

# An *ab initio* Study of Formamide

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Calculated energy and molecular properties of the ground and low-energy excited states of formamide are presented at the ground state geometry. Satisfactory results are obtained except for the  $^1\pi\pi^*$  energy which remains too high by 1 eV (which is nevertheless a large improvement over previous calculations). The predicted triplet energies lie at 5.4 eV ( $^3n\pi^*$ ) and 5.8 eV ( $^3\pi\pi^*$ ).

**Key words:** Formamide, low-energy excited states of ~

## 1. Introduction

Most of the interest in the optical spectrum of the amide group comes from the fact that it is the basic chromophore in polypeptides and hence the spectra of these biologically important molecules cannot be understood unless the component monomer spectrum is properly assigned [1–3]. Formamide is the smallest molecule containing an amide group and has, therefore, been the subject of considerable previous investigation [4–27]. Most of the work has been concerned with rotational barriers and other parameters determining the ground state geometry of polypeptides, but some of it has dealt with the vertical excitation spectrum.

The reported spectrum (below 10 eV) consists of five assigned singlet-singlet transitions. Robin [1] has given an excellent summary of past work on the molecule to which the reader should refer for more details. Table 1 is an attempt to summarize the conclusions of Robin. The  $V_1$  band is the most intense with an oscillator strength of 0.37, but  $R_1$  ( $f=0.06$ ),  $R_2$ , and  $Q$  all have considerable strength. Among the configurations listed, only  $\pi_1\pi^*$ ,  $\pi_2\pi^*$ , and  $n\sigma^*$  give large transition moments although  $n3s$  is appreciable. The transitions assigned as  $W$ ,  $R_1$ , and  $V_1$  are fairly certain but the assignment of  $R_2$  and  $Q$  as well as the location of the many unobserved states is based on reasonable speculation.

The triplet states of formamide have only recently been observed [28] and their location is of paramount interest because of their implication regarding the location of the lowest excited state of polypeptides. Robin estimated the lowest triplet states to be  $^3n\pi^*$  (3.8 eV) and  $^3\pi\pi^*$  (4.4 eV) by Gaussian orbital SCF calculations for the ground and excited states. These should be over 1 eV too low because of differential correlation effects. The Pullmans [2] favor a value of 5.3 eV for  $^3n\pi^*$  and 5.9 eV for  $^3\pi\pi^*$ . Both predictions agree that  $^3\pi\pi^*$  is about 0.6 eV above  $^3n\pi^*$ . Since the  $^3n\pi^*$  state

Band	Energy (eV)	Designation
<i>W</i>	5.7	$^1n\pi^*$
<i>R</i> <sub>1</sub>	6.7	$^1n3s, ^1\pi_23s$ (2 bands)
<i>V</i> <sub>1</sub>	7.3	$^1\pi_2\pi^*$
—	7.5 <sup>c</sup>	$^1n\sigma^*$
—	—	$^1\pi_2\sigma^*$
<i>R</i> <sub>2</sub>	7.9	$^1n3p, ^1\pi_23p$ (6 bands)
<i>Q</i>	9.2	$^1\pi_1\pi^*, ^1n3d, ^1\pi_23d, ^1n4s$ $^1\pi_4s, ^1n4p, ^1\pi_4p$
	10.32	$n \rightarrow \infty$
	10.52	$\pi_2 \rightarrow \infty$
	14.18 <sup>b</sup>	$\pi_1 \rightarrow \infty$
	14.75 <sup>b</sup>	$\sigma \rightarrow \infty$

Table 1. Excited states of formamide<sup>a</sup>

<sup>a</sup> Paraphrased from Robin (Ref. [1]). In cases where several bands are expected to occur near the same energy, the one expected to be responsible for the observed intensity is listed first.

<sup>b</sup> Order reversed by Robin from original assignment (Ref. [41]).

<sup>c</sup> Deduced from polypeptide spectra; not actually observed.

should lie only a little below the  $^1n\pi^*$  state at 5.7 eV, the Pullman estimates seem very reasonable. Maria *et al.* [3] on the other hand, argue strongly for a low-lying  $^3\pi\pi^*$  state near 4.3 eV (3 eV below  $^1\pi\pi^*$ ). Staley *et al.* [28], have reported trapped electron spectra which they interpret as showing the  $^3n\pi^*$  state at 5.30 eV and the  $^3\pi\pi^*$  and/or  $^3n3s$  states (unresolved) at 6.60 eV. The resolution of their spectra make this interpretation somewhat ambiguous, however.

The principal technical difficulty blocking reliable calculations has been felt to be that the authors [4–7] were unable to solve the SCF equations appropriate for certain excited states such as  $^1\pi\pi^*$ . Also, configuration interaction was not always considered. These two factors reduced agreement with experiment and made assignments of the spectrum difficult. Two important questions have not been satisfactorily resolved. Since the triplet states have not been unambiguously assigned, the ordering of the  $n\pi^*$  and  $\pi\pi^*$  triplet states remained uncertain. There is some controversy over the suggestion that the lowest triplet may be of low enough energy to act as an energy sink or transfer route in proteins. The other major problem has been the discrepancy between the experimental assignment of the strong transition occurring at 7.32 eV as  $\pi\pi^*$  and many non-empirical calculations which would predict a significantly higher energy for this transition.

## 2. Calculation Method

The ground state equilibrium geometry was taken from the recent paper by Kitano and Kuchitsu [29] in which they present the results of merging microwave and electron diffraction data. The electron diffraction data were considered superior for the skeleton and the microwave results better for the hydrogen positions. The conclusion of this work was that the data were consistent with a completely planar conformation for the molecule. Formamide had been studied by microwave techniques twice previously. The first study by Kurland and Wilson [30] predicted a planar molecule. The

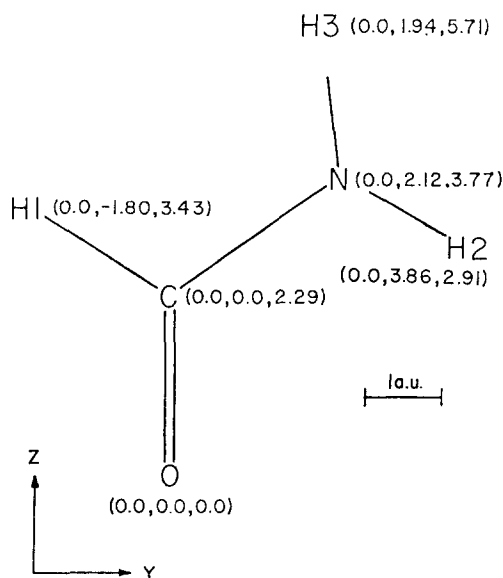


Fig. 1. Molecular coordinate system

second, by Costain and Dowling [31], predicted slight non-planarity of the two amine hydrogens. Concurrently another microwave study was done from which the investigators concluded the molecule was planar. The Kitano and Kuchitsu geometry converted to Cartesian coordinates in Bohr units is shown in Fig. 1. This geometry was also used for all excited states since the purpose of this calculation was to obtain vertical excitation energies.

The basis set adopted was based on contracted Gaussian lobes. These were constructed from Huzinaga's [32]  $10s6p$  sets by first representing each of Huzinaga's  $p$  functions as the difference of Gaussian lobes of exponent  $\alpha$  displaced  $\pm 0.03\alpha^{1/2}$  from the atomic nucleus. The  $s$  orbitals were contracted as  $[6/2/1/1/1]$  and the  $p$  orbitals as  $[4/1/1]$  following Dunning's [33] procedure with coefficients taken from atomic SCF calculations for N, C, and O. The hydrogen orbitals were contracted  $[4/1/1]$  from Huzinaga's  $6s$  set using coefficients from an NH calculation. As in previous calculations, polarization was represented by a clover-leaf pattern of uncontracted lobes around the bond axis between each pair of atoms and in the oxygen lone pair region. Diffuse basis functions to represent the  $3s$  and  $3p$  Rydberg orbitals were constructed from Gaussian lobes with orbital exponent 0.036 centered on the carbon atom. Diffuse  $3d$  functions constructed from lobes could not be included because of loss of significant figures due to differencing in forming the integrals.

All calculations except for the  $^1\pi\pi^*$  state were done by the same procedure. First the SCF equations were solved for the state of interest (using modified SCF methods for excited states as needed) [34]. Then a large CI matrix was formed which included all single excitations and double excitations (based on ICSCF orbitals) selected by perturbation theory. For the  $^1\pi\pi^*$  states a non-orthogonal SCF procedure was followed which allowed the  $\pi$  and  $\pi^*$  orbitals to be non-orthogonal [34]. These non-orthogonal orbitals were then orthogonalized by the transformation which produces the  $^1\pi\pi^*$  configuration

built from orthogonal orbitals which has maximum overlap with the one obtained from the SCF procedure [35].

### 3. Ground State

A reasonable estimate of the experimental energy of a molecule is useful when doing a calculation of this type. The total energy can be estimated by summing the atomic energies and the heat of formation and subtracting the zero point energy. The atomic energies of formamide [36] total  $-169.0781$  a.u. The zero point correction [37] is about  $0.0433$  a.u. The binding energy from thermodynamic tables for the heat of reaction [38]



at  $298^\circ\text{K}$  was corrected for estimated heat capacities of atoms and  $\text{HCONH}_2$  (vapor) to give a binding energy at  $0^\circ\text{K}$  of  $-0.8541$  a.u. This agrees well with a value of  $-0.8514$  obtained by summing standard bond energies [39] plus a typical correction for amide resonance [40]. The atomic energies used here are experimental numbers while the Hamiltonian used in our calculations was non-relativistic. Hence, our expected result will be in error by about  $0.079$  a.u. due to relativistic effects [41]. Therefore the (non-relativistic) result to which our calculations should be compared is about  $-169.896$  a.u.

The SCF energy obtained from the basis set described previously was  $-168.9857$  a.u. This is considerably below the earlier results of  $-168.8661$  by Basch *et al.* [4],  $-168.5259$  by Robb and Czismadia [5], or  $-168.963$  by Christensen *et al.* [13]. With this basis set the sum of SCF atomic energies is  $-168.3896$  compared to the total Hartree-Fock atomic energy of  $-168.399$ . This indicates that at least  $0.01$  a.u. have been lost by use of this basis set at the SCF level. The calculated SCF binding energy is  $-0.60$  or about 70% of the experimental value.

Both the canonical and ICSCF orbital energies are listed in Table 2. It is especially worth noting that, just as for urea, the ICSCF vertical orbitals give a better indication of likely transitions since they place the  $\pi^*$  orbital as the first virtual orbital whereas it was the third canonical orbital following two  $\sigma^*$  orbitals. The other particularly interesting feature is that, although both the canonical and ICSCF results predict the  $\pi$  orbital to be highest in energy with the  $n$  orbital slightly lower, the near-degeneracy is much closer for the ICSCF orbitals. The concept of this near-degeneracy was first broached by Hunt and Simpson [42] as the result of simple Hückel theory and their relative order has been subject to considerable examination. Photoelectron spectroscopy data [43] indicate that the  $n$  orbital actually has the lowest ionization potential. Therefore formamide seems to be an example of a case where reorganization and correlation effects dominate in the determination of the relative binding energies of the electrons. The reported value for the first ionization potential is  $10.3$  eV compared with the Koopmans theorem results of  $11.9$  eV for the  $n$  orbital and  $11.5$  eV for the  $\pi$  orbital.

The set of ICSCF orbitals was truncated to the  $44a'$  and  $16a''$  orbitals of lowest orbital energy. All possible doubly excited configurations were ordered by perturbation

Table 2. Orbital energies of formamide (eV)

Label	Canonical	ICSCF <sup>a</sup>
1a'	-558	-551 1sO
2a'	-424	-420 1sN
3a'	-309	-306 1sC
4a'	-37.8	-38.0 2sO
5a'	-33.0	-34.7
6a'	-23.0	-25.4
7a'	-20.3	-22.7
8a'	-18.3	-20.4
9a'	-16.5	-17.6 ( $\sigma$ ) CC bond
10a'	-11.9	-13.1 ( $n$ )
1a''	-15.6	-17.2 ( $\pi_1$ )
2a''	-11.5	-13.0 ( $\pi_2$ )
11a'	1.7	-3.5 (3s)
12a'	2.2	-2.7 (3py)
13a'	2.9	-1.9 (3pz)
14a'	4.7	-0.7 (3d)
3a''	2.5	-6.0 ( $\pi^*$ )
4a''	3.9	-2.0 (3p $\pi$ )

<sup>a</sup> Biased by  $(V_{ee} - V_{NN})/N$  relative to the usual definition (Ref. [48]).

Table 3. Dominant configurations in the ground state wave function

Configuration	Weight <sup>a</sup>
SCF	0.957
$\pi_2^2 \rightarrow \pi^{*2}$	0.0040
$\pi_1^2 \rightarrow \pi^{*2}$	0.0026
$\pi_1 \rightarrow \pi^*$	0.0023
$\pi_1 \pi_2 \rightarrow \pi^{*2}$	0.0010
$n\pi_2 \rightarrow 19a'\pi^*$	0.0010
$\pi_2^2 \rightarrow \pi^*7a''$	0.0008
$\sigma\pi_2 \rightarrow 26a'\pi^*$	0.0007
$\pi_1 \pi_2 \rightarrow \pi^*6a''$	0.0006
$\sigma\pi_2 \rightarrow 28a'\pi^*$	0.0006
$\pi_1 \pi_2 \rightarrow \pi^*7a''$	0.0006

<sup>a</sup>  $\sum C_i^2$  where sum is over all spin couplings.

theory and the most important ones were retained together with the SCF function and all single excitations to make a list of 1953 orbital products from which 3159 configurations were formed. The CI matrix was formed, taking advantage of the turn-over rule pointed out by Davidson [44], and the lowest eigenvalue and corresponding eigenvector were found by the new method developed by Davidson [45].

The resulting energy was  $-169.2306$  and the coefficient of the SCF configuration was 0.957. The correlation energy was estimated following Snyder's suggestion [46] that the correlation energy for a molecule can be estimated by adding correlation energies for closed shell fragments. For CO and NH<sub>3</sub> this would give  $0.866 \pm 0.01$  and for HCN and H<sub>2</sub>O  $0.876 \pm 0.02$ . This gives a reasonable  $0.87 \pm 0.02$  estimate for formaldehyde. This would mean that the SCF energy is  $0.04 \pm 0.02$  from the Hartree-Fock limit which compares reasonably with the 0.01 error known to be present for the isolated atoms. The CI correlation energy was only  $-0.245$  which is 28% of the total correlation energy. But perturbation theory for all double excitations predicted a second-order correction for this basis set of  $-0.555$  of which  $-0.342$  was given by the configurations retained. If the perturbation result is scaled to agree with the CI result, the estimated CI limit from all double excitations would be  $-(0.555)(0.245)/(0.342)$  or  $-0.40$ . The effect of higher excitations can be estimated from the unlinked cluster estimate [47]  $(1 - C_0^2)\Delta E^{(2)}$  where  $C_0$  is the estimated coefficient of the SCF function if all double excitations are kept (0.892). This gives an estimate of  $-0.08$  from higher excitations or a total correlation energy of  $-0.48$  (55%) representable within the 60 molecular orbitals retained in the CI calculation.

Table 4. Molecular properties (atomic units)

$X1A'$	$1n\pi^*$	$3n\pi^*$	$3\pi\pi^*$	$1\pi\pi^*$	$3n\pi^*$ (spin) <sup>f,g</sup>	$3\pi\pi^*$ (spin) <sup>f,g</sup>	
$f(O)^a$	-22.349	-22.271	-22.263	-22.303	-22.393	-0.710	-0.781
$f(C)$	-14.628	-14.700	-14.701	-14.707	-14.684	-0.539	-0.552
$f(N)$	-18.304	-18.327	-18.330	-18.289	-18.227	-0.417	-0.332
$f(H1)$	-1.074	-1.063	-1.056	-1.118	-1.112	-0.300	-0.346
$f(H2)$	-0.985	-1.007	-1.010	-0.979	-0.927	-0.263	-0.237
$f(H3)$	-0.981	-1.003	-1.006	-0.974	-0.916	-0.247	-0.219
$q_{yz}(O)^b$	0.006	-0.037	-0.032	0.020	0.037	0.001	0.026
$q_{yz}(C)$	0.024	0.015	0.013	0.029	0.051	-0.001	0.001
$q_{yz}(N)$	-0.007	0.012	0.012	-0.029	-0.048	-0.003	-0.016
$q_{yz}(H1)$	-0.046	-0.044	-0.044	-0.045	-0.046	0.011	0.012
$q_{yz}(H2)$	-0.060	-0.060	-0.060	-0.061	-0.058	0.005	-0.000
$q_{yz}(H3)$	-0.014	-0.014	0.014	-0.013	-0.012	0.000	-0.002
$q_z^2(O)$	0.815	0.155	0.095	0.358	0.755	0.945	1.110
$q_z^2(C)$	-0.268	0.259	0.274	0.245	0.115	0.212	0.220
$q_z^2(N)$	0.590	0.658	0.668	0.371	0.055	0.238	0.065
$q_z^2(H1)$	-0.010	0.001	0.001	0.008	0.013	0.005	0.006
$q_z^2(H2)$	-0.047	-0.036	-0.035	-0.050	-0.061	0.014	0.007
$q_z^2(H3)$	0.331	0.335	0.336	0.329	0.317	-0.032	-0.018
$q_x^2(O)$	0.854	-1.579	-1.485	1.303	0.800	-0.925	0.687
$q_x^2(C)$	0.186	-0.195	-0.205	-0.215	-0.226	-0.249	-0.262
$q_x^2(N)$	-0.493	-0.659	-0.673	-0.338	0.049	-0.239	-0.059
$q_x^2(H1)$	-0.077	-0.097	-0.098	-0.096	-0.090	0.006	0.007
$q_x^2(H2)$	-0.150	-0.157	-0.158	-0.149	-0.139	0.011	0.009
$q_x^2(H3)$	-0.027	-0.033	-0.033	-0.023	-0.014	-0.005	-0.001
$\rho(O)^c$	300.747	300.550	300.570	300.442	300.230	0.111	0.129
$\rho(C)$	121.727	121.399	121.391	121.394	121.394	0.024	0.016
$\rho(N)$	197.097	196.097	196.884	197.504	197.504	0.035	0.044
$\rho(H1)$	0.444	0.418	0.412	0.449	0.449	-0.009	0.012
$\rho(H2)$	0.412	0.415	0.414	0.416	0.416	-0.004	-0.002
$\rho(H3)$	0.416	0.414	0.414	0.417	0.417	-0.005	-0.001
$\mu_y^d$	0.462	0.288	0.257	0.754	1.140	0.367	0.679
$\mu_z$	1.546	0.770	0.705	1.065	2.185	0.465	0.731
$Q_{xx}^e$	-14.452	-15.740	-15.809	-14.921	-16.049	-1.616	-1.196
$Q_{yy}$	-11.258	-10.948	-10.983	-11.697	-11.516	-1.523	-1.901
$Q_{zz}$	-13.599	-12.577	-12.413	-12.492	-13.824	-3.065	-3.170
$Q_{yz}$	-0.613	-0.571	-0.588	0.261	0.115	-1.227	-0.795

$$^a f(A) = \sum_{B \neq A} Z_B r_{AB}^{-1} - \left\langle \Psi \left| \sum_i r_{iA}^{-1} \right| \Psi \right\rangle.$$

$$^b q(A) = \sum_{B \neq A} Z_B \mathcal{Q}(r_{AB}) - \left\langle \Psi \left| \sum_i \mathcal{Q}(r_{iA}) \right| \Psi \right\rangle$$

$$\mathcal{Q}_{xy} = xy r^{-5}, \mathcal{Q}_{z^2} = (3z^2 - r^2) r^{-5}, \mathcal{Q}_{x^2} = (x^2 - y^2) r^{-5}.$$

<sup>c</sup> Density evaluated at the nucleus.

$$^d \mu_\alpha = \sum Z_B (r_B)_\alpha - \left\langle \Psi \left| \sum_i (r_i)_\alpha \right| \Psi \right\rangle. \text{ Independent of origin.}$$

The  $\pi^*$  orbital is very important in the CI description of the ground state. This is evident from the list of important configurations given in Table 3. The first ten configurations after the SCF involve the  $\pi^*$  orbital in correlating the  $\pi$  orbitals with each other and with the  $\sigma$  orbitals. The advantage of natural orbitals is obvious from this table also, since many of the smaller contributions could be combined if more efficient orbitals had been used.

Molecular charge distribution properties were calculated from the CI wave function and are listed in Table 4 in atomic units. The dipole moment was computed to be 4.1 D compared to the experimental value [28] of 3.7 D. The moment was found to be rotated  $38^\circ$  from the CN bond toward the oxygen atom compared to the experimental value of  $39.6^\circ$ . The oxygen end of the molecule carries the negative end of the dipole.

The quadrupole coupling constants can be computed from the data given in Table 4 using  $1.56 \times 10^{-2}$  barns for the nitrogen nuclear moment [48] to be 1.78, 1.87 and  $-3.64$  mc compared to 1.9, 1.7, and  $-3.6$  mc found experimentally (relative to the principal axes of inertia). An off-diagonal element of  $-0.07$  mc is also predicted.

#### 4. Excited States

As a first attempt to test the ability of our basis set to represent the low-lying excited states, a CI calculation was done using ground state ICSCF orbitals and the 200 lowest energy singly excited configurations of each symmetry. The results are given in Table 5. There seemed to be a uniform tendency for  $A'$  states to lie too high relative to  $A''$  states so the two groups of states have been shifted to agree with the  $W$  ( $^1n\pi^*$ ) and  $R_1$  ( $^1n3s$ ) band assignments. After this shift all of the states are predicted in reasonable agreement with experiment and with expectations that triplets would lie below the corresponding singlets and  $n \rightarrow$  Rydberg states below the corresponding  $\pi \rightarrow$  Rydberg.

Only one state stands out in this calculation as anomalous. The  $^3\pi\pi^*$  state lies where Maria *et al.* [3] would have predicted rather than where the general consensus would prefer to believe [1, 2]. There is no readily apparent reason why the  $^3\pi\pi^*$  and all the  $^1,^3A''$  states should have been predicted 1.3–1.5 eV more accurately than the other  $^1,^3A'$  states. The  $^1\pi\pi^*$   $^1A'$  state, which is usually anomalous, appears in a reasonable place relative to  $^1n3s$  in this approximation.

<sup>e</sup>  $Q_{\alpha\beta} = \sum Z_B(r_B)_\alpha(r_B)_\beta - \left\langle \Psi \left| \sum_i (r_i)_\alpha(r_i)_\beta \right| \Psi \right\rangle$ . All distances measured from center of mass.

<sup>f</sup>  $-\left\langle \Psi \left| \sum_i s_{zi}\theta(r_i) \right| \Psi \right\rangle$  evaluated with  $M = 1$  component of  $\Psi$ .

<sup>g</sup> The operators  $g_y = yr^{-3}$  and  $g_z = zr^{-3}$  give non-zero values with the spin density as follows:

	$g(O)$	$g(C)$	$g(N)$	$g(H1)$	$g(H2)$	$g(H3)$
$^3n\pi^*$ y	-0.001	-0.022	0.019	-0.003	0.002	0.005
z	-0.108	0.038	0.011	-0.017	0.009	-0.008
$^3\pi\pi^*$ y	-0.006	-0.031	0.007	-0.002	0.006	0.004
z	-0.113	0.042	0.002	-0.007	0.002	-0.002

Table 5. Excitation spectrum (eV) estimated by the Tamm-Dancoff method<sup>a</sup>

Band	$1A'$	$1A''$	$3A'$	$3A''$
$W$			$3.6 (\pi_2\pi^*)$	
$R_1$	$6.7 (n3s, \pi_2\pi^*)$	$5.7 (n\pi^*)$		$5.2 (n\pi^*)$
$V_1$	$6.9 (n3s, \pi_2\pi^*, n3py)$	$7.0 (\pi_23s)$	$7.1 (n3py)$	$6.6 (\pi_23s)$
$R_2$	$7.6 (n3s, \pi_2\pi^*, n3py)$			
	$7.7 (n3p\pi)$		$7.1 (\pi_23p\pi, \pi_1\pi^*)$	
	$8.0 (n3pz)$		$7.5 (n3pz)$	
			$7.6 (\pi_23p\pi, \pi_1\pi^*)$	
$Q$		$8.0 (\pi_23py)$		$7.8 (\pi_23py)$
		$8.8 (\pi_23pz)$		$8.6 (\pi_23pz)$
		$9.3 (n3p\pi)$		$9.2 (n3p\pi)$
		$9.8 (\sigma\pi^*)$		$9.4 (\sigma\pi^*)$
		$10.0 (n3d)$	$9.8 (\pi_23d)$	$9.6 (\pi_23d)$
	$10.2 (n3d, 4s)$			
	$10.3 (\pi_1\pi^*)$			

<sup>a</sup> The  $1,3A'$  states have been shifted downward by 2.1 eV and the  $1,3A''$  states by 0.8 eV in order to match  $W$  and  $R_1$ .

Table 6. Excitation energies estimated by CI methods (eV)

Frozen Orbital	$\Delta E_{SCF}$	$\Delta E_{CI}$	$\Delta E_{CI}$		Ref. [4]	Ref. [5]	Ref. [17]	Ref. [27]	Exptl.
			Extrapolated						
$3n\pi^*$	4.46	5.34	5.38		3.80-6.36	6.15	4.68-5.94	5.39	5.30 <sup>a</sup>
$3\pi\pi^*$	5.15	6.12	5.81		4.40-6.06	6.64	4.07-5.9	6.19	(6.60) <sup>a</sup>
$1n\pi^*$	4.75	5.63	5.70		4.08-6.89	6.75	5.46-5.66	5.65	5.65 <sup>b</sup>
$1\pi\pi^*$	8.23	8.45	8.48		10.41-11.00	11.09	10.70-12.49		7.32 <sup>b</sup>

<sup>a</sup> Ref. [28].

<sup>b</sup> Ref. [1].



#### 4.1. The ${}^3n\pi^*$ State

The lowest triplet state is predicted to be  ${}^3n\pi^*$  by most sources. The SCF energy is  $-168.8217$  corresponding to an excitation energy  $\Delta E_{\text{SCF}}$  of  $4.46$  eV compared to  $6.18$  eV in the frozen orbital approximation. The orbitals show very little change from the ground state. The ICSCF orbital basis was again truncated to  $44a'$  and  $16a''$  orbitals and a CI/perturbation calculation performed. The extrapolated CI excitation energy was  $5.38$  eV. Table 6 summarizes various ways of estimating this excitation energy as well as results from other workers. This result lies near the average of the previous results found by this method for formaldehyde [49] ( $3.4$  eV) and urea [50] ( $6.8$  eV). It is in complete agreement with the calculations of Harding and Goddard [27] and the experimental result [28].

The calculated dipole moment is  $1.96$  D at  $34^\circ$ . This change in moment compared to the ground state agrees with a transition which removes an electron from the  $np$  oxygen orbital and places it in  $\pi^*$  (mostly carbon  $\pi$ ). Other molecular properties are included in Table 4.

Orbital populations for this state compared to the ground state show that the  $n\pi^*$  transition is accompanied by a large rearrangement of charge in other pi orbitals. The net effect is a loss of only  $0.3$  electron from oxygen in spite of a decrease of  $0.8$  in the population of the  $np$  orbital. As expected, there is a significant decrease in both CO and CN pi bond order.

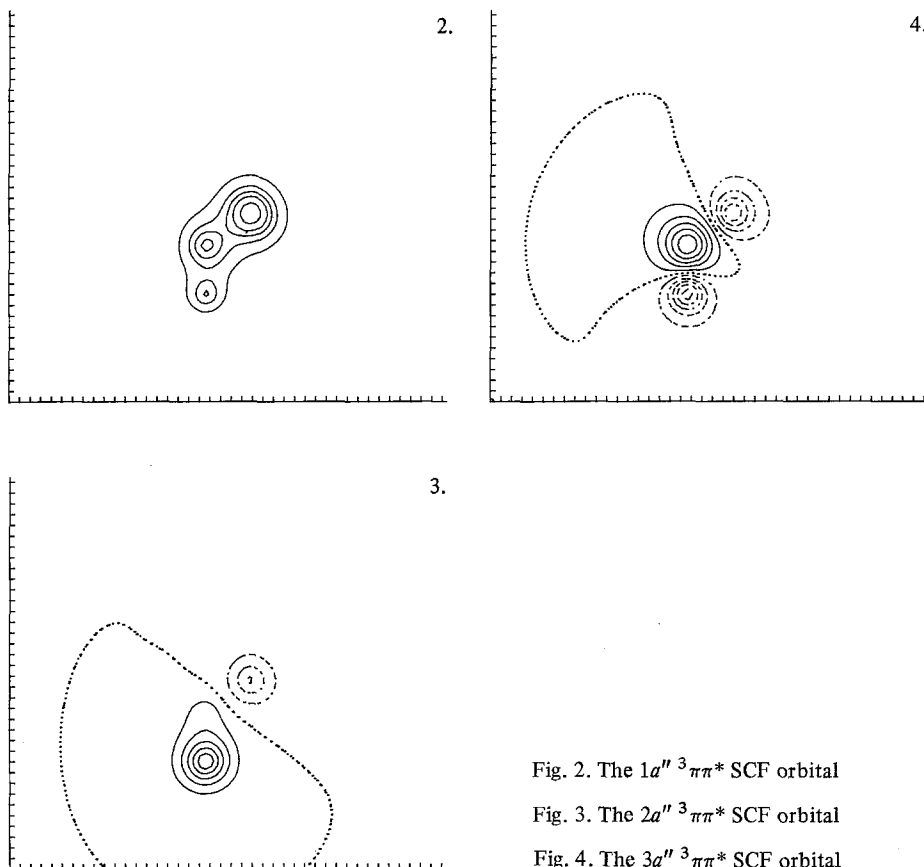
#### 4.2. The ${}^3\pi\pi^*$ State

The  ${}^3\pi\pi^*$  SCF energy was  $-168.7972$ , which gives a  $\Delta E_{\text{SCF}}$  of  $5.15$  eV. The  $1a''$  to  $3a''$  orbitals are shown in Figs. 2-4. Clearly the transition comes primarily from some linear combination of the ground state  $1a''$  and  $2a''$  orbitals and leaves a lone  $\pi$  pair on the nitrogen while exciting the CO  $\pi$  bond. The relaxation energy in this state is less than for the  ${}^3n\pi^*$  state which explains part of the error in Table 5. The ICSCF basis was truncated to  $44a'$  and  $16a''$  orbitals and a CI/perturbation calculation performed. The extrapolated result shown in Table 4 is  $5.81$  eV which is about  $0.5$  eV above the  ${}^3n\pi^*$  state. This relative spacing of the  $n\pi^*$  and  $\pi\pi^*$  states was virtually unchanged from the SCF result. Calculations carried out by the same method for formaldehyde gave excellent results. This result is considerably below the average of formaldehyde ( $5.6$  eV) and urea ( $6.7$  eV). A result above that for formaldehyde is certainly expected.

This result for the  ${}^3\pi\pi^*$  state seems completely reliable. There is no reason to believe that there could be a low energy state corresponding to  ${}^3A'$  symmetry. The result obtained agrees well with the calculation of Harding and Goddard [27]. It seems likely, however, that the trapped electron spectrum failed to resolve this state [28].

#### 4.3 The ${}^1n\pi^*$ State

The  $n\pi^*$  singlet state is an absorption in the electronic spectrum whose assignment seems to be generally agreed upon. This excitation corresponds to the lowest energy

Fig. 2. The  $1a''$   ${}^3\pi\pi^*$  SCF orbitalFig. 3. The  $2a''$   ${}^3\pi\pi^*$  SCF orbitalFig. 4. The  $3a''$   ${}^3\pi\pi^*$  SCF orbital

absorption reported and was missed by the first investigators, Hunt and Simpson [42], since it lies on the edge of the region they studied. Experimentally the band is at 5.6 eV and is weak and poorly resolved with an extinction coefficient of 61. Its assignment is supported by its ORD spectrum and its frequency shift on going from aliphatic to hydroxylic solvents [1]. Previous calculations, both semi-empirical and *ab initio*, also agree with this assignment.

The SCF calculation for this state gives an energy of  $-168.8119$  which corresponds to a  $\Delta E_{\text{SCF}}$  of 4.75 eV. Relaxation effects were even larger for this state than they were for the  ${}^3n\pi^*$  state. A CI/perturbation calculation with a  $44a'$ ,  $16a''$  molecular orbital set gave an extrapolated excitation energy of 5.70 eV in excellent agreement with experiment. This result confirms the validity of this procedure. The small gap between the  ${}^1n\pi^*$  and  ${}^3n\pi^*$  is expected since the  $n\pi^*$  exchange integral is very small. The larger correlation error in the singlet than the triplet state also agrees with expectations. Judging from past work these three excitation energies just discussed should be correct to 0.2 eV.

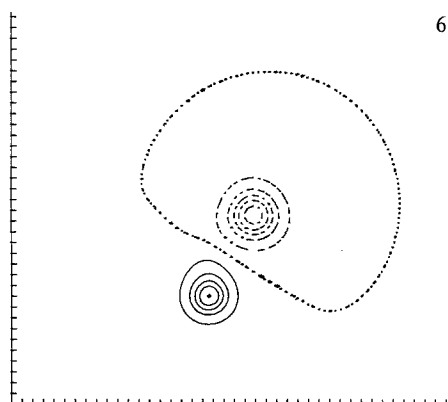
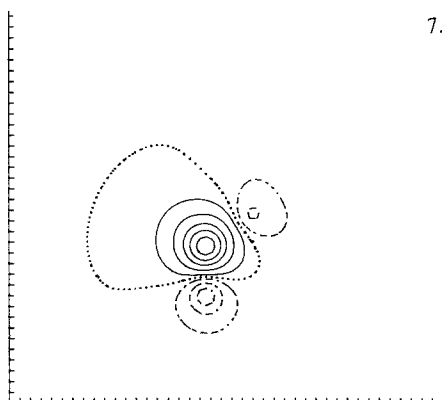
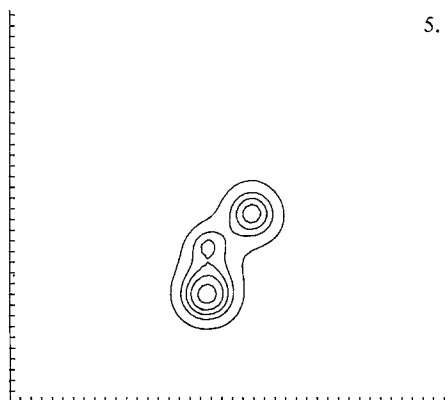


Fig. 5. The  $1a''$   ${}^1\pi\pi^*$  SCF orbital

Fig. 6. The  $2a''$   ${}^1\pi\pi^*$  orthogonalized SCF orbital

Fig. 7. The  $3a''$   ${}^1\pi\pi^*$  orthogonalized SCF orbital

#### 4.4. The ${}^1\pi\pi^*$ State

A state of particular interest in formamide is that corresponding to a  $\pi\pi^*$  excitation from the ground state. The band which is assigned as  ${}^1\pi\pi^*$  was first located by Hunt and Simpson. Pi-electron calculations have been the basis for this assignment. The predicted polarization agrees well with that found for myristamide. This is a very intense band with an oscillator strength of about 0.37.

Ordinary SCF theory does not apply to this state. As shown elsewhere [34], only a non-orthogonal SCF excited state calculation which allows  $\pi$  and  $\pi^*$  to be non-orthogonal is strictly variational. A specially modified non-orthogonal SCF program gave  $-168.6840$  eV for this state. However, the comparable energy for the ground state is not really the usual SCF energy but rather a split shell  $\pi\pi'$  configuration. Hence the result  $\Delta E_{\text{SCF}} = 8.21$  eV is not to be taken too seriously. A split shell description of the ground state would make this result even higher.

The  $\pi$  and  $\pi^*$  non-orthogonal orbitals were transformed to an orthogonal pair of orbitals such that the resulting  $\pi\pi^*$  configuration had least squares difference from

the one with non-orthogonal orbitals. This gave a dominant configuration with energy 8.23 eV above the ground state SCF and very similar orbitals since the extent of non-orthogonality was small. A CI/perturbation calculation using these orbitals gave the final estimated excitation energy of 8.5 eV which is well below all calculations reported previously but still not in good agreement with experiment.

One can well ask why this result for the energy of the  $^1\pi\pi^*$  state is so much worse than the energy of the  $^1n\pi^*$  state (and also worse than the error claimed for  $^3\pi\pi^*$ ). Figs. 5-7 give the  $\pi_1$ ,  $\pi_2$ , and  $\pi^*$  orthogonal orbitals of the dominant configuration. Comparison with Figs. 2-4 which give the corresponding orbitals for the triplet state shows noticeable differences. In the triplet state the  $\pi_1$  orbital is mostly the nitrogen lone pair and the open shell orbitals are mostly oxygen and carbon  $p$  orbitals. Thus the triplet is essentially a carbonyl excitation perturbed weakly by the nitrogen lone pair. The  $^1\pi\pi^*$  orbitals are very different. The lowest (doubly occupied) is localized on the oxygen and the singlet coupled singly occupied orbitals are predominantly carbon and nitrogen. The excitation is better described as leading to the  $O^-C=N^+$  structure which is the amide resonance structure which enters heavily into the ground state [ground state pi bond orders were computed to be 0.78 (CO) and 0.52 (CN)]. This structure has been previously used by Rosa [51] as the basis of the amide resonance theory predictions for the spectra of a series of amide molecules.

The dipole moment listed in Table 4 for the  $^1\pi\pi^*$  state is in agreement with this  $O^-CN^+$  structure since the dipole moment is greatly increased. Also the charge density at the nuclei (due to  $s$  electrons only!) shows a marked increase at nitrogen as would be expected from back charge transfer in the sigma orbitals to compensate for the  $\pi$  charge shift.

In agreement with this ionicity for the  $^1\pi\pi^*$  state the correlation energy was computed to be nearly as large as for the ground state. The CI calculation, however, must be regarded a preliminary result which will be repeated using a different procedure. As it stands it is an illustration of what can go wrong with the method of using only single and double excitations when the SCF configuration is actually not a good approximation. The  $^1\pi\pi^*$  state appeared as the second eigenvalue of the CI matrix when it should really have been third with  $^1n3s$  appearing as the second. This occurred because both the SCF and CI selection were biased in favor of  $^1\pi\pi^*$  so that the  $^1n3s$  state lay 5-7 eV higher. If Table 5 is correct, and it probably is, the  $^1\pi\pi^*$  state is mixed in zeroth order with  $^1n3s$  and  $^1n3p_y$ . Further all three of these configurations have their energies depressed by extensive mixing with  $^1\pi3p\pi$  and  $^1n3p_z$ .

Hence an accurate treatment requires use of an orbital basis and a configuration list which is unbiased in its treatment of all these states. Selection of orbitals is quite difficult since an SCF calculation on any one of these states gives relaxed orbitals which are nearly 5 eV in error for description of any other one. Selection of configurations is equally difficult since the valence states are stabilized mostly by other  $(\pi_1\pi_2\pi^*)^4$  configurations and  $\sigma\pi$  correlation effects. Thus, the result found in the present calculation illustrates the nature of the difficulties ahead but is not terribly discouraging.

#### 4.5. Other Low-Lying Singlet States

The SCF program was run for the  ${}^2A'$  ionic state ( $n \rightarrow \infty$ ) and gave a  $\Delta E_{\text{SCF}}$  of 9.0 eV compared to the experimental value 10.3 and the Koopmans theorem result of 11.9. Thus the large relaxation energy noted for the other  $n\pi^*$  states persists in the ionization limit. Also the differential correlation effect was 1.3 eV compared to the ground state. The SCF calculation for the  $\pi \rightarrow \infty {}^2A''$  ion was not converged as well. It indicated only a 1.6 eV relaxation energy and a differential correlation error of 0.6 eV.

The SCF program for excited states was used to locate approximate energies for a few other states by running for six iterations regardless of convergence. The  ${}^1n3s$  state gave a  $\Delta E_{\text{SCF}}$  (non-orthogonal) of about 6.5 eV compared with the experimental value of 6.8 eV. The SCF program also indicated that the  ${}^1n3p_y$  and  ${}^1n3p_z$  configurations lie about 0.5 and 1.0 eV above  ${}^1n3s$ . If the errors are constant, the indicated location for these states is 7.3 and 7.8 eV respectively. There also appears to be a low energy  ${}^1\pi3s$  state near 7.3 eV.

Neither these SCF calculations nor the simplified CI calculation shown in Table 5 show the  ${}^1n\sigma^*$  and  ${}^1\pi\sigma^*$  states which are believed (according to Table 1) to lie in the 7.5–7.9 eV range. This, however, may just be a question of interpretation. The  $3s$  and  $3p_z$  orbitals have a large amount of  $\sigma^*$  character. The  $3p_y$  orbital, which is more nearly pure, has its maxima where the atoms in a polypeptide chain should occur, so this orbital will become a  $\sigma^*$  orbital in polypeptides. The size of the orbitals bear out this difficulty in interpretation. The average value of  $r^2$  for an  $n = 3$  orbital should be about 81 while for these orbitals it is only 25–40. The “ $3s$ ” orbital does have nearly equal values for  $x^2$ ,  $y^2$ , and  $z^2$  but the standard deviations  $\sigma_y$ ,  $(\sqrt{y^2 - y'^2})$  and  $\sigma_z$  are only about 2.8 which is the same size as the molecule. The orbitals labelled  $3p_y$  and  $3p_z$  have a small value for  $x^2$  and extend along their principal axis to  $\pm 4.6$  which is less than twice as big as the molecule. Hence the  ${}^1n\sigma^*$  state in Table 1 is probably the same as the  ${}^1n3p_z$  state of Table 5.

The oscillator strengths associated with these  $n \rightarrow$  Rydberg configurations are also slightly larger than expected for Rydberg states. At the ground state ICSCF one-configuration level of accuracy,  $n \rightarrow 3s$ ,  $3p_y$ ,  $3p_z$  and  $\pi_1 \rightarrow \pi^*$  all have oscillator strengths around 0.1 while  $\pi_2 \rightarrow \pi^*$  is about 0.9. Configuration mixing should reduce the  $\pi_2 \rightarrow \pi^*$  value to the experimental value (0.4) and increase some of these other band strengths.

## 5. Conclusions

Calculations have been presented for the excited states of formamide. Generally good agreement with experimental excitation energies were obtained.

The computed energy for the  ${}^3\pi\pi^*$  state 5.8 eV, is in good accord with the work of the Pullmans [2]. The 4.3 eV estimate by Maria *et al.* [3] seems very unlikely. The error in the logic of Maria *et al.* arose from the assumption that the  ${}^1\pi\pi^*$  and  ${}^3\pi\pi^*$  states involved similar wave functions. The  ${}^1\pi\pi^*$  energy evaluated in the one-configuration approximation using  ${}^3\pi\pi^*$  orbitals is in fact 3 eV or so above the  ${}^3\pi\pi^*$  state just as Maria *et al.* contend. This, however, gives a  ${}^1\pi\pi^*$  energy above 9 eV. The effects which

are responsible for lowering the  $^1\pi\pi^*$  energy to 7.3 eV do not operate in the triplet state and hence it is incorrect to assume the triplet state will be 3 eV below the experimental singlet state position.

It is interesting to note that in formaldehyde the band originally thought to be due to the  $^1\pi\pi^*$  state has been reassigned as  $^1n3s$  and no  $^1\pi\pi^*$  band is presently known [49]. In formamide the pure carbonyl singlet valence excitation would also lie at high energy and the  $^1n3s$  band would be similar to formaldehyde. The new feature in formamide is the amide resonance possibility which introduces a different kind of  $^1\pi\pi^*$  state nearly degenerate with the  $^1n3s$  and  $^1n3p$  states. In view of the importance of the  $^1n3s$  configuration, the previous work for urea which obtained a  $^1\pi\pi^*$  state at 9.0 eV (also heavily involving amide resonance) needs to be re-examined since diffuse orbitals were not included in that calculation. Presumably a  $^1n3s$  state heavily mixed with  $^1\pi\pi^*$  might well exist at the 7.1 eV observed excitation energy presently assigned as  $^1\pi\pi^*$ .

*Acknowledgements.* The authors wish to thank Larry McMurchie for his help with some of the calculations. This research was supported primarily by the NSF although the later phases of work were supported by an NIH grant.

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*Received September 14, 1976/November 8, 1976*