are automatically satisfied since W is a function of internuclear distances only. The original equation given in ref 11 is obtained by the substitution

$$x_1 = M_1^{1/2}X_1,\ x_2 = M_1^{1/2}Y_1,\ x_3 = M_1^{1/2}Z_1,$$
$$x_4 = M_2^{1/2}X_2,\ x_5 = M_2^{1/2}Y_2,\ x_6 = M_2^{1/2}Z_3, \ldots$$

and this should have explicitly been specified there.

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$$\rho^{\beta}{}_{0,i_\alpha - i_\alpha} = S^{\alpha}{}_{0,i_\alpha - i_\alpha}\rho_{00},\ \rho^{\beta}{}_{i_\alpha - i_\alpha, i_\alpha' - i_\alpha'} = S_{i_\alpha - i_\alpha, i_\alpha' - i_\alpha'}\rho^{\beta}{}_{00},$$
$$\rho^{\alpha}{}_{0,i_\beta - i_\beta} = S^{\alpha}{}_{0,i_\beta - i_\beta}\rho_{00},$$

and

$$\rho^{\alpha}{}_{i_\beta - i_\beta, i_\beta' - i_\beta'} = S^{\alpha}{}_{i_\beta - i_\beta, i_\beta' - i_\beta'}\rho_{00}$$

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(26) The terminology of MO's of the methane part follows C_{3v} symmetry.

Geometries of Acetylene Ions[1]

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Abstract: *Ab initio* SCF-MO calculations on the geometry of acetylene $^2\Pi_u$ cation, $^2\Pi_g$ anion, and $^1\Sigma_g$ neutral ground state using a double-ζ basis set are reported. The SCF calculation with double-ζ basis seems capable of reproducing accurately the ground state experimental geometry and reasonably the C-C and C-H stretching force constants. The anion is predicted to possess stable trans and cis isomers. From a Walsh type analysis the driving force for the bent geometry is found to be due to stabilization of the open shell π_g orbital through σ-π mixing. The $^2\Pi_u$ cation is predicted to be linear. The predicted equilibrium C-C bond lengthening is 0.05 Å for the cation and 0.08 Å for the anion relative to the ground state. The main reason for bond lengthening arises from removal of a bonding π_u electron on going to the cation and from addition of an antibonding π_g electron in the anion. The effects of electronic reorganization on the geometry are discussed. Principal results are that π_u is much more bonding in the cation than in the ground state, and wave functions which do not take into account electron recirculation predict the ionized state geometry poorly. The geometric rearrangement stabilization energy relative to vertical formation of the ions is -1.4 eV for the anion (leading to a predicted electron affinity of -1.3 eV) but only -0.12 eV for the cation. Thus Rydberg absorption spectra converging to the cation is predicted to have short vibrational progressions.

Recently we reported a near Hartree–Fock study of reorganization effects (orbital readjustment from the ground state) caused by π electron loss or capture in acetylene.[2] We discuss here the geometric rearrangements consequent to forming these ions. Because it is a simple polyatomic molecule containing π electrons with high symmetry, acetylene provides special interest in evolving and testing valence concepts. Indeed, a number of studies have been directed to that end.[3,4] A purpose of this study is to attempt to clarify the role that the effect of electronic reorganization from the ground state to the ionic states plays in geometric rearrangement. Additionally, reliable information concerning the equilibrium conformation for the cation will be useful in interpretation of Rydberg spectra, in the expectation that geometries of Rydberg states are mainly controlled by the valence electrons.

The three acetylene states studied are the $^1\Sigma_g$ ground state, the $^2\Pi_u$ cation $[(\sigma_{1g}{}^c)^2(\sigma_{1u}{}^c)^2(\sigma_{2g}{}^c)^2(\sigma_{2u}{}^c)^2(\sigma_{3g}{}^c)^2(\pi_u{}^c)^3]$, and the $^2\Pi_g$ anion $[(\sigma_{1g}{}^a)^2(\sigma_{1u}{}^a)^2(\sigma_{2g}{}^a)^2(\sigma_{2u}{}^a)^2(\sigma_{3g}{}^a)^2(\pi_u{}^a)^4(\pi_g{}^a)^1]$. The orbital forms at the minimal basis set level are discussed in ref 3d. We concluded in our reorganization studies that double-ζ level calculations can include most of the charge circulation effects accompanying ionization. Thus *ab initio* SCF calculations using MOLE programs[5a] were executed on IBM 360-67 and 91 systems with basis set D of ref 2. The calculations were carried out over a C-C and C-H bond distance mesh for a linear acetylene. The C-C-H angle was then allowed to vary using the optimized linear C-C and C-H bond distances. Besides geometry, the stretching force constants are also calculated.

In general, near Hartree–Fock wave functions predict molecular geometries closer to experimental values (within a few per cent) than they do vibrational frequencies (usually off by 20–30%);[5b] *i.e.*, Hartree–Fock wave functions are more capable of describing the position of a potential surface minimum than the shape in the vicinity of the minimum. We thus regard comparison of calculated and experimental ground state geometries as a test of the adequacy of the double-ζ basis set. Qualitative comparison of predicted force constants *vs.* the experimental values provides an additional test (see below).

$^1\Sigma_g$ Ground State

The predicted equilibrium C-C and C-H distances (Table I) for the ground state are 1.06 and 1.20 Å, respec-

Table I. Calculated Geometries, Force Constants, and Energies for Ground and Ionic States of Acetylene

	R_{C-C}, Å	R_{C-H}, Å	θ,[a] deg	$-E_T$,[b] au	ΔE,[c] eV	f_{C-C}, mdyn/Å	f_{C-H}, mdyn/A	f_{C-C-H}, (mdyn Å)/radian^2
$^1\Sigma_g$ ground state	1.203	1.059	0	76.7927		20.0	7.8	0.48[d] (trans) 1.09[d] (cis)
$^2\Pi_u$ cation	1.250	1.072	0	76.4299	0.12	19.2	5.0	0.61 (trans) 0.79 (cis)
$^2\Pi_g$ anion	1.282	1.059	52.5 (trans) 45 (cis	76.6957 76.6859	1.36 1.09	12.8	5.0	1.32 (trans) 0.89 (cis)

[a] θ = C-C-H bending angle. [b] Total energy computed at equilibrium geometry. [c] ΔE = geometric rearrangement stabilization energy. [d] Values calculated from the figure in ref. 4d.

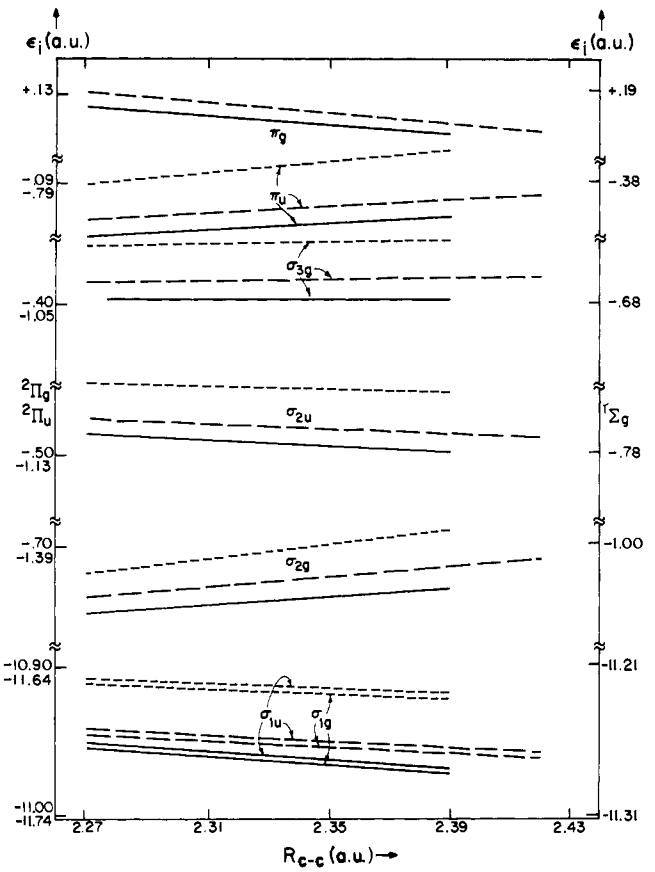

Figure 1. Orbital energy variation with C-C bond distance: (—) $^1\Sigma_g$ ground state, (- -) $^2\Pi_g$ anion, (- - -) $^2\Pi_u$ cation. The energy scale on the right refers to the $^1\Pi_g$ state and that on the left refers to the $^2\Pi_g$ state (lower scale) and to the $^2\Pi_u$ state (upper scale).

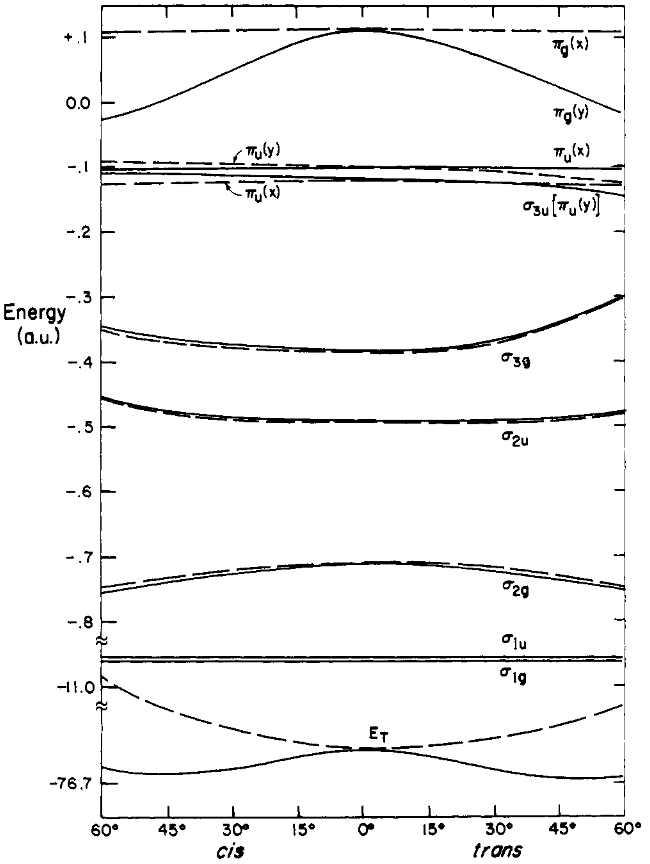

Figure 2. Orbital energy and total energy (E_T) variation with C-C-H bending angle for the $^2\Pi_g$ anion. The bending angle is defined as 0° for linear geometry. The doubly degenerate π_u orbitals in the linear form (along z axis) correlate with $\pi_u(x)$ and σ_{3u} in the bent (in y-z plane) form. The nondegeneracy of the π_u orbitals at the $\theta = 0°$ case is due to use of real functions.[12] The - - curves correspond to the second anionic state with $\pi_{g(x)}$ occupied. Labels such as σ_{xg} and σ_{xu} strictly hold only for the linear case.

tively, in close agreement with the experimental values of 1.060 and 1.203 Å.[6] The calculated C-C and C-H stretching force constants are 20 and 7.8 mdyn/Å also agreeing reasonably with experimental values of 16 and 5.9 mdyn/Å.[7] Thus, as judged by ground state potential functions, the double-ζ function appears reasonably adequate.

$^2\Pi_u$ Cation

The equilibrium C-C distance is predicted to lengthen by nearly 0.05 Å and the C-H distance by 0.01 Å (Table I) upon π electron loss. The ion equilibrium geometry is predicted to be linear. Some understanding of the C-C bond distance change can be obtained from an analysis of the ground state orbital energy *vs.* C-C bond length curves[8] given in Figure 1. According to the analysis, the C-C distance is mainly determined by competition between π_u and $2\sigma_g$ destabilization with the nuclear repulsion decrease (*i.e.*, stabilization) upon bond lengthening. The C-C bond then lengthens in the ionic state simply because there is one fewer π_u electron in the cation than in the ground state.

Comparison of orbital energy-C-C distance curves obtained from the SCF calculation for the $^2\Pi_u$ cation in Figure 1 with those obtained from the ground state reveals that the principal electronic reorganization effects are in the π_u, σ_1, and σ_{2g} orbitals. These orbitals undergo greater destabilization with increasing C-C bond length in the cation than in the ground state.[9] Accordingly, a cation wave function constructed from frozen ground state orbitals predicts an overlengthening of the C-C bond on π electron ionization with deeper minimum than found from the SCF results. Descriptions of the cation which do not properly allow for electron reorganization (such as by a minimal basis set) can be expected to yield significantly erroneous geometries despite the severe symmetry restrictions controlling electron circulation in acetylene. It is of interest to note that the inner shell electron energies are sensitive to π occupancy and significantly change as a function of C–C distance. This latter effect has been attributed by Clementi and Popkie to significant two-center contributions to inner shell orbital energies.[3e]

The energy at the equilibrium geometry of the cation is calculated to be 0.12 eV lower than that for vertical ionization. Since the C–C stretching force constant is somewhat surprisingly predicted to be close to the ground state value (Table I), the vertical energy–equilibrium energy difference is less than one quantum of the C–C stretching vibration. Thus, despite the large C–C bond length change, short vibrational progressions are likely in Rydberg absorption spectra converging to the cation. The observed Rydberg spectra seem to be in accord with these expectations.[10]

$^2\Pi_g$ Anion

The C–C distance is predicted to increase by 0.08 Å on going to the anion, a significantly larger increase than that obtained on going to the cation. The C–H distance is predicted to remain unchanged. Reference to the ground state orbitals in Figure 1 shows the large C–C bond length increase results from occupancy of the antibonding virtual π_g orbital which stabilizes with increasing C–C distance. The orbitals obtained from explicit SCF solution for the anion configuration (Figure 1) confirm that π_g strongly stabilizes as the C–C bond length increases. The anion is predicted to be stabilized in both cis and trans bent geometries as shown in Figure 2 and in Table I. The trans form is calculated to be slightly more stable than the cis form with the energy minimum occurring in the vicinity of 52° for the C–C–H bending angle. Although a C_2 symmetry anion with H_1 out of the H_2–C_2–C_1 plane is predicted to be unstable relative to a planar geometry, the anion should be easily twistable, *i.e.*, the calculated twisting force constant is only 0.17 mdyn Å/radian^2.

Reference to Figure 2 shows that the in-plane component of the open shell π_g orbital is strongly stabilized upon increasing the C–C–H bending angle from 0° to either cis or trans geometries. Occupancy of this orbital clearly provides the driving force for bending in the anion since for small angles the π_g energy changes more drastically than any other orbital energy. Thus, for small bending angles Walsh's rule applies without the complication of competition among several orbitals, *i.e.*, $\partial E_T/\partial\theta \approx \partial\epsilon_{\pi g}/\partial\theta$ for $\theta \sim 0$. The π_g energy variation with the bending angle is very similar for both cis and trans forms, the difference in stability mainly arising from the closed shell (*i.e.*, the ground state configuration) part of the wave function. The slightly increased stability of trans *vs.* cis geometries then can be rationalized from stabilization of the closed shell σ_{3u} orbital (originating in π_u) for trans bending as opposed to destabilization for cis bending. For large trans angles there is a countering destabilization of the σ_{3g} electrons. This observation is parallel with theoretical[4d] and experimental[4a] results that the trans bending frequency in the *ground state* is lower than the cis bending frequency.

The energy at the equilibrium geometry is calculated to be some 1.4 eV lower than for the vertical geometry. Thus the barrier for tunneling between cis and trans forms is predicted to be very high. There is a predicted significant decrease in the C–C stretching force constant (only 60% of the ground state force constant (Table I)), suggesting long vibrational progressions in Rydberg spectra from the as yet unobserved anion. Finally, an estimate of the electron affinity of acetylene can be made by summing: 4.2 eV (vertical SCF electron affinity),[2] −1.5 eV (vertical correlation energy correction),[3f] −1.4 eV (geometric rearrangement stabilization) giving −1.3 eV (equilibrium electron affinity).

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