 0.0$. Figure 1 shows the potential energy curve of $\text{Na}_2(^1\Sigma_g^+)$ and Table I summarizes its spectroscopic properties. Ab initio results from much more extended MCSCF calculations^{12,13} are included in Table I for comparative purposes. It is clear that our basis set and the 4-MCSCF expansion cope nicely with the properties of this system at least in describing the ground state. Notice that the binding energy of Na_2 is "pure correlation energy".

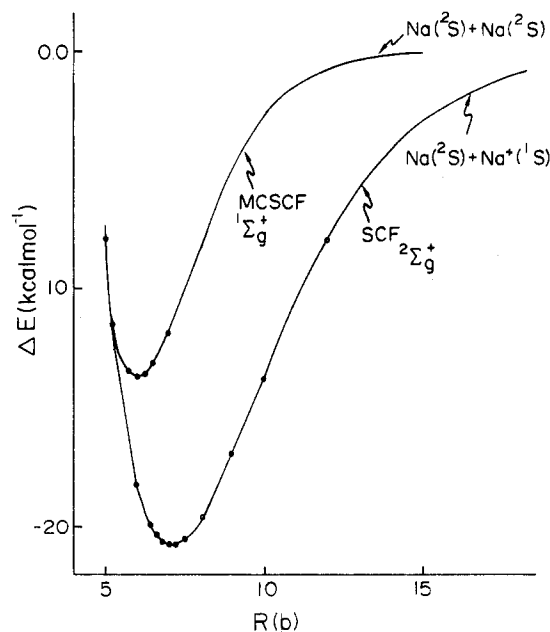


Figure 1. Potential energy curves for $\text{Na}_2(^1\Sigma_g^+)$ and $\text{Na}_2^+(^2\Sigma_g^+)$.

When an electron is removed from the $4\sigma_g$ (bonding) orbital $\text{Na}_2^+(^2\Sigma_g^+)$ is created with just one electron in its valence space. Figure 1 shows the (SCF) potential curve of Na_2^+ and Table I summarizes its spectroscopic properties. We observe the following. In the SCF approximation Na_2^+ separates smoothly to the ground-state atoms $\text{Na}^+(^1\text{S}) + \text{Na}(^2\text{S})$ (in order to pull the molecule apart safely the g,u symmetries of the orbitals were relaxed). The dissociation energy of Na_2^+ is larger than that of Na_2 (in conflict with the usual ideas about bonding molecular orbitals), a common phenomenon for all alkali diatomic positive ions, something speculated as early as 1935 by James¹⁴ in an early ab initio study of Li_2^+ .

It seems that the next bound state of Na_2^+ is a $^2\Pi_u = \mathcal{A}\{(\text{core})2\pi_u^1\alpha\}$ correlating with $\text{Na}^+(^1\text{S}) + \text{Na}(^2\text{P})$. A potential energy calculation gives the values $E = -323.45514$ hartrees, $D_e = 1.1$ kcal mol $^{-1}$ with respect to $\text{Na}^+(^1\text{S}) + \text{Na}(^2\text{P})$, and $R_e \cong 10.3$ bohrs. The energy gap is estimated to be 65.3 kcal mol $^{-1}$. The corresponding pseudopotential values of Bardsley et al.¹⁵ are ~ 6.5 kcal mol $^{-1}$, ~ 9.5 bohrs, and ~ 65.9 kcal mol $^{-1}$.

Our previous experience^{2,3} with the CLi , CLi_2 , as well as our present investigations (vide infra) made clear that expansion of the basis set by adding functions of higher angular momentum are not of importance for this system and for our purposes. If

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(11) We added a set of six functions of d symmetry on each Na atom and varied the exponent around the suggested value of 0.1 (Roos, B.; Siegbahn, P. *Theor. Chim. Acta* **1970**, *17*, 199. Hariharan, P.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. The energy was very insensitive to the d functions, the energy gain being less than 5×10^{-4} hartree.

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TABLE II: Energies (E), Equilibrium Bond Lengths (R_e), Dissociation Energies (E_d), and Spectroscopic

method	E , hartree	R_e , bohr	D_e^a , kcal mol ⁻¹	ω_e , cm ⁻¹	$\omega_e x_e$, cm ⁻¹	B_e , cm ⁻¹	α_e , cm ⁻¹	$10^6 \bar{D}_e$, cm ⁻¹
				$^4\Sigma^-$				
SCF	-199.589 3	4.26	29.7					
MCSCF	-199.594 8	4.294	21.3	409.6	-9.041	0.4140	0.0042	1.69
				$^2\Pi$				
SCF	-199.512 02	4.60	-18.8 ^b					
MCSCF	-199.557 12	~4.60	~-2.30 ^b					

^a 1 hartree = 627.51 kcal mol⁻¹ = 219471.6 cm⁻¹. ^b Unbound with respect to ground state atoms.

the computations are confined in the sp atomic space the CNa molecule is represented by 68 primitives contracted to 32 basis functions while the CNa₂ molecule is composed of 107 primitives contracted to 50 basis functions.

All our calculations were performed with the program ALIS.¹⁶ The underlying idea in the present calculations is that the molecular space can be divided into "core" and "valence" spaces. Assuming that the correlation energy (dynamic, static) of the core can be treated more or less as a constant we are left with a relatively small number of valence or "active" electrons that can be described sufficiently accurately by small, compact, multiconfigurational wave functions (MCSCF functions). Our numerical results show that most of the chemistry can be captured by using carefully constructed MCSCF wave functions.

CNa Results

In what follows we consider the carbon 1s and sodium 1s,2s,2p orbitals as being core orbitals and thus have the SCF configurations

$$^4\Sigma^-: (\text{core})5\sigma^2 6\sigma^1 2\pi_x^1 2\pi_z^1 \alpha\alpha\alpha$$

$$^2\Pi: (\text{core})5\sigma^2 6\sigma^2 2\pi_x^1 \alpha$$

where

$$\text{core} = 1\alpha^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4$$

The SCF wave function for the $^4\Sigma^-$ state predicts an equilibrium bond length of 4.266 bohrs with a total energy of -199.5893 hartrees and a binding energy of 29.7 kcal/mol relative to the separated SCF atoms. At this level the $^2\Pi$ state shows a minimum energy at 4.60 bohrs but is unbound relative to the separated SCF atoms by ~19 kcal/mol. At the SCF level the $^4\Sigma^-$ state is definitely the ground state.

The MCSCF function which permits the $^4\Sigma^-$ state to dissociate correctly to the correlated C(³P) and Na(²S) is composed of the configurations

$$5\sigma^2 6\sigma 2\pi_x 2\pi_z$$

$$6\sigma 7\sigma^2 2\pi_x 2\pi_z$$

$$5\sigma 6\sigma 7\sigma 2\pi_x 2\pi_z$$

While the five open-shell configuration gives rise to four quartet spin eigenfunctions the function in which 5σ and 7σ are singlet coupled was excluded. Table II condenses our results and Figure 2 shows the potential curve to 6.0 bohrs. Around the calculated equilibrium separation of 4.294 bohrs the weight of the SCF configuration in the MCSCF function is 0.997 indicating clearly the adequacy of the SCF ansatz for this state. Note that the binding energy has been reduced to 21.3 kcal/mol because of the loss of the near degeneracy¹⁸ effect in the molecule. Considerable insight into the nature of the bonding in this state is obtained by transforming the 5σ,7σ pair to the GVB¹⁷ representation. The contours of the GVB valence orbitals are shown in Figure 3. They are strikingly similar³ to those of CLi and suggest strongly that we are dealing with a very ionic molecule. It seems that as the Na(²S) atom approaches the C(³P) atom an electron is transferred from the former to the latter resulting in the in situ atoms C(⁴S)

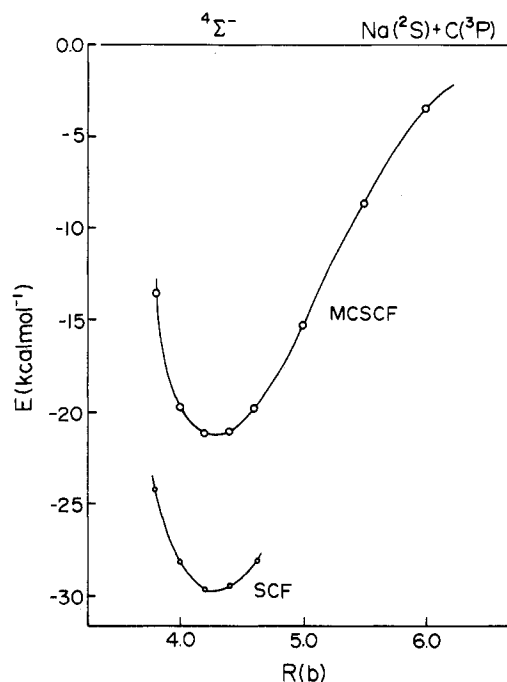


Figure 2. Potential energy curve of CNa($^4\Sigma^-$).

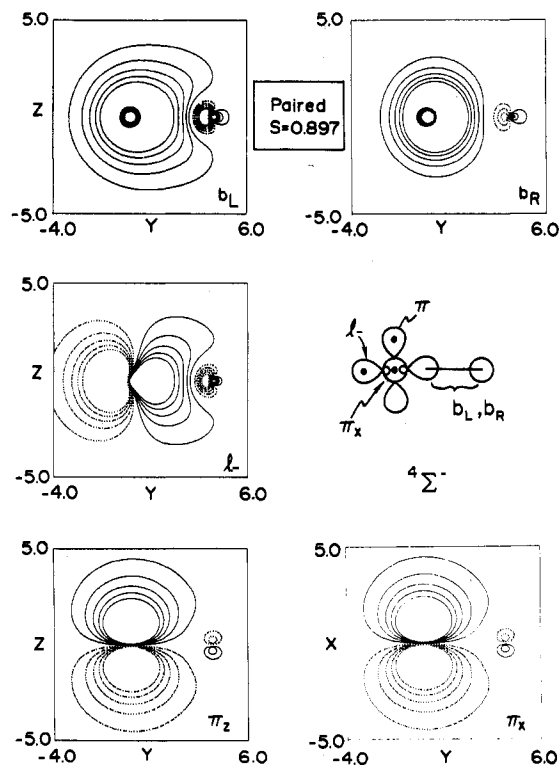


Figure 3. Valence orbital contours of CNa at the equilibrium separation in the $^4\Sigma^-$ state. The plots have uniformly spaced contours with increments of ± 0.02 au beginning with ± 0.02 au. Positive contours are indicated by solid lines and negative contours by dotted lines. The same conventions are used in all plots.

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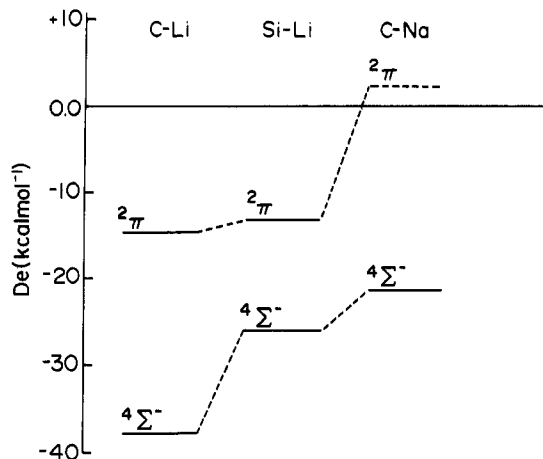


Figure 4. Calculated bond energies of CLi, SiLi, and CNa.

and $\text{Na}^+(^1\text{S})$ which project as $^4\Sigma^-$ in the molecular environment. This picture is identical with that proposed for CLi. Further support for this ionic interpretation is obtained as follows. At infinity the total energy of the system $\text{Na}^+(^1\text{S})$ and $\text{C}^-(^4\text{S})$ is $-161.67213 + (-37.70286) = -199.3750$ hartrees which differs by 0.220 hartree from the MCSCF energy of the molecule listed in Table I. If a pure Coulombic interaction is assumed between C^- and Na^+ a lowering in energy of 0.220 hartree is obtained at $R_{\text{CNa}} = 4.55$ bohrs which compares well with the MCSCF calculated separation of 4.29 bohrs. Certainly polarization effects play a role but the binding energy is essentially due to the ionic attraction.

The MCSCF description of the $^2\Pi$ state includes the SCF configuration and the following three

$$\begin{aligned} &5\sigma^27\sigma^22\pi_x\alpha \\ (\text{core}) &6\sigma^22\pi_z^22\pi_x\alpha \\ &5\sigma^26\sigma7\sigma2\pi_x\alpha\beta\alpha \end{aligned}$$

The first and second configurations take into account left-right and the near degeneracy¹⁸ correlation, respectively. The last configuration ensures the correct asymptotic products. At this MCSCF level the potential curve for the $^2\Pi$ state is purely repulsive.

Figure 4 compares the binding energies of CLi,³ SiLi,³ and CNa calculated with wave functions of comparable accuracy. Substituting Na for Li reduces the bond energy of $^4\Sigma^-$ CX by 16.2 kcal/mol. If this energy difference was purely Coulombic and resulted from the larger separation in CNa (4.29 bohrs) relative to CLi (3.70 bohrs) the charge on the atoms would have to be 0.8 units of an electron further supporting a very ionic molecule.

The Two Lowest Triplet States of Na_2C

By analogy² with Li_2C we anticipate that the $^3\Sigma_g^-$ ($^3\text{B}_1$ in C_{2v} symmetry) or the $^3\text{A}_2$ are the contenders for the ground state of Na_2C . Of the 28 electrons in Na_2C we regard 6 as valence and assign the remaining 22 to the core. Defining

$$(\text{core}) \equiv 1\sigma_g^22\sigma_g^23\sigma_g^24\sigma_g^21\sigma_u^22\sigma_u^23\sigma_u^21\pi_u^41\pi_g^4$$

we may write the various SCF configurations of interest as

$$\begin{aligned} |^3\Sigma_g^- \rangle &= \mathcal{A}(\text{core})5\sigma_g^24\sigma_u^22\pi_{uz}^22\pi_{ux}\alpha\alpha \\ |^3\text{B}_1 \rangle &= \mathcal{A}(\text{core})6a_1^25b_2^27a_1^22b_1\alpha\alpha \\ |^3\text{A}_2 \rangle &= \mathcal{A}(\text{core})6a_1^27a_2^22b_1^25b_2\alpha\alpha \end{aligned}$$

The effect of adding diffuse p functions and d functions to the carbon atom basis was investigated at the SCF level for the $^3\Sigma_g^-$ state and the results are summarized in Table III. Neither of these additional functions are of importance in this case and all

TABLE III: SCF Energies of CNa_2 in Different Basis Sets, $^3\Sigma_g^-$ State

basis set	E_{SCF} , hartree	R_e , bohr
$[5s3p/6s4p/6s4p]^a$	-361.413 79	4.43
$[5s3p1p'/6s4p/6s4p]^a$, $\alpha_{p'} = 0.03$	-361.415 49	4.416
$[5s3p1p'1d/6s4p/6s4p]^a$, $\alpha_{p'} = 0.03$; $\alpha_d = 0.20$	-361.416 90	4.42
$[5s3p/6s4p/6s4p]^b$	-361.413 0	4.43
$[5s3p1d/6s4p/6s4p]^b$, $\alpha_d = 0.75$	-361.413 26	4.43 ^c

^aHuzinaga basis set on Na, ref 10. ^bMcLean-Chandler basis set on Na, ref 8. ^cNo optimization was done.

TABLE IV: Energies (E), Equilibrium Geometries (R_e , θ_e), and MCSCF Expansion Coefficients of Triplet States for the CNa_2 Molecular System

method	E , hartree	R_e , bohr	θ_e , deg	MCSCF coefficients		
				C_{SCF}	C_1	C_2
$^3\Sigma_g^-$						
SCF	-361.413 0	4.43	180	1.0		
MCSCF	-361.458 80	4.480	180	0.827	-0.379	0.414
MCSCF+CI	-361.463 58	4.479	180			
$^3\text{A}_2$						
SCF	-361.403 23	4.815	81.4	1.0		
MCSCF	-361.470 68	4.60	86.0	0.7527	-0.4429	0.4871
MCSCF+CI	-361.475 88	4.60	86.0			

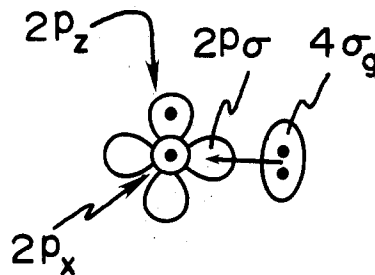
subsequent calculations were done with the McLean-Chandler basis⁸ with no added polarization functions.

Small exploratory CI calculations on the $^3\Sigma_g^-$ state revealed that in addition to the SCF configuration the configurations

$$\begin{aligned} &(\text{core})5\sigma_g^25\sigma_u^22\pi_{uz}2\pi_{ux} \\ &(\text{core})5\sigma_g^24\sigma_u5\sigma_u2\pi_{uz}2\pi_{ux} \end{aligned}$$

are most important. For this last configuration only the eigenfunction in which the $4\sigma_u$, $5\sigma_u$ and $2\pi_{uz}$, $2\pi_{ux}$ are individually triplet coupled is important. Since the $5\sigma_g$ orbital is essentially the 2s on carbon and the $4\sigma_u$ is dominated by the carbon $2p_\sigma$ orbital we interpret these two correlating configurations as allowing for left-right correlation and permitting the proper spin multiplicity on the asymptotic products. An MCSCF function using these three configurations was constructed for the $^3\Sigma_g^-$ state and resulted in the energy and bond length reported in Table IV. At the SCF and MCSCF level the energy rises as the Na-C-Na angle is reduced and as with Li_2C we conclude² the molecule is linear in this configuration. Finally, using the valence orbitals $5\sigma_g$, $6\sigma_g$, $4\sigma_u$, $5\sigma_u$, $2\pi_{uz}$, and $2\pi_{ux}$ which all but the $6\sigma_g$ have been optimized by the MCSaCF process we constructed a complete CI within this space. These results are also collected in Table IV.

We imagine the $^3\text{A}_2$ state resulting from the interaction of a ^3P carbon atom and a $^1\Sigma_g^+$ Na_2 molecule. Specifically, the $4\sigma_g$ bonding orbital of Na_2 interacts with the empty $2p_\sigma$ orbital on carbon with the 2s orbital on carbon remaining doubly occupied and the triplet multiplicity being carried by the unpaired 2p electrons on carbon. Schematically



and in an obvious notation

$$|^3\text{A}_2 \rangle \sim (\text{core})2s^2(p_\sigma + \sigma_g)^2p_xp_y\alpha\alpha$$

or

$$|^3\text{A}_2 \rangle \sim (\text{core})6a_1^27a_2^22b_1^25b_2\alpha\alpha$$

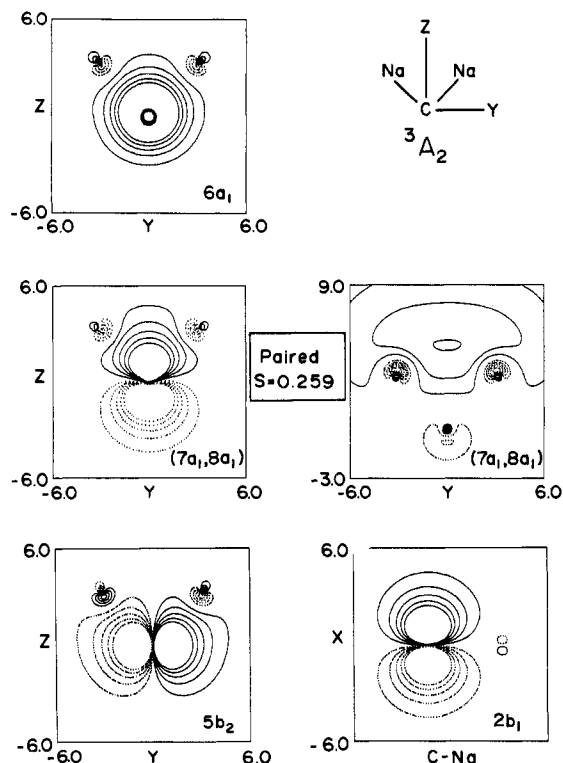


Figure 5. Valence orbital contours of CNa₂ in its equilibrium geometry in the ³A₂ state.

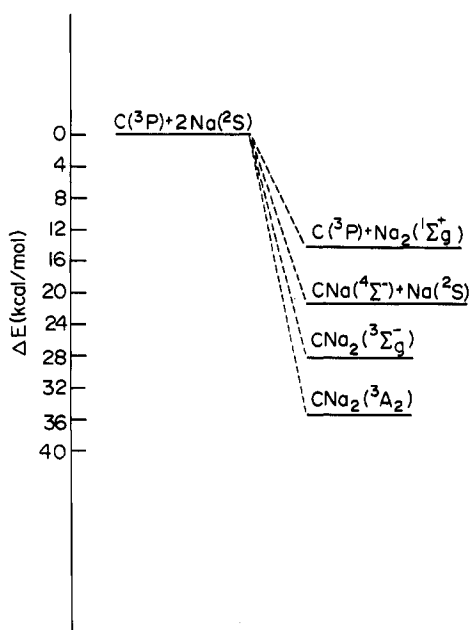
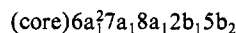
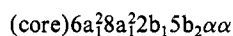


Figure 6. Calculated relative energies of CNa₂ and various neutral dissociation products.

Exploratory CI calculations reveal that in addition to the SCF configurations the most important contributors to the ³A₂ state are



where once again the eigenfunction in which the 7a₁, 8a₁ and 2b₁, 5b₂ are individually triplet coupled is of importance for the four open shell configuration. An MCSCF function constructed with the three configurations results in the energy and geometry reported in Table IV. As with Li₂C the molecule in this state is highly bent and examination of the MCSCF orbitals suggests that the in situ carbon atom is essentially C⁻ while the sodium fragment

is Na₂⁺. Further evidence for this is obtained by transforming the 7a₁, 8a₁ orbitals to the GVB representation and contouring the resulting functions. These contours are shown in Figure 5 and bear a striking resemblance² to the corresponding orbitals in Li₂C.

The remarkably large coefficients for the MCSCF configurations may be understood as follows. If we imagine C⁻(⁴S) and Na₂⁺(²Σ_g⁺) at ∞ we may construct a ³A₂ function as

$$|^3A_2(\infty)(m=+1)\rangle = -(\frac{3}{4})^{1/2} |^4S(m=\frac{3}{2})^2 \Sigma_g^+(m=-\frac{1}{2})\rangle + (\frac{1}{4})^{1/2} |^4S(m=\frac{1}{2})^2 \Sigma_g^+(m=+\frac{1}{2})\rangle$$

where the relative weights are the appropriate Clebsch-Gordan¹⁹ coefficients. Using

$$|^4S(m=\frac{3}{2})\rangle = |2p_x 2p_y 2p_z \alpha \alpha \alpha\rangle$$

$$|^4S(m=\frac{1}{2})\rangle = |2p_x 2p_y 2p_z \left(\frac{\alpha \beta + \alpha \beta \alpha + \beta \alpha \alpha}{3^{1/2}} \right)\rangle$$

$$|^2\Sigma_g^+(m=\frac{1}{2})\rangle = |4\sigma_g \beta\rangle$$

and the association

$$7a_1 = (2p_z + 4\sigma_g)/2^{1/2}$$

$$8a_g = (2p_z - 4\sigma_g)/2^{1/2}$$

$$2b_1 = 2p_x$$

$$5b_2 = 2p_y$$

and the Serber²⁰ spin functions (both triplets)

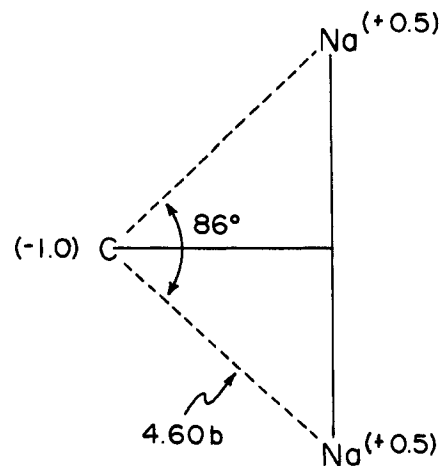
$$|ST\rangle = (\alpha\beta - \beta\alpha)\alpha\alpha/2^{1/2}$$

$$|TT\rangle = [(\alpha\beta + \beta\alpha)\alpha\alpha - \alpha\alpha(\alpha\beta + \beta\alpha)]/2$$

we have the equivalent representation

$$|^3A_2(\infty)(m=+1)\rangle = -0.500|7a_1^2 2b_1 5b_2(ST)\rangle + 0.500|8a_1^2 2b_1 5b_2(ST)\rangle - 0.707|7a_1 8a_1 2b_1 5b_2(TT)\rangle$$

Of course as the C⁻ and Na₂⁺ approach one another maintaining ³A₂ symmetry the relative coefficients and forms of the orbitals change. However, we see from Table IV that the coefficients at equilibrium (-0.75, +0.44, -0.49) are comparable to those characteristic of a purely ionic system (-0.50, +0.50, -0.71). Additional support for this ionic model comes from an estimate of the Coulombic stabilization relative to the C⁻ and Na₂⁺ fragments. The equilibrium geometry and approximate charge distribution of the ³A₂ state is represented schematically as



Assuming this charge distribution we predict a bond length for

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the Na_2 in the molecule larger than the $\text{Na}_2(1^1\Sigma_g^+)$ bond length but smaller than the $\text{Na}_2^+(2^1\Sigma_g^+)$. Indeed from the above geometry we obtain ~ 6.3 bohrs which is $6.0 < 6.3 < 7.0$, where the two extremes refer to Na_2 and Na_2^+ bond lengths, respectively. Our MCSCF+CI calculation predicts a stabilization of the CNa_2 in the 3A_2 state with respect to C^- and Na_2^+ of $+0.214$ hartree. From Coulomb's law and using the above charge distribution and geometry we obtain $2 \times 0.5/4.6 = 0.217$ hartree.

Conclusions

CNa , like CLi , has a $4^2\Sigma^-$ ground state and is quite ionic. It is bound by at least 21 kcal/mol which at the MCSCF level of theory is 16 kcal/mol less bound than CLi . Our calculations suggest that unlike CLi the $^2\Pi$ state of CNa is at best very slightly bound. The ground state of CNa_2 seems to be the highly bent 3A_2 state which like CLi_2 is characterized by electron donation

from the σ_g bonding molecular orbital of the alkali diatomic to the formally empty $2p_x$ orbital of C. As with CLi_2 there seems to be a one-electron bond between the alkali atoms and an essentially ionic interaction between the resulting alkali dimer cation and C^- . This 3A_2 state is bound relative to the separated atoms by at least 35 kcal/mol and is approximately 7 kcal/mol below the linear $^3\Sigma_g^-$ state. These relative energies are summarized in Figure 6. While the energy separations reported in this work will change with more elaborate calculation we expect the physical picture of the bonding in the $4^2\Sigma^-$ state of CNa and the 3A_2 state of CNa_2 to survive.

Acknowledgment. A.M. thanks the North Atlantic Treaty Organization for financial support in the form of a NATO Science Fellowship.

Registry No. CNa , 91585-80-7; Na_2C , 91550-38-8.

pH-Induced Motional and Conformational Changes of Amino Acids. A Reexamination by Deuterium Longitudinal Nuclear Relaxation

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(Received: October 27, 1983; In Final Form: April 18, 1984)

A description of the dynamics of simple amino acids in aqueous solution has been inferred from deuterium relaxation. The deuterium longitudinal relaxation rate, which is dominated by the quadrupolar mechanism, is nearly insensitive to paramagnetic impurities and proves therefore to be an excellent mobility probe for $[^2\text{H}_5]\text{glycine}$ and $2\text{-}[^2\text{H}_1]\text{alanine}$. The experimental results are related to the extent of intra- and intermolecular interactions at different pH values.

Introduction

Nuclear magnetic resonance studies of conformational and motional behavior of simple amino acids like glycine and alanine have been reported in several papers¹⁻⁸ during the past decade, but experimental data and conclusions are partly discordant. From a ^{13}C NMR investigation performed on solutions free of paramagnetic impurities, Pearson et al.⁵ reported that dipole-dipole relaxation rates of glycine carbons do not change between pH 3 and pH 10 for 1.0 M solutions of glycine; this observation would lead to the conclusion that the molecular motion remains unchanged. In later work, Valentine et al.⁶ observed that ^{17}O line widths of enriched glycine and alanine decrease from pH 1 to pH 7 but increase in the higher pH range. The authors attribute the line-width reduction to a higher mobility of the zwitterion, which is of smaller size because of intramolecular ionic interaction and being less solvated.

Recently, Gerotheranassis et al.⁸ discarded this assumption and claimed that the observed line-width decrease is due only to ^{17}O

quadrupole coupling constant variation. In addition, these authors reported that if EDTA^{4-} is added to the solutions, no line-width increase is observed in the higher pH range extending from pH 7 to pH 13. This observation is consistent with other reports of the marked tendency of amino acids toward association with certain paramagnetic ions.^{5,9,10}

Among the possible nuclear probes for molecular dynamic investigation, deuterium is one of the most useful,¹¹⁻¹⁶ owing to its dominant quadrupole nuclear relaxation mechanism. In the present work, we report a study of deuterium longitudinal relaxation rates of glycine and alanine observed in a pH range extending from 0 to 13.

Experimental Section

$[^2\text{H}_5]\text{Glycine}$ and $\text{D,L-2-}[^2\text{H}_1]\text{alanine}$ were purchased from Aldrich and Merck Sharpe & Dohme, respectively. The pH of

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