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Non-Empirical LCAO-MO-SCF-CI Calculations on Organic Molecules with Gaussian Type Functions

IV. Preliminary Investigations on Formamide

M. A. ROBB and I. G. CSIZMADIA

Lash Miller Chemical Laboratories, Department of Chemistry, University of Toronto

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Single detor wavefunctions were calculated for formamide ($HCONH_2$) in the LCAO-MO-SCF framework using a basis of Gaussian type functions (GTF) centered on the individual atoms. Preliminary calculations were carried out on various planar and non-planar configurations of the amide hydrogens. A planar model was found to be the most stable and this planar species was used as the model for the investigation of physical properties. Ground state molecular properties investigated for formamide include ionization potentials, dipole moment, electron populations and one electron and total electron densities. Low lying excited state energies were calculated accurately using a single co-detor wavefunction and the predicted electronic transitions were associated with the previously reported experimental UV spectrum.

Der Grundzustand von Formamid ($HCONH_2$) wurde mittels der LCAO-MO-SCF-Methode mit einem GTF Basissatz berechnet. Dabei ergab sich, daß das planare Molekül am stabilsten ist; für diese Konfiguration wurden Ionisationspotential, Dipolmoment, Elektronen-Population, Ein- und Gesamtelektronendichte berechnet. Die untersten angeregten Zustände wurden mit einem einfachen Co-Detor berechnet und die Elektronenübergänge mit dem experimentellen UV-Spektrum verglichen.

On a calculé des fonctions d'onde simples déterminants pour la formamide ($HCONH_2$) dans le cadre de la méthode LCAO-MO-SCF en utilisant une base de fonctions du type gaussien (GTF) centrées sur les différents atomes. Des calculs préliminaires ont été effectués pour diverses configurations planes et non planes des atomes d'hydrogène du groupement amide. Un modèle plan s'est avéré le plus stable; il a été utilisé pour l'étude des propriétés physiques. Les propriétés moléculaires de l'état fondamental étudiées sont: les potentiels d'ionisation, le moment dipolaire, les populations électroniques et les densités électroniques. Les énergies des états excités inférieure ont été calculées avec précision en utilisant une simple combinaison de déterminants; les transitions électroniques ainsi prédites sont mises en correspondance avec le spectre U.V. expérimental publié auparavant.

The projected work on formyl derivatives (HCOX) has been announced [7]. Results on HCOF have been published [9] and further progress has been reported subsequently [10]. The final conclusions from the calculations on $HCONH_2$ have been presented [29] recently. Just about the time when the work was ready for publication [30] a paper submitted from the Bell Telephone Laboratories [1] reported the results of calculation on $HCONH_2$. Robin and co-workers [1] used a basis set of 36 functions composed of linear combinations of 87 Gaussian type functions (GTF). This contracted basis set yielded a wavefunction approaching the Hartree-Fock limit more closely, on energetic grounds, than the largest uncontracted basis presented here.

A basis set of 59 functions is more flexible than one consisting of 36 functions even if the 36 functions are contracted from 87 GTF. On this basis one would expect the calculated one-electron properties to be better with 59 individual GTF. The only measurable one electron property that has been calculated in this work is the dipole moment, which is in fact closer to the experimental value than that reported by Robin and co-workers [1]. Also, although the method of investigation of electronically excited states was more sophisticated than the present one, the fundamental conclusions from both works are identical. Thus, in order to be able to make comparison between the capabilities of various basis sets (contracted and uncontracted) for the calculation of physical properties, and to be able to judge the relative merits of the calculation of excited state properties at various levels of sophistication, it seemed worthwhile to release the results obtained in this laboratory.

Introduction

The structure and physical properties of formamide are interesting not only chemically and spectroscopically but also biologically. From a biological point of view, it is the simplest molecule containing the peptide bond. From a spectroscopic as well as chemical viewpoint, the non-planarity of the amide hydrogens, and the nature of the so-called intramolecular charge transfer band and the Rydberg series in the UV spectrum are of interest.

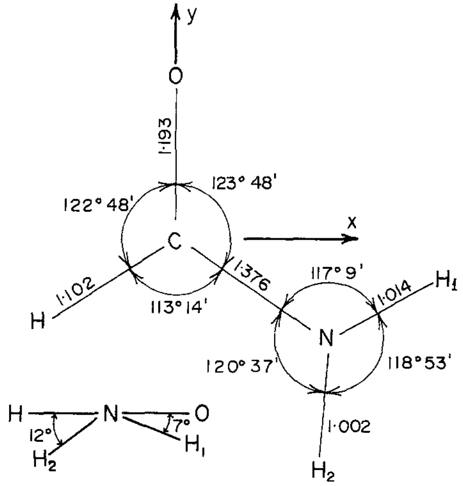

Fig. 1. Observed structure of formamide showing its orientation in a cartesian reference system

The structure of formamide has been investigated by IR [11], NMR [21], and microwave [22, 4] spectroscopy, as well as by X-ray diffraction [27]. The results are in disagreement as to the co-planarity of the two hydrogens bonded to the nitrogen with the N–CHO group. The microwave study by Costain and Dowling [4] on five isotopic species provides a strong indication of a pyramidal model. Their study of the "inversion" satellite lines predicts a barrier of 370 cm^{-1} hindering the "inversion-wagging" type motion. Figure 1 shows the structure proposed by Costain by averaging the final structures for the isotopic species and the orientation of the cartesian reference axes to be used in the present calculations. The structures determined by other workers are collected in Table 1 with Costain and Dowling's data for comparison.

Kurland and Wilson [22] have calculated the dipole moment of formamide from Stark effect measurements on its microwave spectrum. Assuming a planar molecule they obtain a value of 3.714 debye with the vector inclined at an angle of 39.6° from the CN bond directed away from the oxygen. Thus one would expect the negative charge to be in the region of the oxygen and the positive charge in the region of the CNH_2 grouping.

Table 1. *Reported structural characteristics of formamide*

Parameter[a]	Reference			
	[4]	[22]	[21]	[27]
r (N–H′)[b]	1.014	0.995	1.036	—
r (N–H″)	1.002	0.995	1.036	—
r (N–C)	1.376	1.343	—	1.300
r (C–O)	1.193	1.243	—	1.255
r (C–H‴)	1.102	1.094	—	—
<H′NH″	118°53′	118°58′	—	120°
<H″NC	120°37′	120°31′	—	—
<H′NC	117°9′	120°31′	—	—
<NCO	123°48′	123°35′	—	121°30′
<NCH‴	113°14′	103°54′	—	—
<OCH‴	122°58′	132°31′	—	—

[a] Bond lengths (r) are given in Å units.

[b] The prime, double prime and triple prime on the hydrogen denote the two amide hydrogens and the formyl hydrogen (see Fig. 1).

The electronic spectrum of formamide in the gas phase has been studied by Hunt and Simpson [13]. Their observed spectrum is shown in Fig. 8, and has several interesting features. The $V_1 \leftarrow N$ band (the first $\pi^* \leftarrow \pi$ transition) can be identified with the intramolecular transfer of electron density from the electron donating nitrogen group to the electron accepting oxygen group. The presence of a long progression in the C=O stretching vibration suggests that the CO bond may be lengthened in the $V_1 \leftarrow N$ state as in $H_2C{=}O$[1]. Peterson and Simpson [26] have measured the orientation and magnitude of the transition moment vector for the corresponding transition in the myristamide crystal. They find the vector to be inclined away from the NO axis by 9.1 deg. The value for formamide is difficult to measure but should be similar. A well defined Rydberg series is also observed by Hunt and Simpson [13]. The high energy termination point gives a value of 10.2 eV for the ionization potential of the oxygen lone pair.

There have been no previous "ab initio" calculations on formamide other than that of Robin and co-workers [1] but several calculations have been performed using semi-empirical methods [34, 17, 18, 24, 25].

Results and Discussion

Using the infrared data of Evans [11] for zero point vibration: ZPV and bond dissociation energies as well as atomic energies, the experimental energy of formamide can be estimated (Table 2):

$$E_{\mathrm{expt}} = E_{\mathrm{atomic}} + E_{\mathrm{dissoc}} - E_{\mathrm{ZPV}} \,. \tag{1}$$

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[1] See Page 547 of Ref. [15] for discussion of spectrum and bibliography.

This may then be decomposed into quantum mechanically calculable fragments in the following manner:

$$E_{\text{expt}} = E_{\text{HF}} + E_{\text{corr}} + E_{\text{rel}}, \tag{2}$$

where E_{HF} is the energy obtained in the Hartree-Fock limit.

The correlation energy: E_{corr} may be estimated by summing the correlation energy per new electron pair created on forming the molecule from atoms and adding the atomic corrections. The relativistic energy: E_{rel} should be rather small for first row atoms and in the first approximation the relativistic corrections of atoms are used. The breakdown of the experimental energy into these theoretical fractions is shown in Table 2.

Table 2. *Estimation of experimental energy of formamide and its breakdown into theoretically calculable fragments*

Experimental quantity	Energy (hartree)	Theoretical quantity	Energy (hartree)
Atomic energy[a]	−169.076	Hartree-Fock limit[d]	−168.942
Dissociation energy[b]	− 0.888	Correlation energy[e]	− 0.988
Zero-point energy[c]	− 0.045	Relativistic energy[f]	− 0.079
Experimental total energy	−170.009	Experimental total energy	−170.009

[a] The energy obtained by summing the experimental energies of the constituent atoms of formamide [3].

[b] The dissociation energy was estimated by summing the bond dissociation energies of model molecules, CH_3–NH_2 for the HCO–NH_2 bond (Page 640, Ref. [18]), and H_2N–H for the NH–H bond (Page 609, Ref. [18]); and the experimental dissociation energies of N–H (Page 559, Ref. [19]), H–CO (Page 589, Ref. [18]) and C≡O [20] species.

[c] The zero-point vibrational energy was obtained from the fundamental frequencies of formamide [11, 14].

[d] $E_{\text{HF}} = E_{\text{total}} - E_{\text{corr}} - E_{\text{rel}}$.

[e] Assumed to be equal to the sum of the atomic correlation [3] energies (−0.598) and six pair [9] correlations ($6 \times -0.065 = -0.390$).

[f] The sum of relativistic corrections of the C, N, and O atoms [3].

Basis Sets Used in SCF-MO Calculations

In previous work [8], it has been shown that the extrapolation of the results of symmetrically[2] improved basis sets to infinity permits the derivation of a total energy which is as close to the HF limit as orbital exponents will allow. In this work three distinct basis sets were used (Table 3). The *s* and *p*-GTF exponents

Table 3. *GTF basis sets for formamide*

N Basis Set Size	CNO atoms *s*-type	CNO atoms *p*-type	Amide Hydrogens *s*-type	Formyl Hydrogen *p*-type
21	3	1	1	1
39	5	2	2	2
59	7	3	4	3

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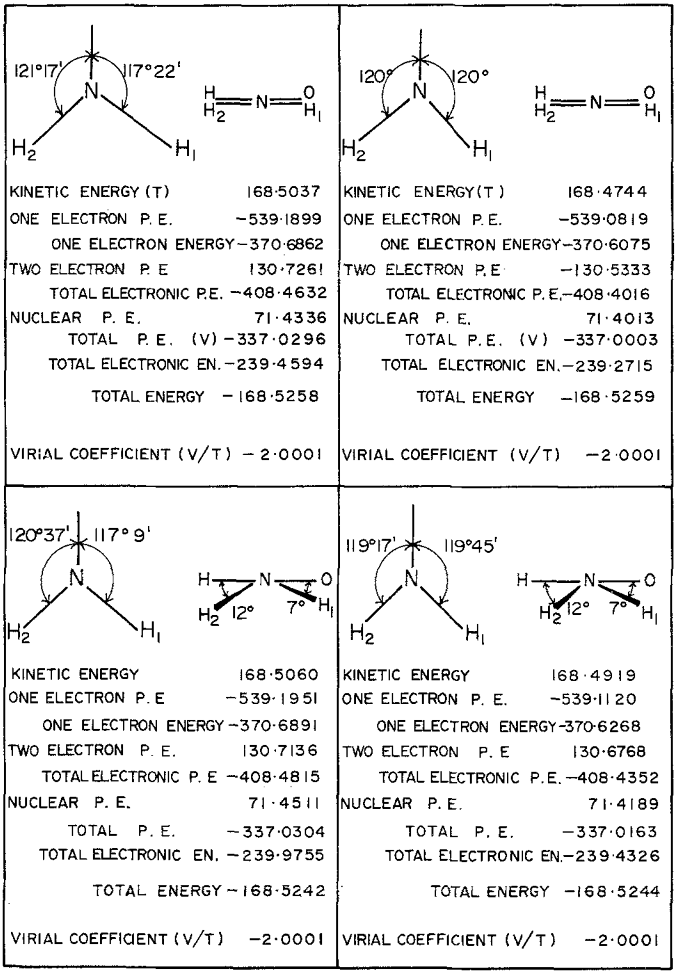
[2] By symmetrically improved basis set we mean that as the basis set is increased, the number of *s*-GTF increases by two and the number of *p*-GTF by one for the C, N, and O atoms and the number of *s*-GTF by one for the H atom.

on C, N and O atoms are those reported in Table 6 of Ref. [8] while the exponents of *s*-GTF on the H atom were those of Reeves [28] for 1^s and Huzinaga [16] for 2^s, 3^s and 4^s.

Variation of Total Energy with Geometry

Because of the experimental uncertainty as to the planarity of the amide hydrogens, preliminary investigations were made on several planar and non-planar models in order to ascertain whether a planar or non-planar geometry should be chosen for further investigations. Fig. 2 shows the assumed geometries and calculated energies (N = 59 GTF) for the pyramidal model of Costain and Dowling (lower left); its corresponding planar derivative (upper left); and a planar model where the hydrogens lie in the plane of the heavy atoms making angles of 120 degrees to the CN bond axis (upper right) and its symmetrical non-planar



KINETIC ENERGY (T)	168·5037
ONE ELECTRON P. E.	−539·1899
ONE ELECTRON ENERGY	−370·6862
TWO ELECTRON P. E	130·7261
TOTAL ELECTRONIC P.E.	−408·4632
NUCLEAR P. E.	71·4336
TOTAL P. E. (V)	−337·0296
TOTAL ELECTRONIC EN.	−239·4594
TOTAL ENERGY	−168·5258
VIRIAL COEFFICIENT (V/T)	−2·0001

KINETIC ENERGY (T)	168·4744
ONE ELECTRON P. E.	−539·0819
ONE ELECTRON ENERGY	−370·6075
TWO ELECTRON P. E	−130·5333
TOTAL ELECTRONIC P. E.	−408·4016
NUCLEAR P. E.	71·4013
TOTAL P. E. (V)	−337·0003
TOTAL ELECTRONIC EN.	−239·2715
TOTAL ENERGY	−168·5259
VIRIAL COEFFICIENT (V/T)	−2·0001

KINETIC ENERGY	168·5060
ONE ELECTRON P. E	−539·1951
ONE ELECTRON ENERGY	−370·6891
TWO ELECTRON P. E.	130·7136
TOTAL ELECTRONIC P. E	−408·4815
NUCLEAR P. E.	71·4511
TOTAL P. E.	−337·0304
TOTAL ELECTRONIC EN.	−239·9755
TOTAL ENERGY	−168·5242
VIRIAL COEFFICIENT (V/T)	−2·0001

KINETIC ENERGY	168·4919
ONE ELECTRON P. E.	−539·1120
ONE ELECTRON ENERGY	−370·6268
TWO ELECTRON P. E	130·6768
TOTAL ELECTRONIC P.E.	−408·4352
NUCLEAR P. E.	71·4189
TOTAL P. E.	−337·0163
TOTAL ELECTRONIC EN.	−239·4326
TOTAL ENERGY	−168·5244
VIRIAL COEFFICIENT (V/T)	−2·0001

Fig. 2. Energies of some planar and non-planar conformations of formamide

analogue using Costain's pyramidal model (lower right). It is readily apparent that the total energy is quite insensitive to the out of plane distortion. The energies of planar and non-planar species are almost identical, with the planar being only very slightly more stable. Recent calculations on CH_3^- [20] showed that the addition of *d*-type Gaussians to an *sp* basis set of carbon greatly increased the inversion barrier for this species. The recent calculation on NH_3 [2] which predicted a planar species using an *sp* basis taken with the results of CH_3^- [20] suggests that inclusion of *d*-type Gaussians in the basis set for heavy atoms (C, N, O, F) may be important. Because of these results, a planar model with the hydrogens making angles of 120 degrees with the CN bond was chosen and the results quoted from this point are for this planar model.

Table 4 shows the variation of the total energy with basis set size with the estimated HF limit shown for comparison. The total energy for the 59 basis set approximates the HF limit within 0.2% and the total energy within 1.2%. Thus one can be reasonably confident that this wavefunction will represent the molecular properties of formamide quite accurately within the Hartree-Fock approach.

Table 4. *Total energies of planar formamide calculated with various basis sets*

Basis Set		Energy (hartree)		
Size	Type	Electronic Attraction	Nuclear Repulsion	Total
21	$3^s\,1^p$	−230.7932	71.4013	−159.3919
39	$5^s\,2^p$	−238.6862	71.4013	−167.2849
59	$7^s\,3^p$	−239.9272	71.4013	−168.5259
Estimated Hartree-Fock Limit				−168.9420

Molecular Orbitals

The orbital energy levels of formamide as calculated by the largest (N = 59) basis set are shown with those of the constituting atoms for comparison in Fig. 3. The MO energy levels obtained with the various basis sets are collected in Table 5.

An assignment of the chemical nature of the occupied MO and the Rydberg or "united atom" classification for the virtual orbitals is also given. The subscripts +, 0, and − for the π MO represent, respectively, bonding, non-bonding and anti-bonding in the quasi-classical concept of the three (allylic) π MO, the two lowest being occupied. Since the computed MO are formed as a linear combination of GTF one no longer has the concept of principal quantum number and the contribution of extravalence shell AO is difficult to assign. Consequently the classification of MO as Rydberg orbitals is qualitative based on the nodal characteristics of the MO (see Fig. 4). Thus in the united atom approach, the π_+ orbital is $2p$, the π_0 and the π_- orbitals are $3d$ and $11\sigma^*$ is $3s$ etc. A more accurate picture of the Rydberg orbitals could be obtained by augmenting the basis set with GTF of *s*, *p*, *d*, and *f* type with very small exponents giving rise to GTF with a large spatial extent.

In accord with Koopmans' theorem each orbital energy represents the energy required to remove one electron from a given orbital to infinity (ionization potential: IP). One notes that the ionization potential of the π_0 orbital is less than the IP of the oxygen lone pair "n_p" in apparent disagreement with the experimental results of Hunt and Simpson's [13] measurement on the Rydberg series involving the oxygen lone pair. However, the apparent discrepancy is at once resolved when one considers that a Rydberg series involving the π_0 orbitals will be of quite low intensity since the $\sigma^* \leftarrow \pi$ transitions will be Z polarized and of low intensity, and

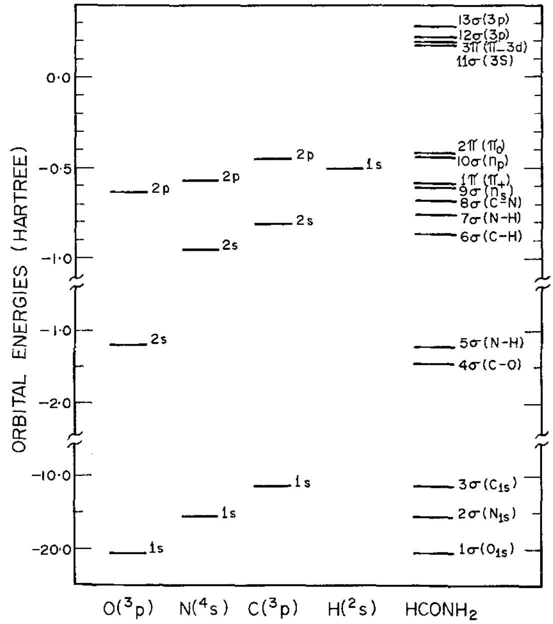
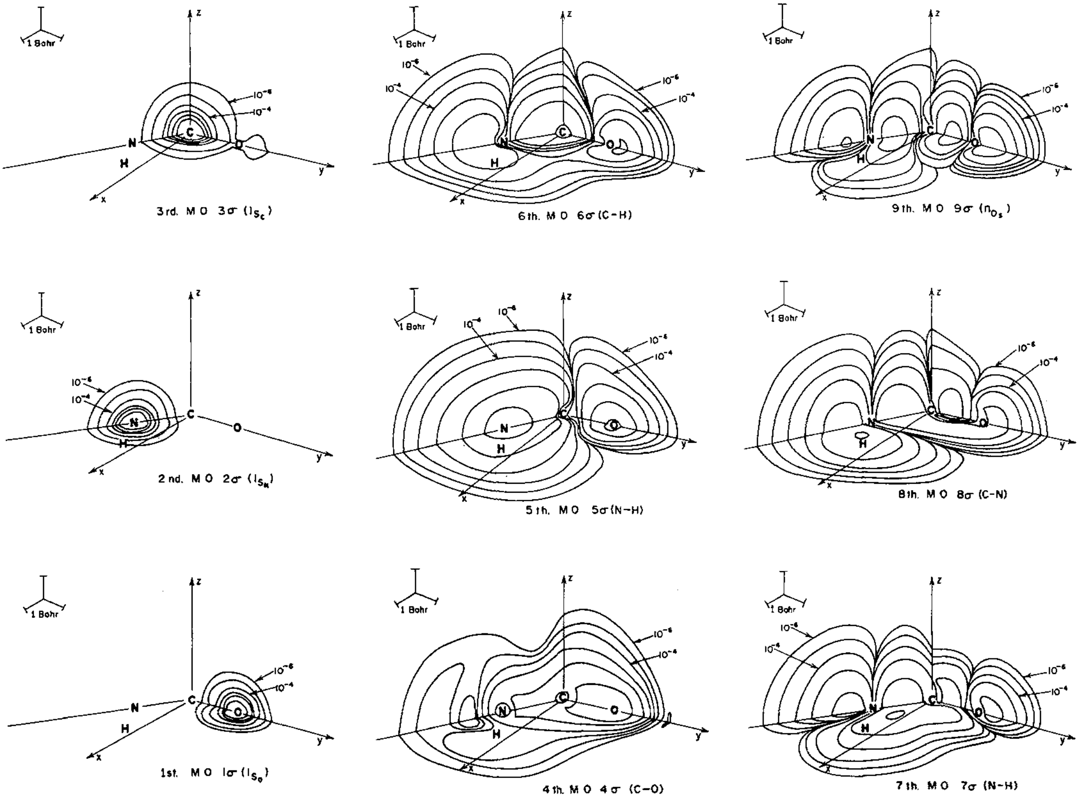


Fig. 3. Atomic and molecular orbital energies of formamide

Table 5. *Orbital energies of formamide calculated with various basis sets*

Orbital	Energy (hartree)		
	$N=21$	$N=39$	$N=59$
$13\sigma^*$	0.724	0.401	0.281
$12\sigma^*$	0.622	0.319	0.215
$3\pi^*$	0.507	0.247	0.187
$11\sigma^*$	0.554	0.316	0.176
2π	− 0.145	− 0.374	− 0.424
10σ	− 0.145	− 0.388	− 0.438
1π	− 0.375	− 0.553	− 0.583
9σ	− 0.342	− 0.558	− 0.613
8σ	− 0.489	− 0.643	− 0.683
7σ	− 0.575	− 0.716	− 0.757
6σ	− 0.736	− 0.836	− 0.881
5σ	− 1.149	− 1.224	− 1.237
4σ	− 1.316	− 1.441	− 1.447
3σ	−11.067	−11.404	−11.393
2σ	−15.378	−15.640	−15.615
1σ	−20.233	−20.614	−20.558


3rd. M O 3σ ($1s_C$)

6th. M O 6σ (C–H)

9th. M O 9σ (n_{O_s})

2nd. M O 2σ ($1s_N$)

5th. M O 5σ (N–H)

8th. M O 8σ (C–N)

1st. M O 1σ ($1s_O$)

4th. M O 4σ (C–O)

7th. M O 7σ (N–H)

Fig. 4. Total and molecular orbital electron densities of formamide

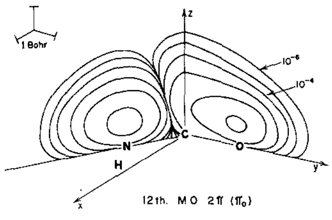
hence not observed. The ionization potential for the π_0 orbital is 11.5 eV, and the n_p orbital is 11.9 eV, wich is to be compared with Simpson's value of 10.2 eV.

From Table 5 it can be seen that the IP of the various MO change substantially with basis set. The IP pattern predicted by the minimal basis set ($N = 21$) is different from that predicted by the medium ($N = 39$) and best ($N = 59$) bases: the order of the n_s and π_+ levels are interchanged. For a minimal basis the energies of the core electrons (1σ, 2σ, and 3σ) are quite good but in going to larger basis sets, the bonding MO improve considerably.

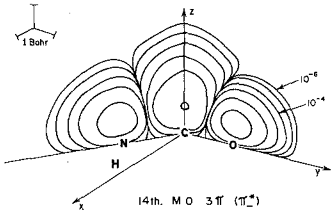
The MO electron densities and the total electron density (Fig. 4) are represented in the form of contours of the xy, yz, and $CN-z$ sections of the electron density surface. The unit of density is the fraction of an electron per cubic bohr atomic unit. The orbitals are numbered in order of increasing energy and the chemical assignment given. One of the amide hydrogens and the aldehyde hydrogen lie behind the planes and are not shown.

Electron Populations

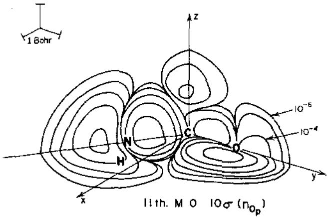
The partitioning of the total electron density into net atomic [23], and valence active [32] populations is shown in Fig. 5 along with the net atomic charges calculated from these populations. Although the method of analysis is rather arbitrary,



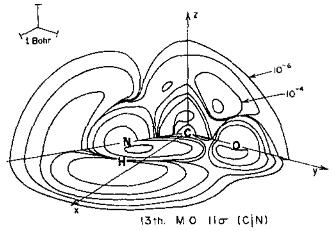
12th. MO 2π (π_0)



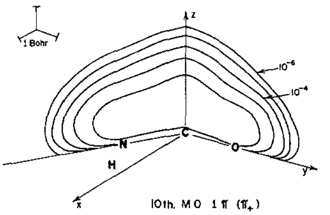
14th. MO 3π (π_-^*)



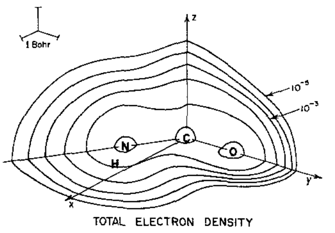
11th. MO 10σ (n_{O_p})



13th. MO 11σ (C|N)



10th. MO 1π (π_+)



TOTAL ELECTRON DENSITY

the net charges thus calculated are a method of visualizing the breakdown, atom by atom, of the total charge distribution given by the dipole moment. The centre of negative charge is localized on the O atom and the centre of positive charge is distributed over the HC–NH_2 grouping.

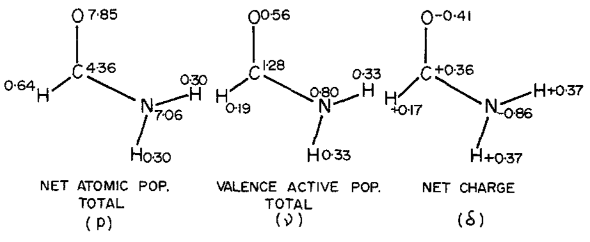


Fig. 5. Results of electron population analysis for formamide

Dipole Moment

The calculation of the dipole moment vector of a molecule with little symmetry gives an excellent criterion for the goodness of the calculated total wavefunction and the accuracy of the geometrical model since the orientation is not completely determined by symmetry. The orientation and magnitude of the calculated dipole moment of formamide as a function of basis set size is shown in Fig. 6 and Table 6 with the experimental value [22] for comparison (note that the Z component is zero for a planar molecule). It can be seen that the best basis set approaches the experimental value quite closely. Thus we can be confident that the calculated wavefunction represents the actual total electron density of the molecule quite well. It is interesting to note that the minimal basis set (N = 21) gives a very poor value indicating that limited basis set calculations do not represent the charge distribution very well. The fact that the orientation and magnitude of the calculated vectors with the medium (N = 39) and large (N = 59) bases are in excellent agreement with experiment also gives a reasonable assurance that the geometry chosen is quite close to the equilibrium value that would be deduced from microwave measurements.

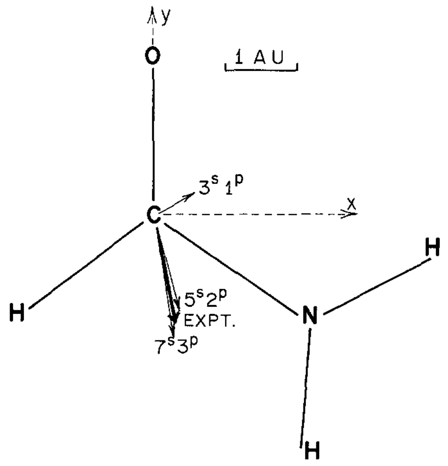


Fig. 6. Physical dipole moment vector of formamide calculated with various basis set sizes

Table 6. *Dipole moments of formamide calculated with various basis sets*

Basis Set		μ_x	μ_y	$\|\mu\|$
Size	Type	Debye		
21	$3^s 1^p$	1.26	0.66	1.41
39	$5^s 2^p$	0.85	−3.28	3.40
59	$7^s 3^p$	0.77	−4.08	4.15
Experimental		0.80	−3.95	3.71

Excited States

Although many investigations have been made on amides in the fields of NMR and IR spectroscopy, there are only a few studies on their vacuum ultraviolet spectra. Nagakura [24, 25] made a theoretical study of the π electron structure of formamide using semi-empirical methods and interpreted the nature of the $V_1 \leftarrow N$ (first π to π^* transition) state. Hunt and Simpson [13] measured the vacuum ultraviolet spectrum of formamide and their spectrum is shown in Fig. 8.

Before discussing the observed spectrum and the results obtained in this work, it is worthwhile to consider the possible pathways of excitation. It is useful to distinguish two types of excitation; sub-Rydberg transitions, including $V \leftarrow N$ $(\pi^* \leftarrow \pi)$ bands, the $Q \leftarrow N$ or $A \leftarrow N$ $(\pi^* \leftarrow n)$ bands, and $B \leftarrow N$ $(\sigma^* \leftarrow \pi)$ bands, and Rydberg transitions $R \leftarrow N$. For formamide one can expect sub-Rydberg excitations $Q_1 \leftarrow N$ $(\pi^*_- \leftarrow n_p)$, $Q_2 \leftarrow N$ $(\pi^*_- \leftarrow n_s)$, and $V_1 \leftarrow N$ $(\pi^*_- \leftarrow \pi_0)$, $V_2 \leftarrow N$ $(\pi^*_- \leftarrow \pi_+)$, although the $V_2 \leftarrow N$ could also be identified as a Rydberg transition. For each filled orbital in the ground state there will arise three Rydberg series np, five Rydberg series nd, and only one Rydberg series ns. Rydberg series originating from orbitals lower in energy than the two highest occupied MO will probably be of very high energy.

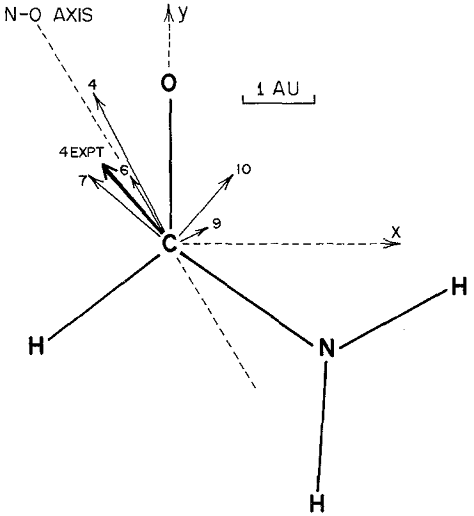


Fig. 7. Transition moment vectors for in-plane polarized transitions of formamide

On the basis of molecular symmetry one can classify excitations into two types: $\pi^* \leftarrow \sigma$ and $\sigma^* \leftarrow \pi$ excitations which will be out of plane polarized (Z polarized); and the $\pi^* \leftarrow \pi$ excitations which will be polarized in the plane of the molecule (XY polarized). There are no symmetry forbidden transitions but the Z polarized transitions should be several orders of magnitude less intense than the XY polarized transitions (overlap forbidden).

For the theoretical study of the formamide electronic spectrum only those excited states that can be constructed from the four lowest energy virtual orbitals have been considered. Since excited state wavefunctions are strongly affected by CI, the theoretical spectrum predicted by the SCF-MO calculation will be shifted to higher energy than the observed and the spacing of the energy levels may not be too accurate since configuration mixing may affect some states more than others, but the order of the predicted transitions should be correct at least for the low lying states. The calculated spectrum of formamide is shown in Fig. 8 with the transition moment squared as the intensity scale. The transition moment vectors for the XY polarized transitions are illustrated in Fig. 7. The excitation energies and transition moments are collected in Table 7 for the singlet-singlet excitations

Table 7. *Singlet-singlet excitations of formamide*

Code[b]	State		Excitation	Transition moment (Debye)			
	Excitation	C_s Symmetry[a]	Energy (eV)	M_x	M_y	M_z	$\lvert M\rvert$
1	$3\pi^* (\pi_- 3d) \leftarrow 10\sigma (n_p)$	A''	6.75			−0.71	0.71
2	$11\sigma^* (3s) \leftarrow 2\pi (\pi_0)$	A''	9.62			0.67	0.67
3	$12\sigma^* (3p) \leftarrow 2\pi (\pi_0)$	A''	10.85			−0.14	0.14
4	$3\pi^* (\pi_- 3d) \leftarrow 2\pi (\pi_0)$	A'	11.09	−2.66	5.35		5.97
5	$3\pi^* (\pi_- 3d) \leftarrow 9\sigma (n_s)$	A''	11.87			0.26	0.26
6	$11\sigma^* (3s) \leftarrow 10\sigma (n_p)$	A'	12.01	−0.54	0.92		1.07
7	$12\sigma^* (3p) \leftarrow 10\sigma (n_p)$	A'	12.33	2.93	1.94		3.52
8	$13\sigma^* (3p) \leftarrow 2\pi (\pi_0)$	A''	12.77			0.08	0.08
9	$13\sigma^* (3p) \leftarrow 10\sigma (n_p)$	A'	13.82	1.19	0.92		1.50
10	$3\pi^* (\pi_- 3d) \leftarrow 1\pi (\pi_+)$	A'	14.59	2.14	2.53		3.31
11	$11\sigma^* (3s) \leftarrow 1\pi (\pi_+)$	A''	14.74			−0.86	0.86

[a] Symmetry classification refers to the excited states involved.

[b] Code refers to the numerical code used in Figs. 7 and 8 to denote the different excitations.

and Table 9 for the singlet-triplet excitations while the excited state dipole moments are shown in Table 8. The excitation energies calculated will be for vertical excitations (geometry in the excited state assumed the same as in ground state) and the calculated term values should therefore be compared with the maxima of the observed spectrum and not the O–O bands. The experimental spectrum of Hunt and Simpson [13] is shown with the calculated spectrum in Fig. 8.

Table 8. *Dipole moment vectors for electronic excited states of planar formamide*

Excitation	Dipole moment		
	μ_x	μ_y	$\lvert\mu\rvert$
$3\pi^* \leftarrow 10\sigma$	0.53	−1.53	1.62
$11\sigma^* \leftarrow 2\pi$	−2.52	3.27	4.12
$12\sigma^* \leftarrow 2\pi$	0.425	−1.07	1.15
$3\pi^* \leftarrow 2\pi$	3.95	−5.16	6.50
$3\pi^* \leftarrow 9\sigma$	1.20	−2.09	2.40
$11\sigma^* \leftarrow 10\sigma$	−5.94	6.90	9.11
$12\sigma^* \leftarrow 10\sigma$	−3.00	2.56	3.94
$13\sigma^* \leftarrow 2\pi$	3.84	−0.37	3.86
$13\sigma^* \leftarrow 10\sigma$	0.417	3.27	3.29
$3\pi^* \leftarrow 1\pi$	2.12	−3.88	4.42
$11\sigma^* \leftarrow 1\pi$	−4.35	4.55	6.30

From Fig. 8 it can be seen that the calculated and observed spectra are in good agreement with respect to band intensity and band separation, with the calculated spectrum displaced to the blue as expected. Some general features of the observed and calculated spectra will now be discussed.

A fragmentary Rydberg series is identified in the region below 1500 Å by Hunt and Simpson [13]. After much searching they found a progression in that region fitting the formula:

$$\nu(\mathrm{cm}^{-1}) = 82{,}566 - R/(n-0.639)^2, \quad n = 3, 4, 5, 6, 7, \ldots, R = 109{,}677\ \mathrm{cm}^{-1},$$

giving a value of 10.2 eV (82,566 cm^{-1}) for the ionization potential of the oxygen lone pair. With a quantum defect of 0.639 the series obviously involves *ns* type Rydberg orbitals. For the oxygen lone pair the calculated term values for the Rydberg excitations for the first members of three series are shown in Fig. 8. Bands 6, 7, and 9 are the first members of the *ns* and two *np* series respectively. The separation of these first values is in qualitative agreement with the Rydberg series reported for formaldehyde[3] and acrolein[4]. Although Hunt and Simpson [13] only observed one Rydberg series for the oxygen lone pairs there should be at least four series (a single *ns* and three *np*) converging on the same ionization limit.

Table 9. *Singlet-triplet excitations of formamide*

Excitation	Excitation Energy (eV)
$3\pi^* \leftarrow 10\sigma$	6.15
$11\sigma^* \leftarrow 2\pi$	9.22
$12\sigma^* \leftarrow 2\pi$	10.69
$3\pi^* \leftarrow 2\pi$	6.64
$3\pi^* \leftarrow 9\sigma$	10.93
$11\sigma^* \leftarrow 10\sigma$	11.54
$12\sigma^* \leftarrow 10\sigma$	11.78
$13\sigma^* \leftarrow 2\pi$	12.63
$13\sigma^* \leftarrow 10\sigma$	13.17
$3\pi^* \leftarrow 1\pi$	9.66
$11\sigma^* \leftarrow 1\pi$	14.53

Presumably if the spectrum were obtained at sufficiently high resolution the Rydberg series corresponding to *np* would be found since their predicted intensity in these calculations is of the same order of magnitude as the *ns* Rydbergs.

No Rydberg series involving the π_0 MO is observed. The reason is that these Rydberg series must involve $\sigma^* \leftarrow \pi$ excitations which must be of lower intensity than the $\sigma^* \leftarrow \sigma$ excitations. If a Rydberg series were observed one would expect it to converge at a lower energy than the one involving the oxygen lone pair. Transitions 2, 3, and 8 may be regarded as borderline between Rydberg and sub-Rydberg transitions involving π_0. If as an approximation we regard them as Rydberg state corresponding to the first members of the *ns* and two *np* series respectively, then their term values are of lower energy than the corresponding terms for the n_p MO and we would expect the ionization limit to be lower than n_p MO. However, these $\pi^* \leftarrow \sigma$ excitations involve no change in principal quantum number and are probably more correctly classified as sub-Rydberg $B \leftarrow N$ excitations.

The sub-Rydberg bands calculated agree well in intensity and position with the observed spectrum. Bands 4 and 10 are the two $V \leftarrow N$ transitions. The $V_1 \leftarrow N$ transition (band 4) is of special interest since the orientation and magnitude of the transition moment vector for the corresponding band in myristamide have been measured experimentally by Peterson and Simpson [26]. Their observed value

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[3] See Page 547 of Ref. [18].

[4] See Page 518 of Ref. [18].

and the calculated value can be seen in Fig. 7. Nagakura [24, 25] has called this transition an intramolecular charge transfer band (after the analogous phenomenon observed with inorganic ligands and a similar high intensity band in acrolein). He identifies this band with the intramolecular migration of electron density via a bridge of conjugated double bonds from the electron donating nitrogen grouping to the strongly electron accepting oxygen. The calculated transition

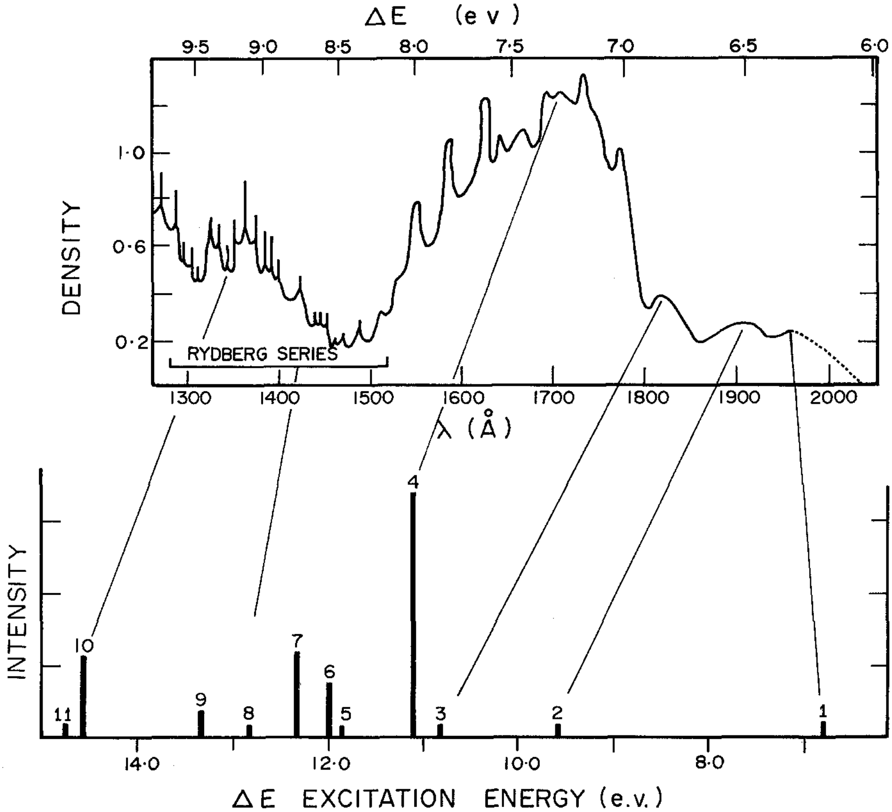

Fig. 8. Correlation of experimental and calculated electronic spectrum of formamide

moment is inclined at an angle of 4 degrees away from the NO axis directed from nitrogen to oxygen, strongly reinforcing this interpretation. The process may be visualized by considering the calculated values of the ground state dipole moment (Fig. 6), the transition moment, and the excited state dipole moment (Table 8). The ground state dipole moment is about one half the value of the excited state dipole moment, but both have the same direction suggesting a greater separation of charge between the oxygen and the nitrogen groupings in the excited state. The transition moment, however, is almost exactly opposite in orientation to the two dipole moments showing the migration of electron density from the nitrogen to the oxygen during the excitation.

The $Q \leftarrow N$ transitions are bands 1 and 5 corresponding to the $\pi^* \leftarrow n$ excitations of the oxygen long pairs. Unlike formaldehyde, these bands are not symmetry forbidden but rather are out of plane polarized (and consequently of low intensity).

Naive π electron MO theory predicts that the two non-bonding electron pairs n_p and π_0 should be approximately degenerate and on this basis Hunt and Simpson concluded [13] that the $Q_1 \leftarrow N$ band is probably buried in the high intensity $V_1 \leftarrow N$ band. This view is not consistent with the large energy separation predicted in this work which predicts that the $Q_1 \leftarrow N$ band comes at much lower energy than the $V_1 \leftarrow N$ band.

Computational Details

The calculations performed in this work were carried out using an extensively modified and expanded version of the POLYATOM SYSTEM [6]. The program has been tailored to operate under the University of Toronto's version of the IBSYS batch processor for an IBM 7094 II Computer and numerical methods have been improved. Faster integral evaluation routines have been incorporated resulting in a substantial decrease in integral computation time. In the SCF, in order to reduce round-off error to an absolute minimum, all matrix operations are performed in double precision. A new highly sophisticated matrix diagonalization routine, using a variable threshold Jacobi technique [19] has been used in order to secure maximum accuracy in the solution of the eigenvalue problem.

For the treatment of excited states, it was assumed that the excited states in question could be represented by a single codetor in which one of occupied molecular spin orbitals of the ground state detor is replaced by a virtual spin orbital. The excitation energy for the transition is calculated from Eq. 68 of Ref. [31]. The transition moments were found by evaluating matrix elements for the dipole length operator between the ground and excited state single co-detor wavefunctions.

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Professor I. G. Csizmadia
Department of Chemistry
University of Toronto
80 St. George Street, Toronto 5/Canada