

Electronic spectroscopy of propadiene (allene) by electron impact*

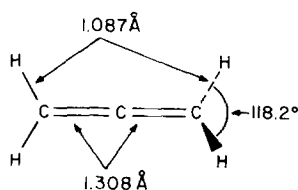
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(Received 15 March 1974)

The electron impact excitation of propadiene (allene) has been studied experimentally at impact energies of 20, 40, and 60 eV and scattering angles from 6° to 80°. Two transitions with maxima at 4.28 and 4.89 eV are identified as singlet \rightarrow triplet excitations. The magnitude of the splitting between these transitions is a measure of the interaction between the two perpendicular π molecular orbitals. The significance of these triplet excited states in the interpretation of previous electronic energy transfer experiments and sensitized photochemical studies is briefly discussed. Two very weak transitions are observed between 5.0 and 6.5 eV. The angular dependence of the corresponding cross sections indicates that these are spin-allowed but symmetry-forbidden transitions. A weak singlet \rightarrow singlet transition is seen with a maximum at 6.74 eV. This feature has also been optically observed and attributed to an electric dipole-allowed $\tilde{X}^1A_1 \rightarrow 1^1E$ transition. This assignment is discussed in the light of the present results. The first strong transition, the $\tilde{X}^1A_1 \rightarrow 1^1B_2 \pi \rightarrow \pi^*$ transition, appears with a maximum at 7.24 eV. Higher energy-loss features between 7.95 and 10 eV probably involve excitations to Rydberg states. A previously unreported transition to a superexcited state is observed with a maximum at 11.25 eV.

I. INTRODUCTION

Allene (propadiene) is the simplest example of a cumulene or adjacent carbon-carbon double bond system. The ground electronic state is probably non-planar,^{1,2} with the CH_2 planes at 90° to each other. The molecule then has D_{2d} symmetry with the following structure.¹



The π electron molecular orbitals (MO's) are at right angles and should have only limited interaction with each other. The observed $\pi \rightarrow \pi^*$ excitation energies may then be compared with those values in ethylene to furnish an estimate of the π MO interaction. An electron impact study of allene was undertaken to locate accurately the positions of the low-lying $\pi \rightarrow \pi^*$ forbidden transitions. Previous unpublished 90° electron scattering³ and trapped electron studies⁴ indicated the presence of one or more triplet excited states in the region from 4 to 5 eV, and it was hoped that the present study would provide more detailed information and a better understanding of this energy-loss region. Semiempirical and *ab initio* theoretical calculations are available for comparison with experimental results.

II. SUMMARY OF THEORETICAL CALCULATIONS

There have been a number of studies⁵⁻⁹ of allene using either Pariser-Parr-Pople or related methodologies. Table I summarizes the results of these studies. The ground state total energy and configuration has been the subject of an extensive *ab initio* calculation¹⁰ using Gaussian type molecular orbitals as the basis set. The ground state configuration is $(1a_1)^2(1b_2)^2(2a_1)^2(3a_1)^2(2b_2)^2 \times (4a_1)^2(3b_2)^2(1e)^4(2e)^4 = \tilde{X}^1A_1$. In a separate *ab initio* calculation,¹¹ both the ground and excited electronic states

were studied. The excited states that are lowest in energy arise from promoting an electron from a $2e$ to a $3e$ orbital. This produces four singlet and four triplet states. The $2e$ and the $3e$ molecular orbitals are each composed of two accidentally degenerate π or π^* orbitals, respectively. Thus, the $2e$ orbital may be thought of as two π orbitals, say π_a and π_b . The four pairs of excited states can then be thought of as arising from the $\pi_a \rightarrow \pi_a^*$, $\pi_a \rightarrow \pi_b^*$, $\pi_b \rightarrow \pi_a^*$, and $\pi_b \rightarrow \pi_b^*$ excitations. The *ab initio* calculations are also included in Table I. Although the energy values differ from study to study, the order of the triplet states remains the same. The lowest two triplets (1^3A_1 and 1^3B_2) are predicted to have quite similar energies and to lie significantly below the 1^3B_1 and 1^3A_2 states. The order of the singlet states in all these calculations is the same except for the 2^1A_1 state. The lowest electric dipole-allowed transition is predicted¹¹ to be the $\tilde{X}^1A_1 \rightarrow 1^1B_2$. The calculations indicate that two or possibly three weak transitions should be observed below the first strong singlet \rightarrow singlet transition.

III. SUMMARY OF PREVIOUS EXPERIMENTAL STUDIES

The results to be discussed below are summarized in Table II.

A. Optical absorption

The optical spectrum has been studied by several authors¹²⁻¹⁴ and some of the results have been listed by Herzberg.² Very weak continuous absorption starts around 4.8 eV and extends to about 6.5 eV. Rabalais *et al.*¹³ tentatively attributed an excitation in the region from 4.8 to 5.5 eV to the $\tilde{X}^1A_1 \rightarrow 1^1A_2$ transition and a very small inflection point at 5.76 eV to the $\tilde{X}^1A_1 \rightarrow 2^1A_1$ transition. The first transition that shows vibrational structure is a weak band system¹³ ($f \approx 3 \times 10^{-2}$) between about 6.4 and 6.9 eV with a maximum at 6.70 eV. An $\tilde{X}^1A_1 \rightarrow 1^1E$ assignment has been suggested¹³ for this excitation based on an analogy with linear triatomic groupings containing 16 valence electrons.

TABLE I. Summary of theoretical calculations.

Electronic state	Orbital transition	Calculated energy (eV)						
		<i>Ab initio</i>		Semiempirical				
		Schaad <i>et al.</i> ^a	Buenker ^c	Parr and Taylor ^d	Serre ^e	Borden ^{f,g}	Pellégatti ^h	Tai and Allinger ⁱ
\tilde{X}^1A_1	None	-114.8392 ^b	-115.6979 ^b					
1^3A_1	$2e \rightarrow 3e$	4.887eV		0.9		4.39		
1^3B_2	$2e \rightarrow 3e$	5.078		1.4		4.61		
1^3B_1	$2e \rightarrow 3e$	6.522		4.5		6.39		
1^3A_2	$2e \rightarrow 3e$	6.713		5.0		6.69		
1^1A_2	$2e \rightarrow 3e$	6.865		5.1	5.44	6.77	4.64	6.03 ^j
1^1B_1	$2e \rightarrow 3e$	7.263		5.5	5.76	7.15	4.86	6.55 ^j
2^1A_1	$2e \rightarrow 3e$	9.633		11.1	6.87	6.46	4.73	7.62 ^j
1^1B_2	$2e \rightarrow 3e$	10.792		8.9	7.05	7.85	7.40	7.84
1^1E	$2e \rightarrow 5a_1$	13.908						

^aReference 11.^bThis is the total energy of the ground electronic state in hartrees.^cReference 10.^dReference 5.^eReference 6.^fReference 7.^gAs measured from graph in Ref. 7.^hReference 8.ⁱReference 9.^jThese states were identified as forbidden singlets, but not specifically identified by symmetry.

The first strong optical absorption occurs¹²⁻¹⁴ between 6.9 and 7.9 eV with prominent peaks at 7.24 and 7.38 eV. This transition is optically allowed and has been assigned¹³ as $\tilde{X}^1A_1 - 1^1B_2$. Additional strong transitions with vibrational structure are seen in the region from 7.95 to 10 eV.¹²⁻¹⁴ Some of the observed bands have been arranged¹²⁻¹⁴ into Rydberg series, but a number of the peaks are not yet assigned.

B. Electron scattering experiments

The 90° spectrum of allene³ showed a weak feature at 4.5 ± 0.2 eV as well as stronger features at 7.6, 8.7,

and 9.5 eV. The trapped electron spectrum,⁴ which measures a quantity proportional to the integral cross section in a narrow energy band above the threshold energy, showed a broad peak from 3.5 to 5.5 eV with small maxima at 4.4 and 4.8 eV. Five stronger peaks were seen between 6.1 and 9.0 eV. The features observed from 4 to 5 eV were associated with triplet excited states in both studies.

IV. RESULTS AND DISCUSSION

A. Experimental procedure

The electron impact spectrum of allene was studied at

TABLE II. Summary of experimental observations on allene.

Nature of transition	Possible upper state ^a	Optical studies		Electron scattering ^c		
		Iverson and Russell ^d	Rabalais <i>et al.</i> ^e	90° scattering ^f	Trapped electron ^g	Present study
Singlet-triplet	1^3A_1 and 1^3B_2			4.5(± 0.2)	4.4	4.28 ± 0.05(3.6 → 4.8) ^h
Singlet-triplet					4.8	4.89 ± 0.05(4.3 → 5.6)
Symmetry-forbidden or weak allowed	1^1A_2 , 1^1B_1 ,		4.8 → 5.5		6.1	5.0 → 6.2
singlet-singlet	2^1A_1 , or 1^1E ^b	6.71	5.76			5.5 → 6.5
			6.70		6.6	6.74 ± 0.02(6.2 → 7.1)
Electric dipole-allowed						
singlet-singlet	1^1B_2	7.25	7.23	7.6	7.2	7.24 ± 0.02(6.5 → 7.9)
Rydberg bands						
$\pi \rightarrow 3p$		8.05	8.02	8.7	8.1	8.07 ± 0.03(7.95 → 8.48)
$\pi \rightarrow 4s$		8.58	8.57	9.5	9.0	8.60 ± 0.03(8.48 → 10)
Superexcited state						11.25 ± 0.05

^aNone of these identifications are certain. They represent an assignment based on an analysis of experiments and theoretical calculations.^bFor a discussion of the ordering of these states, see Sec. IV. C and IV. D^cAll transition energies are in eV.^dReference 14.^eReference 13.^fReference 3.^gReference 4.^hThe onsets and ends of the transitions are estimates based on band shapes in this study.

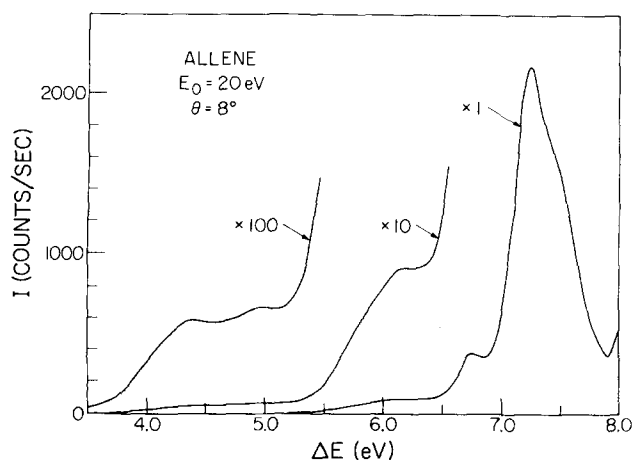


FIG. 1. Electron energy-loss spectrum of allene at $\theta = 8^\circ$; 20 eV incident electron energy; 3×10^{-8} A incident beam current; 3.7×10^{-3} torr sample pressure reading from an uncalibrated Schulz-Phelps gauge; resolution approximately 0.12 eV.

impact energies of 20, 40, and 60 eV and at scattering angles θ ranging from 6° to 80° in a modified version of an apparatus previously described.^{15,16} The size of the energy analyzers has been increased from 5.08 cm to 7.62 cm diameter, and the lens support system has been modified to facilitate assembly and insure accurate alignment. Allene (97% minimum purity) from the Matheson Co. was subjected to several liquid nitrogen freeze-pump-thaw cycles before use in this study. The pressure in the scattering chamber was 5×10^{-3} torr as indicated by an uncalibrated Schulz-Phelps ionization gauge. The resolution (defined as the full width at half-maximum of the elastic peak) was typically 0.13 to 0.15 eV. One spectrum was run at a resolution of 0.065 eV.

Figures 1 and 2 show the 20 eV impact energy spectra of allene at scattering angles of 8° and 60° , respectively. Figure 3 shows a higher resolution spectrum at 40 eV impact energy and $\theta = 0^\circ$.

The differential cross section (DCS) ratios with respect to either the elastic peak or the $\bar{X}^1A_1 \rightarrow 1^1B_2$ transition at 7.24 eV energy loss are taken from the areas under each peak in the energy-loss spectrum as previously described.¹⁶ The peaks in allene overlapped strongly, so that the measured cross section ratios are accurate to no better than $\pm 25\%$. The ratio of the DCS of several transitions to that of the $\bar{X}^1A_1 \rightarrow 1^1B_2$ at im-

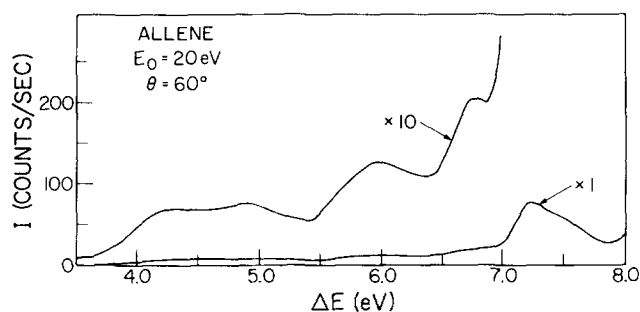


FIG. 2. Same as Fig. 2 at $\theta = 60^\circ$.

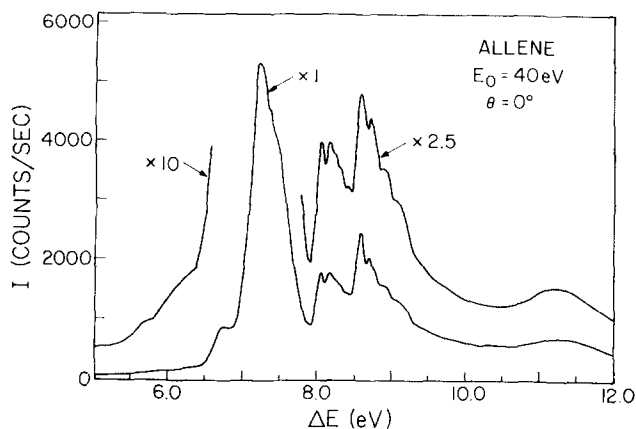


FIG. 3. Electron energy-loss spectrum of allene in the 5.0–12.0 eV energy-loss region for $\theta = 0^\circ$; 40 eV incident beam energy; 2×10^{-8} A incident beam current; 7.0×10^{-3} torr sample pressure reading from an uncalibrated Schulz-Phelps gauge; resolution approximately 0.06 eV.

pect energies of 20 and 40 eV are displayed in Figs. 4 and 5, respectively.

The elastic DCS in arbitrary units shown in Figs. 6 and 7 at impact energies of 20 and 40 eV, respectively, were determined by multiplying the observed count rates by the scattering volume correction¹⁷ appropriate to each scattering angle and normalizing the results to an arbitrary value of 1.0 at $\theta = 45^\circ$. The precision of these measurements is about 10%.

The $\bar{X}^1A_1 \rightarrow 1^1B_2$ DCS between 22.5° and 80° was ob-

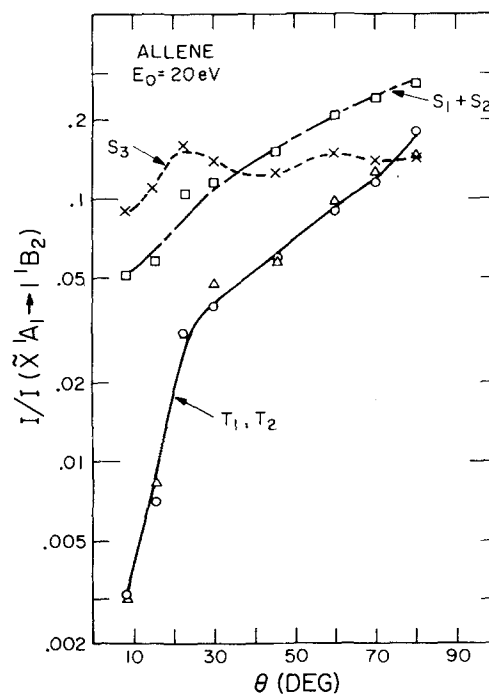


FIG. 4. Intensities of several electronic transitions in allene divided by the intensity of the $\bar{X}^1A_1 \rightarrow 1^1B_2$ transition as a function of θ at an incident electron energy of 20 eV; the excited states for the curves shown are T_1 (\circ), T_2 (Δ), S_1+S_2 (\square), and the 6.74 eV singlet (\times).

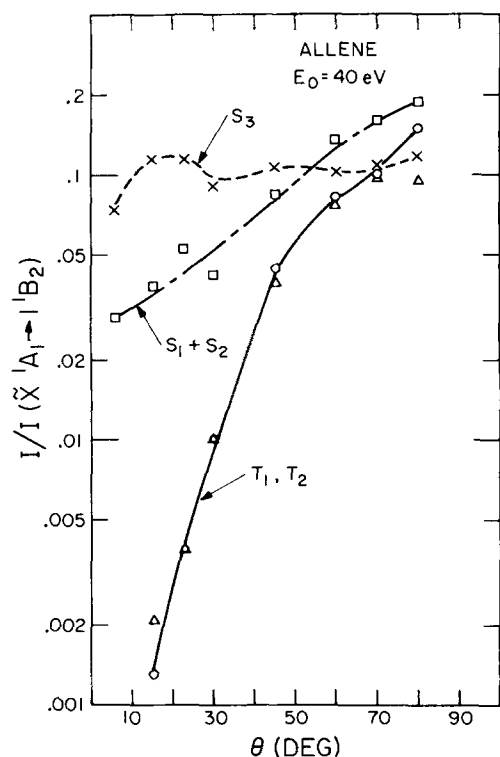


FIG. 5. Same as Fig. 4 at an incident electron energy of 40 eV.

tained by multiplying the $\bar{X}^1A_1 \rightarrow 1^1B_2$ to elastic DCS ratio by the elastic DCS at each scattering angle. In addition, for angles of 30° and below, the $\bar{X}^1A_1 \rightarrow 1^1B_2$ DCS was determined without reference to the elastic peak using the same procedure as for the elastic DCS, except that the normalization procedure was to make the result at 22.5° agree with the one obtained by the ratio method. These two methods agreed well at 30° .

The DCS's for the other inelastic transitions displayed in Figs. 6 and 7 were determined by the ratio method using the elastic DCS as a reference for angles of 22.5° and above, and the $\bar{X}^1A_1 \rightarrow 1^1B_2$ DCS below 22.5° . The estimated uncertainty in the inelastic DCS's is 35%. The arbitrary units in Figs. 6 and 7 are the same for all curves displayed.

B. The triplet states (T_1 and T_2)

1. Electron impact spectroscopy

Two weak features are observed with maxima at 4.28 ± 0.05 eV and 4.89 ± 0.05 eV (the uncertainty refers to the range of peak positions observed). The apparent onset of the lowest excitation is below 3.6 eV. The DCS ratios (see Figs. 4 and 5) of both these transitions are equal within experimental error. Each shows the sharp increase^{15,16,18} with scattering angle characteristic of a spin-forbidden transition. The inelastic DCS values (see Figs. 6 and 7) for both transitions do not vary by more than a factor of three over the angular range from 10° to 80° , which confirms¹⁵⁻¹⁸ the triplet nature of the excited states. These transitions are designated as $S_0 \rightarrow T_1$ and $S_0 \rightarrow T_2$.¹⁹

All available theoretical calculations^{5,7,11} suggest that

the upper states of these transitions are the 1^3A_1 and 1^3B_2 states. Although these calculations indicate that the 1^3A_1 should be the lowest triplet state, they may not be sufficiently accurate to insure the correctness of this prediction.

The lowest triplet excited state in ethylene has a maximum intensity at a transition energy of 4.40 eV.¹⁸ The average excitation energy of the two lowest triplet states in allene is 4.58 eV with an energy splitting of 0.61 eV. In *s-trans*-1, 3-butadiene, the corresponding values¹⁶ are 4.07 and 1.69 eV. The similarity of the $\pi \rightarrow \pi^*$ triplet excitation energy in ethylene with the average triplet excitation energies in both allene and butadiene supports a valence bond or "molecules-in-molecules" description of these systems.²⁰ The magnitude of the energy splitting (0.61 eV) in allene is substantially less than in butadiene (1.69 eV). This result is in qualitative agreement with simple MO theory. The coplanar butadiene π MO's have considerable interaction with each other, even though they are physically separated by a C-C single bond, and this interaction produces the large energy splitting. The relatively small energy split in allene reflects the fact that although the

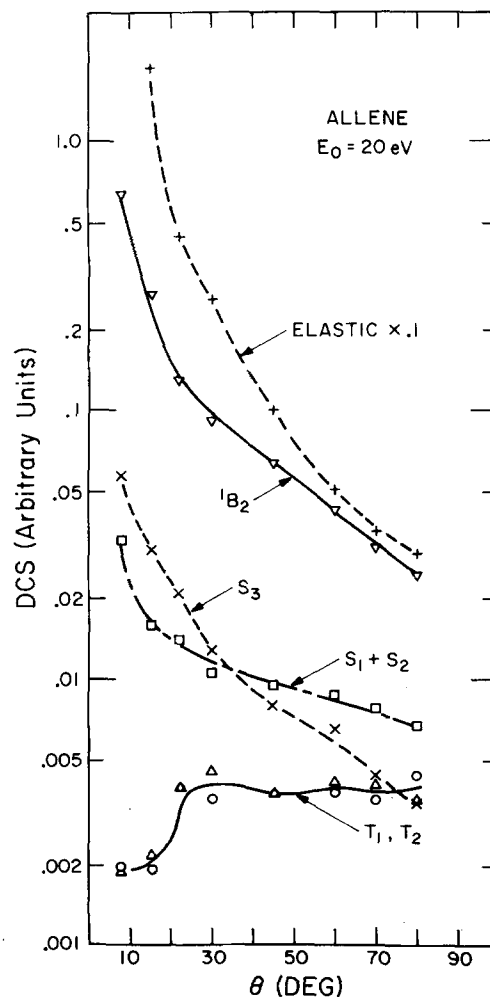


FIG. 6. Differential cross sections as a function of θ at an incident electron energy of 20 eV for elastic scattering (+) and for transitions to the following excited states: T_1 (\circ), T_2 (Δ), $S_1 + S_2$ (\square), 6.74 eV singlet (\times), 1^1B_2 (∇).

π MO's are closer, they are perpendicular to each other and have a relatively small overlap.

2. Role in energy-transfer and sensitized-photochemical studies

The results of recent experiments²¹ involving π -bonded molecules have led to the suggestion that the rate of triplet-triplet energy transfer in the gas phase is proportional to the energy overlap of the donor molecule phosphorescence spectrum with the $S_0 \rightarrow T$ optical absorption spectrum of the acceptor molecule. This finding is consistent with the theoretical prediction of Dexter,²² developed for solid state systems, for triplet-triplet energy transfer rates due to exchange interactions. The shape and location of the low energy side of the T_1 electron impact excitation in allene is quite similar to that of ethylene¹⁸ and, according to Dexter's theory, both molecules might be expected to have similar cross sections for quenching benzene in the 1^3B_{1u} state ($T_{00} = 3.66$ eV)²³. Indeed, the experimental quenching rate coefficients^{21b} of these two systems are equal within experimental error. In contrast, a molecule such as acetylene, which has an $S_0 \rightarrow T_1$ electron impact excitation spectrum with an onset above 4.0 eV,²⁴ has a benzene 1^3B_{1u} quenching rate coefficient^{21b} which is more than fifty times smaller than that of allene. These observations support the suggestion of Schmidt and Lee^{20b} that the shape and location of the acceptor $S_0 \rightarrow T_1$ electron impact excitation spectrum and of the donor phosphorescence spectrum may be useful for predicting relative quenching efficiencies of different acceptors.

The second triplet state may be the state that is initially excited in the Hg photosensitized decomposition of allene.²⁵ The decomposition²⁵ following photosensitization into propargyl radicals ($\cdot\text{CH}_2 - \text{C}\equiv\text{CH} + \text{H}\cdot$) may occur from T_2 , T_1 , or vibrationally excited levels of the ground state. Hg in the $3P_1$ state is 4.89 eV above its ground state, and this energy appears to be insufficient to excite the lowest singlet state of allene.

C. S_1 and S_2

A weak feature in the electron impact excitation spectrum of allene is observed between about 5.0 and 6.5 eV. The cross section ratios and the shape^{18,26} and magnitude of the differential cross sections shown in Figs. 4-7 are consistent with theoretical predictions that the transitions in this region are spin allowed but symmetry forbidden. This inference is also consistent with the weakness of the optical absorption.¹³ In the low resolution spectra (Figs. 1 and 2), the region shows only one maximum, but its location is angle dependent and varies from 5.93 to 6.10 eV. This behavior indicates that in this region there are at least two transitions occurring which have differential cross sections that vary differently with scattering angle. The high resolution spectrum (Fig. 3) shows a slope break at 5.79 ± 0.03 eV in agreement with optical results.¹³ Figure 3 shows that one state is located between about 5.0 and 6.2 eV while another has an onset around 5.5 eV and extends to about 6.5 eV. Several theoretical calculations^{5,6,11} predict that the lowest excited singlet state is the 1^1A_2 and that the second one is the 1^1B_1 state. These assignments

are consistent with our observation that the transitions to the first two excited singlet states are symmetry forbidden.

D. The 6.74 eV singlet (S_3)

Another transition is observed from 6.2 eV to beyond 7.0 eV with a maximum at 6.74 ± 0.02 eV, in agreement with optical observations.¹²⁻¹⁴ Rabalais *et al.*¹³ assign this region to the optically allowed $\tilde{X}^1A_1 - 1^1E$ transition. These authors¹³ argue that it is a weak transition because it is analogous to the symmetry-forbidden $1^1\Sigma_g^+ - 1^1\Pi_g$ transition in linear triatomic molecules of $D_{\infty h}$ symmetry, like CO_2 . However, the *ab initio* calculation of Schaad, Burnelle, and Dressler¹¹ places the 1^1E excited state 13.9 eV above the ground state. An alternate assignment of this transition in allene as spin allowed but symmetry forbidden is also consistent with the observed facts. Indeed, the observed ratio of the DCS for this transition to that of the optically allowed $\tilde{X}^1A_1 - 1^1B_2$ transition oscillates weakly with scattering angle, as shown in Figs. 4 and 5. Such behavior has been observed in the past¹⁶ for spin-allowed, symmetry-forbidden transitions. Nevertheless, this oscillatory behavior is not inconsistent with the $\tilde{X}^1A_1 - 1^1E$ assignment. An example¹⁵ occurs in CO, in which the intensi-

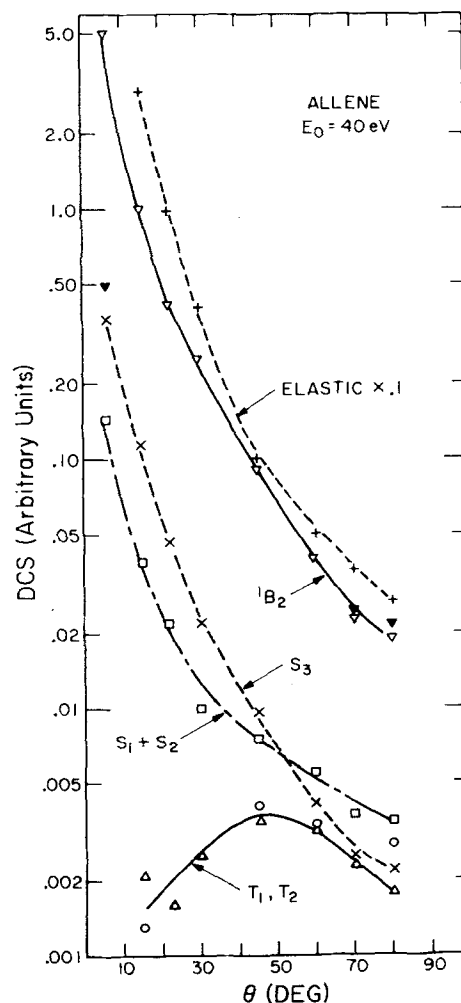


FIG. 7. Same as Fig. 6 for an incident electron energy of 40 eV.

ty ratios of two fully allowed transitions, the $\bar{X}^1\Sigma^+ \rightarrow B^1\Sigma^+$ and the $\bar{X}^1\Sigma^+ \rightarrow C^1\Sigma^+$, to that of the fully allowed $\bar{X}^1\Sigma^+ \rightarrow A^1\Pi$ transition show oscillatory behavior with θ .

E. The 7.24 eV (1^1B_2) state

A strong transition is observed from below 6.5 eV to about 8.0 eV, with a maximum at 7.24 ± 0.02 eV. The DCS for this transition (Figs. 6 and 7) is consistent with its fully allowed nature. The peak location is in excellent agreement with optical studies¹²⁻¹⁴ and the transition has been assigned¹³ as the optically allowed $\bar{X}^1A_1 \rightarrow 1^1B_2$ excitation.

F. Higher transitions

Two features at higher energy loss are observed with peaks at 8.07 and 8.60 eV. These features are also observed optically,¹²⁻¹⁴ although the lack of resolution in this study masks many of the finer details of each band system.

A previously unreported transition to a superexcited state (i. e., above the first ionization potential) is seen with a peak at 11.25 eV. No further peaks were observed out to 16 eV energy loss.

V. CONCLUSIONS

The results of this study are summarized in the last column of Table II. Excitations to two low-lying triplet states have been observed at 4.28 and 4.89 eV. The region from 5.0 to 6.5 eV contains at least two singlet \rightarrow singlet transitions which may be symmetry forbidden.

A singlet \rightarrow singlet transition from about 6.2 to 7.1 eV with a peak at 6.74 eV shows a behavior that suggests that it is either a symmetry-forbidden excitation or analogous to a transition that in the isoelectronic molecule CO_2 is symmetry forbidden. A previously unreported superexcited state 11.25 eV above the ground state is observed.

*Work supported in part by the United States Atomic Energy Commission Report Code CALT-767P4-128.

†Work performed in partial fulfillment of the requirements for the Ph. D. degree in Chemistry at the California Institute of Technology.

‡Contribution No. 4842.

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¹⁹The notation used here does not indicate the spatial symmetry of the electronic state. Singlet spin states are designated S_0, S_1, \dots , where the state energy increases with increasing numerical subscript. In a similar manner, the triplet electronic states are designated as T_1, T_2, \dots . This notation is commonly used in spectroscopic and photochemical studies of large molecules. For further discussion, see S. P. McGlynn, T. Azumi, and M. Kinoshita, *Molecular Spectroscopy of the Triplet State* (Prentice-Hall, Englewood Cliffs, New Jersey, 1969), pp. 1-3.

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