

Excited electronic states of cyclohexene, 1,4-cyclohexadiene, norbornene, and norbornadiene as studied by electron-impact spectroscopy^{a)}

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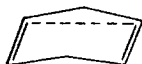
The excited electronic states of cyclohexene, 1,4-cyclohexadiene, norbornene (bicyclo[2.2.1]-2-heptene), and norbornadiene (bicyclo[2.2.1]-2,5-heptadiene) have been studied by electron impact at scattering angles from 5° to 80°, and impact energies of 30 and 50 eV. Low-lying features with intensity maxima at 4.24 eV in cyclohexene and 4.10 eV in norbornene are identified as singlet → triplet transitions. Similar features in the spectra of 1,4-cyclohexadiene and norbornadiene extending from 3.4 to 5.4 eV and 2.9 to 4.5 eV, respectively, are believed to result from superposition of two low-lying singlet → triplet transitions in each molecule. In norbornadiene, these features have estimated intensity maxima at 3.4 and 3.9 eV, while in 1,4-cyclohexadiene they appear to be more highly overlapped, yielding a single intensity maximum at 4.29 eV. The singlet → triplet excited state spectra of these molecules are discussed from the point of view of a model in which ethylene units interact via through-bond and through-space effects. In each of these four molecules, transitions to several superexcited states are observed.

I. INTRODUCTION

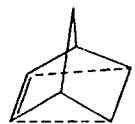
Low energy, variable angle, electron-impact spectroscopy is a powerful technique for studying both optically forbidden and optically allowed electronic transitions.^{1,2} Using this technique, we have investigated the electronic spectra of cyclohexene, 1,4-cyclohexadiene, norbornene (bicyclo[2.2.1]-2-heptene), and norbornadiene (bicyclo[2.2.1]-2,5-heptadiene). In this paper we report the observation of the lowest singlet → triplet transition in each of these molecules and discuss the effects of ground-state molecular geometry on the excited state manifold. This geometry is indicated below:



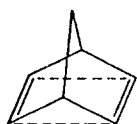
Cyclohexene



1,4 Cyclohexadiene



Norbornene



Norbornadiene

All four molecules have a boat-shaped, six-membered carbon ring with either one or two double bonds on opposite sides of the planar or nearly planar four-carbon

portion of that ring (indicated with the help of the dashed lines, which do not represent bonds). In addition, for the norborna- compounds there is a one-carbon, two-bond bridge connecting the two carbons of the six-membered ring on the "bow" and "stern" of the boat.

Spectroscopic investigation of both the singlet and triplet excited states of norbornadiene and 1,4-cyclohexadiene permits us to probe the interaction of non-conjugated ethylenic units. These two molecules represent, respectively, systems in which through-space and through-bond interactions are believed to be important.^{3,4} Norbornene and cyclohexene have been studied to provide a comparison between the isolated double-bond and the dienyl systems. In addition, the spectra of norbornene and cyclohexene are interesting when compared to those of methyl-substituted ethylenes.⁵

Information about the nature of the excited electronic states observed in an electron-impact spectrum can be obtained by studying the dependence of the intensity of each transition on the impact energy (E_0) and scattering angle (θ).^{1,2} In electron-impact spectroscopy at impact energies about 15 eV or more above the excitation threshold, the differential cross section (DCS) of a transition which is both electric dipole- and spin-allowed is sharply forward peaked, decreasing by approximately one to two orders of magnitude as the scattering angle increases from 10° to 80°. ^{1,2} In contrast, transitions involving changes of unity in the molecular spin quantum number, such as singlet → triplet excitations, have a more nearly isotropic DCS over the same angular region.^{1,2} Such transitions occur by the mechanism of electron exchange.⁶ Excitations which are spin-allowed but electric dipole-forbidden have DCS curves which are forward peaked, but often not as much as those of fully allowed transitions.^{7,8} Finally, for impact energies about 15 eV or more 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.^{1,2}

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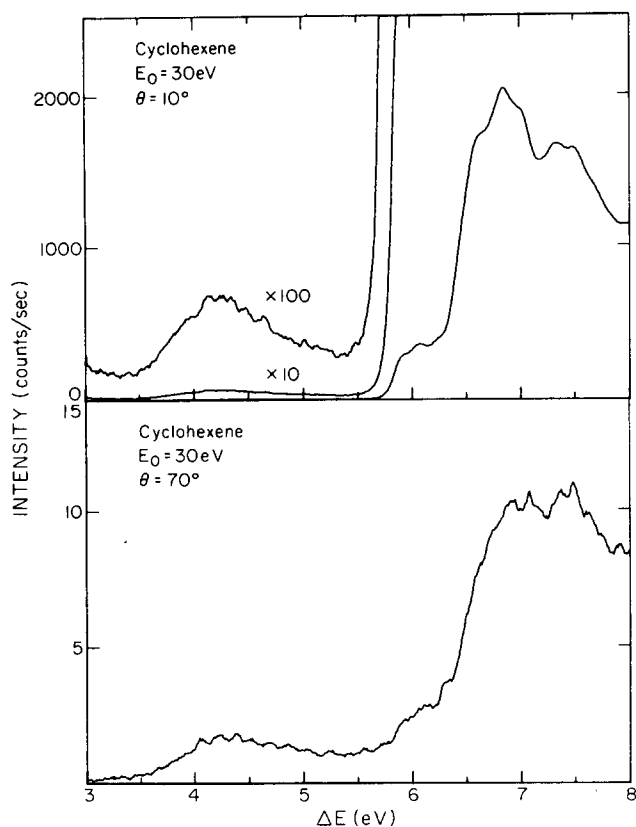


FIG. 1. Electron energy-loss spectrum of cyclohexene at scattering angles of 10° and 70° ; 30 eV incident electron energy; 60 nA incident beam current; 6 mtorr sample pressure, as indicated by an uncalibrated Schulz-Phelps ionization gauge. Apparent spectral features whose intensity is less than 2 counts/sec and whose width is less than 0.2 eV are irreproducible and are due to instrumental noise.

II. EXPERIMENTAL

The apparatus used in this study has been described previously by Kuppermann and co-workers.^{1,2} In the present experiments, the electron-impact spectra of cyclohexene, 1,4-cyclohexadiene, norbornene, and norbornadiene in the energy-loss region 0–13 eV were studied at impact energies of 30 and 50 eV, and scattering angles from 5° to 80° . Sample pressures in the scattering chamber were typically 7 mtorr, as indicated by an uncalibrated Schulz-Phelps ionization gauge, while the incident electron beam current was approximately 100 nA. The energy resolution, as measured by the full width at half maximum (FWHM) of the elastically scattered peak, was set at about 0.15 eV. The norbornene and norbornadiene samples were obtained from Aldrich Chemical Company, with stated purities of 99%. Two samples of cyclohexene, from Aldrich Chemical Co. (99% stated purity) and Chemical Samples Co. (99.8% stated purity) were used. Structure due to trace impurities was observed in the cyclohexene spectra at scattering angles less than 20° when using the Aldrich sample. This structure was not present when using the sample supplied by Chemical Samples Co. Samples of 1,4-cyclohexadiene were obtained from Aldrich Chemical Co. (97% stated purity) and from PCR Inc. (99% stated purity). The sample from Aldrich was

used for only a few spectra because a benzene impurity gave a noticeable peak at 6.93 eV. Most of the spectra were taken with the PCR sample where the benzene peak was not discernible. All samples were subjected to several liquid nitrogen freeze-pump-thaw cycles prior to use. The data were analyzed and the DCS values were calculated as described previously.⁸

III. RESULTS AND DISCUSSION

A. Cyclohexene and Norbornene

Figures 1 and 2 show spectra of cyclohexene and norbornene at both low and high scattering angles. These spectra are quite similar to those of the methyl-substituted ethylenes, in which three principal transitions, due to excitations from the carbon-carbon double bond, are observed.⁵ These three principal kinds of transitions are $\pi \rightarrow \pi^*$, singlet-triplet valence excitations, designated $N-T$; the corresponding $\pi \rightarrow \pi^*$, singlet-singlet transitions, designated $N-V$; and $\pi \rightarrow 3s$ Rydberg transitions, designated $N-R$.^{5,9,10} The lowest energy excitations of the two molecules being considered occur with maximum intensity at 4.24 eV in cyclohexene and 4.10 eV in norbornene. Figures 3 and 4 give the DCS curves at 30 eV impact energy for several of the

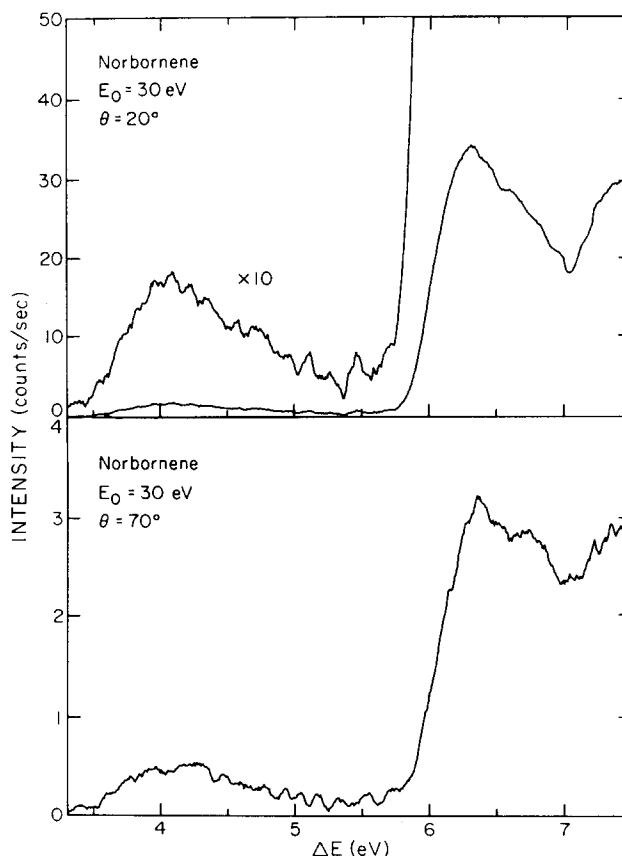


FIG. 2. Electron energy-loss spectrum of norbornene at scattering angles of 20° and 70° ; 30 eV incident electron energy; 70 nA incident beam current; 8 mtorr sample pressure, as indicated by an uncalibrated Schulz-Phelps ionization gauge. Apparent spectral features whose intensity is less than 2 counts/sec and whose width is less than 0.2 eV are irreproducible and are due to instrumental noise.

transitions observed in these spectra. The DCS's of the 4.24 and 4.10 eV excitations are relatively independent of angle. As noted previously, this behavior allows us to assign them as singlet-triplet transitions. For comparison, the $N \rightarrow T$ transition intensity maxima in the methyl substituted ethylenes fall between 4.32 and 4.10 eV.⁵ The excitations presently reported are undoubtedly the analogous $\pi \rightarrow \pi^*$, $N \rightarrow T$ transitions of cyclohexene and norbornene.

The next transition detected in the cyclohexene spectrum occurs with an intensity maximum at 6.11 eV. Upon close study of the low-angle spectrum (Fig. 1), we find that three vibronic peaks are observed at 5.92, 6.07, and 6.22 eV. These have been seen optically and are believed to result from the excitation of zero, one, and two C=C vibration quanta, respectively. Initially, this transition was assigned by Potts¹¹ as the $N \rightarrow T$ excitation. Subsequent optical studies performed by Evans,¹² involving the effects of high-pressure nitrogen, led, however, to a $\pi \rightarrow 3s$, $N \rightarrow R$, Rydberg assignment. Our results leave no doubt as to the singlet-singlet nature of this transition: The DCS of this feature, shown in Fig. 3, is sharply forward peaked. In norbornene, optical studies, with inherently higher resolution than our electron-impact spectra, reveal a sharp absorption at $48\,150\text{ cm}^{-1}$ (5.97 eV) followed by a second peak 280 cm^{-1} higher in energy.¹³ These have been assigned to the $\pi \rightarrow 3s$ Rydberg transition.¹⁰ We do not observe these features.

The most intense feature in both the cyclohexene and norbornene spectra is the $N \rightarrow V$ transition occurring at 6.85 and 6.35 eV, respectively, in these two molecules.

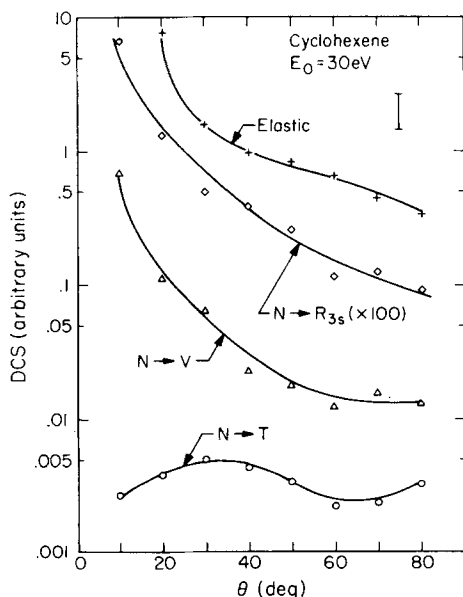


FIG. 3. Relative elastic and inelastic differential cross sections for cyclohexene at an incident electron energy of 30 eV. The elastic differential cross section is normalized to 1.0 at $\theta = 40^\circ$. The arbitrary units for all transitions of a given molecule at a particular impact energy are the same. The arbitrary units are not the same for different molecules or the same molecule at different impact energies. The error bar beneath the heading represents the estimated uncertainty ($\pm 30\%$) for an inelastic DCS value.

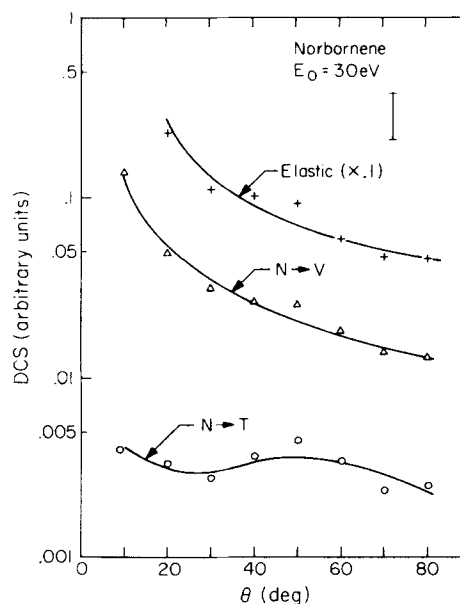


FIG. 4. Relative elastic and inelastic differential cross sections for norbornene at an incident electron energy of 30 eV. The normalization procedure for the arbitrary ordinate units is the same as for Fig. 3. The error bar beneath the heading represents the estimated uncertainty ($\pm 30\%$) for an inelastic DCS value.

These excitations, as expected for singlet-singlet excitations, have sharply forward peaked DCS curves (Figs. 3 and 4). The positions of their intensity maxima are in good agreement with optical studies, which give transition energies of 6.79 eV for cyclohexene¹¹ and 6.34 eV for norbornene.¹³ In cyclohexene, shoulders appear on both the low and high sides of the $N \rightarrow V$ transition. These are most likely either vibronic components of the $N \rightarrow V$ transition, or superimposed Rydberg structure. In both molecules, additional transitions, which appear to be singlet-singlet in nature, are observed at higher energy losses (Table I). The exact nature of these excitations is unknown; it seems likely that they are elements of various Rydberg series converging to the first and higher ionization potentials.

It is interesting to note that while the $N \rightarrow R$ transitions in norbornene and cyclohexene occur at 5.97 and 6.07 eV, respectively, and have nearly identical term values of 3.00 and 3.05 eV, the $N \rightarrow V$ transition intensity maxima differ by 0.50 eV. It seems that in norbornene the V state is stabilized relative to the ground state as compared to cyclohexene. This stabilization cannot be presently explained and further theoretical studies would be helpful.

B. 1,4-cyclohexadiene and norbornadiene

1. Introduction

In order to understand the spectroscopy of these molecules, the interaction of the ethylenic units must be considered. Hoffmann and co-workers^{3,4} give a summary of the interactions of orbitals through space and through bonds. When the geometry of a molecule permits direct spatial overlap of the orbitals on each of the chromophores, the interaction is of the through-

TABLE I. Transition energies of cyclohexene, norbornene, 1,4-cyclohexadiene, and norbornadiene.^a

	$N \rightarrow T$	$N \rightarrow R$	$N \rightarrow V$	Additional singlet \rightarrow singlet transitions		
Cyclohexene	4.24[3.4-5.3] ^b	5.92 ^c , 6.07 ^c , 6.22 ^c (6.10) ^d	6.85 (6.79) ^e	7.40, 8.10, 8.40, 8.93, 9.50, 10.35 11.07, 11.85, 12.15, 13.60, 13.95 14.65		
Norbornene	4.10[3.4-5.1] ^b	(5.97) ^f	6.35 (6.34) ^f	7.4, 8.25, 8.97, 10.3, 11.90 12.8		
	$N \rightarrow T_1 + T_2$	$N \rightarrow V_1$ or $\pi_2 \rightarrow 3s$	$N \rightarrow V_2$ or $\pi_2 \rightarrow 3p$	$\pi_1 \rightarrow 3s$	$N \rightarrow V_3$	Additional singlet \rightarrow singlet transitions
1,4-Cyclohexadiene	4.29[3.4-5.4] ^b (4.3) ^g	6.15 (6.20) ^g	6.4, 6.6	7.1 ^c , 7.3 ^c	7.95 (8.1) ^g	9.00, 9.25, 9.90, 10.30, (10.14) ^h , (10.45) ^h 11.30, 12.05, 12.95 (11.3) ^h , (12.0) ^h , (13.0) ^h
	$N \rightarrow T_1 + T_2$	$N \rightarrow V_1$	$N \rightarrow V_2$ or $\pi_2 \rightarrow 3s$	$N \rightarrow V_3$ or $\pi_1 \rightarrow 3s$	Additional singlet \rightarrow singlet transitions	
Norbornadiene	3.4, 3.9 [2.9-4.5] ^b	5.23 (5.39) ⁱ	5.95 (5.89) ⁱ	6.85 (6.88) ^j	7.2, 7.5, 7.9, 8.8, 9.8 10.4, 11.45, 13.0	

^aTransition energies listed correspond to intensity maxima. The estimated accuracy of these values is ± 0.05 eV. Values in parentheses are from previous experiments. All other values are from the present study.

^bApparent Franck-Condon region observed in present study.

^cThese are believed to be vibronic components of the same electronic transition.

^dReference 10.

^eReference 11.

^fReference 13.

^gReference 22.

^hReference 24.

ⁱAppears as a shoulder in the optical spectrum of Ref. 19.

^jReference 21a.

space type. Norbornadiene provides an example of this form of interaction.^{3,4} It splits both sets of degenerate π and π^* orbitals of the isolated ethylenic moieties. This splitting is evidenced by a comparison of the vertical π ionization potential of norbornene, 8.97 eV¹⁴ and the vertical π ionization potentials of norbornadiene, 8.69 and 9.57 eV.¹⁴

The through-space interaction is expected to be small in 1,4-cyclohexadiene because the molecule is almost planar. The dihedral angle of 1,4-cyclohexadiene is 159.3°,¹⁵ compared to 115.6° for norbornadiene.¹⁶ This near-planar geometry gives poor direct overlap between the p -type π orbital lobes. However, a through-bond interaction, via hyperconjugative effects of the σ_{CH} bonds, can couple the ethylenic π systems. This through-bond interaction leads to two separate π ionization potentials. Indeed, whereas the lowest (vertical) π ionization potential of cyclohexene is 9.12 eV, the corresponding photoelectron state in 1,4-cyclohexadiene splits into two levels at 8.80 and 9.80 eV.³

The effects of these interactions are expected to manifest themselves in the electronic spectra of norbornadiene and 1,4-cyclohexadiene (Figs. 5-7). The resulting spectra should be significantly different from their monoethylenic counterparts. Following the simple procedure used by Mulliken¹⁷ in discussing the spectra of *s-cis* and *s-trans*-1,3-butadiene, we note that the interaction of the two ethylenic units should result, in the first approximation, in four molecular orbitals. These are, in order of increasing energy, the a_1 , b_1 , b_2 , and a_2 orbitals of the C_{2v} point group. This π orbital ordering is believed to be correct for norbornadiene.^{3,4} However, for 1,4-cyclohexadiene, where a through-bond rather than a through-space interaction couples the ethy-

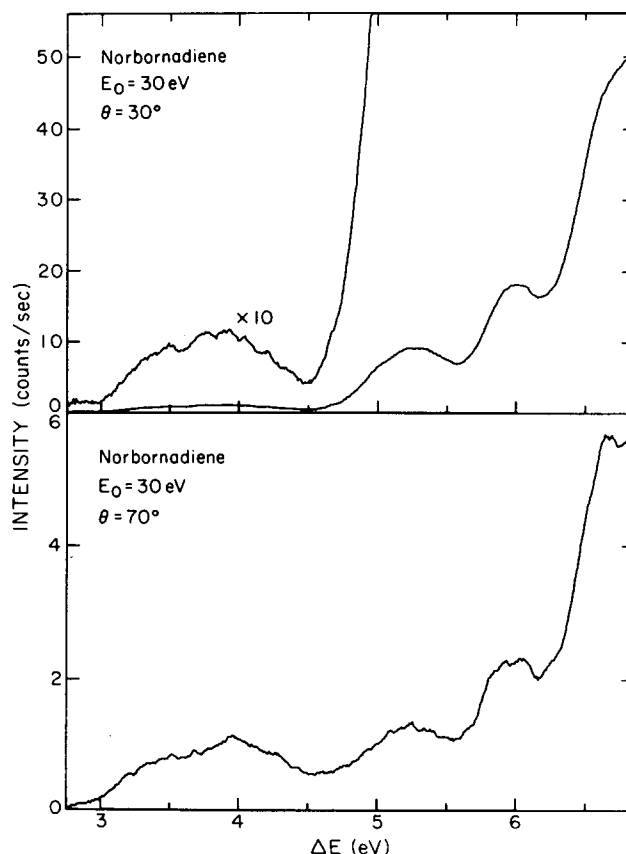


FIG. 5. Electron energy-loss spectrum for norbornadiene at scattering angles of 30° and 70°; 30 eV incident energy; 90 nA incident beam current; 8 mtorr sample pressure, as indicated by an uncalibrated Schulz-Phelps ionization gauge. Apparent spectral features whose intensity is less than 2 counts/sec and whose width is less than 0.2 eV are irreproducible and are due to instrumental noise.

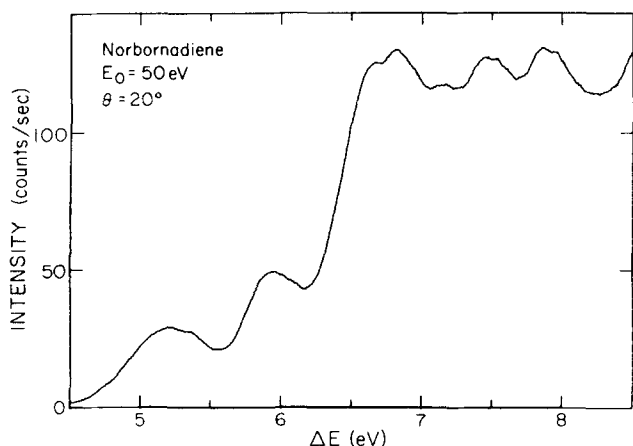


FIG. 6. Electron energy-loss spectrum for norbornadiene at a scattering angle of 20° and 50 eV incident energy. Experimental conditions as described in Fig. 5.

lenic units, the π orbital ordering is believed to be b_1 , a_1 , a_2 , and b_2 .^{3,4} In the ground states of both molecules, the a_1 and b_1 orbitals are doubly occupied. For either π orbital ordering, four excited singlet states belonging, in order of increasing energy, to the irreducible representations A_2 , B_2 , B_2 , and A_2 , result from excitation of a single electron to the a_2 and b_2 orbitals. Transitions from the ground state (A_1) to the A_2 states are symmetry

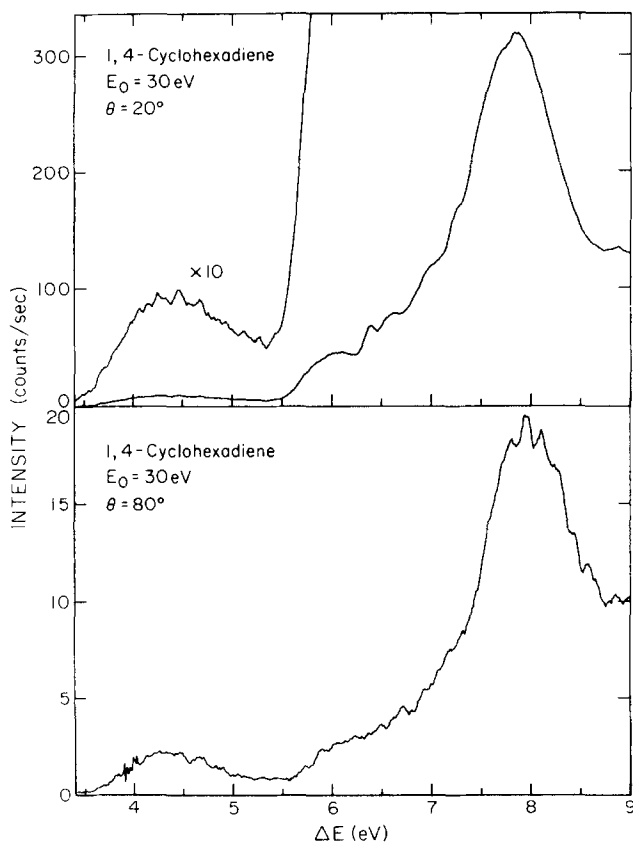


FIG. 7. Electron energy-loss spectrum for 1,4-cyclohexadiene at scattering angles of 20° and 80° ; 30 eV incident electron energy; 40 nA incident beam; 6 mtorr sample pressure, as indicated by an uncalibrated Schulz-Phelps ionization gauge. Apparent spectral features whose intensity is less than 2 counts/sec and whose width is less than 0.2 eV are irreproducible and are due to instrumental noise.

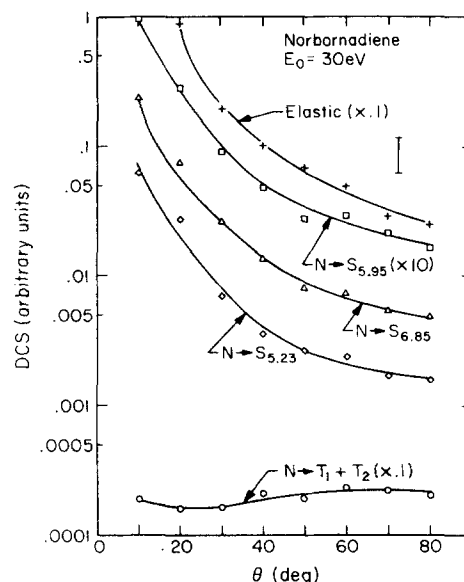


FIG. 8. Relative elastic and inelastic differential cross section for norbornadiene at an incident electron energy of 30 eV. The normalization procedure for the arbitrary ordinate units is the same as for Fig. 3. The error bar beneath the heading represents the estimated uncertainty ($\pm 30\%$) for the inelastic DCS value.

forbidden, while transitions to the B_2 states are symmetry allowed. Mulliken¹⁷ has designated these transitions, in order of increasing energy, as $N-V_1$, V_2 , V_3 , V_4 . Four corresponding excited triplet states should also occur.

Unfortunately a correlation between these simple ideas and our experimental results is difficult to establish. One source of difficulty is the possibility of other transitions in addition to those within the π system. Transitions to Rydberg excited states are observed and $\sigma \rightarrow \pi^*$ transitions may also be possible.

2. Norbornadiene

The lowest energy feature in the spectrum of norbornadiene has an apparent Franck-Condon envelope extending from about 2.9 to 4.5 eV (Fig. 5). As shown in Fig. 8, the DCS of this feature (labeled $T_1 + T_2$) is nearly isotropic. It is also observed that the relative intensity of this feature increases at a given scattering angle as the impact energy is lowered. This behavior is characteristic of a singlet-triplet transition. The band shape of this feature (Fig. 5) seems to indicate the presence of two overlapping singlet-triplet transitions. We estimate the locations of the intensity maxima of these transitions to be approximately 3.4 and 3.9 eV, yielding a splitting between the two lowest triplet states of norbornadiene, T_1 and T_2 , of about 0.5 eV. The magnitude of this splitting seems reasonable in view of the fact that the interaction of the two ethylenic units results in two π ionization potentials of 8.69 and 9.57 eV.¹⁴ The feature occurring between 2.9 and 4.5 eV in the spectrum of norbornadiene is therefore suggested to be due to the superposition of the $N-T_1$ and $N-T_2$ singlet-triplet transitions. Although these transitions have not been reported previously in the literature, Wei and Kuppermann¹⁸ did detect a broad,

weak singlet \rightarrow triplet feature peaking at 3.8 eV in their fixed scattering angle ($\theta = 90^\circ$) electron-impact spectra of norbornadiene.

The remaining features in the norbornadiene spectrum are believed to result from singlet \rightarrow singlet transitions. Unlike the optical spectrum, where only a shoulder is observed at 5.4 eV,¹⁹ the electron-impact spectrum displays a well-defined peak at 5.23 eV (Figs. 5 and 6).

Figure 8 shows that the DCS of this transition is sharply forward peaked, indicating its singlet \rightarrow singlet nature. The assignment of the excitation is uncertain. Its term value, $30\,000\text{ cm}^{-1}$ (3.72 eV), is large enough to rule out the possibility of a Rydberg identification.¹⁰ A semiempirical Pariser-Parr-type calculation by Hermann²⁰ places the lowest $\pi \rightarrow \pi^*$ transition at 5.50 eV, while a second calculation using different empirical parameters increases this excitation energy to 5.98 eV. It seems reasonable to suggest that the 5.23 eV feature is the lowest $\pi \rightarrow \pi^*$ singlet \rightarrow singlet transition, i.e., the symmetry-forbidden, $N \rightarrow V_1$, $\bar{X}^1A_1 \rightarrow ^1A_2$ excitation predicted by simple arguments.

The next feature in the present norbornadiene spectra peaks at 5.95 eV. Its DCS behavior with respect to scattering angle (Fig. 8) indicates that it also is a singlet \rightarrow singlet transition. Robin and Kuebler²¹ have observed it optically at 5.89 eV. Their vibronic study indicates that this is an allowed transition. The effects of high pressure helium on the optical spectrum and the characteristics of its rare gas matrix spectrum and neat film low temperature spectrum show that this feature is due to a Rydberg transition, most likely the $\pi_2 \rightarrow 3s$ excitation. Consistent with this assignment is the $22\,000\text{ cm}^{-1}$ (2.74 eV) term value of this feature.

In the same excitation energy region, Robin and Kuebler^{21a} found that underlying the $\pi_2 \rightarrow 3s$ Rydberg transition in norbornadiene was a second transition. They assigned it as the lowest $\pi \rightarrow \pi^*$, $N \rightarrow V_1$ excitation, since they did not detect the peak at 5.23 eV. This assignment must be viewed with caution. If this underlying excitation is indeed $\pi \rightarrow \pi^*$ in nature, it is more likely the $N \rightarrow V_2(\bar{X}^1A_1 \rightarrow ^1B_2)$ transition, because, as indicated above, the $N \rightarrow V_1(\bar{X}^1A_1 \rightarrow ^1A_2)$ transition in norbornadiene probably occurs at 5.23 eV.

The most intense feature in the norbornadiene spectrum (Fig. 6) has an intensity maximum at 6.85 eV and also exhibits a DCS characteristic of a singlet \rightarrow singlet transition (Fig. 8). This excitation is also observed optically at 6.88 eV.^{21a} It is probably due to the symmetry allowed $N \rightarrow V_3(\bar{X}^1A_1 \rightarrow ^1B_2)$ transition. Hermann's²⁰ calculations place an $X^1A_1 \rightarrow ^1B_2$ excitation at 7.13 or 6.61 eV, depending on the choice of parameters. These energies are consistent with the experimental value.

We also observe structure superimposed on top of the 6.85 eV feature (Fig. 6). More detailed vibronic structure is detected in the optical spectrum.¹⁹ Most probably it is due to a superimposed Rydberg excitation, whose term value with respect to the first π ionization potential is $14\,800\text{ cm}^{-1}$ (1.84 eV). This value does not seem to be consistent with an assignment of this structure to either an *s* or *p* Rydberg series converging to

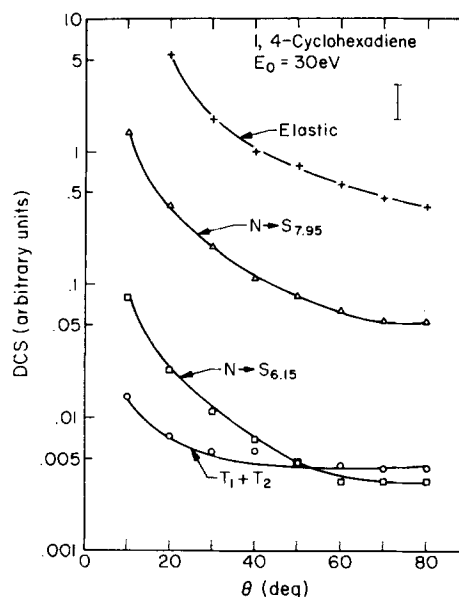


FIG. 9. Relative elastic and inelastic differential cross sections for 1,4-cyclohexadiene at an incident electron energy of 30 eV. The normalization procedure for the arbitrary ordinate units is the same for Fig. 3. The error bar beneath the heading represents the estimated uncertainty ($\pm 30\%$) for an inelastic DCS value.

the first I.P. However, the term value with respect to the second π ionization potential of norbornadiene is $21\,900\text{ cm}^{-1}$ (2.72 eV). This value is almost identical to the $\pi_2 \rightarrow 3s$ term value and hence a possible assignment of this structure is the $\pi_1 \rightarrow 3s$ Rydberg transition. Several additional features are observed at excitation energies above 6.85 eV. These relatively weak peaks, whose locations are listed in Table I, are probably elements of Rydberg series converging to the first or higher ionization potentials.

3. 1,4-cyclohexadiene

The lowest feature in the 1,4-cyclohexadiene spectrum (Fig. 7) extends from 3.4 to 5.4 eV, with maximum intensity occurring at 4.29 eV. The DCS of this feature (Fig. 9, $T_1 + T_2$ curve) varies by about a factor of 3 over the angular range 10° to 80° . This behavior is characteristic of a spin-forbidden transition. This feature could be due to a single transition. However, as mentioned in Sec. III. B.1, the two lowest π ionization potentials for 1,4-cyclohexadiene are split by about 1.0 eV. This fact, and the splitting of the two lowest triplets in norbornadiene, suggest that the low-lying 1,4-cyclohexadiene feature being considered may be due to the superposition of the $N \rightarrow T_1$ and $N \rightarrow T_2$ singlet \rightarrow triplet transitions, having approximately equal intensity, and split by about 0.3 to 0.4 eV. Brongersma²² has also observed this feature in threshold electron-impact studies with an intensity maximum occurring at 4.3 eV. The experimental results are in fairly good agreement with the theoretical calculations of Allinger *et al.*,²³ who place the lowest triplet state of 1,4-cyclohexadiene at 4.07 eV.

The next feature in the spectrum of 1,4-cyclohexadiene has an intensity maximum at 6.15 eV. The DCS of this transition (Fig. 9), is forward peaked, indicating

that it is a singlet \rightarrow singlet excitation. This excitation is also observed in the optical spectrum at 6.20 eV,²³ in the threshold electron-impact spectrum at 6.3 eV,²² and in high impact energy electron impact at 6.23 eV.²⁴ The theoretical calculations of Allinger *et al.*,²³ predict the forbidden $N \rightarrow V_1$, $\pi \rightarrow \pi^*$, singlet \rightarrow singlet transition to occur at 6.42 eV. This is about 0.5 to 0.9 eV above the calculated²⁰ excitation energy of the $N \rightarrow V_1$ excitation in norbornadiene. The difference of the corresponding experimental values is 0.9 eV, in reasonable agreement with theory. The low intensity of this 6.15 eV feature in our spectra relative to a fully allowed transition occurring at 7.95 eV is consistent with such an $N \rightarrow V_1$ assignment.

The possibility also exists that the 6.15 eV feature could be a $\pi \rightarrow 3s$ Rydberg transition similar to the $N \rightarrow R$ excitation observed in cyclohexene and norbornene. In the spectrum of norbornadiene, the transition occurring at 5.95 eV, with term value 22 000 cm^{-1} (2.74 eV), was shown by Robin and Kuebler^{21b} to be a Rydberg excitation and tentatively assigned in the present study to the $\pi_2 \rightarrow 3s$ transition (see Sec. III. B. 2). The 6.15 eV feature in the spectrum of 1,4-cyclohexadiene has a term value of 21 400 cm^{-1} (2.65 eV). Recalling the similarity of the term values for the $N \rightarrow R$ transitions for cyclohexene and norbornene, we feel that this 6.15 eV transition could alternatively be assigned to the $\pi_2 \rightarrow 3s$ excitation. High pressure optical studies would be required to establish the valence or Rydberg nature of this feature.

Further comparisons between the spectra of norbornadiene and 1,4-cyclohexadiene yield additional information. The structure observed at 6.85 eV in norbornadiene, with a term value of 21 900 cm^{-1} (2.72 eV) with respect to the second ionization potential, was suggested to be due to the $\pi_1 \rightarrow 3s$ Rydberg excitation (Sec. III. B. 2). On the basis of term value similarities, we would predict structure due to the $\pi_1 \rightarrow 3s$ excitation to occur near 7.1 eV in the spectra of 1,4-cyclohexadiene. Examination of the latter (Fig. 7) reveals indeed two weak features at 7.1 and 7.3 eV. These features may be due to vibronic components of that $\pi_1 \rightarrow 3s$ Rydberg excitation. Two other weak features in the spectrum of 1,4-cyclohexadiene occur at 6.4 and 6.6 eV. These peaks have term values of about 18 500 cm^{-1} (2.3 eV) and may be due to vibronic components of the $\pi_2 \rightarrow 3p$ Rydberg transition. Alternatively, they could be the $N \rightarrow V_2$ valence excitation. Our spectra do not allow a differentiation between these possibilities.

The most intense feature found in 1,4-cyclohexadiene peaks at 7.95 eV. The DCS of this transition at 30 eV impact energy (Fig. 9) decreases by a factor of 27 as the scattering angle increases from 10° to 80°. This forward peaked behavior is characteristic of a fully allowed excitation. As discussed earlier in this section, this feature probably does not correspond to the first $\pi \rightarrow \pi^*$ transition, which is expected to be symmetry forbidden. It may instead be the second or third $\pi \rightarrow \pi^*$ excitation. This transition is observed at 8.1 eV in the threshold electron-impact spectrum²² and 7.9 eV in the high incident energy electron-impact spectrum.²⁴

The only available theoretical calculations are those of Allinger *et al.*,²³ which predict that the lowest optically allowed $\pi \rightarrow \pi^*$ transition should occur at 7.37 eV. This is in relatively poor agreement with the experimental results. Several additional weak features observed at excitation energies above 7.95 eV are believed to be elements of various Rydberg series. Their transition energies are listed in Table I.

We see, then, that there are similarities between the presumed valence singlet \rightarrow singlet portions of the spectra of 1,4-cyclohexadiene and norbornadiene. If the spectrum of norbornadiene is shifted upwards by approximately 0.5–1.0 eV, it becomes qualitatively similar to the spectrum of 1,4-cyclohexadiene. This similarity would be expected if the simple model of interacting ethylene units is valid. The upward shift seems to indicate that the valence-excited states of norbornadiene are somewhat stabilized with respect to those of 1,4-cyclohexadiene. This behavior is similar to the lowering of the $N \rightarrow V$ transition energy by 0.5 eV in going from cyclohexene to norbornene. The stabilization of the norbornadiene valence excited states with respect to the 1,4-cyclohexadiene ones, like that of the norbornene levels with respect to the cyclohexene ones, is not readily explained. Appropriate theoretical studies of these systems would be useful.

IV. SUMMARY AND CONCLUSION

The Franck–Condon envelopes and locations of the lowest singlet \rightarrow triplet transitions in each of the four molecules studied have been obtained. In norbornadiene and 1,4-cyclohexadiene, the lowest excitation energy features are believed to be the result of the superposition of two singlet \rightarrow triplet transitions. For norbornadiene these excitations have estimated intensity maxima occurring at 3.4 and 3.9 eV, and are interpreted in terms of interacting ethylenic units. The singlet state spectra have also been discussed in terms of such an interaction. While the lower excitation energy regions of norbornene (below \sim 6.5 eV) and cyclohexene (below \sim 7 eV) are fairly well understood, the equivalent regions in the spectra of norbornadiene (below \sim 7 eV) and 1,4-cyclohexadiene (below \sim 8 eV) are not. The valence states of norbornene and norbornadiene appear to be stabilized with respect to the corresponding states in cyclohexene and 1,4-cyclohexadiene. This apparent stabilization is also not presently understood.

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