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Author
Dykstra, Clifford E.

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Clifford E. Dykstra

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Molecular Structure of Acrolein Electronic States[*]

Clifford E. Dykstra[**]

Department of Chemistry and Materials and Molecular Research Division
Lawrence Berkeley Laboratory, University of California
Berkeley, California 94720

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[**] University of California Regents Fellow, 1975-1976.

ABSTRACT

The ground and low-lying singlet and triplet states of acrolein, CH_2CHCHO, have been studied with ab initio SCF methods using a double-zeta basis set of Gaussian orbitals. The cis and trans ground state geometries were optimized and vertical excitation energies were determined for $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ singlet and triplet states. The separation between the cis and trans ground states was found to be 540 cm^{-1}. Optimization of major bond lengths placed the $\pi \rightarrow \pi^*$ states very close energetically to the $n \rightarrow \pi^*$ states. For all excited states, the carbon-oxygen bond length was substantially longer than in the ground state. For the $\pi \rightarrow \pi^*$ singlet and triplet, the single/double bond character of the carbon-carbon bonds is interchanged with respect to the ground state. The ground and lowest excited singlet and triplet states are planar.

INTRODUCTION

Acrolein is isoelectronic with glyoxal and butadiene, but has not received as much experimental attention as glyoxal and has been the subject of fewer theoretical investigations than butadiene. Nonetheless, because of conjugation of the carbon-carbon double bond with a carbon-oxygen bond, acrolein is of unique spectroscopic and electronic structure interest.

Among the early studies of acrolein is that of Walsh who characterized the vacuum ultraviolet spectrum, identifying a high energy singlet state.[1] Inuzuka studied the $n \rightarrow \pi^*$ excitation and placed the 0-0 band for the $^1A' \rightarrow {}^1A''$ transition[2-3] at 25851 cm^{-1}. From vibrational analysis of the spectrum, Inuzuka estimated the lengthening of the C=O bond in the $^1A''$ state to be 0.1 Å. Brand and Williamson[4] studied the spectrum under high resolution and derived barrier heights for internal rotation about the two carbon-carbon bonds in the ground state and the excited singlet state and concluded that there was increased π electron density in the central carbon bond in the excited state. They also determined that the C=O bond lengthening for the $^1A''$ state was about 0.12 Å. At about the same time, Hollas[5] had studied the acrolein spectrum and proposed possible structures for the excited singlet of acrolein and also of glyoxal. Hollas also made a tentative identification of a singlet to triplet transition with a band origin at about 4060 Å. Brand had identified the 4122 Å band as the $n \rightarrow \pi^*$ triplet transition.[4] In 1966, Cherniak and Costain[6] provided very accurate information on the trans ground state structure of acrolein from microwave spectra.

In recent years, the spectrum of acrolein has been of continued interest. Trying to demonstrate *cis-trans* photoisomerization, Becker, Inuzuka and King[7] considered *cis* and *trans* states arising from not only an $n \rightarrow \pi^*$ excitation, but also from a $\pi \rightarrow \pi^*$ excitation. They used emission spectra and semi-empirical calculations to suggest that the $\pi \rightarrow \pi^*$ triplet is energetically quite close to the $n \rightarrow \pi^*$ triplet. They concluded that largely because of potential barriers between *cis* and *trans* excited states and internal conversion, photoisomerization did not occur. In 1970, Alves, Christoffersen and Hollas[8] presented some of the most interesting spectroscopic results of studies on acrolein. Their rotational band contour analysis of the 4060 Å system indicated that it was due to a *cis* $^1A' \rightarrow {}^1A''$ $(n\pi^*)$ transition. They determined the *cis-trans* ground state energy difference to be 700 cm^{-1} and the difference of the $^1A''$ states to be -522 cm^{-1}. The 4120 Å band was confirmed to arise from the *trans* $n \rightarrow \pi^*$ triplet transition. The magnetic rotation spectrum was investigated by Bair, Goetz and Ramsay,[9] who not only reconfirmed the 4120 Å band assignment, but also identified a 4322 Å band to be the corresponding *cis* transition. They determined the *cis-trans* energy difference of the $^3A''$ states to be -420 cm^{-1}.

Theoretical studies of acrolein include the early semi-empirical calculations of Inuzuka[10] and Kato and coworkers.[11] The latter authors performed calculations on acrolein, butadiene and glyoxal. For glyoxal, the vertical excitation energies of the lowest states which they present are in qualitative agreement with recent *ab initio* calculations.[12] Their calculated vertical excitation energies of acrolein place the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ triplets very close in energy, less than 0.1ev.

These are shown as the lowest excited states followed by the $n \rightarrow \pi^*$ singlet and $\pi \rightarrow \pi^*$ singlet. The cis set of electronic states were quite similar to the trans.

Ab initio SCF calculations on acrolein were performed by Devaquet and Salem[13] and later by Devaquet.[14] These calculations used a minimum basis set of Slater type orbitals and the reported ground state energy was -190.185 hartrees.[14] Interest in both studies was centered around the triplet excited states. It was shown that the bond lengths in the triplet states are probably substantially different from the ground state. Unfortunately, the C=C, C-C and C=0 bond lengths were not varied independently so that the molecular structures and relative energies of the states are only qualitatively determined. Four excited states of trans-acrolein were studied by Iwata and Morokuma in work on the water-acrolein complex.[15] For all states, the ground state experimental geometry was assumed. The vertical transition energies they report are 3.40 eV for triplet $\pi \rightarrow \pi^*$, 3.77 eV for triplet $n \rightarrow \pi^*$, 4.53 eV for singlet $n \rightarrow \pi^*$ and 7.86 eV for singlet $\pi \rightarrow \pi^*$. A diffuse p function was found to be important in the $\pi \rightarrow \pi^*$ singlet which was associated with the high energy state studied by Walsh.[1]

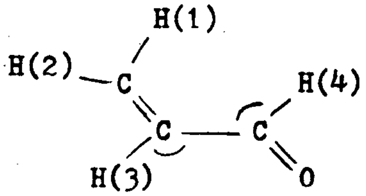
Conjugated C=C and C=0 groups can be involved in very interesting chemistry. One exciting example is the thermal ring opening of an oxetene intermediate.[16] A model of the reverse reaction is, of course, ring closure such as in acrolein. This has been studied recently by van der Meer and Mulder using ab initio methods.[17] They predicted a ring closure activation energy of 3.4 ev for the ground state of cis-acrolein. An analagous reaction is the formation of cyclobutadiene which has been studied extensively by Hsu, Buenker and Peyerimhoff[18-20] among others. Another interesting area of acrolein chemistry concerns Diels-Alder reactions. Frontier orbital calculations have been used to investigate such Diels-Alder reactions[21-22] and also regioselectivity in the dimerization of acrolein.[23]

In our recent ab initio SCF study of glyoxal, we predicted the existence of a low-lying biradical triplet state.[12] If an analagous acrolein state exists, its electronic structure could make it quite reactive and potentially important in ring closure and dimerization. Indeed, if it is sufficiently low-lying, such an excited state may provide a pathway (for some of the reactions mentioned above) which is competitive with the ground state. But before considering reactions, it is necessary to know the relative energies of the excited states and their geometric structures. This is the primary purpose of this work. It seems clear, that while spectroscopic studies have provided much information on the $n \rightarrow \pi^*$ states, there is still uncertainty regarding the $\pi \rightarrow \pi^*$ states. The existing theoretical studies have not been extensive enough to provide such information. Calculations on acrolein may also help explain the difficulties of the molecules-in-molecules model which proved unsuccessful for glyoxal.[12] This is an important consideration since it leads to predicting correlation effects in large systems on the basis of more easily studied small systems, e.g. formaldehyde and ethylene.

THEORETICAL APPROACH

A double-zeta basis set of Dunning-contracted functions,[24-26] C (9s5p/4s2p), O (9s5p/4s2p) and H (4s/2s), was used in the SCF calculations. In the C_S symmetry of planar acrolein, the ground state occupancy for both cis and trans is 1-13 a'^2 1-2 a''^2. π type orbitals are a'' and oxygen n orbitals are a', giving A'' $n \rightarrow \pi^*$ states and A' $\pi \rightarrow \pi^*$ states.

A simple cyclic individual optimization of structure parameters, previously used with ketene[27] and glyoxal,[12,28] was used for eight parameters in the trans ground state. A simple sketch of the molecule is given below (1). For all calculations the carbon-hydrogen bond lengths were fixed at 1.075 Å. This distance was chosen on the basis of calculations on other carbonyls done with the same basis set. The methylene H(2)-C-H(1) angle was optimized, but H(1) and H(2) were kept in symmetric positions relative to the C=C bond. As shown in Table I, the bond angles of H(3) and H(4) were not optimized for the cis ground state. Trans values were assumed and the effect of optimization should certainly be small. In the eight excited states, the most important stucture parameters, the carbon-carbon and carbon-oxyben bond distances were optimized.



(1)

Tests were made to determine if any states were non-planar. The HCO group was twisted about the central carbon-carbon bond by 6° with other structure parameters fixed as values optimized for the given state.

Only one type of symmetry orbitals exist for the non-planar structures, so that $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excited states cannot be distinguished by symmetry. Therefore, non-planar tests on the higher open shell singlet and triplet states were performed by starting with planar symmetrized orbitals and minimizing mixing of orbitals of different planar symmetries. This forces the Hartree-Fock procedure to converge to a higher root, which should be the desired state. Not surprisingly, these calculations required very many more iterations to converge than the lowest root states.

RESULTS AND DISCUSSION

Table I gives the optimized molecular geometries. The only experimental values are for the ground state of the trans form. Cherniak and Costain[6] give a C=C bond length of 1.345 Å, about 0.01 Å longer than we have determined, and C-C-C bond angle of 119.8° or 3.6° smaller than our theoretical result. The other structural parameters agree quite well. The C-C bond length was 1.470 Å, the C=O bond length 1.219 Å, C-C-O angle 123.3°, and all hydrogen angles agreed with calculated values to within 2°. The double zeta basis set is sufficient for describing the acrolein ground state and since the excited states being considered are all low-lying valence excitations, we believe the basis is adequate for the excited states as well. Morokuma[15] concluded that some diffuse functions are necessary to account for Rydberg character of the $\pi \rightarrow \pi^*$ singlet. However, we feel that with a sufficiently large basis set, e.g. a double zeta set, the $\pi \rightarrow \pi^*$ singlet is essentially entirely a valence excitation without Rydberg character. This was demonstrated[12] to be the case for glyoxal. We note that the vertical excitation energy of this state which we have determined is much less than the 3G (minimum basis) or 3G + p energies of Morokuma.

The vertical excitation energies are given in Table II. The energies for the $n \rightarrow \pi^*$ states are lower than observed 0-0 transition energies. This result, however, is consistent with related theoretical predictions on other systems. In calculations on formaldehyde with the same basis set, the $n \rightarrow \pi^*$ vertical transition energies were also too small.[12] This is due to a greater correlation energy correction in the ground state than in the open shell excited states. The optimized state energies are presented in Table III. The ordering of excited states is $n \rightarrow \pi^*$ triplet, $\pi \rightarrow \pi^*$ triplet, $\pi \rightarrow \pi^*$ singlet, and $n \rightarrow \pi^*$ singlet. The geometry optimization lowered the $n \rightarrow \pi^*$ state energies by around 5000 cm^{-1} and the $\pi \rightarrow \pi^*$ states by around 12,000 cm^{-1}. The geometries of corresponding cis and trans states are very similar and correlation effects should be nearly identical. Thus, it is reasonable to compare cis-trans state energy differences with experiment.[9] The cis $^3A''$ state lies 120 cm^{-1} below the trans $^3A''$, compared with an experimental value of 420cm^{-1}. The theoretical energy difference for the $^1A''$ state was 250 cm^{-1} with the cis state lower in energy, while the experimental result was 540 cm^{-1}. The ground states differ by 540 cm^{-1}, with the cis state being higher, compared to a well determined experimental value of 700 cm^{-1}. While the theoretical energy differences are consistently smaller than experiment, the calculations do correctly order the states even with small energy differences of a few hundred wavenumbers.

The structure of the excited states is the most important result of the calculations because there are neither complete experimental nor theoretical values. For the $n \rightarrow \pi^*$ states, the carbon-carbon single bond is shortened slightly. This is consistent with spectroscopic estimates of Brand and Williamson.[4] The change is also similar to $n \rightarrow \pi^*$ excited states of glyoxal.[12] Unlike glyoxal, however, the $n \rightarrow \pi^*$ excitation in acrolein also results in a lengthening of the carbon-oxygen bond by about 0.15 Å, compared with the approximate experimental result of 0.12 Å.[4] The carbon-carbon double bond is lengthened only slightly in these states. Consistent with the large energy change upon optimization, the most dramatic changes in structure occur for

$\pi \rightarrow \pi^*$ excitations. In these states, the carbon-oxygen bond lengthens at least as much as for the $n \rightarrow \pi^*$ states. In addition, the two carbon-carbon bond lengths change greatly. The single bond contracts to a distance typical of double bonds, as occurs in glyoxal, while the double bond increases in length by about 0.13 Å.

The structure optimizations were performed with the molecule constrained to be planar. However, tests were made on slightly twisted structures and the results are shown in Table IV. It seems likely that most of the states are planar. The $^3A'$ state may, however, have a potential minimum in a gauche form. The probable crossing of the triplets in internal rotation was shown by the potential sheets of Devaquet.[14] Semiempirical calculations of Inuzuka and coworkers gave internal rotation barriers for all states except the higher triplet where the potential curve was flat.[7] In the reduced symmetry of the non-planar structures, the triplets can mix and thus, a one-configuration representation of the wavefunction becomes inappropriate. In glyoxal, C_2 symmetry is maintained in internal rotation so that the states analagous to acrolein $^3A''$ and $^3A'$ do not have the same symmetry and cannot mix. That is, the crossing is allowed. Furthermore, the reason for the crossing is seen to be a correlation, upon internal rotation, of $n \rightarrow \pi^*$ states with $\pi \rightarrow \pi^*$ states, and the reverse. The lack of symmetry in acrolein means there will be an avoided crossing in the internal rotation potential curves of the triplets. This can be described accurately only with a correlated wavefunction. Qualitatively, however, this avoided crossing makes it likely that the higher triplet curve may have a minimum between the cis and trans forms or may be nearly flat. The small energy change at the test geometry (see Table IV) and the lack of a CI calculation does not make it possible to confidently predict the true form of the potential. If the mixing were sufficiently large, it could also imply that the $\pi \rightarrow \pi^*$ singlet is non-planar. If there is a minimum for singlet or triplet states, the closeness of the $n \rightarrow \pi^*$ states which gives rise to the avoided crossing means that the effect on total energy of the state is likely to be small. On the other hand, a larger $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ state separation would increase the likelihood of the higher singlet and triplet being non-planar.

A degree of freedom not considered in this work is rotation around the terminal carbon-carbon bond. The calculations of Devaquet[14] show this rotation also results in an avoided crossing between the triplets. With the methylene group perpendicular to the molecular plane, the triplets remain separated by about the same energy. The mixing in the region of the avoided crossing should raise the barrier for the lower state and lower the barrier of the upper state. The effect on the singlet states should be similar. Nonetheless, the methylene hydrogens are probably in the molecular plane at the equilibrium geometries of the states, due to an overall upward energy shift upon rotation. Our conclusion on the structures of the excited states is that the lowest triplet and singlet are planar. The higher triplet and singlet may be non-planar or at least have shallow internal rotation potentials for the central carbon-carbon bond.

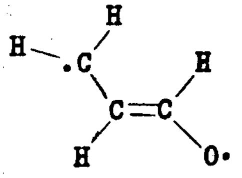
Electronic Structure

Using the Mulliken populations in Table V and the orbital energies in Table VI, some understanding can be reached concerning the nature of the electronic structure of the states of acrolein. The identification of the 13a' orbital as an oxygen n orbital is clearly indicated. The 2a" π orbital has a higher orbital energy than the n orbital and the π^* orbital is quite low-lying. Interestingly, the two occupied π orbitals are very localized. The 1a" in the ground state is almost entirely a carbonyl π orbital. The 2a" is an ethylene π bond. Symmetry restrictions in glyoxal do not allow such localization in glyoxal. Instead, these orbitals correspond to plus and minus combinations of a carbonyl π orbital.

For $n \rightarrow \pi^*$ excitations, it can be seen that the remaining n electron is completely localized on the oxygen. The 3a" electron is primarily centered on the carbonyl carbon, which had the greatest positive partial charge in the ground state. As a result of the increased electron density on carbon, the 1a" orbital changes by shifting electron density back to the oxygen. It becomes a much weaker bonding orbital. The change in 1a", which is always doubly occupied, probably accounts for the increase of the C=0 bond length for the A" states. This effect is not seen in glyoxal because the orbitals are delocalized. As expected, the $n \rightarrow \pi^*$ excitation in acrolein reduces the charge on oxygen.

Changes are seen in all the highest filled orbitals for the $\pi \rightarrow \pi^*$ excitation. The remaining electron in the 2a" orbital, which was an ethylene orbital, is shifted to the oxygen. The 1a" orbital now becomes localized on the central carbons rather than over the carbonyl. The π^* orbital is highly localized on the terminal carbon. It is clear that the lengthening of the C=C bond is due to the change in the 2a", the lengthening of the C=O bond is due to the change in 1a" and 13a', and the central carbon-carbon bond length contraction is the result of an additional C-C bond, specifically the 1a" orbital. Comparison of the 2a" orbital in the ground state with the 1a" orbital in the excited state suggests that the single/double bond character of the carbon-carbon bonds has been interchanged.

The low-lying $\pi \rightarrow \pi^*$ triplet of glyoxal is predicted to be a biradical state.[12] This is equally likely for acrolein and in addition, the $\pi \rightarrow \pi^*$ singlet may also be a biradical. For the acrolein $\pi \rightarrow \pi^*$ states, the 2a" is a half-filled orbital localized on oxygen. The electron in the half-filled 3a" orbital is localized on the methylene carbon. The lack of any delocalization of these orbitals suggests the following representation (2). The double



(2)

bonded central carbons mean that this biradical structure is close to an oxetene structure. The unpaired electrons on the terminal carbon and on oxygen could facilitate ring closure. It seems reasonable, then, that ring opening of an oxetene may proceed quite readily to a $\pi \rightarrow \pi^*$ state. Following the relaxation of the bond angles, this state may internally convert to the ground state.[7]

The localized nature of the valence molecular orbitals points toward a description of the electronic structure of acrolein as simply ethylene plus formaldehyde. In this model, we would expect the $\pi \to \pi^*$ states to be higher than the $n \to \pi^*$ states. As in formaldehyde, SCF calculations predict the $n \to \pi^*$ states to be too low-lying;[12,29] that is, the closed shell ground state should be lowered relative to these states by adding correlation energy. This would bring excitation energies into agreement with experiment. To the extent of the small carbonyl character of the $\pi \to \pi^*$ excitations, correlation effects should further separate the ground state and these states, as in formaldehyde.[30] A further upward shift in the $\pi \to \pi^*$ states would lead to a direct energy correlation of the acrolein excited states with either a formaldehyde or ethylene excitation. However, the conjugation of the double bonds makes the association of the $\pi \to \pi^*$ states with a pure ethylene excitation inappropriate. In glyoxal, the situation is worse, for $n \to \pi^*$ excitations are far different from molecules-in-molecules formaldehyde excitations,[12] while for butadiene, the model is successful.[31-32]

SUMMARY

The $\pi \rightarrow \pi^*$ triplet and singlet states of acrolein are quite low-lying and, depending on correlation effects, may be very close to the $n \rightarrow \pi^*$ singlet and triplet states. The manifold of excited states shows only minor differences between the *cis* and *trans* forms. The structure of the $n \rightarrow \pi^*$ states has as its primary feature a lengthened carbon-oxygen bond. For the $\pi \rightarrow \pi^*$ states, the single and double bonds between the carbons are interchanged relative to the ground state. The higher triplet and singlet states may be *gauche* forms, but if so, the potential minimum should be only slightly below the energy of the planar forms. The $\pi \rightarrow \pi^*$ states are biradicals and it is possible that the *cis* forms of these states are involved with oxetene ring opening. Finally, the localized valence orbital nature of the electronic states suggests that to some extent, correlation effects may be estimated from formaldehyde and ethylene. That is, the relative energy of the ground state should be shifted downward, while the $\pi \rightarrow \pi^*$ states should be shifted at least slightly upward.

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Table I. Optimized Geometries of Acrolein Electronic States.[a]

	State	$R_{C=C}$	R_{C-C}	$R_{C=O}$	$\angle_{CCC}$	$\angle_{CCO}$	$\angle_{CH_2}$	$\angle_{CCH(3)}$	$\angle_{CCH(4)}$
<u>trans</u>	$^1A'$ gs	1.336	1.477	1.222	123.4	121.4	116.5	116.3	116.2
	$^3A''$ $n\rightarrow\pi^*$	1.344	1.445	1.373					
	$^1A''$	1.347	1.430	1.389					
	$^3A'$ $\pi\rightarrow\pi^*$	1.465	1.346	1.396					
	$^1A'$	1.467	1.345	1.398					
<u>cis</u>	$^1A'$ gs	1.336	1.482	1.225	122.6	124.3	117.5		
	$^3A''$ $n\rightarrow\pi^*$	1.350	1.440	1.371					
	$^1A''$	1.354	1.432	1.386					
	$^3A'$ $\pi\rightarrow\pi^*$	1.466	1.344	1.387					
	$^1A'$	1.469	1.342	1.391					

[a] Bond lengths are in Angstrom and angles in degrees. Ground state values were assumed for bond angles not optimized. The $\angle_{CCH(3)}$ and $\angle_{CCH(4)}$ angles, optimized for the <u>trans</u> ground state were used for all other states.

Table II. Acrolein Vertical Excitation Energies.

	State		a. u.	cm^{-1}
Trans	$^1A'$	gs	-190.7054	0
	$^3A''$	$n\to\pi^*$	-190.6154	19,760
	$^1A''$		-190.6036	22,350
	$^3A'$	$\pi\to\pi^*$	-190.5805	27,420
	$^1A'$		-190.5760	28,410
Cis	$^1A'$	gs	-190.7030	0
	$^3A''$	$n\to\pi^*$	-190.6172	18,820
	$^1A''$		-190.6061	21,250
	$^3A'$	$\pi\to\pi^*$	-190.5850	25,880
	$^1A'$		-190.5815	26,660

Table III. Acrolein Optimized Electronic State Energies.

State		a. u.	cm^{-1}	Dipole Moment (Debyes)
Trans	$^1A'$ gs	-190.7054	0.0	4.11
	$^3A''$ $n \to \pi^*$	-190.6387	14,640	1.72
	$^1A''$	-190.6314	16,250	1.91
	$^3A'$ $\pi \to \pi^*$	-190.6356	15,320	3.06
	$^1A'$	-190.6344	15,590	2.96
Cis	$^1A'$ gs	-190.7030	0.0	3.48
	$^3A''$ $n \to \pi^*$	-190.6393	13,980	1.93
	$^1A''$	-190.6325	15,460	2.05
	$^3A'$ $\pi \to \pi^*$	-190.6384	14,170	2.78
	$^1A'$	-190.6369	14,500	2.69

Table IV. Energy changes from twisting.[a]

Trans	$^1A'$	g.s.	0.77
	$^3A''$	$n \to \pi^*$	0.11
	$^3A'$	$\pi \to \pi^*$	-0.30
	$^1A'$	$\pi \to \pi^*$	0.18
	$^1A''$	$n \to \pi^*$	0.13

[a] Energy change, in millihartrees, from internal rotation about the central C-C bond for the given states at their optimum geometries. The internal rotation angle for the excited states was 6° and for the ground state 10°.

Table V. Mulliken Populations.[a]

M.O.			Trans	${}^1A'$ gs	${}^3A''$	${}^1A''$	${}^3A'$	${}^1A'$
13a'	Oxygen	s		0.0	0.0	0.0	0.0	0.0
		p		1.290	0.964	0.968	1.375	1.366
	Carbon_1	s		0.003	0.0	0.0	0.008	0.008
		p		0.130	0.002	0.002	0.167	0.170
	Carbon_2	s		0.016	0.003	0.002	0.0	-0.001
		p		0.221	0.011	0.010	0.148	0.151
	Carbon_3	s		0.0	0.0	0.0	0.001	0.001
		p		0.035	0.001	0.001	0.021	0.021
1a"	Oxygen	p		1.011	1.696	1.762	0.091	0.076
	Carbon_1	p		0.721	0.240	0.163	1.007	1.010
	Carbon_2	p		0.195	0.046	0.046	0.851	0.865
	Carbon_3	p		0.073	0.017	0.019	0.051	0.049
2a"	Oxygen	p		0.321	0.123	0.136	0.871	0.947
	Carbon_1	p		-0.001	0.057	0.096	-0.005	-0.003
	Carbon_2	p		0.827	0.963	0.967	0.066	0.060
	Carbon_3	p		0.852	0.855	0.801	0.067	-0.004
3a"	Oxygen	p			0.074	0.033	0.064	-0.005
	Carbon_1	p			0.764	0.768	0.098	0.089
	Carbon_2	p			-0.006	-0.004	-0.017	-0.017
	Carbon_3	p			0.168	0.204	0.856	0.933
Net Charge	Oxygen			-0.358	-0.209	-0.236	-0.260	-0.256
	Carbon_1			0.112	-0.070	-0.041	-0.083	-0.080
	Carbon_2			-0.119	-0.045	-0.048	-0.028	-0.033
	Carbon_3			-0.428	-0.494	-0.492	-0.440	-0.441

[a] Carbon_1 is the carbon nearest oxygen and carbon_2 is the central carbon. Populations given are sums over all s or p atomic basis functions on each center.

Table VI. Ground State Occupied and Virtual Orbital Energies.[a]

	Trans $^1A'$ gs	Cis $^1A'$ gs
5 a'	-1.4115	-1.4075
6 a'	-1.1000	-1.0875
7 a'	-0.8973	-0.9087
8 a'	-0.8029	-0.7682
9 a'	-0.6831	-0.7152
10 a'	-0.6726	-0.6397
11 a'	-0.6055	-0.6136
12 a'	-0.5642	-0.5512
1 a"	-0.5446	-0.5410
13 a'	-0.4364	-0.4343
2 a"	-0.4009	-0.3946
3 a"	0.0700	0.0632
4 a"	0.1951	0.2165
14 a'	0.2474	0.2534
15 a'	0.2674	0.2781

[a] Energies are in hartrees. The highest four orbitals are unoccupied and their energies were determined from an improved virtual orbital (IVO) calculation.

FIGURE CAPTION

Energies of acrolein electronic states.

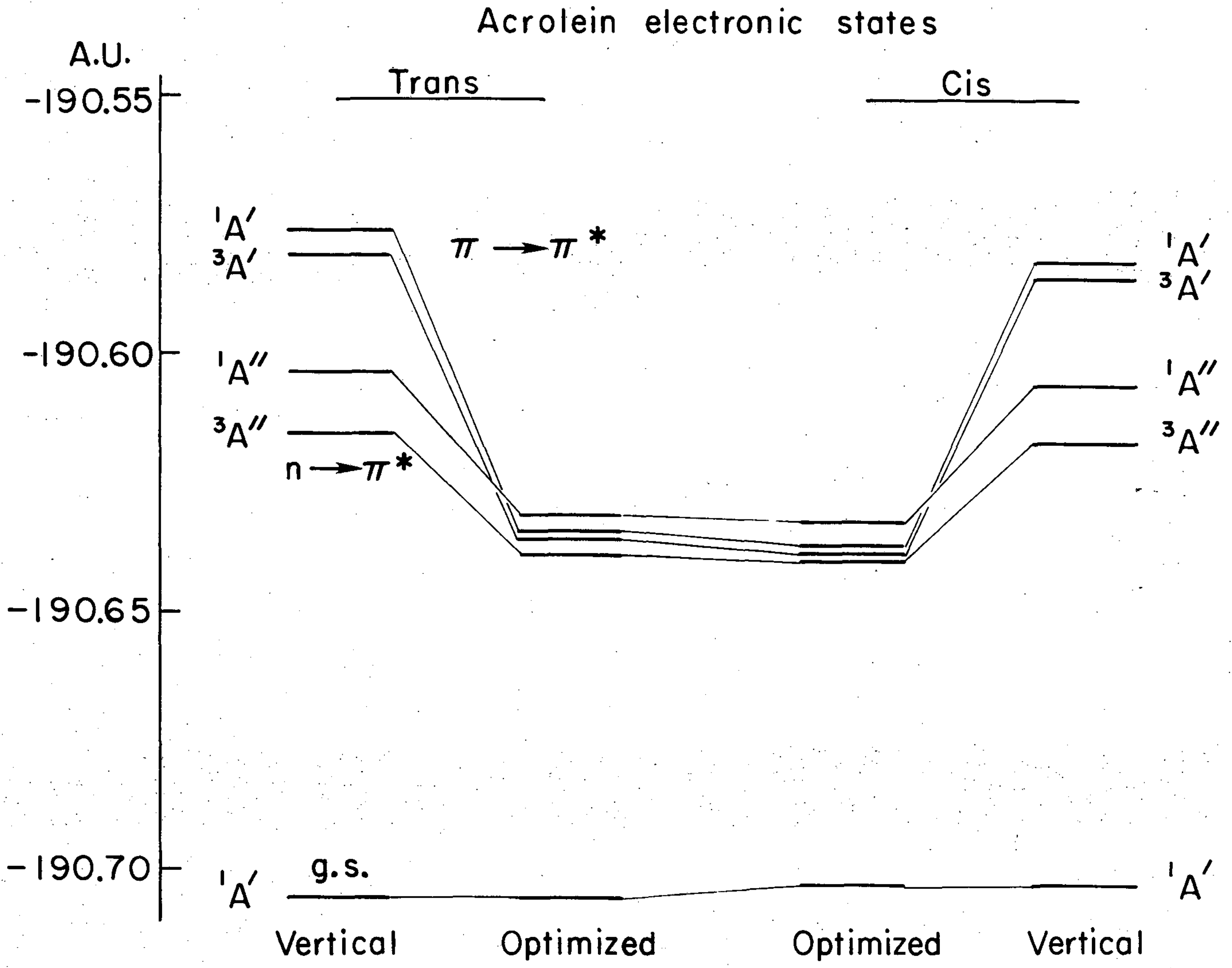

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Fig. 1

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720