Electronic spectroscopy of 1,3-cyclopentadiene, 1,3-cyclohexadiene and 1,3-cycloheptadiene by electron impact[a]

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The electronic spectra of three conjugated *cis*-dienyl systems, 1,3-cyclopentadiene, 1,3-cyclohexadiene, and 1,3-cycloheptadiene have been investigated using electron-impact spectroscopy. Spectra were obtained at impact energies ranging from 20 to 75 eV and scattering angles from 5° to 80°. A single singlet → triplet transition was observed for each molecule at 3.10, 2.94, and 2.99 eV, respectively. Information on the Franck–Condon envelopes was obtained for these transitions. The $N \rightarrow V_1$, $N \rightarrow V_2$ and V_3, and several Rydberg transitions were also observed in each substance. Some previously unreported superexcited states lying above the first ionization potential were detected.

I. INTRODUCTION

The electronic spectra of three cyclic conjugated dienes, 1,3-cyclopentadiene, 1,3-cyclohexadiene, and 1,3-cycloheptadiene, have been investigated by the method of low-energy, variable angle electron impact.[1-3] Previously, these dienyl systems have been the object of numerous photochemical[4-15] and spectroscopic studies.[16-26] Due to the cyclic nature of these compounds, the two double bonds are locked in the s-cis conformation. The planes of the double bonds in 1,3-cyclopentadiene and 1,3-cycloheptadiene are the same while those of 1,3-cyclohexadiene intersect at an angle of 18°.[27-29] Figure 1 shows the ground state geometrical configurations of the molecules studied as obtained from electron diffraction and microwave rotational studies.[27-29]
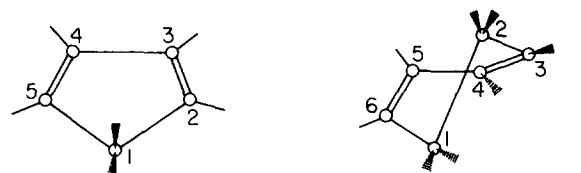
Over the last forty years, several groups of researchers have used ultraviolet spectroscopy to investigate the excited states of these molecules.[16-22] High energy electron impact has also been used to study spin-allowed electronic transitions in cyclohexadiene.[23] Spin-forbidden, singlet → triplet transitions in these molecules have been studied to a much lesser extent. Researchers have used both the O_2 perturbation technique and external heavy atom perturbations to increase the optical intensity of singlet → triplet transitions.[22,25,26]

Knowledge of the location and Franck–Condon profiles of singlet → triplet excitations in these molecules would be of considerable importance when attempting to interpret results of photochemical experiments involving triplet–triplet energy transfer, as in the case of cyclopentadiene.[4-7] According to a theory developed for solids,[30] and as applied to gases,[3a,31-33] the rate of triplet–triplet energy transfer due to exchange interactions depends upon the energy overlap of the $S_0 \rightarrow T$ absorption spectrum of the acceptor and the phosphorescence spectrum of the donor.
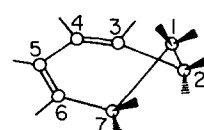
The photochemistry of these molecules is of considerable interest. Investigations of the stereochemical aspects of the photosensitized cycloaddition to cyclopentadiene, in the presence of various photochemical sensitizers, have been made.[4-7] It is believed that after photoexcitation of the sensitizer and a subsequent intersystem crossing to an excited triplet state, this energy is collisionally transferred to cyclopentadiene, resulting in a reactive cyclopentadiene triplet intermediate.[4] The photochemical reactions of 1,3-cyclohexadiene are interesting because they are typical of those of the vitamin D system.[8,9,11] Photolysis of gas phase 1,3-cyclohexadiene with ultraviolet lights leads to 1,3,5-hexatriene, benzene, H_2, and other products.[10,11] The photoisomerization of 1,3-cycloheptadiene has also been investigated.[15]

The method of low-energy, variable angle, electron-impact spectroscopy has been used successfully to in-

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1,3-Cyclopentadiene (C_{2v}) 1,3-Cyclohexadiene (C_2)

1,3-Cycloheptadiene (C_S)

FIG. 1. Molecular geometries and symmetries of 1,3-cyclopentadiene, 1,3-cyclohexadiene, and 1,3-cycloheptadiene.

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vestigate spin-forbidden and other dipole-forbidden transitions in molecules.[1-3] With this technique, high-quality Franck–Condon envelopes of singlet → triplet transitions may be measured. Information about the nature of the excited electronic states observed in an electron-impact spectrum can be obtained from the dependence of the intensity of each transition on impact energy and scattering angle.[1,2] A transition which, in optical spectroscopy, is both electric dipole and spin allowed has, in electron-impact spectroscopy, a differential cross section (DCS) vs scattering angle curve which is peaked in the forward direction. For impact energies 15 eV or more above excitation threshold, the corresponding DCS decreases by 1 to 2 orders of magnitude as the scattering angle varies from 10° to 80°.[1,2] In contrast, transitions involving changes in the electron spin quantum number of unity, such as singlet → triplet excitations, have a more nearly isotropic DCS curve, which usually varies by a factor smaller than 3 over that angular range. Such transitions occur by the mechanisms of electron exchange.[34] Spin-allowed but electric dipole-forbidden processes are forward peaked, but often not as much as fully allowed transitions.[3b,35] Finally, for impact energies about 15–100 eV above threshold, optically forbidden processes, and in particular spin-forbidden ones, become more intense with respect to optically allowed ones as the impact energy is lowered.

II. SUMMARY OF PREVIOUS STUDIES

A. Introduction

In a first approximation, the interacting ethylenic groups produce two filled π molecular orbitals (MO's) and two antibonding π^* MO's. The four lowest $\pi \rightarrow \pi^*$ singlet → singlet transitions were designated by Mulliken[36] as $N \rightarrow V_1$, V_2, V_3, and V_4, respectively. The symmetry of the cyclic dienes makes all of these excitations electric dipole allowed. Experimentally, these dienes exhibit the $N \rightarrow V_1$ transition and, at higher excitation energies, an intense region of absorption which has been attributed by Robin[37] to the overlapping of the $N \rightarrow V_2$ and $N \rightarrow V_3$ transitions. In addition to valence excitations, transitions from the highest π orbital to Rydberg-like orbitals are expected, with the Rydberg series converging to the first ionization potential.

B. Theoretical calculations

Calculations of the electronic spectrum of cyclic cis-dienes have thus far been limited to semiempirical investigations. For cyclopentadiene, which has C_{2v} symmetry, the V_1, V_2, V_3, and V_4 states transform according to the $^1B_2$, $^1A_1$, $^1A_1$, and $^1B_2$ irreducible representations of that symmetry group. Del Bene and Jaffe[38] performed semiempirical CNDO calculations yielding the following transition energies from the ground ($\tilde{X}^1A_1$) to the indicated excited state: $^1B_2 - 4.8$ eV, $^1A_1 - 6.3$ eV, $^1B_1(\sigma - \pi^*) - 7.5$ eV, and $^1A_1 - 7.9$ eV. More recent CNDO/2 calculations performed by Hayashi and Nakajima[39] yield $\pi \rightarrow \pi^*$ excitation energies of $^1B_2 - 5.11$ eV, $^1A_1 - 6.36$ eV, $^1B_2 - 7.27$ eV, and $^1A_1 - 8.12$ eV. In addition, $\sigma \rightarrow \pi^*$ excitations were calculated to occur at

$^1B_1 - 6.01$ eV, $^1A_2 - 6.29$ eV, $^1A_2 - 6.94$ eV, and $^1A_2 - 8.03$ eV.[39] The excitation energy of the lowest state of cyclopentadiene ($N \rightarrow T_1$, $\tilde{X}^1A_1 - {}^3B_2$) was calculated by Barfield, using a semiempirical valence bond technique, to lie at 3.4 eV.[40]

Allinger, Tai, and Stuart[41] performed semiempirical variable electronegativity self-consistent field (VESCF) configuration interaction calculations on the π system of 1,3-cyclohexadiene. Singlet → singlet transitions were predicted to occur at 5.21 and 5.71 eV, while the two lowest-lying triplet states were calculated to have excitation energies of 3.01 and 4.61 eV. The lowest excited singlet state (V_1) energies of all three cyclic 1,3-dienes considered in the present paper were calculated by Allinger and Miller[42] using the Pariser–Parr method. These energies were found to be 5.0, 5.1, and 5.4 eV, for 1,3-cyclopentadiene, 1,3-cyclohexadiene, and 1,3-cycloheptadiene, respectively. Table I summarizes the results of the various theoretical investigations.

In addition to the theoretical investigations on the molecules being considered, ab initio SCF–CI calculations on s-cis-1,3-butadiene were performed by Buenker and Whitten[43] and Shih, Buenker, and Peyerimhoff.[44] Their results should be useful for comparison with those of the cyclic cis-dienes, particularly if the diene portion of the ring is more important in determining the transition energy than the overall ring size and conformation. Results by Shih et al.[44] indicate that the lowest excited singlet state is the 1^1B_2 one and that the 2^1A_1 state is 0.31 eV about it. These results are different from those of an earlier investigation[42] which had placed the 2^1A_1 state below the 1^1B_2 one. For the s-trans configuration of butadiene, Buenker et al.[45] found that the lowest ^1B_u state had significant diffuse character and may correspond to a Rydberg excitation observed at 6.66 eV.[46] The observed $N \rightarrow V_1$ transition may be due to a non-vertical valence excitation to an "n ^1B_u" state.[45]

For s-cis-1,3-butadiene Shih et al.[44] have predicted singlet → triplet transitions with excitation energies of 2.95 eV ($\tilde{X}^1A_1 - 1$ $^3B_2$) and 4.90 eV ($\tilde{X}^1A_1 - 1$ $^3A_1$). The accuracy of these values is expected to be quite good. Similar investigations[44] for s-trans-butadiene yielded triplet excitation energies of 3.24 and 4.95 eV, which are in excellent agreement with the electron-impact measurements of Mosher, Flicker, and Kuppermann,[3a] who observed singlet → triplet excitations at 3.22 and 4.91 eV.

C. Previous experimental results

The optical spectrum of 1,3-cyclopentadiene has been previously studied by Scheibe and Grieneisen,[16] Pickett, Paddock, and Sackter,[17] and Price and Walsh.[18] The first observed singlet → singlet transition was designated $N \rightarrow V_1$ ($\tilde{X}^1A_1 - {}^1B_2$) by Mulliken.[36] Absorption begins at about 4.75 eV and continues to 5.90 eV with the absorption maximum located at 5.34 eV. Superimposed on the low-energy side of the $N \rightarrow V_1$ transition, both Scheibe and Grieneisen[16] and Pickett et al.[17] observed weak, but sharp transitions. On the high-energy side of the $N \rightarrow V_1$ feature an additional set of five excitation peaks is ob-

TABLE I. Transition energies (in eV) for 1,3-cyclopentadiene, 1,3-cyclohexadiene, and 1,3-cycloheptadiene.[a]

Transitions[b]	s-cis-butadiene[c]	Previous theoretical results			Previous experimental results			Present experimental results		
		C_5H_6	C_6H_8	C_7H_{10}	C_5H_6	C_6H_8	C_7H_{10}	C_5H_6	C_6H_8	C_7H_{10}
$N \to T_1(\tilde{X}^1A_1 \to {}^3B_2)$	2.95	3.4[d]	3.01[h]		3.1[i]	2.9[i]		3.10(2.5 → 3.9)[p]	2.94(2.1 → 3.8)[p]	2.99(2.4 → 3.9)[p]
$N \to T_2(\tilde{X}^1A_1 \to {}^3A_1)$	4.90		4.61[h]					Above 4.7	Above 4.5	Above 4.5
$N \to V_1(\tilde{X}^1A_1 \to {}^1B_2)$	6.35	4.8,[e] 5.11,[f] 5.0[g]	5.21,[h] 5.1[g]	5.4[g]	5.34[j]	4.95[m]	5.00[o]	5.26	4.94	5.08
$N \to V_2(\tilde{X}^1A_1 \to {}^1A_1)$	6.66	6.3,[e] 6.36[f]								
$N \to V_3(\tilde{X}^1A_1 \to {}^1A_1)$	7.89	7.9,[e] 8.12[f]	5.71[h]		8.06[k]	8.04[h]		8.03	7.88	8.24
$N \to V_4(\tilde{X}^1A_1 \to {}^1B_2)$	8.53									
$\pi \to 3s$					{5.68, 5.77, 5.8, 5.94, 5.99[j]}			5.68, 5.77; 5.94		5.41, 5.61
$\pi \to 3p$					{6.24, 6.35, 6.43, 6.49[j]}	6.05, 6.22; 6.40[l]		6.28, 6.41	6.05, 6.20; 6.39	5.95, 6.13; 6.27
apparent Rydberg transitions					7.88[l], 8.13[l], 8.28[l], 8.36[l]	6.90[n], 7.23[n], 7.46[n], 7.75[n], 8.5[n], 8.95[n], 10.49[n], 12.28[n], 15.5[n], 18.8[n]		6.80, 7.05, 7.61, 7.84, 8.03, 8.19, 9.2, 10.4, 11.8, 14.0	6.90[q], 7.21, 7.42, 7.73, 7.88, 8.05, 9.05	6.65, 6.79, 6.97, 7.18, 7.38, 7.66, 7.86, 8.24, 8.80, 9.52, 10.00, 11.33, 13.78

[a]The uncertainty in the location of these intensity maxima is ±0.05 eV.
[b]None of the experimental identifications are definite. They represent an assignment based on analysis of experiments and theoretical calculations. Symmetry designations are those appropriate for the C_{2v} point group.
[c]Reference 44.
[d]Reference 40.
[e]Reference 38.
[f]Reference 39.
[g]Reference 42.
[h]Reference 41.
[i]Reference 25.
[j]Reference 17.
[k]Reference 37.
[l]Reference 18.
[m]Reference 21.
[n]Reference 23.
[o]Reference 24.
[p]Values in parentheses are the effective Franck–Condon regions.
[q]This feature may be due to a small benzene impurity (≲ 2%).

served. The next region of absorption occurs from 6.20 to 6.90 eV. This region consists of a complicated system of vibronic bands. Price and Walsh[18] have interpreted these in terms of a single electronic transition, while Pickett et al.[17] assigned them to two superimposed electronic excitations. At higher transition energies, four additional features are observed.[18] These were suggested to be members of a Rydberg series ($\delta = 0.28$) converging to the first ionization potential, 8.566 eV (vert.).[47] These features appear to be superimposed on a broad region of intense absorption which has its onset at approximately 7.32 eV. Derrick et al.[47] have arranged these transitions and those occurring at about 6.3 eV into three Rydberg series. The lowest triplet state of 1,3-cyclopentadiene was studied by Evans,[25] using the high pressure O_2 perturbation technique. An absorption maximum was observed at 3.1 eV in an oxygen and chloroform solution, and the 0–0 band of this transition was placed at 2.53 eV.

The spectrum of 1,3-cyclohexadiene has been studied previously both optically[18–22] and by high-incident energy electron-impact spectroscopy.[23] An intense transition is observed with onset at about 4.4 eV and an absorption maximum at 4.95 eV.[21] It has been assigned by Mulliken[36] to the $N \rightarrow V_1$ (or $\bar{X}\,^1A_1 \rightarrow\,^1B_2$, in C_{2v} symmetry notation)[48] transition, analogous to its counterpart in 1,3-cyclopentadiene. The earlier optical spectra of Henri and Pickett[20] showed this peak to have some vibrational structure. However, subsequent studies[21,22,49] have shown only a smooth feature. The previous vibrational structure was shown to be that of 1,3,5-hexatriene produced by photochemical conversion of the 1,3-cyclohexadiene sample.[21] Three peaks centered at 6.22 eV[18,19,22] are observed above the $N \rightarrow V_1$ transition and are believed to correspond to the vibronic components of a single Rydberg transition. High incident energy electron-impact studies by Killat[23] have provided information about the more energetic excitations. Below the first vertical ionization potential at 8.25 eV,[50] several transitions were assigned as having Rydberg character while at 8.04 eV a strong excitation has been attributed to a combination of the $N \rightarrow V_2$ and V_3 excitations. In an O_2 plus chloroform solution, Evans[25] detected the lowest singlet $\rightarrow$ triplet transition of 1,3-cyclohexadiene, with maximum absorption intensity occurring at 2.9 eV and the 0–0 band at 2.32 eV. In a methyl iodide solution, the intensity maximum shifted downwards to 2.79 eV.[22]

The spectrum of 1,3-cycloheptadiene has received considerably less attention than those of the other molecules. The $N \rightarrow V_1$ transition is observed to have an onset at approximately 4.5 eV with an absorption maximum at 5.00 eV.[24] No singlet $\rightarrow$ triplet transitions have been reported. The previously obtained experimental and theoretical results are summarized in Table I.

III. EXPERIMENTAL METHODS

The electron-impact spectrometer used in these studies has been described previously.[1,2] In brief, a beam of electrons generated by a tungsten filament at about 2100 °C is injected into a hemispherical electrostatic energy analyzer where it is monochromatized, and accelerated to an impact energy E_0. The electron beam is then scattered off the target gas contained in a flexible, metal bellows scattering chamber. The scattered electrons are energy-analyzed by another hemispherical device identical to the monochromator. A continuous dynode electron multiplier serves as the detector. Its output pulses are amplified, shaped, and stored in a 1024 channel scaler.

In the present experiments, the electron-impact spectra of 1,3-cyclopentadiene, 1,3-cyclohexadiene, and 1,3-cycloheptadiene were obtained at impact energies of 30 and 50 eV, 20 and 40 eV, and 25 and 50 eV, respectively, over scattering angles ranging from 5° to 80°. Electron beam intensities incident into the scattering chamber were typically 40 nA, while sample pressure ranged from 3–6 mtorr, as indicated by an uncalibrated Schulz–Phelps ionization gauge. The energy resolution, as measured by the full width at half maximum (FWHM) of the elastic peak, was usually chosen to lie in the range 0.10–0.15 eV; however, some spectra were obtained at higher resolutions of 0.07–0.09 eV.

The 1,3-cyclopentadiene used in these studies was prepared using dicyclopentadiene obtained from Matheson, Coleman, and Bell with a stated purity of 95%. This substance was cracked by boiling on a distillation apparatus, and the pure 1,3-cyclopentadiene was collected from the head of the distillation column.[51] Electron-impact spectra of the uncracked dicyclopentadiene were taken at several angles and used to check the completeness of the cracking procedure. No structure in any of the 1,3-cyclopentadiene results could be attributed to dicyclopentadiene. The samples of 1,3-cyclohexadiene and 1,3-cycloheptadiene, with stated purities of 99% and 97%, respectively, were obtained from the Aldrich Chemical Company. The 1,3-cyclohexadiene sample was used as soon after its arrival as possible to minimize build up of benzene, cyclohexene, or 1,3,5-hexatriene impurities.[12] The cycloheptadiene sample was kept in an ice bath prior to its use, and its spectra showed no change with sample age over the period of two weeks during which these spectra were obtained.

IV. RESULTS AND DISCUSSION

Figures 2–4 display the low-energy portion of the spectra of the three cyclic dienes at both high and low scattering angles. Figure 5 shows the higher energy-loss region of the spectra of these molecules. The differential cross sections (DCS) for the elastic peak and various transitions are shown for both high and low impact energies in Figs. 6–8. The technique for obtaining these differential cross sections has been described previously.[1–3] The DCS values are given in terms of arbitrary units specified by setting the elastic DCS at $\theta = 40°$, for a given impact energy, equal to unity. The arbitrary units thus determined are different for each molecule and impact energy but are the same for all curves of a given molecule at a given impact energy.
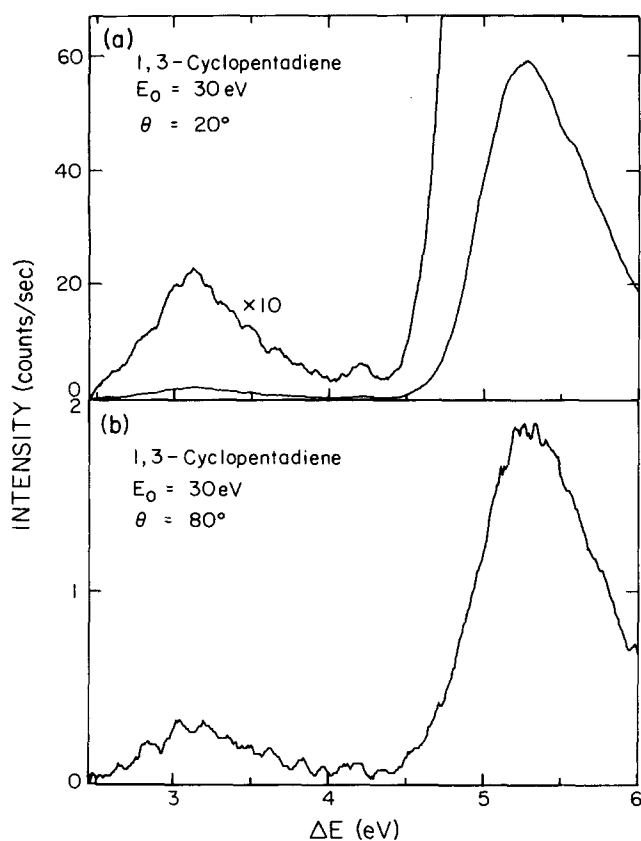
FIG. 2. Electron energy-loss spectrum of 1,3-cyclopentadiene at a scattering angle of (a) 20° and (b) 80°; 30 eV incident electron energy; 50 nA incident beam current; 8 mtorr sample pressure reading from an uncalibrated Schulz–Phelps gauge; resolution approximately 0.15 eV (FWHM). Flat sections in the 80° spectrum are the result of computer roundoff.

A. Spectral features

1. 1,3-Cyclopentadiene

The lowest energy transition observed in the 1,3-cyclopentadiene spectrum has an effective Franck–Condon region (outside of which we can no longer detect the transition) extending from 2.5 to 3.9 eV, with the intensity maximum occurring at 3.10 eV. The DCS of this transition at 30 eV impact energy [see Fig. 6(a)] is much more isotropic than are the other DCS curves, decreasing monotonically by less than a factor of 5 over the angular range 10° to 80°. At 50 eV impact energy this transition is relatively less intense with respect to the other transitions of Fig. 6(b) and its DCS is also much more isotropic than are the DCS curves for the other transitions in that figure. This DCS behavior permits us to assign this transition to a singlet → triplet excitation.[1,2] Our value of 3.10 eV for the excitation energy corresponding to the intensity maximum is identical to that obtained by Evans[25] using the oxygen perturbation technique. It is also in good agreement with the value of 3.4 eV predicted by the semiempirical calculations of Barfield,[40] and very close to the ab initio calculated value of 2.95 eV for the first triplet in s-cis-butadiene.[44] On this basis we assign this transition to the $\tilde{X}\,^1A_1$ → $1\,^3B_2$ ($N \to T_1$) excitation.

At 5.26 eV we observe an intensity maximum of a broad transition [Figs. 2(a) and 5(a)]. The DCS of this excitation at 50 eV impact energy [Fig. 6(b)] decreases by a factor of 90 as the scattering angle increases from 10° to 80°, while at 30 eV impact energy [Fig. 6(a)], the corresponding change in the DCS is greater than a factor of 100. This forward-peaked property of the DCS is characteristic of a singlet → singlet symmetry-allowed transition, and is consistent with its assignment as the $\tilde{X}\,^1A_1$ → $^1B_2$ ($N \to V_1$) excitation. Both Scheibe and Grieneisen[16] and Pickett et al.[17] observed five weak peaks separated by approximately 0.095 eV on the low-energy side of the $N \to V_1$ absorption. The resolution we used in obtaining these spectra, about 0.15 eV, did not permit us to observe this structure. On the high-energy side of the $N \to V_1$ transition, between 5.5 and 6 eV energy loss, we detect several apparently superimposed peaks which have been previously reported in optical studies.[16–18] They will be discussed in Sec. IV. B.

Between 6.15 and 6.7 eV, there is another intense feature with resolvable peaks at 6.28 and 6.41 eV [Fig. 5(a)]. In the corresponding optical spectra,[17,18] complex higher resolution vibronic structure has been observed and interpreted in terms of either one or two electronic transitions. At 50 eV impact energy, the DCS of this feature decreases by a factor of nearly 200 as the scat-
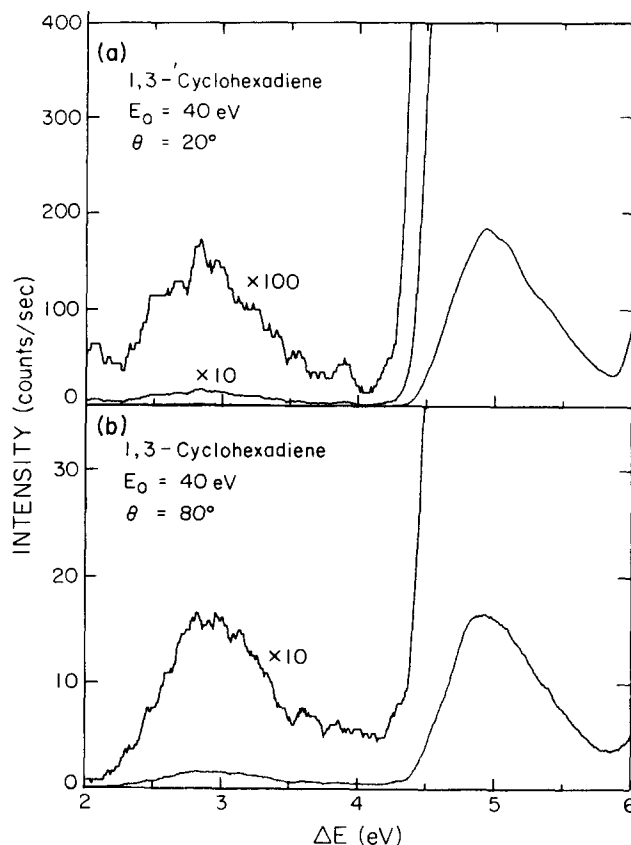

FIG. 3. Electron energy-loss spectrum of 1,3-cyclohexadiene at a scattering angle of (a) 20° and (b) 80°; 40 eV indicent electron energy; 40 nA incident beam current; 5 mtorr sample pressure reading from an uncalibrated Schulz–Phelps gauge; resolution approximately 0.12 eV(FWHM). Flat sections in the spectra are the result of computer roundoff.
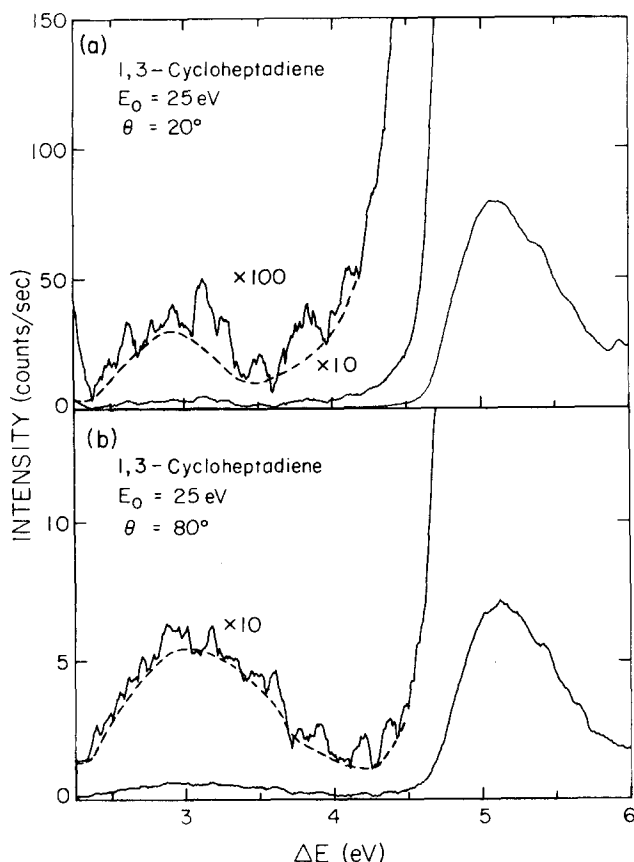
FIG. 4. Electron energy-loss spectrum of 1,3-cycloheptadiene at a scattering angle of (a) 20° and (b) 80°; 25 eV incident electron energy; 30 nA incident beam current; 4 mtorr sample pressure; resolution approximately 0.09 eV(FWHM). The dashed line represents our estimate for the $S_0 \rightarrow T_1$ band system profile.

tering angle increases from 10° to 80°. In addition, the ratio of this DCS to that of the $N \rightarrow V_1$ excitation changes by a factor of only 2 over the same angular range. The observed band shape shows no discernible change over the angular region studied. This behavior is consistent with that expected for either a single electronic transition,[52] or for two superimposed transitons which have essentially the same angular dependence. As a result, we cannot differentiate between these two possibilities.

The region of the most intense inelastic scattering in the 1,3-cyclopentadiene spectrum occurs from approximately 7.2 to 8.6 eV with an intensity maximum at 7.88 eV. This feature appears to be due to a broad and structureless transition with smaller peaks superimposed on it. Robin[37] has suggested that the corresponding feature in the optical spectra results from the superposition of the $N \rightarrow V_2$ ($\bar{X}\,^1A_1 \rightarrow \,^1A_1$) and $N \rightarrow V_3(\bar{X}\,^1A_1 \rightarrow \,^1A_1)$ excitations. For s-cis-butadiene, these transitions are calculated to occur at 6.66 and 7.89 eV.[44]

2. 1,3-Cyclohexadiene

Figure 3 shows the lower energy-loss portion of the 1,3-cyclohexadiene spectrum. With an effective Franck–Condon region extending from 2.1 to 3.8 eV, the lowest energy, electronic transition is observed to have an

intensity maximum at 2.94 eV. As seen in Fig. 7, the DCS curves for this transition at both 20 and 40 eV impact energies are nearly isotropic over the angular range, 20° to 80°. This behavior is typical of a singlet → triplet transition. The close correlation between the observed excitation energy and that calculated for s-cis-butadiene by Shih et al.[44] (2.95 eV) and Allinger et al.[41] (3.01 eV), confirms the expected assignment of this transition as the $N \rightarrow T_1$ ($\bar{X}\,^1A_1 \rightarrow 1\,^3B_2$) excitation. There is also excellent agreement between our result and that obtained from O_2 perturbation (2.9 eV).[25]

The intense transition peaking at 4.94 eV was assigned to the $N \rightarrow V_1$ ($\bar{X}\,^1A_1 \rightarrow \,^1B_2$) transition by Mulliken.[36] The
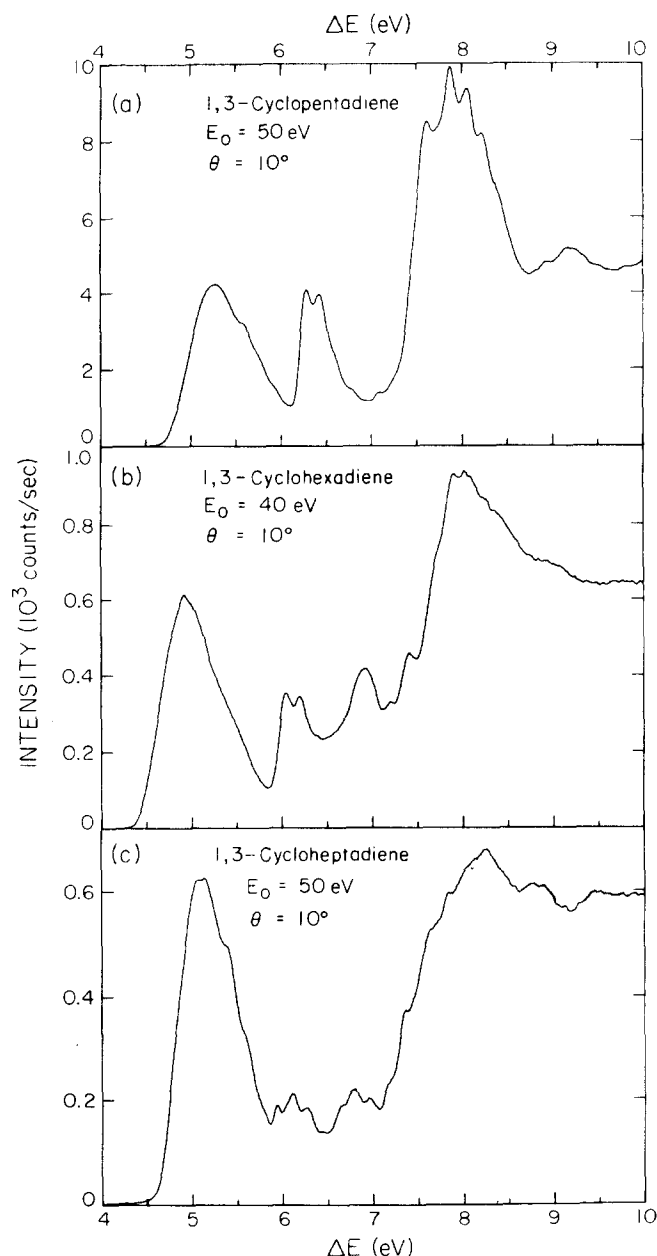

FIG. 5. Electron energy-loss spectra of 1,3-cyclopentadiene, 1,3-cyclohexadiene, and 1,3-cycloheptadiene over the energy-loss region 4–10 eV. Experimental conditions for each molecule are those given in the captions of Figs. 2–4.
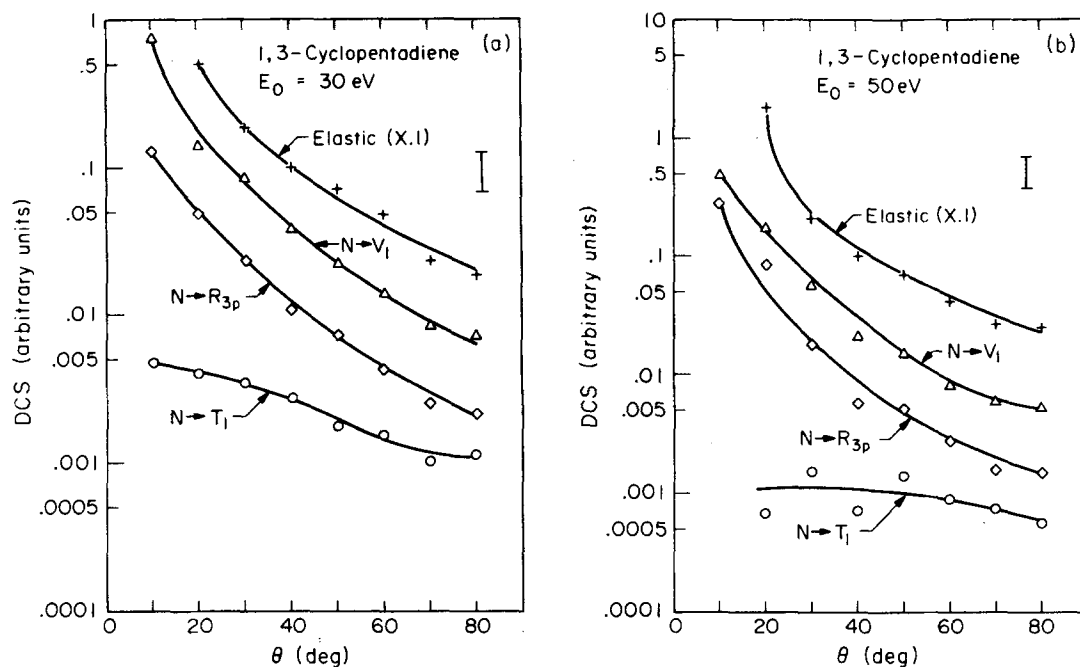
FIG. 6. Relative differential cross sections of 1,3-cyclopentadiene as a function of scattering angle at an incident energy of (a) 30 eV and (b) 50 eV. The elastic DCS was multiplied by 0.1 before plotting. The $N \rightarrow R_{3p}$ is the DCS for the $\pi \rightarrow 3p$ Rydberg transition occurring at about 6.3 eV. The error bar beneath the heading represents the uncertainty ($\pm 30\%$) for an inelastic DCS value.

DCS curves for this excitation (Fig. 7) are forward peaked, decreasing by factors of 16 and 80 as the scattering angle increases from $10°$ to $80°$, at impact energies of 20 and 40 eV, respectively. On the high energy side of the $N \rightarrow V_1$ transition, there is a slight indication of vibrational structure suggesting the possibility of the presence of a very small amount of 1,3,5-hexatriene (Fig. 3). At higher energy losses, three peaks are ob-

served at 6.05, 6.20, and 6.39 eV [Fig. 5(b)]. These transitions were also observed in previous optical studies.[18,19,22] The next transition is observed at 6.90 eV. A peak is seen at about 7.0 eV in a recent optical study[22] and at 6.9 eV in a 50 keV incident electron energy electron-impact study.[23] However, an earlier optical study showed a feature peaking at 6.81 eV and smooth continuous absorption in the 6.85–7.1 eV region. Ben-
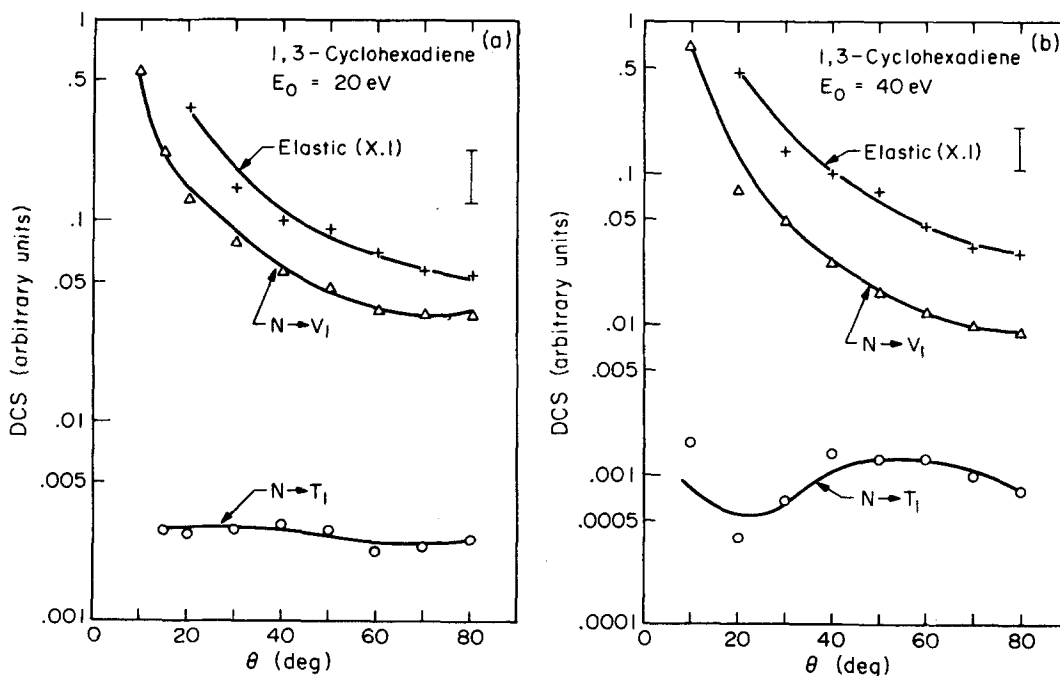

FIG. 7. Same as Fig. 6 except for 1,3-cyclohexadiene at (a) 20 eV and (b) 40 eV.
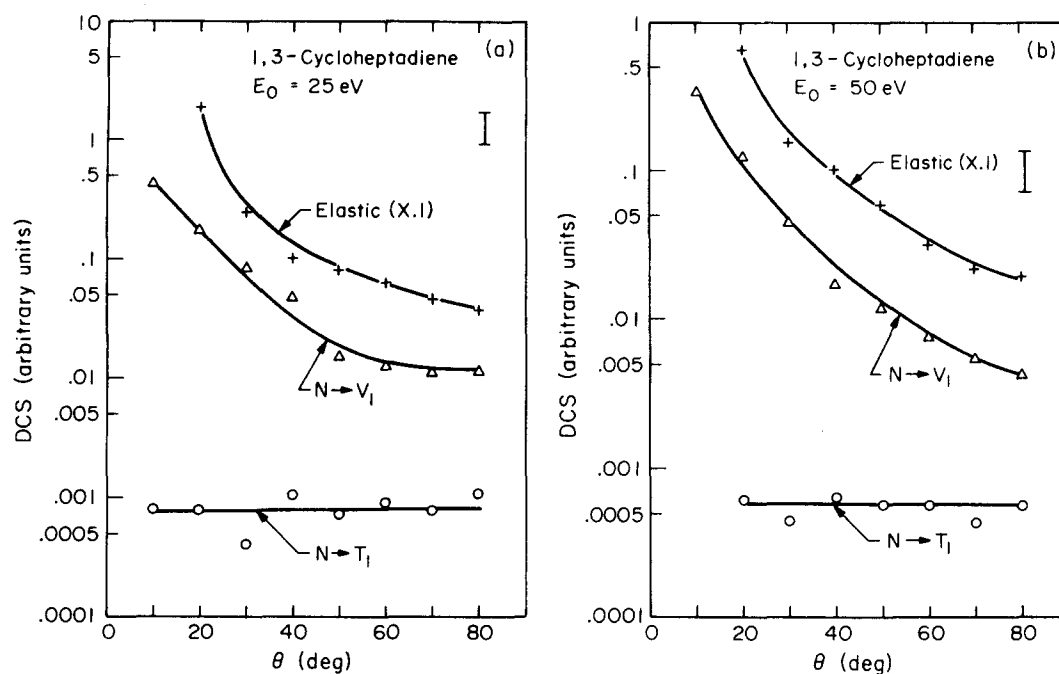
FIG. 8.   Same as Fig. 6 except for 1,3-cycloheptadiene at (a) 25 eV and (b) 50 eV.

zene is known to have an extremely intense transition peaking at 6.93 eV and having an optical oscillator strength of 1.2.[53] At low scattering angles, the intensity ratio in the electron-impact spectrum between two singlet→singlet transitions is of the same order as that of their optical oscillator strengths. Consequently, the observed ratio of the area under the $N \rightarrow V_1$ transition to that of the 6.90 eV transition could result from the presence of as little as a 2% benzene contamination, since the f value for the $N \rightarrow V_1$ excitation in 1,3-cyclohexadiene is 0.13.[22] This 6.90 eV peak may therefore be the result of a benzene impurity. On the other hand, the intensities of the transitions observed at 7.0 eV in the optical study,[22] at 6.90 eV in the high incident energy electron impact spectra,[23] and at 6.90 eV in our 40 eV, 0° spectra relative to the other transitions in those spectra are about the same. If these features were attributed to a benzene impurity, this would require the concentration of this impurity to be approximately the same in all three studies. While such a coincidence is possible, it seems unlikely. Nevertheless, to determine more reliably whether this excitation is due to a benzene impurity requires further experimental study in which special care is taken with respect to sample purity. As in 1,3-cyclopentadiene, a broad intense transition, which has been suggested to be due to $N \rightarrow V_2$, V_3 excitations,[37] is observed between approximately 7.2 and 8.8 eV. Several distinct peaks appear to be superimposed on this feature.

3. 1,3-Cycloheptadiene

Figures 4 and 5(c) show both the low and high energy-loss portions of the 1,3-cycloheptadiene spectrum. At 2.99 eV, the intensity maximum of a low-lying transition is observed. This transition has an effective Franck–Condon region extending from 2.4 to 3.9 eV.

The DCS for this transition is essentially isotropic at both 25 and 50 eV impact energies (Fig. 8). This allows us to assign this excitation as the $N \rightarrow T_1$ singlet→triplet transition, analogous to similar transitions observed in 1,3-cyclopentadiene and 1,3-cyclohexadiene.

The next feature in the 1,3-cycloheptadiene spectrum is a broad excitation with an intensity maximum occurring at 5.08 eV. The DCS of this transition decreases by factors of 80 and 36 at impact energies of 50 and 25 eV, respectively, as the scattering angle increases from 10° to 80° (Fig. 8). This transition is analogous to the corresponding excitations observed in the other two molecules. We can assign it to the $N \rightarrow V_1$ ($\tilde{X}\,^1A_1 \rightarrow {}^1B_2$) excitation. We also observe two weaker shoulders superimposed on the high-energy side of the $N \rightarrow V_1$ transition with estimated intensity maxima occurring at 5.41 and 5.61 eV. The available optical spectrum extends to 5.46 eV,[24] but does not show the first additional feature just mentioned. This optical spectrum was obtained in the liquid phase and if the transitions being considered correspond to Rydberg excitations, we would expect that under these conditions they would be less intense than in the gas phase. The spacing of 0.20 eV (~ 1600 cm^{-1}) between those two transitions is in the range expected for vibrational splittings, since for the ground state of 1,3-cycloheptadiene, the symmetric and asymmetric C=C–C fundamental vibration wavenumbers are 1613 and 1646 cm^{-1}, respectively.[54] This spacing is consistent with features which are different vibronic peaks of the same electronic transition. Their electronic nature is discussed in Sec. IV. B.

Several additional transitions occur above the $N \rightarrow V_1$ excitation. Between 5.9 and 7.0 eV, six sharp, but weak transitions are observed [Fig. 5(c)]. These appear to correspond to two different electronic excitations,

each with three vibronic components occurring at 5.95, 6.13, and 6.27 eV, and 6.65, 6.79, and 6.97 eV, respectively. Possible assignments of these features are discussed in Sec. IV. B. The region of most intense absorption above the $N \rightarrow V_1$ transition occurs between 7.2 and 8.6 eV. It is analogous to the presumed $N \rightarrow V_2$, V_3 features observed to peak at 8.03 and 7.88 eV in 1,3-cyclopentadiene and 1,3-cyclohexadiene, respectively. There appear to be several smaller peaks superimposed on this absorption.

B. Rydberg transitions

In each of the three molecules studied in this investigation, we have observed many transitions in addition to the $N \rightarrow V_1$ and apparent $N \rightarrow V_2$, V_3 excitations. These additional transitions appear to have fairly sharp structure and occur both as isolated peaks and as superimposed structure on other peaks. Specific assignment of them is quite difficult. McDiarmid[55] recently completed a new interpretation of the ultraviolet spectrum, and in particular the Rydberg states, of s-trans-1,3-butadiene. The analysis was based on the separation of electronic origins and an assignment of the vibronic transitions related to each origin by studying the spectra of different deuterium-substituted molecules. This procedure for assignment of Rydberg series is much more reliable than one which bases the entire interpretation on the spectrum of a single isotopic molecule. However, we cannot use this multiple isotope technique because the resolution of our experiment is not high enough. Rather than attempting to make definitive assignments of Rydberg series, we will discuss the likely assignments of the more apparent of these transitions. Although these excitations are most likely Rydberg in nature, the possibility that they are valence transitions cannot be entirely ruled out, since an $N \rightarrow V_4$ transition is expected to occur above the $N \rightarrow V_1$ excitation in the spectra of these molecules.[36]

In both 1,3-cyclopentadiene (vertical I.P. = 8.566 eV[47]) and 1,3-cycloheptadiene (vertical I.P. = 8.31 eV[50]), the structure we observed superimposed on the high-energy side of the $N \rightarrow V_1$ transition has a term value of about 23,000 cm^{-1} (2.9 eV). This value is quite appropriate for a $\pi \rightarrow 3s$ Rydberg excitation.[56,57] In 1,3-cyclohexadiene (vertical I.P. = 8.25 eV),[50] we also observe structure in the equivalent energy-loss region but in this case it could be due to a small amount of 1,3,5-hexatriene impurity.[21,22,49] Another group of transitions are clearly observed in the 6.0–6.4 eV region in all three molecules studied. The corresponding term values lie near 17 500 cm^{-1} (2.2 eV), which is reasonable for $\pi \rightarrow 3p$ Rydberg excitations.[56,57] In addition, high pressure and crystal spectra of 1,3-cyclohexadiene obtained by Robin[37] indicate that the transition at 6.3 eV is definitely Rydberg in nature.

In each of the molecules studied, some structure is observed superimposed on the presumed $N \rightarrow V_2$, V_3 features. In the spectra of 1,3-cyclohexadiene and 1,3-cycloheptadiene, these transitions are quite weak and appear to be higher elements of Rydberg series. However, in 1,3-cyclopentadiene this structure is quite pronounced [Fig. 5(a)]. It is interesting to consider

whether this structure corresponds to vibronic components of the (apparent) $N \rightarrow V_2$, V_3 transitions or is Rydberg in nature. Byrne and Ross[58] arrived at the empirical rule that the lowest singlet excited state of a polyatomic molecule in the gas phase will exhibit the sharpest vibronic structure. The higher states tend to show much more diffuse vibrational structure, due to the many means of intramolecular relaxation available, which shorten the excited state lifetime, leading to major uncertainty broadening. They also point out that Rydberg transitions may be exceptions to this rule because they are only weakly coupled to the valence manifold and their relaxation times are consequently longer. With this information and noting that the $N \rightarrow V_1$ transition is structureless, we feel that the peaks on the apparent $N \rightarrow V_2, V_3$ transitions of 1,3-cyclopentadiene are probably Rydberg in nature. In all of these molecules, broad superexcited transitions were observed above the first ionization potential. These superexcited state transition energies are listed in Table I.

C. Discussion

The data obtained in this study clearly demonstrate that there are many similarities between the spectra of these three cyclic dienes. As indicated in Table I, each molecule exhibits an $N \rightarrow T_1$, $(\tilde{X}^1A_1 \rightarrow 1\,^3B_2)$ transition near 3.0 eV, with quite similar effective Franck–Condon envelopes. Since the $N \rightarrow T_2$ $(\tilde{X}^1A_1 \rightarrow 1\,^3A_2)$ excitation is predicted to occur at 4.90 eV in s-cis-1,3-butadiene,[44] a second spin-forbidden transition should exist at approximately this energy in each of the cyclic dienes. This transition has not been observed and probably is hidden under the $N \rightarrow V_1$ excitations. However, we can at least estimate a lower bound above which this transition should lie. In 1,3-cyclopentadiene we would not be able to observe the $N \rightarrow T_2$ transition if it lay above 4.7 eV (due to masking by the $N \rightarrow V_1$ transition), while in the other two molecules this limit is 4.5 eV.

Each molecule exhibits a strong structureless $N \rightarrow V_1$ transition, as well as the even more intense feature presumed to be the $N \rightarrow V_2$, V_3 excitations. We also see (Fig. 5) that as the ring size increases, the $N \rightarrow V_1$ transition becomes more intense relative to the $N \rightarrow V_2$, V_3 feature. The relative insensitivity of the locations of valence transitions to increasing ring size is consistent with excitations being localized to the dienyl portion of the molecule, and therefore somewhat insensitive to overall molecular geometry. Although the suggested assignments of Rydberg transitions in these molecules are tentative, it appears that the term value of the 3s and 3p Rydberg states vary little with ring size.

It is also interesting to compare the present results for the triplet states of 1,3-cyclopentadiene with those from previous investigations of furan (C_4H_4O), thiophene (C_4H_4S), and pyrrole (C_4H_4NH),[59,60] three heterocycles which also contain two conjugated double bonds locked into an s-cis conformation. In these molecules, two low-lying triplets (T_1 and T_2) were observed, with excitation energies listed in Table II. The locations of these triplet states and the energy splitting between them are similar to those of the first two triplet states

TABLE II. Triplet excitation energies in some cyclic molecules.

	T_1	T_2
Benzene	3.89[a]	4.85[a]
Furan	3.99[b]	5.22[b]
Thiophene	3.75[b]	4.62[b]
Pyrrole	4.21[b]	5.1[c]
1,3-Cyclopentadiene	3.10	>4.7[d]

[a]Reference 61.
[b]Reference 59.
[c]Reference 60.
[d]The second singlet → triplet transition in 1,3-cyclopentadiene is estimated to lie above this value in the present study.

of benzene.[61] This correlation suggests that for these valence transitions, the five-membered heterocycles may be considered to have appreciable aromatic character, resulting from partial participation of two formally nonbonding electrons on the heteroatom in the resonance π electron system.

In contrast, the lowest triplet state energy in 1,3-cyclopentadiene is 0.85 eV less than both the lowest benzene triplet state energy as well as the average energy of this state in furan, thiophene, and pyrrole. Furthermore, the splitting between T_1 in 1,3-cyclopentadiene and the unobserved T_2 is probably greater than 1.6 eV, which is considerably larger than the 0.96 eV T_1-T_2 splitting in benzene,[61] or the 1.0 eV average splitting in the five-membered heterocycles.[59,60] These results indicate that 1,3-cyclopentadiene can be regarded as a typical conjugated diene, and that, to a first approximation, hyperconjugation of the double bond π orbitals with the CH_2 orbitals does not play an important role in determining the excitation energies of the lowest triplet states.

V. SUMMARY

A single, low-lying triplet state has been observed near 3 eV energy loss in cyclic 1,3-dienes with five, six, and seven carbon atoms. $N \to V_1$ and presumed $N \to V_2$, V_3 singlet → singlet transitions were also observed in each molecule. The excitation energies of these valence transitions are relatively insensitive to the ring size and geometry. This behavior is consistent with the concept that these transitions are localized in the dienyl region of the molecule. Assignments of transitions to $3s$ and $3p$ Rydberg states have been made on the basis of the term values of these features. Several previously unreported states lying above the first ionization potential have been located. Comparison of the location of the two lowest lying triplet states in 1,3-cyclopentadiene with those in furan, thiophene, pyrrole, and benzene indicates that 1,3-cyclopentadiene is a typical dienyl π electron system and that hyperconjugation of the CH_2 orbitals to the dienyl π electron system is negligible in those states.

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