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Commentationes

Theoretical Assignments of the Electronic Spectrum of Acetylene

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Non empirical calculations of energies and properties of some excited states of acetylene are presented. A frozen core approximation is used and excitations to σ, π and δ MO's are taken into account. Both valence and Rydberg states are considered. Assignments of the UV and electron impact spectra are proposed and some questions are raised.

Key words: Acetylene, excited states of ~

1. Introduction

The present non empirical theoretical study is an attempt to elucidate the nature and relative energies of the low lying excited states of acetylene, and their valence or Rydberg character, as well as to describe the first few terms of the observed Rydberg series. We will call Rydberg states those states of the molecule where one electron is, on the average, much farther from the nuclei than the other electrons [i.e. in a diffuse Molecular Orbital (MO)]. Expectation values of x^2 and z^2 will be taken as a measure of diffuseness. This article will deal only with vertical transitions. A forthcoming paper will be devoted to potential surfaces for some excited states.

2. Experimental Background

The ground state electronic configuration of acetylene is: $(1\sigma_g)^2\,(1\sigma_u)^2\,(2\sigma_g)^2\,(2\sigma_u)^2\,(3\sigma_g)^2\,(1\pi_u)^4$. It's UV absorption spectrum shows two weak features at low energy [1]. System $\tilde{A}$ at 5.23 eV, (we will use Herzberg's notation [1] throughout this article), has been assigned to a transition to a ^1A_u state of trans bent acetylene, derived from a $^1\Sigma_u^-$ state of the linear molecule [2]. System $\tilde{B}$ extends from 6.1–8.0 eV, with maximum at 7.3 eV and has been analyzed only recently [35]. Mulliken has suggested [2] that it is due to transitions to a $^1\Sigma_u^-$ or a $^1\Delta_u$ state.

Three Rydberg series have been observed [1, 3], converging to the first ionisation potential (IP) of the molecule at 11.40 eV [14]. The first two start with peaks $\tilde{C}$ [1] at 8.16 eV and $\tilde{F}$ [3] at 9.27 eV, and are usually assigned to the allowed transitions to $^1\Pi_u$ $(\sigma_g^* \leftarrow 1\pi_u)$ and $^1\Sigma_u^+$ $(\pi_g^* \leftarrow 1\pi_u)$ states [3]. $\tilde{D}$ at 9.24 eV could be a $^1\Pi_g$ $(\sigma_u^* \leftarrow 1\pi_u)$ state [3]. The third Rydberg series [3] starts at 9.97 eV and has been assigned to transitions to $^1\Pi_u(\delta_g^* \leftarrow 1\pi_u)$ states. We will present numerical support for that assignement. State $\tilde{G}$ [1] at 9.93 eV could be the second member of the first Rydberg series.

There is still uncertainty in the assignments for the peaks around 9.25 eV, where the presence of non linear states has been suggested [1]. Additional peaks are found only in electron impact spectra. Trajmar *et al.* [4] with incidence electrons of 45 eV, found peaks at 5.2 and 6.1 eV which they assign to ${}^3\Pi$ states. Dance and Walker [5] in threshold electron impact experiments detected two peaks near the same energies, but assigned them to triplet states belonging to the $(1\pi_g^* \leftarrow 1\pi_u)$ electronic configuration. They assigned a further peak at 8.05 eV to a ${}^3\Pi(\sigma^* \leftarrow 1\pi_u)$ state.

Quenching experiments by Burton and Hunziker [6] suggest that the lowest triplet state of acetylene has an energy between 2.6 and 4.7 eV above the ground state.

3. Theoretical Background

Early theoretical studies of the excited states of acetylene are reviewed by Kammer [7]. Recently, Duncan *et al.* [8] presented approximate calculations which support the interpretation of the first two Rydberg series of acetylene as *ns* and $nd\pi$ series respectively. Kammer [7] carried out *ab-initio* SCF-CI studies on the excited states of acetylene in linear and bent geometries. In these calculations, no diffuse (small exponent) basis functions were used, excitation was allowed only to σ_u^* and π_g^* MO's, but not to σ_g^* or π_u^*, and virtual orbitals from the ground state SCF calculation were used. Thus neither Rydberg states, like the ${}^1\Sigma_u^+$ state (Table 5), nor the ${}^1\Pi_u$ state, which are thought to be responsible for the two most intense transitions, $\tilde{F}$ and $\tilde{C}$, of the spectrum [3], could be satisfactorily described. Indeed both have computed excitation energies higher than the experimental first IP [7]. For the valence states (Table 5), we will show that the method used here gives lower total energies than using the virtual MO's from a ground state SCF calculation in a CI treatment. These considerations, and the lack of calculations with MO's of delta symmetry, prompted this study.

4. Theoretical Methods

Truhlar [9] has given a review of computational methods appropriate for excited states. Other recent work of interest include calculations on CO_2 by Winter *et al.* [10] and on C_2H_4 by Kowalewski and Fischer-Hjalmars [11]. Our calculations are of the *ab-initio* frozen core type; this approach was first used by Lefebvre-Brion [12] on N_2, NO, CO, and BF, and recently by Hunt and Goddard on H_2O [13], and in Ref. [11].

In the present case, the core is the acetylene cation in its ${}^2\Pi_u$ ground state, corresponding to the ionization of one pi electron. The first three IP's of acetylene are: 11.40, 16.36, and 18.38 eV [14]. Since the second IP is 5 eV greater than the first, we feel confident that states arising from excited ionic cores will not be important in the description of the states observable at energies up to near the first IP.

With a basis set containing no diffuse functions, of the type needed to describe Rydberg states, one carries out an SCF calculation to obtain the core. One can do a closed shell calculation for the neutral ground state and obtain the ion via Koopmans theorem [33] or one can obtain the core directly by an open shell calculation for the ion. This second method might lead to better results for Rydberg states, which one describes as an ionic core plus one electron on a large orbit. We have investigated both possibilities.

When the core is obtained, for each type, sigma, pi or delta MO's, one enlarges the basis with diffuse functions; one computes the additional integrals due to the increase of the basis, forms the effective operators (Table 2) for the appropriate symmetries, and diagonalizes them. The eigenvalues of the effective operators (orbital energies) are the ionisation potentials of the excited states: Koopmans' theorem applies exactly for the excited MO's (since a frozen core approximation is used). The total energy of an excited state, $E=E_{\text{core}}+\varepsilon$, obeys the variation principle. This must be remembered when one compares the goodness of different cores. The wave function for the excited state is the antisymmetrized product of $\Psi(\text{core})\cdot\Psi(\text{excited MO})$. Orthogonality of excited state MO's to ground state MO's is easily taken care of by projecting the operators out of the space of the occupied core MO's before diagonalizing. Strictly speaking, if one uses the SCF ion as core, the excited $^1\Sigma_g^+$ states are not orthogonal to the $^1\Sigma_g^+$ molecular ground state. In practice, no difficulty was met, and we obtained results similar to those obtained with a core taken from a ground state calculation of the molecule.

Our method is quite similar to that of Fischer-Hjalmars and Kowalewski [11]. We use the same integrals and optimise the excited MO's in the field of the frozen core. However, we save computer time by doing only one SCF calculation without the diffuse functions in the basis. This affects the computed ionisation potentials of our excited states by an amount negligible compared to the errors introduced by the neglect of electron correlation and zero point vibrational energy differences. Indeed computing valence states without diffuse functions changes their computed IP's by 0.04 eV in the worst case. Computation of the expectation values of x^2, y^2, and z^2 and of oscillator strengths is made easy by the frozen core approximation, and the excited states can thus easily be characterized.

The results presented in this article emphasize the usefulness of optimizing the excited state MO. Except for the ground state, and with a basis set similar to that of Ref. 7, but with diffuse functions, we obtain lower total energies. For Rydberg states, the lowering is 0.1–0.4 a.u. (1 a.u. = 27.21 eV), for valence states, about 0.02 a.u. Since contribution from the diffuse basis is only 0.001 a.u., for valence states, the energy lowering compared to Kammer's results is a reflection of the use of optimized MO's for the excited state, as opposed to virtual MO's from an SCF calculation.

5. Computational Details

The ground electronic configuration of acetylene is: $\ldots(3\sigma_g)^2\,(1\pi_u)^4$. We considered all excited states arising from the configurations $\ldots(1\pi_u)^3\,(X)$ where X

is an MO of one of the following types: σ_u, σ_g, π_u, π_g, δ_u, δ_g. The excited states one obtains are the following:

$$\begin{array}{ll} \ldots(\pi_u)^3\,(n\sigma_g) & {}^1\Pi_u,\ {}^3\Pi_u \\ \ldots(\pi_u)^3\,(n\pi_g) & {}^1\Sigma_u^+,\ {}^3\Sigma_u^+,\ {}^1\Sigma_u^-,\ {}^3\Sigma_u^-,\ {}^1\Delta_u,\ {}^3\Delta_u \\ \ldots(\pi_u)^3\,(n\delta_g) & {}^1\Pi_u,\ {}^3\Pi_u,\ {}^1\Phi_u,\ {}^3\Phi_u \end{array}$$

and the corresponding states of g symmetry arising from MO's of u symmetry.

Table 1. Wavefunctions for some excited states of acetylene

State	Form of the wavefunction[a]
${}^1\Sigma_g^+$	$\pi_{ux}^2\pi_{uy}^2$
${}^{1,3}\Pi_u$	$\begin{cases}\pi_{ux}^2\pi_{uy}\,3s\sigma_g{}^{\mathrm{b}} \\ \pi_{uy}^2\pi_{ux}\,3s\sigma_g\end{cases}$
${}^3\Sigma_u^+$	$\pi_{ux}^2\pi_{uy}\pi_{gy}+\pi_{uy}^2\pi_{ux}\pi_{gx}{}^{\mathrm{b}}$
${}^{1,3}\Delta_u$	$\begin{cases}\pi_{ux}^2\pi_{uy}\pi_{gy}-\pi_{uy}^2\pi_{ux}\pi_{gx} \\ \pi_{ux}^2\pi_{uy}\pi_{gx}+\pi_{uy}^2\pi_{ux}\pi_{gy}\end{cases}$
${}^{1,3}\Sigma_u^-$	$\pi_{ux}^2\pi_{uy}\pi_{gx}-\pi_{uy}^2\pi_{ux}\pi_{gy}$
${}^1\Sigma_u^+$	$\pi_{ux}^2\pi_{uy}\,3d\pi_{g,yz}+\pi_{uy}^2\pi_{ux}\,3d\pi_{g,xz}$
${}^{1,3}\Pi_u$	$\begin{cases}\pi_{ux}^2\pi_{uy}\,3d\delta_{g,x^2-y^2}-\pi_{uy}^2\pi_{ux}\,3d\delta_{g,xy} \\ \pi_{ux}^2\pi_{uy}\,3d\delta_{g,xy}+\pi_{uy}^2\pi_{ux}\,3d\delta_{g,x^2-y^2}\end{cases}$
${}^{1,3}\Phi_u$	$\begin{cases}\pi_{ux}^2\pi_{uy}\,3d\delta_{g,x^2-y^2}+\pi_{uy}^2\pi_{ux}\,3d\delta_{g,xy} \\ \pi_{ux}^2\pi_{uy}\,3d\delta_{g,xy}-\pi_{uy}^2\pi_{ux}\,3d\delta_{g,x^2-y^2}\end{cases}$

[a] The wave function of the lowest state of each symmetry is shown. In each case the configuration $(1\sigma_g)^2\,(1\sigma_u)^2\,(2\sigma_g)^2\,(2\sigma_u)^2\,(3\sigma_g)^2$ is present. The wave function is multiplied by the appropriate spin function and antisymmetrized. π_{ux}, π_{uy} are the ground state $1\pi_u$ MO components. The excited MO's are optimized (see text).

[b] By $3s\sigma_g$ etc. we mean a diffuse σ_g MO which can best be described as a $3s$ atomic orbital at the molecular center. π_{gx}, π_{gy} are components of a valence-like π_g MO.

Table 2. Effective operators for some excited states of acetylene

States	Operators[a]
${}^{1,3}\Pi$	$h+2\,J^\sigma-K^\sigma+1.5\,J^\pi-0.5\,K^\pi\pm 0.5\,K^\pi$
${}^1\Sigma^+$	$h+2\,J^\sigma-K^\sigma+0.5\,J^x+2.5\,J^y+3\,K^x-5\,K^y$
${}^3\Sigma^+$	$h+2\,J^\sigma-K^\sigma+0.5\,J^x+2.5\,J^y-K^x-K^y$
${}^{1,3}\Sigma^{-\,\mathrm{b}}$	$h+2\,J^\sigma-K^\sigma+2.5\,J^x+0.5\,J^y-K^x-K^y$
${}^1\Delta$	$h+2\,J^\sigma-K^\sigma+1.5\,J^x+1.5\,J^y-K^x+3\,K^y$
${}^3\Delta$	$h+2\,J^\sigma-K^\sigma+1.5\,J^x+1.5\,J^y-K^x-K^y$
${}^1\Phi^{\mathrm{c}}$	$h+2\,J^\sigma-K^\sigma+1.5\,J^\pi-7/12\,K^\pi$
${}^1\Pi^{\mathrm{c}}$	$h+2\,J^\sigma-K^\sigma+1.5\,J^\pi+7/12\,K^\pi$
${}^3\Phi\,{}^3\Pi^{\mathrm{b}}$	$h+2\,J^\sigma-K^\sigma+1.5\,J^\pi-K^\pi$

[a] h is the monoelectronic part of the Hamiltonian. The coulomb, J, and exchange, K, operators are defined in the standard way. $J^\pi=J^x+J^y$, $K^\pi=K^x+K^y$.

[b] In the SCF approximation the ${}^1\Sigma^-$ and ${}^3\Sigma^-$ states are degenerate and also the ${}^3\Pi$ and ${}^3\Phi$ $(n\delta^*\leftarrow 1\pi_u)$ states.

[c] The operators for the ${}^1\Phi$ and ${}^1\Pi$ $(n\delta^*\leftarrow 1\pi_u)$ states are approximate; see text and appendix.

The symmetry adapted linear combinations of determinants and the resulting effective one electron operators are listed in Tables 1 and 2. The operators do not depend on $u-g$ symmetry. They are obtained by the usual rules for matrix elements between determinantal wave functions [34], and the high symmetry of the problem has been used to simplify them. For the $\ldots(1\pi_u)^3\,(n\pi^*)$ configurations, the operators given in the table determine real π_x^* MO's. Operators for π_y^* MO's can be obtained by interchanging x and y in the formulae. However, they need not be explicitly considered.

For the $(1\pi_u)^3\,(n\delta^*)$ configurations, the operators of Table 2 are approximate ones. They have been used to generate the data of Table 7. In Appendix A the exact expressions are given, and the results of the exact and approximate treatments are compared, using a smaller basis set. For the lowest $^1\Pi_u$ and $^1\Phi_u$ states, the difference between the two treatments is only 0.04 eV; it is even smaller for higher states. The approximate treatment allows one to use only one type of function of delta symmetry: d_{xy} or $d_{x^2-y^2}$.

6. Geometry and Basis Sets

In all our calculations, we used the following geometry: $R_{\mathrm{C-C}}=2.281$ a.u. and $R_{\mathrm{C-H}}=2.002$ a.u. (1 a.u. $=0.529177$ Å). The molecular axis was taken as Z axis.

This corresponds to the experimental geometry of the molecule in its ground state [15] and is very close to the minimum energy geometry obtained with a double zeta basis set comparable to ours [16]. All our basis functions were of the gaussian lobe type. For an exponent α, the separation d between two lobes was obtained from $d/2=0.2/(\alpha)^{\frac{1}{2}}$ for p functions, $d/2=0.35\,(\alpha)^{\frac{1}{2}}$ for d pi and delta functions, and $d/2=0.5/(\alpha)^{\frac{1}{2}}$ for d sigma functions. The d sigma functions were made of two positive lobes plus one negative lobe at the center. We could have ignored the negative part, since s functions at the center could simulate it, but we choose to keep it to facilitate the characterisation of the MO's.

For the SCF calculations, several basis sets were tried. Our final choice was a double zeta plus polarization set constructed as follows: Huzinaga's $4s$ hydrogen and $9s$, $5p$ carbon basis [17] in the double zeta contraction of Dunning [18], increased with a p sigma function of exponent 0.4 on each hydrogen and a s function of exponent 0.3 and p pi functions of exponents 0.26 at the molecular center. We will not give a detailed comparison of the results obtained with different basis sets, since this has been done recently by Siegbahn and Fischer-Hjalmars [19]. Like them, we found that separate optimisation of the exponents of p sigma and p pi functions is unimportant for double zeta basis sets. (Optimisation caused an energy lowering of 0.005 a.u., while with minimum basis sets of STO's, the lowering was 0.036 a.u. [20]). In Table 3, our results for the energy and a few molecular properties are compared with the near Hartree-Fock results of McLean and Yoshimine [21], and with experiments when possible.

Our results for molecular properties are close enough to the Hartree-Fock results that we can have confidence in the corresponding values for the ion. Table 3 shows that Koopmans theorem works fairly well for acetylene. This im-

Table 3. SCF results for the acetylene molecule and ion

	This work	Hartree-Fock[a]	Experiment
C_2H_2			
Energy (a.u.)	−76.81178	−76.85397	
IP (Koopmans) (eV)	11.15	11.17	11.40[b]
Θ (esu)	7.19	7.23	8.4 ± 1.0[c]
χ_L (esu)	−48.39	−48.52	
χ (esu)	−22.33		-20.8 ± 0.8[d]
$\Delta\chi$ (esu)	3.28		4.5 ± 0.5[c]
MO	$\langle x^2 \rangle$	$\langle z^2 \rangle$ [(a.u.)^2]	
$2\sigma_u$	0.69	6.57	
$3\sigma_g$	0.53	6.15	
$1\pi_{ux}$	2.35	1.68	
$C_2H_2^+$			
Energy (a.u.)	−76.44542		
IP (SCF) (eV)	9.97		11.40[b]
Θ (esu)	9.40		
χ_L (esu)	−40.97		

[a] Ref. [21].

[b] Ref. [14].

[c] Flygare, W. H. *et al.*: Chem. Phys. Letters **18**, 153 (1973).

[d] Barter, C. *et al.*: J. Phys. Chem. **64**, 1312 (1960). Molecular properties are computed from the center of mass. All properties are as defined in Neumann and Moskowitz, J. Chem. Phys. **49**, 2056 (1968) and **50**, 2216 (1969). Conversion factors from atomic units to e.s. units were taken from Rothenberg, S., Schaefer, H.: J. Chem. Phys. **53**, 3014 (1970).

Θ is the molecular quadrupole moment in 10^{-26} esu. χ_L is the average diamagnetic susceptibility. $\chi = \chi_L + \chi_P$, the total magnetic susceptibility. $\Delta_\chi = \chi_\perp - \chi_{\|}$, the magnetic susceptibility anisotropy, all in 10^{-6} erg/Gauss^2 mole.

The value for χ_P was obtained as in: Y. Kato *et al.*, Chem. Phys. Letters **13**, 453 (1972), but using for $g_\perp$ the positive value, as suggested by Flygare[c]. Our $\Delta\chi$ value is now in good agreement with Flygare's estimate and lends further support to his assignment of a positive sign to $g_\perp$. If one takes $g_\perp$ as negative, one obtains $\Delta = 9.16 \cdot 10^{-6}$ esu.

plies a near cancellation between the reorganisation energy of the ion and the difference in correlation energy between molecule and ion.

$$\Delta E(\text{Reorganisation}) = \text{IP(Koopmans)} - \text{IP(SCF)} = 1.18\ \text{eV}$$

$$\Delta E(\text{Correlation}) = \text{IP(Experimental)} - \text{IP(SCF)} = 1.43\ \text{eV}\,.$$

Sinanoğlu *et al.* [22] with a minimum STO basis set, obtained ΔE(Reorganisation) = 0.66 eV and ΔE(Correlation) = 1.52 eV.

For the excited state calculations, three sets of functions were used. In each set, the lowest exponent for each type (*p*, *s*, etc.) of function was used for one function on each carbon atom. The other exponents were each used for one function at the molecular center. The following type of functions and exponents were used:

For sigma MO's: 0.06, 0.015, 0.005, 0.0015 (s and d_z^2 functions)
0.052, 0.013, 0.0042, 0.0013 (p_z functions)
For pi MO's: 0.048, 0.012, 0.0036, 0.0012 (p_x and d_{xz} functions).

Table 4. $n\sigma^* \leftarrow 1\pi_u$ excited states

State	MO type	ΔE	$n-\delta$	$\langle x^2\rangle$	$\langle z^2\rangle$	f	ΔE (exp)[a]
$^1\Pi_u$	$3s$	8.43	2.14	18.5	20.2	0.072	8.16
	$3d\sigma$	9.70	2.82	17.1	66.9	0.042	
	$4s$	10.05	3.17	96.5	65.7	0.015	9.93
	$4d\sigma$	10.49	3.87	70.5	312.5	0.019	
	$5s$	10.63	4.20	335.4	176.3	0.0035	10.57
	$5d\sigma$	10.84	4.93	191.1	1075.2	0.0083	
$^3\Pi_u$	$3s$	8.35	2.12	17.8	18.0		
	$3d\sigma$	9.60	2.75	13.6	61.0		
	$4s$	10.03	3.16	96.3	57.9		
	$4d\sigma$	10.44	3.77	61.8	295.3		
	$5s$	10.62	4.18	338.6	167.0		
	$5d\sigma$	10.82	4.85	192.3	1082.9		
$^1\Pi_g$	$3p\sigma$	8.915	2.34	12.9	45.1		
	$4p\sigma$	10.22	3.38	64.9	200.5		
	$5p\sigma$	10.72	4.44	243.6	750.6		
$^3\Pi_g$	$3p\sigma$	8.83	2.30	11.6	42.1		
	$4p\sigma$	10.18	3.34	60.5	187.2		
	$5p\sigma$	10.71	4.45	232.2	715.6		

[a] ΔE in eV (see definition in the text), $\langle x^2\rangle$, $\langle z^2\rangle$, f in atomic units, ΔE (exp) in eV; data from Ref. [3].

Table 5. $n\pi_g^* \leftarrow 1\pi_u$ excited states

State	MO type	ΔE	$n-\delta$	$\langle x^2\rangle$	$\langle z^2\rangle$	f	ΔE (exp)[a]
$^1\Sigma_u^+$	$3d\pi$	9.83	2.98	53.0	53.0	0.0495	9.267[b]
	$4d\pi$	10.54	3.98	235.6	235.6	0.0222	10.31[b]
	$5d\pi$	10.875	5.09	802.3	802.3	0.0080	10.74[b]
$^3\Sigma_u^+$	Valence	5.02		2.83	3.62		
	$3d\pi$	9.97	3.09	68.4	68.4		
	$4d\pi$	10.60	4.13	265.4	265.4		
	$5d\pi$	10.90	5.22	808.1	808.1		
$^{1,3}\Sigma_u^-$	Valence	6.69		3.51	4.27		
	$3d\pi$	10.05	3.18	76.2	76.2		
	$4d\pi$	10.63	4.21	277.6	277.6		
	$5d\pi$	10.90	5.22	797.5	797.5		
$^1\Delta_u$	Valence	7.04		3.88	4.63		
	$3d\pi$	10.04	3.17	75.7	75.7		
	$4d\pi$	10.63	4.21	276.7	276.7		
	$5d\pi$	10.90	5.22	798.6	798.6		
$^3\Delta_u$	Valence	5.87		3.11	3.89		
	$3d\pi$	10.01	3.13	72.1	72.1		
	$4d\pi$	10.62	4.18	271.1	271.1		
	$5d\pi$	10.90	5.22	803.7	803.7		

Notations and units as in Table 4.

[a] Data from Ref. [3].

[b] Uncertain assignment; this series could be assigned to $nd\sigma$ (Table 4), see text.

Table 6. $n\pi_u^* \leftarrow 1\pi_u$ excited states

State	MO type	ΔE	$n-\delta$	$\langle x^2 \rangle$	$\langle z^2 \rangle$
$^1\Sigma_g^+$	$3p\pi$	9.29	2.54	56.5	19.5
	$4p\pi$	10.34	3.59	252.9	83.3
	$5p\pi$	10.78	4.69	882.4	286.4
$^3\Sigma_g^+$	$3p\pi$	9.065	2.42	45.0	16.3
	$4p\pi$	10.27	3.48	228.0	74.2
	$5p\pi$	10.76	4.62	853.0	276.8
$^{1,3}\Sigma_g^-$	$3p\pi$	9.24	2.51	51.0	18.4
	$4p\pi$	10.32	3.56	242.2	78.9
	$5p\pi$	10.77	4.65	871.7	283.0
$^1\Delta_g$	$3p\pi$	9.19	2.49	49.5	17.8
	$4p\pi$	10.31	3.54	238.9	77.8
	$5p\pi$	10.77	4.65	862.5	281.9
$^3\Delta_g$	$3p\pi$	9.16	2.47	48.0	17.4
	$4p\pi$	10.30	3.52	235.5	76.7
	$5p\pi$	10.76	4.62	864.2	280.5

Notations and units as in Table 4.

For delta MO's (one function on each carbon for each exponent):

0.15, 0.05, 0.015, 0.005, 0.0015 (d_{xy} functions).

Higher Rydberg states will thus be described effectively by one center functions, and no polarization functions for them are included. As a result, for e.g. *d* pi MO's $x^2 = z^2$ exactly (Table 5). Use of smaller double zeta basis sets to describe the core changed the excitation energies by less than 0.05 eV. All excitation energies given in Tables 4–8 were stable within 0.05 eV against further increase of the diffuse basis sets. For delta MO's, the function with exponent 0.15 had nearly no influence on the results.

We now compare the effect of SCF and Koopmans core on total and excitation energies. For most states, excitation energies were not sensitive to which core was used, but total energies were lower when an SCF core was used. For each of the lowest states of the $^{1,3}\Sigma_u^-$, $^{1,3}\Delta_u$, and $^3\Sigma_u^+$ symmetries, a Koopmans core gave lower total and excitation energies. It turns out that the states in the first set are diffuse Rydberg states, while those in the second set were valence states (independent of the core used). The results in Tables 4–7 are always those of lowest total energy.

We may conclude that at least for acetylene, the use of a Koopmans core is sufficient to describe Rydberg states properly, and much to be preferred for valence states.

7. Results

In Tables 4–7, we present our results for the low lying excited states of acetylene which can be described as single excitations from the $1\pi_u$ MO to a MO of sigma, pi or delta symmetry. The excitation energies are taken as the ex-

Table 7. $n\delta^* \leftarrow 1\pi_u$ excited states

State	MO type	ΔE	$n-\delta$	$\langle x^2 \rangle$	$\langle z^2 \rangle$	f	ΔE (exp)[a]
$^1\Pi_u$	$3d\delta$	9.99	3.11	64.3	20.5	0.0079	9.97
	$4d\delta$	10.60	4.13	246.1	76.2	0.005	10.59
	$5d\delta$	10.88	5.12	570.3	175.5	0.003	10.88
$^1\Phi_u$	$3d\delta$	9.97	3.09	61.5	19.6		
	$4d\delta$	10.59	4.11	236.2	73.1		
	$5d\delta$	10.87	5.08	578.5	178.0		
$^3\Pi_u$, $^3\Phi_u$	$3d\delta$	9.96	3.08	60.3	19.3		
	$4d\delta$	10.58	4.08	231.9	71.8		
	$5d\delta$	10.87	5.08	581.7	179.1		
$^1\Pi_g$	$4f\delta$	10.55	4.01	127.9	118.6		
	$5f\delta$	10.87	5.08	502.7	463.9		
$^1\Phi_g$	$4f\delta$	10.55	4.01	127.8	118.5		
	$5f\delta$	10.87	5.08	502.3	463.5		
$^3\Pi_g$, $^3\Phi_g$	$4f\delta$	10.55	4.01	127.7	118.5		
	$5f\delta$	10.87	5.08	502.2	463.3		

Notations and units as in Table 4.

[a] Data from Ref. [3].

Table 8. Excitation energies for states of acetylene below 10.0 eV

Present work			UV data	Electron impact data	
State	ΔE (eV)	Assignments	ΔE (eV) (T_0)	ΔE (eV)	
$^1\Sigma_g^+$	0		0	[c]	[d]
$^3\Sigma_u^+$	5.02	$(\tilde{a})$		5.2 ($^3\Pi$)	5.3 $^3(\pi_g^* \leftarrow \pi_u)$
$^3\Delta_u$	5.87	$(\tilde{b})$		6.1 ($^3\Pi$)	5.9 $^3(\pi_g^* \leftarrow \pi_u)$
$^1\Sigma_u^-$	6.69	$(\tilde{A})$	5.23 $\tilde{A}(^1A_u)$[a]		
$^3\Sigma_u^-$	6.69				
$^1\Delta_u$	7.04	$(\tilde{B})$	6.71 $\tilde{B}(^1B_u)$[e]	7.2	7.6
$^3\Pi_u$	8.35	$(\tilde{c})$			8.05 ($^3\Pi$)
$^1\Pi_u(s)$	8.43	$(\tilde{C})$	8.16 $\tilde{C}(^1\Pi_u)$[b]		
$^3\Pi_g$	8.83				
$^1\Pi_g$	8.91	$(\tilde{D}?)$	9.24 $\tilde{D}(^1\Pi_g)$[b]		
$^1\Sigma_g^+$[f]	9.29	$(\tilde{D}?)$			
$2\,^3\Pi_u$	9.60				
$2\,^1\Pi_u(d\sigma)$	9.70	$(\tilde{F}?)$	9.27 $\tilde{F}(^1\Sigma_u^+)$[b]		
$^1\Sigma_u^+$	9.83	$(\tilde{F}?)$			
$^3\Pi_u$, $^3\Phi_u$	9.96				
$^1\Phi_u$	9.97				
$^1\Pi_u(\delta)$	9.99		9.97 $^1\Pi_u(\delta^*)$[b]		
$3\,^1\Pi_u(s)$	10.05		9.97 $\tilde{G}(^1\Pi_u)$[a]		

[a] Ref. [1].

[b] Ref. [3].

[c] Ref. [4].

[d] Ref. [5].

[e] Ref. [35].

[f] All other states of the $(1\pi_u)^3\,(2\pi_u)$ configuration are within 0.1 eV from $^1\Sigma_g^+$. UV data are estimates of T_0, calculated values are for T_v (see text). In parentheses: assignments by the experimentalists.

perimental first IP, 11.4 eV, minus the calculated IP of the excited state. The uncertainty in our excitation energies should approximately be equal to the difference between the exact and Koopmans' theorem values for the IP, 0.25 eV. The values of x^2 and z^2, computed from the molecular center, give an idea of the shape and sizes of the MO's, that is, of their description in terms of united atom orbitals (UAO), and their degree of Rydberg character. The sizes one deduces from these numbers are in approximate agreement with those given by Mulliken's formula [23] $R_{\max} = Ry/T = (n-\delta)^2$ (in atomic units). Ry is the Rydberg constant, T the IP of the state, $n-\delta$, its effective principal quantum number. R is the maximum in the radial electron density of the hydrogen atom. Oscillator strengths are computed as: $f = (2/3)\,\Delta E|\langle\psi|\mu|\psi\rangle|^2$ (taking into account degeneracies). Experimental transition energies for the Rydberg series [1, 3] are included for comparison.

In Table 8, our results for the excited states of acetylene below 10.0 eV are compared with UV and electron impact data, and assignments are proposed.

8. Discussion

According to the x^2 and z^2 values of Tables 4–7, only the lowest state of each of the ${}^3\Sigma_u^+$, ${}^{1,3}\Sigma_u^-$, and ${}^{1,3}\Delta_u$ symmetries are valence states. The first ${}^{1,3}\Pi_u$ ($\sigma_g^* \leftarrow 1\pi_u$) states are borderline cases since the $4\sigma_g^*$ MO is only twice as large as the $3\sigma_g$ MO. All other states which we computed are Rydberg states.

We have computed vertical transition energies, T_v, for which the upper state is at the same geometry as the ground state. From *UV* data one obtains values for T_0, the difference between the ground vibrational levels of the two electronic states. Rydberg states are usually thought [1] to have the same geometry as the corresponding ion. $C_2H_2^+$ is linear [1] or slightly bent [24], and its C–C bond length is slightly greater than that of the molecule [25]. Therefore, we do not expect large differences between T_0 and T_v for Rydberg states. Most valence states are strongly bent, and some have much longer C–C bond lengths than the ground state [2, 25]. Difference of 1 eV or more between T_0 and T_v can then be expected [7].

9. Rydberg States

The use of the Rydberg formula: $T_n = T_\infty - Ry/(n-\delta)^2$ for molecular Rydberg series implies that the molecule is treated as a distorted hydrogen atom. It is thus convenient to use a UAO notation for the Rydberg MO's, which describes them in terms of one atomic orbital of the appropriate size and symmetry placed at the molecular center.

To assign principal quantum numbers to these UAOs, we must decide upon an UAO notation for the occupied MO's of the ground state, although the lower the MO, the more arbitrary the UAO notation becomes. We adopt the following notation:

MO	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	$1\pi_u$
UAO	—	—	$1s$	$2p\sigma$	$2s$	$2p\pi$.
The alternative notation	—	—	$2s$	$2p\sigma$	$3d\sigma$	$2p\pi$

is often preferred, based on two [19] and three [25] dimensional plots of the MO's. However, Huzinaga for N_2 and Jungen for NO [26] found that they could best fit the highest occupied sigma MO by a mixture of 2*s* and 3*d* sigma AO's at the molecular center.

We choose our notation as better adapted to describe Rydberg states; indeed the 3*d* sigma Rydberg series (Table 4) starts now at $n=3$, and has a quantum defect of 0.16, a value close to that often found for *d* electrons [27]. Also, the computed order of the states is 3*s*, $3p\sigma$, $3p\pi$, $3d\sigma$, $3d\pi$, ... [the 3*s* state is the $^1\Pi_u(3s\sigma_g^* \leftarrow 1\pi_u)$ state, etc.]. This is more satisfactory than ...$3p\pi$, $4d\sigma$, $3d\pi$....

Tables 4–7 show that except for the $\ldots(1\pi_u)^3\,(1\pi_g^*)$ electronic configuration the component states of one configuration are nearly degenerate, and that the excited MO for each of those states are nearly identical. For example, the $4\sigma_g^*$ MO's of $^1\Pi_u$ and $^3\Pi_u$ states are nearly identical, and the energy separation is only 0.08 eV. The six states of the $\ldots(1\pi_u)^3\,(2\pi_u^*)$ configuration are spread by 0.22 eV, and for second and third members of Rydberg series, the spreads are 0.05 and 0.01 eV typically. This occurs because the energy separation can be described in the frozen core approximation as arising from one exchange integral over the Rydberg MO and the $1\pi_u$ ground state MO. Such integrals represent the repulsion of two overlap charge distributions of the type $1\pi_u(1)\cdot Ry(1)$, and will be small because a diffuse and a non diffuse MO overlap very little.

Figure 1 represents a UAO diagram for the Rydberg states of acetylene. Average energies of configurations are used, except for the $d\pi$ UAO's, for which we used the $^1\Sigma_u^+$ values. The size of the π^* orbital of the components of the second $\pi^* \leftarrow \pi$ excited configuration is much alike the size of the Rydberg orbital of $1\,^1\Sigma_u^+$ ($\tilde{F}$, see Table 5) except for $2\,^1\Sigma_u^+$ which in turn has the same size as the π^* orbital of the $3\,^1\Delta_u$ etc. states. We therefore consider the $1\,^1\Sigma_u^+$, $2\,^3\Sigma_u^+$, $2\,^3\Delta_u$, $2\,^3\Sigma_u^-$, $2\,^1\Delta_u$ states as the components of the first $\pi^* \leftarrow \pi$ excited Rydberg configuration. The fact that $^1\Sigma_u^+$ is the lowest and not the highest of them is due to the orthogonality of the remaining components with respect to the valence states of the same symmetry. There is a striking simplicity in the diagram, which recalls those built from experimental atomic spectra [28]. As in simple MO theory, one can describe the spectrum in terms of one electron jumps from an occupied to an excited MO. However, the present excited MO's differ from

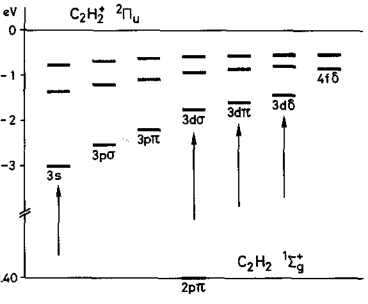

Fig. 1. Aceylene: UAO diagram for Rydberg states. The arrows indicate optically allowed transitions

the usual virtual orbitals in that they are diffuse and have been optimized to describe properly one electron in the field of the other electrons and the nuclei. Excluded from this picture are the valence states of the $(\pi_u)^3\,(1\pi_g^*)$ configuration, the states which arise from single excitation from a lower ground state MO, and those which can only be described as multiple excitations from the ground state. The first set of states is observed as weak, forbidden transitions in the UV spectrum and in electron impact. The other are probably not important spectroscopically below 11 eV; except may be the $^5\Sigma_g^+$ state (vide supra, and also [7]).

Figure 1 and Tables 4–7 show that the states of each symmetry form Rydberg series, converging to the $^2\Pi_u$ ground state of the ion. The values of the quantum defects δ fall in three groups: near 1.0 for s series, between 0.4 and 0.7 for p electrons, and between 0.15 and -0.10 for d and f series. This agrees with trends observed for other polyatomic molecules [27].

Most Rydberg series of acetylene are not observed, and on the basis of selection rules [1], one would expect four intense Rydberg series:

$$ns(^1\Pi_u)\,, \quad nd\sigma(^1\Pi_u)\,, \quad nd\pi(^1\Sigma_u^+)\,, \quad nd\delta(^1\Pi_u)\,.$$

Only three series are observed, [1, 3] in the UV spectrum of acetylene; we will presently discuss their identities.

We compute the $3d\delta$ Rydberg state at 9.99 eV and the $4s$ state at 10.05 eV (Table 7); experimental assignments are $4s$ at 9.93 eV (80110 cm^{-1}) and $3d\delta$ at 9.97 eV (80400 cm^{-1}). The separation between the two states is so small that we cannot be certain of the correct ordering. The energies predicted for the $4d\delta$ and $5d\delta$ levels (10.60 and 10.88 eV) are in good agreement with the energies of the second and third members of the third Rydberg series of Ref. [3] (10.59 and 10.88 eV). Thus our calculations strongly support the assignment of that series as $d\delta$ [3].

The $^1\Pi_u(\sigma_g^* \leftarrow 1\pi_u)$ states (Table 4) divide into two series, ns and $nd\sigma$; this is clearly shown by the shapes of the Rydberg MO's. The $3s$ MO is spherical; due to their orthogonality to the s and d sigma MO's of the lower states of $^1\Pi_u$ symmetry, the $4s$ and $5s$ MO's are distorted into oblate discs perpendicular to the molecular axis. The $d\sigma$ MO's are prolate, extending along the axis. The quantum defects also reveal two series, ns with $\delta = 0.84$ and $nd\sigma$ with $\delta = 0.15$.

Intensities within a Rydberg series should decrease regularly [1]. Assuming similar Franck Condon factors for the members of a series, the oscillator strengths should also decrease regularly (although their values only represent the order of magnitude). They do if again one considers s and d states as two series.

It seems well established that the series starting with $\tilde{C}$ at 8.16 eV is made of $^1\Pi_u(\sigma_g^* \leftarrow 1\pi_u)$ states [1], probably ns [8]. Our calculations support this assignment. The computed excitation energy is 0.27 eV too high for the first term of the series, $\tilde{C}$, and the agreement is much better for higher terms (Table 4).

The calculations predict two other intense Rydberg series: $nd\sigma$ and $nd\pi$. Only one is observed; it starts with $\tilde{F}$ at 9.27 eV and it's next terms are at 10.31 and 10.74 eV [3].

It is generally thought that $\tilde{F}$ is a ${}^1\Sigma_u^+ (1\pi_g^* \leftarrow 1\pi_u)$ state and the series $nd\pi$ [3, 8]. We compute the first three ${}^1\Sigma_u^+$ states at 9.83, 10.54, and 10.875 eV. The lowest is thus 0.56 eV higher than the experimental value for $\tilde{F}$. This discrepancy seems rather high in view of our other results. SCF calculations with diffuse functions, on the ground state of the molecule and the ion and on the ${}^1\Sigma_u^+$, ${}^1\Pi_u$, and ${}^1\Pi_g$ excited states give excitation energies identical with the frozen core results of Tables 4–7 within 0.01 eV. This illustrates the validity of the ionic frozen core concept. But since our ${}^1\Sigma_u^+$ state is rather diffuse, we cannot explain such a large error. Calculations on the singlet $(\pi^* \leftarrow \pi)$ state of ethylene have also met difficulties, see [11, 36]. If we assume that $\tilde{F}$ is a ${}^1\Sigma_u^+$ state, then $\tilde{D}$, a state which gains intensity from $\tilde{F}$ through a vibration of π_u symmetry [3], should be ${}^1\Pi_g$. The only ${}^1\Pi_g$ state near the experimental position of $\tilde{D}$, 9.19 eV, is the $3p\sigma$ state at 8.92 eV (Table 4).

As to where the $d\sigma$ series would be found, we can only note that there are unexplained features in the spectrum between 9.5 and 10.0 eV and an underlying continuum [3], and await the results of further studies. Another set of assignments which our results support somewhat better, but not perfectly, indicate that $\tilde{F}$ and its series would be $d\sigma({}^1\Pi_u)$. Duncan's results in favor of a $d\pi$ series [8] are based on too many approximations to be a strong counterargument. The experimental assignment is based on Price's observation that the bands of the $\tilde{F}$ series are single-headed whereas the bands of other observed Rydberg series are double-headed [1, 37].

The $d\sigma$ series fits the experimental term values [3] better than the $d\pi$ one, (Tables 4 and 5), but the error for the first term $\tilde{F}$ is still 0.43 eV. $\tilde{D}$ at 9.19 eV would then be a ${}^1\Sigma_g^+$ state, which we compute in good agreement at 9.29 eV. Again the ${}^1\Sigma_u^+$ state could really be in the 9.8–9.9 eV region, where there are unexplained peaks about 20 times less intense than $\tilde{F}$. We cannot at the present stage explain why any one of the two series, $nd\sigma$ or $nd\pi$, should be unseen. Oscillator strengths are about equal for the two series.

10. Valence States

The five excited valence states arise from the $\ldots(1\pi_u)^3(1\pi_g)$ electronic configuration. Their $1\pi_g$ MO's are only 20–30% greater than the $1\pi_u$ MO. We predict the same order by increasing energy as Mulliken [2] and Kammer [7]: ${}^3\Sigma_u^+$, ${}^3\Delta_u$, ${}^{1,3}\Sigma_u^-$, ${}^1\Delta_u$. ${}^1\Sigma_u^+$, the sixth member of the configuration, a Rydberg state, is much higher in energy. This ordering has been explained as follows by Buenker and Peyerimhof [29]: from the wave functions of the six states (Table 1) one sees that Σ_u^+ states result from in plane (e.g. $\pi_x^* \leftarrow \pi_x$) excitation while Σ_u^- states from out of plane (e.g. $\pi_y^* \leftarrow \pi_x$) excitation and Δ_u states from both. Singlet-triplet separations correspond to an exchange integral between the $1\pi_g$ and the $1\pi_u$ MO (Table 2). This integral will be small when the overlap distribution $1\pi_g(1) \cdot 1\pi_u(1)$ is small. Thus singlet triplet separations increase from Σ_u^- states to Δ_u and to Σ_u^+ states. We obtain:

$$\Sigma_u^- \; 0.0 \quad \text{eV}, \qquad \Delta_u \; 1.17\,\text{eV}, \qquad \Sigma_u^+ \; 4.8\,\text{eV}.$$

Refs. [7] and [29] obtain:

$$\Sigma_u^- \ 0.002\,\mathrm{eV}, \quad \Delta_u \ 1.17\,\mathrm{eV}, \quad \Sigma_u^+ \ 7.2\,\mathrm{eV}.$$

We obtain a smaller separation for the Σ_u^+ states, because ${}^1\Sigma_u^+$ is diffuse. For the $(1\pi_u)^3\,(2\pi_u^*)$ configuration, we obtain the following separations (triplets lower than singlets): Σ_g^- 0.0 eV, Δ_g 0.03 eV, Σ_g^+ 0.22 eV. They are small because the $2\pi_u$ MO is diffuse (Table 6).

The fact that ${}^1\Sigma_u^+$ is diffuse while all other states of the $\ldots(1\pi_u)^3(1\pi_g)$ configuration are valence states has been discussed by Jungen [30]. The transitions to the valence states of acetylene are thought to be observed in the weak forbidden bands $\tilde{A}$ and $\tilde{B}$ [1, 35]. Before discussing possible assignments, we want to estimate the difference between T_0 and T_v for those states. Preliminary results indicate a contribution of 0.5 eV from C–C stretching, and we take Kammer's calculations to estimate energy changes on trans bending [7]. We obtain the following values for $T_0(T_v)$: ${}^3\Sigma_u^+$ 3.14 eV (5.02), ${}^3\Delta_u$ 4.31 eV (5.87), ${}^1\Sigma_u^-$ 5.27 eV (6.69), ${}^3\Sigma_u^-$ 6.17 eV (6.69), ${}^1\Delta_u$ 6.51 eV (7.04) (${}^3\Sigma_u^-$, ${}^1\Delta_u$ are nearly linear). Similarly we can estimate that for the Π_g, and probably Π_u states T_0 is nearly equal to T_v.

We conclude that band $\tilde{A}$ is probably due to the ${}^1\Sigma_u^-$ state, and $\tilde{B}$ to the ${}^1\Delta_u$ state in concordance with Ref. [35]. The existence of a triplet state of acetylene as low as 3.14 eV above the ground state is supported by quenching experiments [6]. Both ${}^3\Sigma_u^+$ and ${}^3\Delta_u$ are below 4.6 eV and each could thus be involved in the process described.

Assignments for the triplet states observed in electron impact experiments are made difficult by the lack of knowledge of the processes involved and of strict selection rules [32]. With low energy electrons [4, 5], one does not seem to know whether T_0 or T_v is measured [4]. For example, for CO_2 a good correlation was found between computed T_v [10] and experimental data obtained with very low energy electrons [31], but not all the data could be explained that way.

Our results suggest the following assignments: peaks $\tilde{a}$ and $\tilde{b}$, observed by Dance and Walker in threshold electron impact [5] and by Trajmar *et al.* with 45 eV electrons [4] (thus plausibly vertical transitions) correspond to calculated vertical transitions to the ${}^3\Sigma_u^+$ and ${}^3\Delta_u$ states, in agreement with Dance and Walker's suggestion [5]. Both T_0 and T_v for the ${}^3\Pi_g$ and ${}^3\Pi_u$ states are near 8.0 eV and cannot be assigned to peaks $\tilde{a}$ and $\tilde{b}$ as suggested by Trajmar *et al.* [4]. The analogy with N_2 is limited because ${}^3\Pi$ states arise from $\pi^* \leftarrow \sigma_g$ excitation, while in acetylene they arise from $\sigma^* \leftarrow \pi_u$ excitation. Finally, the ${}^3\Pi_u$ state at 8.35 eV would be Dance and Walker's $\tilde{c}$ state [5].

11. Conclusions

Our assignment are collected in Table 8. We review them briefly and emphasize where further work is needed.

We think that our calculations identify clearly the *ns* and *nd*δ Rydberg series. The region of the UV spectrum between 9.0 and 10.0 eV needs to be reexamined to understand which of the *nd*σ and the *nd*π series is missing and why. Further theoretical work is also needed which would reproduce the small (0.07 eV) separation between $\tilde{D}$ and $\tilde{F}$, allowing an unambiguous assignment.

Our calculations do not find any valence state above 7.0 eV. However, our definition of valence states may be more restrictive than that of the experimentalist [e.g. for the $\tilde{C}$ (*ns*) state]. Also it may be that some of our Rydberg states will turn out to be stable in bent geometries. The valence state assignments require also a study of the geometry of some excited states. Such a study is presently being performed in this laboratory.

Appendix

Treatment of the Delta Rydberg MO's

The correct energy expression for the $^1\Pi$ and $^1\Phi$ states are

$$E(^1\Phi, {}^1\Pi) = h_{d_1} + (2J-K)^{\sigma}_{d_1} + 1.5\,J^{\pi}_{d_1} \pm 2(d_1 x/y d_2)\,. \qquad (1)$$

The notation is that of Table 2.

Because of the last integral, the energy is not the eigenvalue of an effective operator for d_1 (or d_2). Such non-diagonal terms appear also for pi MO's, but can be eliminated by symmetry. For complex MO's $d_\pm = (d_1 \pm i d_2)/(2)^{\frac{1}{2}}$ one obtains an energy expression which is diagonal in d_+ or d_-. Because the delta MO's are all diffuse (Table 7) one expects small separations between the states of one configuration. This justifies the use of an approximation, which was obtained as follows: One center calculations with $2p$ and $3d$ STO's showed that $(d_1 x/y d_2) = 7/12(d_1 x/x d_1)$ (or symmetry related integrals).

Straub [38] obtained this result analytically and showed that for other principal quantum numbers slightly different ratios occured. Two center gaussian lobe functions gave ratios differing from 7/12 only by a few percents. So we decided to use the approximate operator of Table 2 to generate d_{xy} MO's. This allowed us to use only one type of d delta basis functions.

With a small double zeta basis and only two diffuse exponents for basis functions of d_{xy} and $d_{x^2-y^2}$ type, we carried out the approximate and the exact treatment. The results are given in Table 9. They show that the exact answer differs very little from the approximate one. The order of the states is reversed however; the size of the MO's change by less than 0.1%.

We now describe the exact treatment. By symmetry,

$$2(d_1 x/y d_2) = (d_1 x/y d_2) - (d_2 x/y d_1)\,.$$

Consider the right hand side as the $d_1 \times d_2$ block of the operator K^{-xy}. Such an operator has only off-diagonal blocks. It can be constructed with the integrals over the basis functions and the transition density matrix constructed form the $1\pi_{ux}$ and $1\pi_{uy}$ MO's.

A diagonal operator K' is constructed, which has, as it's $d_1 \times d_1$ and $d_2 \times d_2$ blocks the $d_1 \times d_2$ block of K^{-xy}. The operator:

$$F(^1\Phi, {}^1\Pi) = h + (2J-K)^{\sigma} + 1.5\,J^{\pi} \pm 2K'$$

determines the correct MO's and it's eigenvalues are the IP's of the excited states. Indeed the MO's which diagonalise F, used with the correct energy expression (1) give back exactly the eigenvalues of F.

Table 9. Delta molecular orbitals

Configuration	State	ε_1	ε_2	$\varepsilon_{\text{exact}}$
$\ldots(1\pi_u)^3(1\delta_g)$	$^1\Phi_u$	-0.0534	-0.0550	-0.0552
	$^1\Pi_u$	-0.0508	-0.0497	-0.0498
	$^3\Pi_u$, $^3\Phi_u$			-0.0547
$\ldots(1\pi_u)^3(1\delta_u)$	$^1\Phi_g$	-0.02307		-0.02310
	$^1\Pi_g$	-0.02296		-0.02293
	$^3\Pi_g$, $^3\Phi_g$			-0.02312

See appendix for definitions; all energies in atomic units.
ε_1: approximate energies computed with formulae of Table 2.
ε_2: approximate energies computed with exact formula (appendix) and with the approximate MOs obtained with the operators in Table 2.
$\varepsilon_{\text{exact}}$: exact energies, computed as in the appendix. For the triplet states the exact formula is that of Table 2.

A less correct procedure would be to use the approximate MO's with expression (1) to obtain a corrected energy. Table 9 shows that the results are already quite good. However, the computational effort is not much less than that required for the correct treatment.

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