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Commentationes

The Excited States of Allene*

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Excited states of allene are calculated using virtual orbitals from a Gaussian SCF calculation on the ground state. The ground state ionization potential is predicted to be 10.14 eV. Although the calculated transition energies are too high, the spectrum is predicted to consist of 3 weak transitions followed by a strong transition at shorter wavelength, in good qualitative agreement with experiment. States of the flattened (D_{2h}) molecule were also studied. The rotation barrier of the ground state is predicted to be 3.12 eV. The lowest triplet state is predicted to be planar.

Aus einer SCF Rechnung mit Gauß-Funktionen für den Grundzustand des Allens werden die virtuellen Orbitale für die Berechnung angeregter Zustände übernommen. Das Ionisationspotential des Grundzustands ergibt sich dabei zu 10,14 eV. Die Rechnungen zeigen, daß das Spektrum aus drei schwachen Übergängen und einem starken Übergang kürzerer Wellenlänge besteht. Dies steht in guter Übereinstimmung mit dem experimentellen Befund, obwohl die Übergangsenergien zu hoch berechnet werden. Die Zustände des Moleküls mit der Symmetrie D_{2h} werden studiert. Die Energieschranke für die Rotation wird zu 3,12 eV berechnet und der tiefste Triplett-Zustand als eben vorausgesagt.

Calcul des états excités de l'allène à l'aide des orbitales virtuelles fournies par un calcul SCF en gaussiennes sur l'état fondamental. Le calcul prédit un potentiel d'ionisation de 10.14 eV. Les énergies de transition caculées sont trop hautes mais le spectre calculé consiste en 3 transitions peu intenses suivies par une transition intense à plus courte longuer d'onde, ce qui est en bon accord qualitatif avec l'expérience. On a aussi étudié les états de la molécule «aplatie» (D_{2h}). La barrière de rotation est de 3.12 eV dans l'état fondamental. L'état triplet le plus bas devrait être plan.

Introduction

There have been a number of semiempirical calculations [1–4] on the excited states of allene, and more recently a thorough paper by Buenker [5] describing an SCF calculation on the allene ground state using Gaussian lobe functions. Buenker's main interest was in studying the twisting of allene from its normal D_{2d} geometry to a planar D_{2h} form; he did not look at excited states of the D_{2d} molecule.

The work to be reported here is the first *ab initio* study of allene excited states in which all electrons are taken into explicit account. Results will be presented for both the D_{2d} and D_{2h} geometries.

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Method of Calculation

For the D_{2d} form all calculations were done using the experimental ground state geometry from Maki and Toth's [6] high-resolution infrared study: r(C–H) = 1.087 Å = 2.054 a.u.[1], r(C–C) = 1.308 Å = 2.472 a.u., ∢ HCH = 118° 10′. The same angles and lengths were used for the D_{2h} molecule.

The SCF computations were carried out with New York University's POLYATOM program on a CDC 6600 computer using a Gaussian basis of five *s* orbitals with exponents 0.32, 1.6, 8.0, 40.0 and 200.0, and two *p* orbitals in each of the *x*, *y* and *z* directions with exponents 0.2469 and 1.4810 on each carbon atom, and two *s* orbitals with exponents 0.27 and 1.8 on each hydrogen. These exponents were obtained by Moskowitz and Harrison [8] from atomic calculations. Results of the SCF calculations are given in Table 1.

Table 1. SCF *results for the allene ground state*[a]

D_{2d} geometry		D_{2h} geometry	
orbital	orbital energy	orbital	orbital energy
$1a_1$	−11.3321	$1a_g$	−11.4363
$1b_2$	−11.3012	$1b_{1u}$	−11.2580
$2a_1$	−11.3003	$2a_g$	−11.2571
$3a_1$	− 1.1061	$3a_g$	− 1.1284
$2b_2$	− 0.9822	$2b_{1u}$	− 0.9912
$4a_1$	− 0.7124	$4a_g$	− 0.7045
$3b_2$	− 0.6067	$1b_{2u}$	− 0.6155
$1e$	− 0.6036	$3b_{1u}$	− 0.6082
$2e$	− 0.3728	$1b_{3g}$	− 0.5576
$3e$	+ 0.1863	$1b_{3u}$	− 0.4894
$5a_1$	+ 0.3830	$1b_{2g}$	− 0.2474
		$2b_{2u}$	+ 0.0459
		$2b_{3u}$	+ 0.2511
		$5a_g$	+ 0.3853
		$4b_{1u}$	+ 0.4101
		$2b_{3g}$	+ 0.4376
		$6a_g$	+ 0.5342
Total energy =	−114.8392	Total energy =	−114.7233

[a] All energies are in a.u.; the total energies include nuclear repulsion. Orbitals through $2e$ are filled in the D_{2d} molecule and through b_{2g} in the D_{2h}.

Excited states were approximated using virtual orbitals from the ground state LCAO SCF calculations. This is simpler, though not as rigorous as doing a separate SCF calculation on each state. Since the orbitals we use are appropriate to the ground state, we might expect the computed excitation energies to be too large.

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[1] The units used in this paper are 1 a.u. of length = 0.52917 Å and 1 a.u. of energy = 27.211 eV = 627.5 kcal/mole [7].

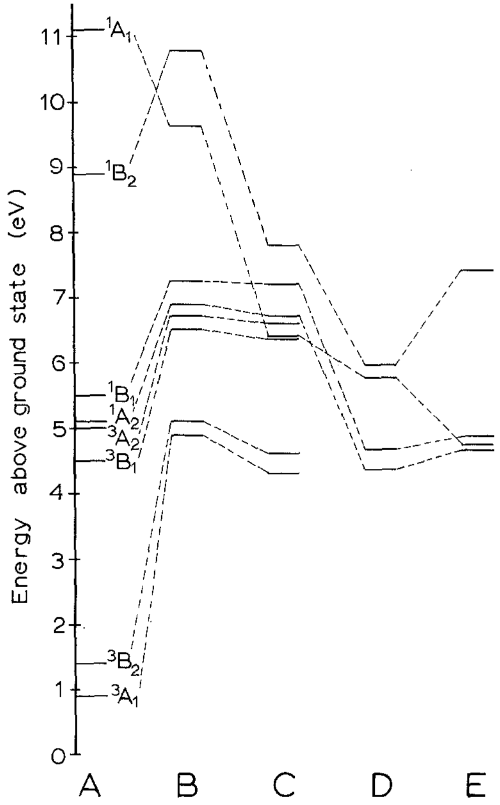

Fig. 1. Excited states from the $(1a_1)^2 \ldots (1e)^4\,(2e)^3\,(3e)^1$ configuration of allene. A, Parr and Taylor's π electron calculation; B, the present *ab initio* all electron calculation; C, Borden's Pariser-Parr-Pople calculation; D, Serre's Pariser-Parr-Pople calculation; E, Pellégatti's results using Jülg's "Improved LCAO method"

For D_{2d} geometry, the lowest excited electronic configuration is obtained by removing 1 electron from the $2e$ orbital to the $3e$. This gives rise to eight states whose energies relative to the ground state are

$$\left.\begin{aligned}
E(^3A_1) &= E_0 + \varepsilon_{12} - \varepsilon_{10} - (2e\,2e|3e\,3e) - (2e\,2\bar{e}|3e\,3\bar{e})\\
E(^3B_2) &= E_0 + \varepsilon_{12} - \varepsilon_{10} - (2e\,2e|3e\,3e) + (2e\,2\bar{e}|3e\,3\bar{e})\\
E(^3B_1) &= E_0 + \varepsilon_{12} - \varepsilon_{10} - (2e\,2e|3\bar{e}\,3\bar{e}) - (2e\,2\bar{e}|3e\,3\bar{e})\\
E(^3A_2) &= E_0 + \varepsilon_{12} - \varepsilon_{10} - (2e\,2e|3\bar{e}\,3\bar{e}) + (2e\,2\bar{e}|3e\,3\bar{e})\\
E(^1A_2) &= E(^3A_2) + 2(2e\,3\bar{e}|2e\,3\bar{e}) - 2(2e\,3\bar{e}|2\bar{e}\,3e)\\
E(^1B_1) &= E(^3B_1) + 2(2e\,3\bar{e}|2e\,3\bar{e}) + 2(2e\,3\bar{e}|2\bar{e}\,3e)\\
E(^1A_1) &= E(^3A_1) + 2(2e\,3e|2e\,3e) + 2(2e\,3e|2\bar{e}\,3\bar{e})\\
E(^1B_2) &= E(^3B_2) + 2(2e\,3e|2e\,3e) - 2(2e\,3e|2\bar{e}\,3\bar{e})\,.
\end{aligned}\right\} \qquad (1)$$

In these expressions, ε_{10} and ε_{12} are the orbital energies of the $2e$ and $3e$ orbitals, respectively; $2e$ and $2\bar{e}$ are the two wavefunctions of the degenerate $2e$ level and similarly for 3*e* and $3\bar{e}$. The convention

$$(2e\,2\bar{e}\,|\,3e\,3\bar{e}) \equiv \int 2e(1)\,2\bar{e}(1)\,\frac{1}{r_{12}}\,3e(2)\,3\bar{e}(2)\,d\tau_{12}$$

is used for the integrals. The situation is similar to that of benzene except that the D_{2d} group contains only one kind of doubly degenerate representation. These states are compared in Fig. 1 to those from semiempirical calculations.

Borden [2] does not list numerical values of his states; he plots his results on two graphs, one for singlets and one for triplets. Consequently there is some uncertainty about the relative order of his $^1A_1$ and $^3B_1$ states shown in Fig. 1. Serre [1] and Pellégatti [3] compute only singlet states. Although there is considerable variation in the absolute position of each state from calculation to calculation, all states except the $^1A_1$ which wanders over the graph, are in the same relative order in all calculations. We can suggest no reason why the $^1A_1$ state should be more erratic than the others. Of the five calculations Parr's [4] using only the π electrons gives energies that are in least agreement with the others. In particular, his $^3A_1$ and $^3B_2$ states lie much lower than in any of the other calculations. This disagreement is not surprising since we find that the hydrogen orbitals which he neglects do contribute slightly to the 2*e* and strongly to the 3*e* MO. (The $1s_H$ with exponent 0.27 has coefficient 0.13 in 2*e* and 0.43 in 3*e*.)

Table 2. *Excited states of D_{2d} allene*

State	Configuration[a]	Energy (eV above D_{2d} ground state)
$^3A_1$	$2e \rightarrow 3e$	4.887
$^3B_2$	$2e \rightarrow 3e$	5.078
$^3B_1$	$2e \rightarrow 3e$	6.522
$^3A_2$	$2e \rightarrow 3e$	6.713
$^3B_1$	$1e \rightarrow 3e$	12.392
$^3A_2$	$1e \rightarrow 3e$	12.468
^3E	$2e \rightarrow 5a_1$	13.157
$^3A_1$	$1e \rightarrow 3e$	13.589
$^3B_2$	$1e \rightarrow 3e$	13.663
^3E	$2e \rightarrow 4b_2$	13.943
$^1A_2$	$2e \rightarrow 3e$	6.865
$^1B_1$	$2e \rightarrow 3e$	7.263
$^1A_1$	$2e \rightarrow 3e$	9.633
$^1B_2$	$2e \rightarrow 3e$	10.792
$^1B_1$	$1e \rightarrow 3e$	12.917
$^1A_2$	$1e \rightarrow 3e$	12.947
^1E	$2e \rightarrow 5a_1$	13.908
^1E	$2e \rightarrow 4b_2$	14.514
$^1B_2$	$1e \rightarrow 3e$	14.800
$^1A_1$	$1e \rightarrow 3e$	16.226

[a] The configurations are described in terms of excitations from the ground configuration $(1a_1)^2\,(1b_2)^2\,(2a_1)^2\,(3a_1)^2\,(2b_2)^2\,(4a_1)^2\,(3b_2)^2\,(1e)^4\,(2e)^4$; for example, the first $^3A_1$ state is from a configuration in which 1 electron is excited from the 2*e* level to the 3*e*.

Excitations from the $1e$ to the $3e$ level were also investigated, as well as from both $1e$ and $2e$ to $5a_1$ and $4b_2$. Energy expressions for the first of these are analogous to those for $2e \rightarrow 3e$ above. Each of the other four excitations gives rise to a doubly degenerate singlet and triplet. The quintet arising from the promotion of two electrons from $2e$ to $3e$ is of A_1 symmetry and was computed to be 0.3427 a.u. above the ground state. Singlets and triplets from this configuration would presumably lie still higher in energy and were not investigated.

Several kinds of excitations were considered for the D_{2h} molecule. Single excitations all give nondegenerate singlets and triplets. Exciting two electrons

Table 3. *States of D_{2h} allene*

State	Configuration[a]	Energy (eV above D_{2d} ground state)
^3A_u	$1b_{2g} \rightarrow 2b_{2u}$	3.032
$^3B_{1u}$	$1b_{2g} \rightarrow 2b_{3u}$	7.353
$^3B_{1g}$	$1b_{3u} \rightarrow 2b_{2u}$	7.620
$^3B_{1u}$	$1b_{2g}, 1b_{3u} \rightarrow 2b_{2u}^2$	7.688
^3A_u	$1b_{3u}, 1b_{2g} \rightarrow 2b_{2u}, 2b_{3u}$	10.105
$^3B_{1g}$	$1b_{2g}^2 \rightarrow 2b_{2u}, 2b_{3u}$	11.518
$^3B_{1u}$	$1b_{3g} \rightarrow 2b_{2u}$	11.544
$^3B_{3g}$	$3b_{1u} \rightarrow 2b_{2u}$	11.778
^3A_g	$1b_{2u} \rightarrow 2b_{2u}$	12.377
$^3B_{2g}$	$1b_{2g} \rightarrow 5a_g$	12.690
^3A_g	$1b_{3u} \rightarrow 2b_{3u}$	12.766
$^3B_{3u}$	$1b_{2g} \rightarrow 4b_{1u}$	13.609
$^3B_{1g}$	$1b_{2g} \rightarrow 2b_{3g}$	14.271
$^3B_{3u}$	$3b_{1u}, 1b_{2g} \rightarrow 2b_{2u}^2$	14.940
$^3B_{2u}$	$4a_g \rightarrow 2b_{2u}$	15.046
$^3B_{2g}$	$1b_{2g} \rightarrow 6a_g$	15.430
$^3B_{1g}$	$1b_{3g}, 1b_{2g} \rightarrow 2b_{2u}^2$	15.558
^1A_u	$1b_{2g} \rightarrow 2b_{2u}$	3.122
^1A_g	D_{2h} "ground state"	3.152
^1A_g	$1b_{2g}^2 \rightarrow 2b_{2u}^2$	7.925
$^1B_{1g}$	$1b_{3u} \rightarrow 2b_{2u}$	8.330
$^1B_{1g}$	$1b_{2g}^2 \rightarrow 2b_{2u}, 2b_{3u}$	12.126
$^1B_{1u}$	$1b_{2g} \rightarrow 2b_{3u}$	12.494
$^1B_{1u}$	$1b_{2g}, 1b_{3u} \rightarrow 2b_{2u}^2$	12.932
$^1B_{3g}$	$3b_{1u} \rightarrow 2b_{2u}$	12.997
$^1B_{1u}$	$1b_{3g} \rightarrow 2b_{2u}$	13.247
$^1B_{2g}$	$1b_{2g} \rightarrow 5a_g$	13.680
$^1B_{3u}$	$1b_{2g} \rightarrow 4b_{1u}$	14.330
$^1B_{1g}$	$1b_{2g} \rightarrow 2b_{3g}$	14.605
^1A_g	$1b_{3u}^2 \rightarrow 2b_{2u}^2$	15.076
^1A_g	$1b_{2u} \rightarrow 2b_{2u}$	15.226
$^1B_{3u}$	$3b_{1u}, 1b_{2g} \rightarrow 2b_{2u}^2$	15.598
$^1B_{2g}$	$1b_{2g} \rightarrow 6a_g$	16.156
$^1B_{1g}$	$1b_{3g}, 1b_{2g} \rightarrow 2b_{2u}^2$	16.160

[a] Configurations are described in terms of excitations from the "ground state" D_{2h} configuration $(1a_g)^2 (1b_{1u})^2 (2a_g)^2 (3a_g)^2 (2b_{1u})^2 (4a_g)^2 (1b_{2u})^2 (3b_{1u})^2 (1b_{3g})^2 (1b_{3u})^2 (1b_{2g})^2$. See Footnote to Table 2.

from orbital i to orbital a gives only a singlet. Excitation of one electron each from orbitals i and j both into orbital a gives a singlet and triplet as does excitation of 2 electrons from orbital i, one into orbital a and one into orbital b. The configuration obtained by exciting one electron from orbital i and one from j into a and b is more complicated and gives 1 quintet, 3 triplets, and 2 singlets. Spin eigenfunctions were obtained as described by Pauncz [9], and the 3×3 and 2×2 configuration interaction matrices diagonalized to give the triplet and singlet energies.

States of lowest calculated energy are collected in Table 2 for the D_{2d} geometry and in Table 3 for D_{2h}.

Discussion

The experimental ionization potential of the allene ground state has been found to be 10.19 ± 0.01 eV from the convergence limit of allene Rydberg series [10], 10.16 ± 0.02 eV by electron impact [11], and very recently Parr and Elder [12] have published a photoionization result of 9.62 ± 0.04 eV[2]. The photoionization experiment is thought to give an adiabatic ionization potential. A spectroscopic value could be an adiabatic or a vertical result depending upon the series followed. Parr and Elder say that the Sutcliffe and Walsh series must refer to an excited state of the ion. The electron impact result [11] is presumably a vertical ionization potential and hence most appropriate for comparison with our value of 0.3728 a.u. = 10.14 eV calculated, using Koopmans' theorem, as minus the energy of the highest filled orbital. This good agreement must be partly accidental, however; Buenker's [5] ground state energy of -115.6979 a.u. is considerably lower than ours, but his predicted ionization potential is 11.45 eV, in rather poor agreement with experiment.

There is only the single vacuum ultraviolet spectrum of allene by Sutcliffe and Walsh [10] to compare with our calculated levels. The study was done at low resolution, bands were diffuse and not analyzed in detail; consequently the symmetry of no excited state was determined. Roughly, the spectrum can be divided into three regions: a weak, continuous absorption from 2030 Å (6.11 eV) to 1800 Å (6.89 eV); strong absorption from 1800 Å to 1600 Å (7.75 eV); and a number of bands of medium strength from 1600 Å to 1200 Å (10.33 eV). Sutcliffe and Walsh fit these short wavelength bands to several Rydberg series, hence they should correspond to nothing in our calculations. The strong absorption starts with a band at 7.17 eV and is of such intensity that they feel it must correspond to a transition from the vibrationless ground state to an allowed upper state. It is difficult to say much about the weak absorption longer than 1800 Å, but from a comparison with the spectrum of ethylallene, Sutcliffe and Walsh suggest that it arises from at least three and perhaps five valence shell transitions.

Note in Table 2 that the eight lowest excited states of D_{2d} allene all arise from the configuration $(1a_1)^2 \ldots (2e)^3 (3e)^1$ as might be expected. Of these, electric dipole transition is allowed only to ${}^1B_2$. This is somewhat unfortunate from our point of

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[2] A photoionization ionization potential of 10.19 eV is also listed in Kiser's tables [13] and attributed to Isaacs, Price and Ridley [14]. However, in fact, these authors do not report a photoionization result, but merely quote the spectroscopic value of Sutcliffe and Walsh [10].

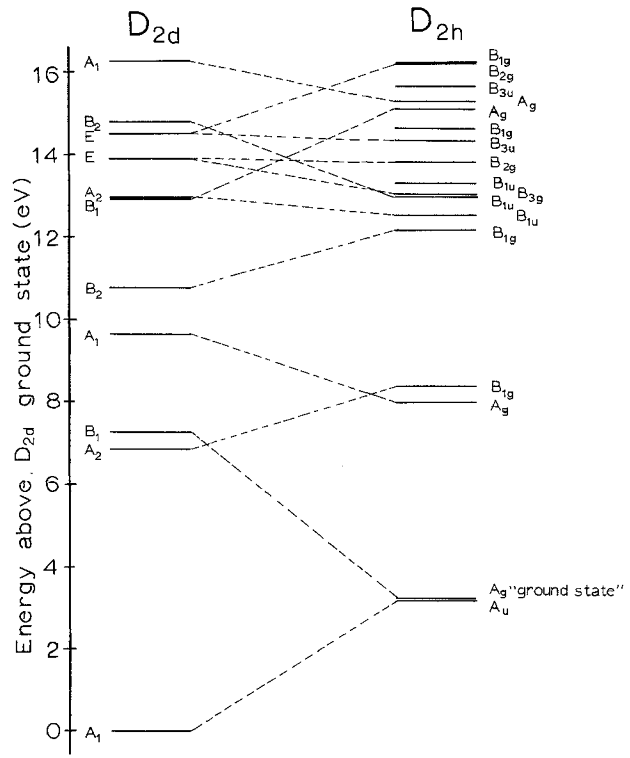

Fig. 2. Correlation of allene singlets

view since we calculate $^1B_2$ to be the highest state of the eight. It might therefore be expected to be least accurately represented by virtual ground state orbitals, and its energy most poorly calculated. It seems reasonable to suppose that the state found by Walsh and Sutcliffe at 7.17 eV and giving the strongest absorption is this $^1B_2$ state. Although it is not necessarily in contradiction to this assignment, it should be pointed out that Sutcliffe and Walsh suppose the state at 7.17 eV to be the start of a Rydberg series (with an error of some 0.6 eV for this first member). (See also Herzberg [15].)

For molecules made of first-row elements one usually expects spin-forbidden transitions to be at least an order of magnitude weaker than transitions forbidden by symmetry. Our three singlets below $^1B_2$ might therefore correspond to the three states that Walsh and Sutcliffe might see between 6.11 and 6.89 eV.

Thus although our calculated transition energies are too large, and although the experimental data are more ambiguous than one would like, experiment and theory seem to agree that the spectrum of allene consists of three weak transitions followed by a strong. Our calculations also agree with Sutcliffe and Walsh's supposition that the transitions are due to electrons which are concentrated mainly in the C–C–C bonds of the ground state.

States of D_{2h} and D_{2d} geometry are correlated in Figs. 2 and 3 using the subgroup D_2. A_1 and B_1 states of D_{2e} both go either to A_g or A_u states of D_{2h}. A_2 and B_2

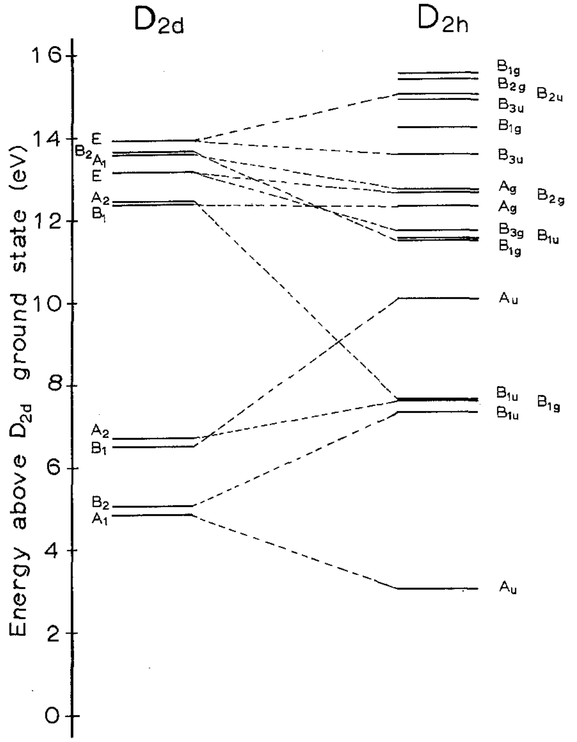

Fig. 3. Correlation of allene triplets

go to B_{1g} and B_{1u}, and an E state of D_{2d} gives one of B_{2g} or B_{2u} and one of either B_{3g} or B_{3u}. Fig. 3 shows that the lowest triplet state of allene would be expected to rotate to planar form. This agrees with the semiempirical result of Borden [2]. Although Borden finds the lowest ^1A_u and ^3A_u states to be of the same energy, he suggests that the degeneracy may be due to his approximation of zero differential overlap, and that in a higher approximation the triplet may lie below the singlet. We in fact do get this result, with the triplet lower in energy by 0.09 eV. Note that the singlet $(1b_{2g} \rightarrow 2b_{2u})\,^1A_u$ is lower than the "ground state". This also agrees with Borden's results.

Otherwise however, our order of the D_{2h} excited states does not agree well with Borden's. In particular we find, like Buenker [5], that the $(1b_{2g}^2 \rightarrow 2b_{2u}^2)\,^1A_g$ state lies above the "ground state" ^1A_g level, whereas Borden places it below.

There seems to be no experimental value for the rotation barrier in allene. Our calculated value of 3.12 eV to the lowest ^1A_u state may be compared with about 2.9 eV estimated from Borden's Fig. 1 or with a value of 2.8 eV reported by Preuss [16]. Buenker computes a barrier of 3.56 eV for rotation to the lowest ^1A_g state, compared to our estimate of 3.15 eV.

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