Electronic Spectroscopy of Polyatomic Molecules by Low-Energy, Variable-Angle Electron Impact[†]

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Contents

I. Introduction

A large number of molecules of interest to chemistry are constituted by atoms of atomic number low enough for electronic spin angular momentum to be a good constant of the motion. For such molecules, electronic transitions involving a change of spin multiplicity, such as singlet → triplet transitions, are strongly forbidden in optical excitations. Nevertheless, electronically excited states of different spin multiplicity from the ground state play important roles in organic photochemistry, radiation chemistry, atmospheric chemistry, plasmas, and lasers. The technique of low-energy, variable-angle, electron-impact spectroscopy permits the investigation of electronic transitions to excited molecular states which are not accessible by optically allowed transitions from the ground electronic state. In addition, it is a useful tool for studying optically allowed electronic transitions, including those with excitation energies not readily accessible to ultraviolet spectroscopy (i.e., >10 eV). A large number of molecules have been investigated with this technique, resulting in the detection and characterization of many new transitions, both spin-forbidden and spin-allowed. The present paper is a review and evaluation of some of the work done in this field over the last few years. Previous reviews have been published elsewhere.[1,2]

II. Physical Picture of Electronic Excitation by Electron Impact

The theory of electronic excitation by electron impact is discussed in great detail in the monograph by Mott and Massey,[3]

and we direct the interested reader to it and to the more recent review by Rudge.[4] What we wish to do here, however, is to present a physical picture of this process using a classical mechanical language and to compare the electron-impact excitation process with the corresponding optical excitation.

The phenomenon of light-induced electronic transitions can be viewed as due to the effect of the radiation's electromagnetic field on the molecular electrons. Analogously, the force exerted on a molecular electron by an incident electron is of similar electromagnetic origin, and the main component of this force is due to the coulombic interaction between these electrons. If the incident electron has a relatively large energy, most of the effective collisions will occur at large electron–molecule distances because of the long range of coulomb forces. As a result, the incident electrons which have produced a given (coulombic) electronic excitation will be deflected relatively little, and the corresponding angular distribution will be forward-peaked, as seen for the 6.27-eV transition in carbon disulfide[5] (Figure 1). The selection rules will, for this case, be analogous to those for optical excitations, because of the similarity of the interactions involved.[6]

If the incident electron has low energy, of the order of a few tens of an electron volt, those collisions in which it penetrates the electron cloud of the molecule can give rise to a different phenomenon, that of electron exchange. In such a process, the electron that emerges can be "different" from the incident one (with due respect to Pauli) and may have a different spin. This phenomenon, first proposed theoretically by Oppenheimer,[7] is called exchange scattering, and results in an electronic transition in which the spin angular momentum quantum number changes by one. If the initial state is a singlet, the final state will be a triplet, even though there is no spin flip but only a spin exchange. The integral cross section for such a process will, in general, be smaller than that of an optically allowed one. Typically, the cross section ratio for these two processes will have a value of the order of 10^{-2} at an incident electron energy of about 30 eV. This is a great relative enhancement compared with optical excitation, for which the equivalent ratio may be 10^{-6} or lower. In addition, because of the mixing between incident and molecular electrons which is required for the exchange to take place, the scattered electron is emitted much more isotropically than for a spin-allowed transition, as seen for the 3.36-eV transition in carbon disulfide in Figure 1. This behavior is largely due to the short range of the electron exchange interaction.[2] In some cases, spin-forbidden transitions can be more intense than optically allowed ones, especially at large scattering angles. An example of this pattern occurs in the energy-loss spectrum of helium obtained at an incident electron energy of 34 eV and a scattering angle of 70°. Under these experimental conditions, the spin-forbidden $1^1S \rightarrow 2^3P$ transition is more intense than the optically allowed $1^1S \rightarrow 2^1P$ excitation.[1]

Spin-allowed but symmetry-forbidden electronic transitions can also be excited by low-energy electron impact. In these
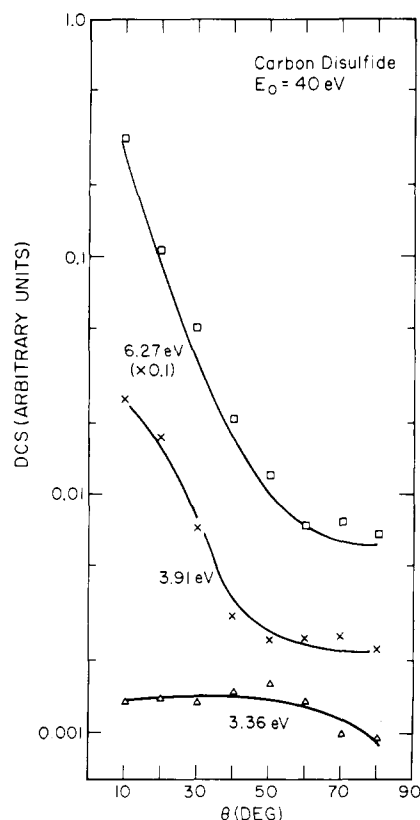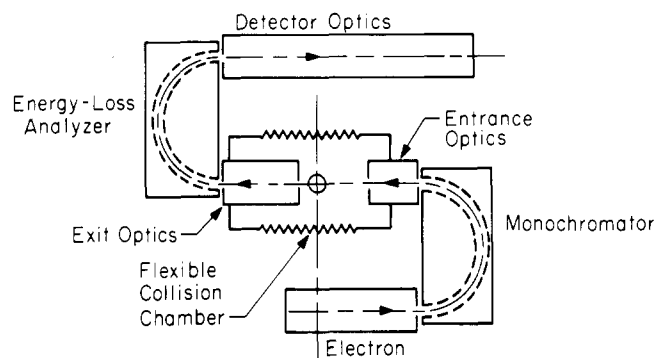
Figure 1. Differential cross sections (DCS) for three kinds of electronic transitions in carbon disulfide, as a function of scattering angle (θ), for an incident electron energy (E_0) of 40 eV. The arbitrary units in the ordinate are the same for all transitions. The one at 6.27 eV energy loss is optically allowed, the one at 3.91 eV energy loss is spin-allowed but symmetry-forbidden, and the one at 3.36 eV is spin-forbidden. Scale factors are numbers by which DCS values were multiplied before being plotted.

SPECTROMETER BLOCK DIAGRAM

Figure 2. Block diagram of variable-angle, low-energy, electron scattering spectrometer. The center of the circle inside the flexible collision chamber is the center of the scattering region. The part of the spectrometer preceding this region along the electron beam path (indicated by arrows) can be rotated with respect to the rest of the spectrometer about the vertical axis which passes through the scattering region.

collisions the incident electron polarizes the electron cloud of the target atom or molecule,[8] thereby changing its symmetry characteristics. The shape of the angular distribution of scattered electrons may be complex, showing maxima and minima,[9] and is frequently less sharply forward-peaked than for an optically allowed transition, as shown by the curve for the 3.91-eV transition in carbon disulfide depicted in Figure 1. This behavior is often observed[5,10-12] and can be of use in identifying the orbital symmetry of excited electronic states.

In general, the integral cross section for a spin-allowed transition shows a maximum as a function of impact energy at a few tens of electron volts above threshold and then falls off rather slowly as the energy further increases, over a range of a few hundred electron volts. In contrast, the cross section for a spin-forbidden transition usually peaks within 5 eV of threshold, and by 50 eV above threshold has fallen by more than two orders of magnitude below its maximum value.

The angle and impact energy dependence of the differential cross sections of different kinds of electronic transitions permits not only the detection but also the characterization of such transitions. In particular, spin-forbidden transitions can easily be distinguished from spin-allowed ones. At about 30 eV above threshold, the ratio of the intensity of a spin-forbidden transition to that of an optically allowed transition increases between one and three orders of magnitude as the scattering angle increases from 0° to about 80°. Furthermore, only spin-forbidden transitions show this behavior. As a result, low-energy variable-angle electron-impact spectroscopy is an extremely useful tool for studying such spin-forbidden excitations.

In concluding this section, we should mention another form of low-energy, electron-impact spectroscopy, the threshold excitation method, which probes transitions to states of both

short-lived negative ions as well as neutral molecules. This technique, which in many respects is complementary to the variable-angle method, has been reviewed by Walker.[111] In addition, close to excitation threshold, resonances in the corresponding integral cross sections can occur as a result of temporary negative ion formation. We shall not concern ourselves with this phenomenon in this paper but direct the interested reader to appropriate reviews.[13,14]

III. Apparatus

The equipment used in this form of spectroscopy is depicted in Figure 2. It consists of an electron gun, two hemispherical electrostatic energy analyzers, a flexible collision chamber, and a detector system.[1,2] Electrons emitted by a cathode or filament are accelerated and collimated by an electron gun, and energy-selected by the first electrostatic analyzer (the monochromator). After the electrons collide with sample molecules in the form of a gas at 1 to 10 mTorr pressure, their energy loss is determined by the second analyzer and they are detected by an electron multiplier and pulse-counting system. The basic design is that of Simpson and Kuyatt.[15]

The angle between the incident and scattered electron beams can be changed owing to the flexible bellows construction of the scattering chamber. Further details of the apparatus are described elsewhere.[1,2,11] The best energy resolution of the instrument for clean gases such as hydrogen is about 50 meV. Most of the spectra displayed in this paper were taken at a resolution between 100 and 150 meV.

IV. Results and Discussion

In this section we review some of the spectroscopic information obtained by electron-impact investigations of a number of series of related molecules. These include (1) triatomics, (2) methylated ethylenes, (3) fluoroethylenes, (4) alkynes, (5) polyenes, (6) fluorobenzenes, (7) five-membered heterocycles, (8) azo compounds, and (9) additional molecules. This discussion will focus on only a few selected features of the spectra. A complete list of the transition energies observed for the above compounds is given in Table I. In particular, we call attention to the column containing transition energies of superexcited states (SES), which lie above the lowest ionization potential (IP). Most of the SES listed in Table I were first detected by variable-angle, electron-impact spectroscopy. The assignments of all transitions as either spin-forbidden or spin-allowed were made on the basis of the angular and impact energy dependences of the differential cross sections (DCS) and DCS ratios, as discussed in section II.

A. Triatomics

The electronic excitation spectra of carbon disulfide (CS_2), carbonyl sulfide (OCS), and sulfur dioxide (SO_2) are considerably more complex than that of the related molecule carbon dioxide (CO_2) in the energy-loss range below 8 eV (Figure 3). In contrast to CO_2, in which no vertical excitations below 7 eV are known,[16] each of these sulfur-containing triatomics has at least one low-lying (i.e., <5 eV) spin-forbidden transition.[5] These features are clearly caused by excitations out of relatively weakly bound π orbitals formed in part from sulfur 3p orbitals.

In CS_2, three separate features are observed between 3-eV and 4-eV energy loss, although some or all of these peaks may actually consist of excitations to several excited states of similar energy.[17,18] The lowest feature, at 3.36 eV, exhibits predominantly spin-forbidden behavior. This supports a previous suggestion,[19] based on Zeeman splittings in the optical spectra,[20] that the band system corresponds to a singlet $\rightarrow$ triplet transition. Analysis of ultraviolet observations[18] of this transition indicates that it is the $\tilde{X}^1\Sigma_g^+ \rightarrow {}^3A_2(1^3\Delta_u)$ excitation. The feature at 3.65 eV also exhibits some of the characteristics of a spin-forbidden excitation, and it may represent transitions to one or more triplet states predicted to lie in this region, e.g., ${}^3B_2 (1^3\Sigma_u^+)$, ${}^3B_2 (1^3\Delta_u)$, and ${}^3A_2(1^3\Sigma_u^-)$.[18] However, a weak optically observed transition,[18] $\tilde{X} {}^1\Sigma_g^+ \rightarrow {}^1A_2(1^1\Delta_u)$, also occurs at 3.65 eV, and it may contribute some intensity to the feature we observe, particularly at low impact energies and small scattering angles. A weak, electric dipole-forbidden $\tilde{X} {}^1\Sigma_g^+ \rightarrow {}^1B_2(1^1\Delta_u)$ transition is observed with maximum at 3.91 eV, in agreement with optical observations.[17]

In OCS, the lowest observed feature,[5,21,22] which consists of at least one singlet $\rightarrow$ triplet excitation,[22] has a maximum intensity at 4.94-eV energy loss. The excited triplet state is believed[21] to participate in mercury photosensitization experiments involving OCS. A definite assignment has not been made for this state, or for the weak, spin-allowed transition observed at 5.53 eV, but it has been suggested, on the basis of optical data, that the latter feature is either a ${}^1\Sigma^+ \rightarrow {}^1\Sigma^-$ transition[23,24] or a ${}^1\Sigma^+ \rightarrow {}^1\Delta$ transition.[17,24] Additional information on this assignment has been obtained by applying a rigorous electron-impact selection rule,[25] which states that ${}^1\Sigma^+ \rightarrow {}^1\Sigma^-$ transitions are forbidden at scattering angles of $0°$ and $180°$. Since the 5.53-eV transition becomes increasingly strong as the scattering angle is lowered toward $0°$, it seems unlikely that the ${}^1\Sigma^+ \rightarrow {}^1\Sigma^-$ assignment is correct. Instead, as with CO_2 and CS_2, the lowest lying singlet excited state of OCS is probably of ${}^1\Delta$ symmetry.

In SO_2, the only observed singlet $\rightarrow$ triplet transition occurs at 3.40 eV.[5] On the basis of a rotational analysis[26] of the optical data, it has been assigned to the $\tilde{X} {}^1A_1 \rightarrow \tilde{a} {}^3B_1$ transition. A good Franck–Condon band system profile has been determined for this transition (Figure 3), and this should be of use in the interpretation of electronic energy transfer experiments.[27,28] There is no evidence in the electron-impact spectra for transitions to two other nearby triplet states which have been postulated to occur in the vicinity of the $\tilde{a}$ state.[26b-29]

These spectroscopic results for the triatomics demonstrate that the substitution of a sulfur atom for either a carbon atom or an oxygen atom in CO_2 results in a major perturbation of the electronic structure of the molecule. Although the energy-loss spectra of these four molecules are quite different from one another, a crude relationship can be discerned among the spectra of CO_2, OCS, and CS_2, which have isoelectronic valence shells. We first note that the lowest ionization potentials decrease in the order CO_2 (13.79 eV), OCS (11.19 eV), and CS_2 (10.07 eV),[30] as would be expected both from the decrease in the atomic ionization potential from O to S, and from the decrease in the π bond energy expected in this sequence. Although a similar decrease is expected to occur among the transition energies of corresponding Rydberg states[31] (vide infra), we
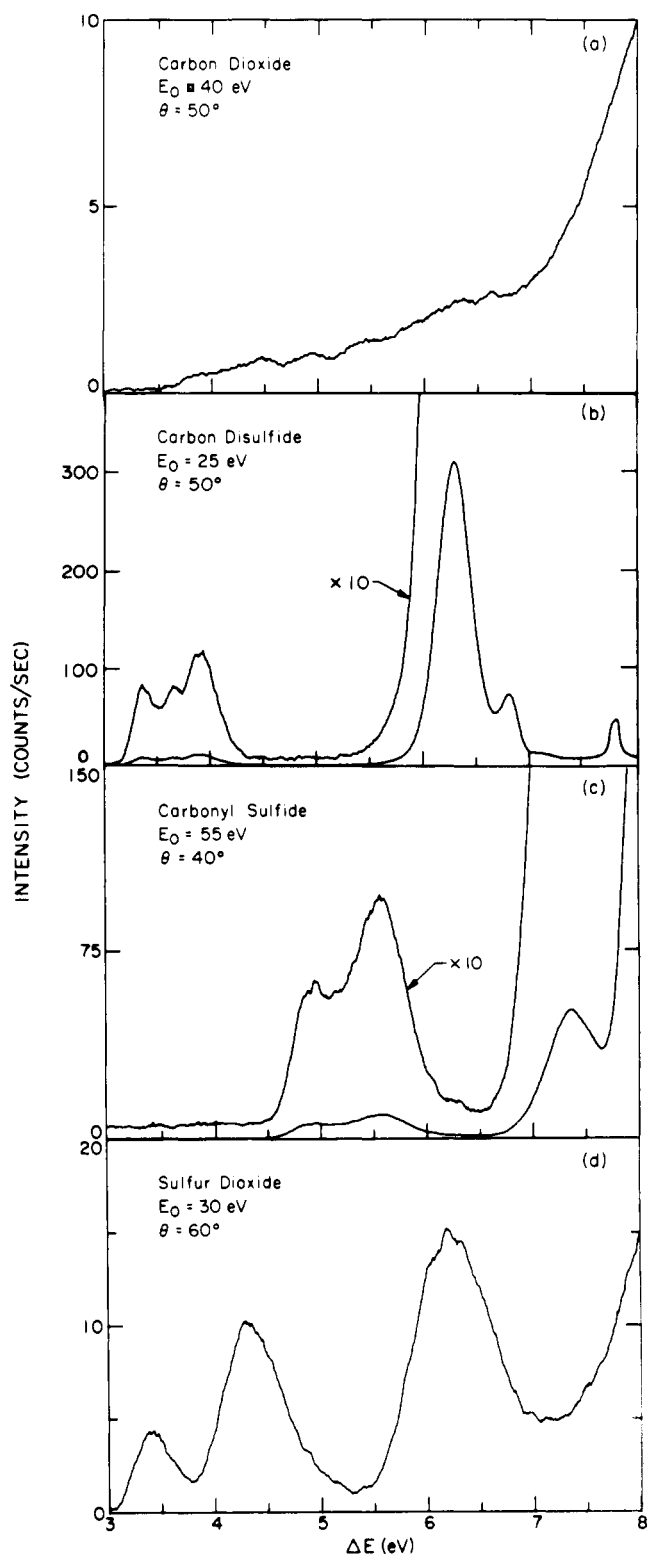

Figure 3. Energy-loss spectra of CO_2, CS_2, OCS, and SO_2. The values of E_0 and θ indicated represent the incident electron energy and scattering angle, respectively. The abscissa (ΔE) represents the energy loss of the incident electron and the ordinate represents the detected scattered electron intensity. Scale factors indicated are numbers by which this intensity was multiplied before being plotted.

would not expect valence states to scale with the ionization potential. Surprisingly, we find that the transition energy of the low-lying valence triplet state, ${}^3\Sigma_u^+$ or ${}^3\Sigma^+$, displays a similar bathochromic shift, decreasing in the order 7.5 eV (CO_2),[21] 4.94 eV (OCS),[5] and 3.65 eV (CS_2).[5] An analogous, rough correlation exists among the observed transition energies to the valence 1 ${}^1\Delta_u$ or 1 ${}^1\Delta$ state. This pattern presumably reflects the decreasing π bond energy in these molecules.

TABLE I. Excited State Transition Energies Determined by Variable-Angle, Electron-Impact Spectroscopy

| molecule | transition energies (eV)[a] | | ionization[b] | superexcited singlets |
	triplets	singlets		
carbon dioxide		8.6, 9.35, 11.04, 11.41, 11.62, 11.71, 11.84, 12.01, 12.18, 12.31, 12.48, 12.65, 12.99, 13.27, 13.47, 13.75	13.79	14.59, 14.69, 14.83, 14.97, 15.11, 15.25, 15.48, 15.89, 16.03, 16.21, 16.49, 16.87, 17.07, 17.49, 17.85, 18.50, 18.82, 19.05, 19.19
Carbon disulfide	3.36 3.65[c]	3.91, 6.27, 6.79, {7.12, 7.22, 7.33}, 7.78, 7.97, 8.23, 8.61, 8.78, 9.02, 9.24, 9.53	10.07	10.61, 11.13, 11.40, 11.96, 12.52, 12.97, 13.32, 13.61, 13.82, 13.94, 14.49, 14.99, 15.44
carbonyl sulfide	4.94	5.53, 7.36, {8.02, 8.11}, 8.88, 9.11, 9.59, 10.07, 10.36, 10.66	11.19	11.6, 12.22, 13.30, 13.93, 14.38, 14.82, 14.93, 15.08, 15.39
sulfur dioxide	3.40	4.31, 6.20, 8.30, 8.8, {9.35, 9.44}, 9.87, 10.98, 11.68	12.50	13.0, 15.08
ethylene	4.32	{7.11, 7.28, 7.45, 7.60}, 7.6, 8.25, 8.60, {8.91, 9.08, 9.23}, 9.36, {9.63, 9.70}, 10.09, 10.27	10.51	11.25, 12.06, 14.4
propene	4.28	6.6, 7.17, 7.61, 7.78, 7.97, 8.14, 8.36, 8.49, 8.67, 8.87, 9.01, 9.41, 9.52	10.03	10.1, 10.86, 11.39, 12.54, 13.14, 14.3
isobutene	4.22	6.1$_5$, {6.60, 6.71}, 6.90, 7.08, 7.27, 7.45, 7.59, 7.78, 7.96, 8.17, 8.37, 8.59	9.45	9.89, 11.10, 14.3
cis-2-butene	4.21	{6.03, 6.20}, 6.36, 7.10, 8.29, 8.45, 8.76, 8.92, 9.16	9.36	9.9$_5$, 11.51
trans-2-butene	4.24	{6.14, 6.3}, 6.95, {7.41, 7.55}, 7.82, 8.00, 8.22, 8.38, 8.57, 8.75	9.37	9.28, 10.95, 12.4
trimethylethylene	4.16	5.76, 6.47, {6.84, 6.97}, {7.31, 7.49}	8.86	8.9, 9.60, 10.64, 11.1
tetramethylethylene	4.10	5.55, 6.57	8.44	9.82, 10.98, 11.4
fluoroethylene	4.40, 6.4	7.02, 7.50, 8.08, 8.67, 8.87, 9.37, 9.72, 9.84, 10.03, 10.22	10.58	11.1, 12.5$_5$, 15.2
1,1-difluoroethylene	4.63	6.95, 7.50, 8.23, 9.08, 9.26, 9.44, 9.81, 10.01, 10.11	10.72	11.0$_5$, 12.2, 13.8, 14.2, 14.7
cis-1,2-difluoroethylene	4.43	6.52, 7.82, 8.38, 8.81, 9.01, 9.20, 9.55, 10.25	10.43	10.9, 11.4, 11.9, 12.3, 13.0, 13.8, 14.8
trans-1,2-difluoroethylene	4.18	6.44, 7.39, 7.88, 8.68, 8.80, 8.97, 9.53, 10.2	10.38	10.9, 12.0, 12.4$_5$, 12.9, 13.2, 13.7, 15.2, 16.9
trifluoromethylene	4.43	6.56, 7.65, 7.98, 8.74, 8.91, 9.31, 9.53	10.53	11.4, 12.0, 12.9, 13.8, 15.2
tetrafluoroethylene	4.68	6.62, 8.28, 8.84, 9.04, 9.44, 9.65	10.52	13.3, 13.9, 15.0, 15.7
chlorotrifluoroethylene	4.43	6.51, 7.80, 8.26, 8.50, 8.94, 9.60	10.24	11.4, 12.0, 12.7, 13.2, 14.3, 15.4
chloroethylene	4.08	{6.72, 6.83}, 7.63, {7.81, 7.97, 8.13}, 8.53, {9.12, 9.25, 9.38}	10.18	10.06, 10.19, 10.31, 10.42, 10.54, 10.77, 10.88, 11.55, 12.87
acetylene	5.2, 6.0	7.1, {8.16, 8.37, 8.61}, 9.02, {9.26, 9.47, 9.66}, 9.94, {10.29, 10.54}, 10.74, 10.96, 11.19	11.40	
propyne	5.2, 5.8$_5$	6.7, {7.18, 7.38}, 7.88, {8.06, 8.30}, 8.47, {8.84, 9.08}, {9.25, 9.44, 9.71}, 9.36, 9.96, 10.19, 10.28	10.37	10.57, 10.72, 12.7, 14.7
1-butyne	5.2, 5.8$_5$	6.7, 7.18 {7.78, 7.93, 8.11}, 8.37, {8.57, 8.78}, 9.02, 9.20, 9.45, 9.70, 9.91	10.18	10.24, 10.43, 10.68, 10.90, 12.3, 14.7
3,3,3-trifluoropropyne	5.0, 5.8	7.01, 8.80, 9.60, 10.10, 10.88, 12.08	12.12	13.66, 16.6
1,3-butadiene	3.22, 4.91	{5.76, 5.92, 6.05}, {6.64, 6.80}, {7.08, 7.28, 7.48}, 7.60, 8.00, 8.18, 8.54, 8.69, 8.90	9.07	9.53, 11.04
1,3-pentadiene (trans)	3.14, 4.87	5.80, 6.87, 7.06, 7.69, 7.92	8.56[d]	9.3$_3$, 11.6
1,3-hexadiene (mixed isomers)	3.20, 4.93	5.77, 6.90, 7.09, 7.29, 7.69		9.3
cis-2-trans-4-hexadiene	3.11, 4.8$_5$	5.69, 6.78	8.23[c]	9.13, 9.78, 10.85
1,3,5-hexatriene (cis and trans)	2.61, 4.07	{4.95, 5.13, 5.30, 5.5, 5.7}, 6.06, 6.25, 6.42, 6.57, 6.75, 6.93, 7.08, 7.48, 7.77, 7.93, 8.06	8.29 (trans) 8.32 (cis)	9.1, 9.7, 10.5
1,3-cyclohexadiene	2.94	4.94, {6.05, 6.20, 6.39}, 7.21, 7.42, 7.73, 7.88, 8.05	8.25	
1,4-hexadiene (mixed isomers)	4.25	6.84		9.4
1,5-hexadiene	4.25	7.00, 8.3, 9.1	9.59	
1,4-cyclohexadiene	4.29	6.15, 7.95	8.80	
propadiene (allene)	4.28, 4.89	5.0–6.2,[e] 5.5–6.5,[e] 6.74, 7.24, 8.07, 8.60	10.05	11.25

TABLE I *(Continued)*

| molecule | transition energies (eV)[a] | | ionization[b] | superexcited singlets |
	triplets	singlets		
benzene	3.90, 5.59	4.80, 6.25, 6.95, 8.14, 8.41, 8.72, 8.88	9.25	9.50, 9.76, 9.90, 10.01, 10.51, 11.08, 11.61, 12.15, 13.08, 13.96, 14.26, 15.21, 15.81, 17.45
fluorobenzene	3.90, 5.72	4.78, 6.23, 6.99, 8.87	9.40	9.73, 10.75, 11.38, 11.72, 12.33, 12.73, 13.93, 14.63, 15.27, 16.97
o-difluorobenzene	3.92, 5.67	4.76, 6.22, 7.02, 8.46	9.51	9.60, 9.93, 10.73, 11.39, 12.13, 12.99, 14.09
1,3,5-trifluorobenzene	3.95, 5.62	4.87, 6.20, 6.94, 8.20, 8.56, 8.73, 9.43, 9.56	9.81	10.40, 11.33, 12.51, 13.08, 13.55, 13.96, 15.16
1,2,3,4-tetrafluorobenzene	3.95	4.85, 6.43, 7.21, 8.13, 8.43, 9.05	9.80	9.90, 10.40, 10.90, 11.91, 12.58, 13.08, 13.58, 14.33, 15.50, 16.31, 17.21
1,2,4,5-tetrafluorobenzene	4.0	4.69, 6.3, 7.25, 8.07, 8.26, 8.59, 9.14	9.56	10.16, 11.06, 12.39, 13.26, 13.64, 13.96, 14.49, 15.62
pentafluorobenzene	3.90	4.79, 5.85, 6.36, 7.12, 9.91	10.1	11.11, 11.61, 12.35, 13.41, 14.25, 15.58, 16.40
hexafluorobenzene	3.86	4.80, 5.32, 6.36, 7.10, 9.82	10.11	10.26, 10.99, 11.14, 11.39, 11.72, 12.49, 12.79, 13.46, 13.89, 15.81, 18.32
furan	3.99, 5.22	6.06, {6.44, 6.61}, 7.42, 7.82, 8.05, 8.52	8.89	11.0, 11.95
thiophene	{3.66, 3.82}, 4.62	5.48, 5.93, 7.05, 8.21, 8.39	8.87	9.08, 9.65, 10.20, 10.7, 11.1, 12.1, 13.9
pyrrole	4.21	5.22, 5.89, 5.98, 6.2–6.5, {6.80, 6.93}, 7.26, 7.43, 7.54, {7.69, 7.86}	8.21	9.63, 10.18, 11.06, 11.76
azomethane	2.75, 4.8$_4$	3.50, 6.0$_1$, 6.71, 7.8	8.98	9.5
azo-tert-butane	2.67, 4.9	3.37, 6.1, 7.3$_5$, 8.1		8.20
nitromethane	3.8	4.45, 6.23, 7.8, 8.3, 8.85, 9.43, 10.35, 10.91	11.34	11.73
thiophosgene	3.1	2.61, 4.89		9.68
ammonia	5.9[f] ...[g]	{5.7, 5.82, 5.95, 6.06, 6.16, 6.27, 6.39, 6.51, 6.62, 6.72, 6.83, 6.97, 7.11, 7.22}	10.85	
dimethyl ether		6.74, 7.36, 7.64, 8.52, 9.19, 9.34	10.04	
hydrogen sulfide	5.8	6.27, 7.14, 7.34, 7.89, 8.01, 8.21, 8.52, 8.65, 8.81, 8.89	10.48	
methylamine		5.78, 7.05	9.7	10.31, 11.40, 12.67
nitric oxide[h]	5.60, 6.29	{5.47, 5.75, 6.04, 6.33}, {6.48, 6.76}, 6.59	9.54	
acetonitrile	5.5–7.5[i]	8.0, 8.5, 9.0, {9.60, 9.72, 9.83}, 10.30, 10.54, {10.76, 10.93}, {11.26, 11.47, 11.69, 11.93}	12.20	12.28, 12.58, 12.76
pyridine	3.95	4.91, 6.45, 7.21	9.67	10.2
1,3-cyclopentadiene	3.1	5.26, (5.58, 5.75, 5.93), 6.28, 6.41, 6.80, 7.05, 7.61, 7.84, 8.03, 8.19	8.57	9.2, 10.4, 11.8, 14.0

[a] Values correspond to maximum intensity of a transition. The estimated uncertainty of most transition energies is 0.05 eV. Some of the transition energies of weak or broad features have uncertainties of 0.1 eV. Values in brackets represent vibronic bands of a single band system. [b] Vertical ionization energies are listed, unless otherwise noted. These values were obtained from the literature, and most are based upon photoelectron spectroscopic studies. [c] The assignment of this transition as spin-forbidden is tentative. [d] Adiabatic ionization potential. [e] Two transitions overlap in this energy-loss range, and, as a result, the observed maximum intensity varies considerably with impact energy and scattering angle. The values listed correspond to estimated Franck–Condon limits for each transition. [f] Reference 120. [g] Two features have been observed in energy-loss spectra with peaks at 3.9$_5$ and 4.8 eV. The existence and identity of these features are uncertain. They may be analogous to the weak feature in H_2O at 4.5 eV energy loss, which is also of unknown identity.[123] [h] Since the ground state of NO is a doublet state, the excited states are doublets and quartets, rather than singlets and triplets. [i] Reference 122.

B. Ethylene and Methylated Ethylenes

The optical[32,33] and electron-impact[34–37] excitation spectra of ethylene and its six methyl-substituted derivatives are well known in the transition energy range from 5 to 9 eV. The most intense feature (Figure 4) is a transition with maximum intensity at 7.60 eV in ethylene, which shifts to lower energy loss with increasing methyl substitution, and occurs at 6.57 eV in tetra-methylethylene. This feature is commonly referred to as the N → V, $\pi \rightarrow \pi^*$ transition.[32] The V state appears to be intermediate in character between a pure valence and a pure Rydberg state,[38,39] but this conclusion is still controversial. A second band system,[32,40] consisting of sharp peaks superimposed on the N → V continuum, begins at 7.11 eV in ethylene, rapidly shifts to lower energies with methyl substitution, and peaks at 5.55 eV in tetramethylethylene. This band system, known as N → R, has
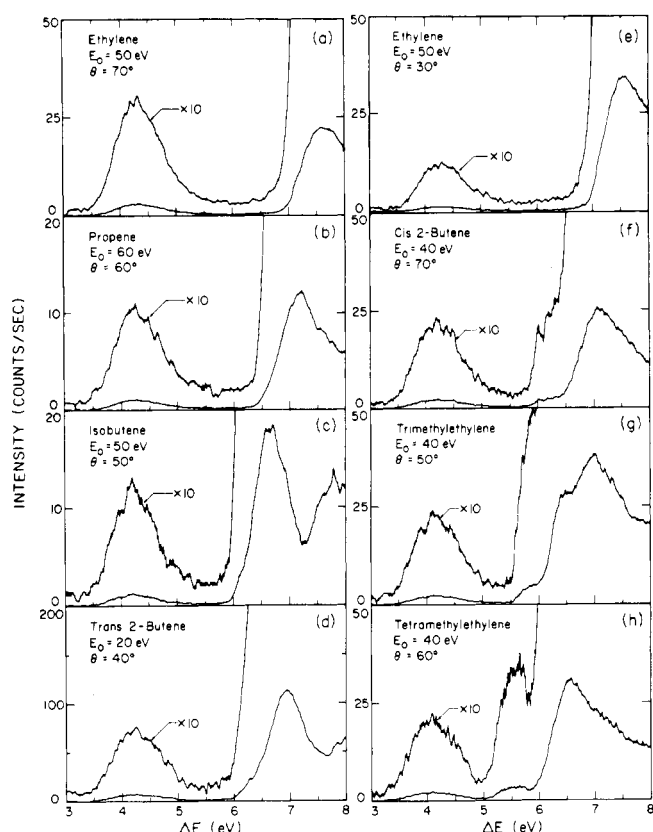
Figure 4. Electron energy-loss spectra for ethylene and six methylated derivatives. Symbols have same meaning as in Figure 3.

been assigned[32,33,40] with reasonable certainty to a singlet → singlet $\pi \rightarrow 3s\sigma$ Rydberg excitation. No weak low-lying singlet → singlet Rydberg transitions (N → R*) or singlet → triplet Rydberg excitations (N → T_R) have been observed in variable-angle, electron-impact studies of these molecules, although such transitions may have been detected with other methods.[33,36] We also do not observe either of the Rydberg states, $(\pi, 3p\sigma)$ $^1B_{2g}$ and $(\pi, 3p_y)$ $^1B_{1g}$, believed to occur in the 7 to 8 eV transition energy region. Excitations to both of these states are produced by electric dipole-forbidden transitions and may have been observed recently in magnetic circular dichroism spectra[112] ($^1B_{2g}$) and threshold electron impact spectra[113] ($^1B_{1g}$) of ethylene.

The N → T singlet → triplet transition is observed in the electron energy-loss spectra[37] of all members of the series (Figure 4) with maximum intensity between 4.32 eV (ethylene) and 4.10 eV (tetramethylethylene). Each additional methyl substituent added to ethylene lowers the peak maximum by about 0.06 eV. The small size of this bathochromic shift validates the theoretical description of the T state as a valence $^3(\pi,\pi^*)$ state with a charge density similar to that of the ground state. This behavior contrasts with that of the V state and even more so with that of the R state. The strong dependence of the N → V and N → R transition energies upon the number of substituents indicates that the relatively diffuse π-electron cloud in these states interacts differently with the methyl substituents than do the ground-state π electrons. This differentiation of valence excitations from diffuse or Rydberg excitations presupposes that highly substituted members of a series have a first ionization potential substantially different from that of the "parent" compound. This is clearly the case with methyl group substitution of ethylene, since the first IP drops from 10.51 eV in ethylene to 8.44 eV in tetramethylene.[30] If no such shift occurs, the dependence of transition energies on substitution may yield no information about the spatial spread of the excited states.

An alternative explanation for the effect of methyl substituents upon the alkene transition energies is based upon the valence

bond theory, in which the N and T states are covalent, while the V and R states are ionic or ion-like. In this model, the V and R states will be stabilized by hyperconjugation with alkyl substituents, but the N and T states will not be similarly affected.

C. Fluoroethylenes

In contrast with the methylated ethylenes, the fluoroethylenes have received, until recently, relatively little attention from spectroscopists. However, systematic studies of both the optical absorption spectra[41] and the electron-impact spectra[42] of these molecules are now available. While the basic olefinic pattern of N → T, N → R, and N → V transitions is present in the fluoroethylenes, there are some interesting differences between the effects of fluorine substitution and those of methyl group substitution on the electronic spectrum of ethylene.

One such difference involves the N → T transition energy. In contrast with the results for the methylated ethylenes,[37] there appears to be no systematic correlation between the number of fluorine substituents and the location of the N → T maximum intensity transition energy (Figure 5). Nevertheless, all the N → T peak values are within the range 4.42 ± 0.25 eV.[42] Although the N → T transition in the fluoroethylenes is undoubtedly an intravalence excitation, we cannot use the independence of its transition energy from fluorine substitution as corroboration of this assertion. This is due to the fact that fluorine substitution has little effect on the lowest molecular ionization potential, since the first IP of C_2F_4 (10.52 eV) is essentially indistinguishable from that of ethylene (10.51 eV). We would expect, therefore, that all transitions below the first IP, both valence and Rydberg, would show relatively little energy dependence on fluorine substitution. With one exception, which is discussed below, this is indeed the case.

In one molecule of this series, vinyl fluoride, a second, weaker singlet → triplet transition is observed at about 6.4 eV.[42] This could be the N → T_R transition to the triplet Rydberg state associated with the singlet R state at 7.0 eV. We have detected no analogous N → T_R transitions in the other fluoroethylenes,[42] presumably due to overlapping of stronger nearby transitions.

The N → V transition energies[41,42] of the first five members of the fluoroethylene series vary much less than they do in the analogous methylated ethylenes,[32] ranging nonmonotonically from 7.39 eV in trans-1,2-difluoroethylene to 7.82 eV in cis-1,2-difluoroethylene. This relatively small nonmonotonic shift is analogous to what is observed for the N → T transition. However, in tetrafluoroethylene, the N → V maximum intensity transition energy occurs near 8.84 eV.[41,42] This large shift was ascribed to an increased barrier to torsional rotation in the excited state of tetrafluoroethylene.[41] Nevertheless, no similar hypsochromic shift is observed in chlorotrifluoroethylene, which has an N → V maximum at 7.80 eV.[42b,43] This result casts doubt on the torsional barrier explanation, since chlorine should provide an even larger resistance to torsion than does fluorine. A more likely explanation takes into account the relative effects of configuration mixing involving C-C-H, C-C-Cl, and C-C-F σ orbitals.[44]

Transitions to many superexcited states have been observed in the fluoroethylenes (Figure 6). Using the term value approach,[31,45,46] we have assigned a majority of these features as members of Rydberg series converging to the second or third ionization potential.[42b] The remaining transitions to SES are most probably intravalence excitations of electrons which are more strongly bound than the π electrons.

D. Alkynes

The electronic structure of alkynes is expected to be more complex than that of the corresponding alkenes, and, in fact, the alkyne spectra are among the least understood of the systems frequently studied by molecular spectroscopists.[47] Transitions
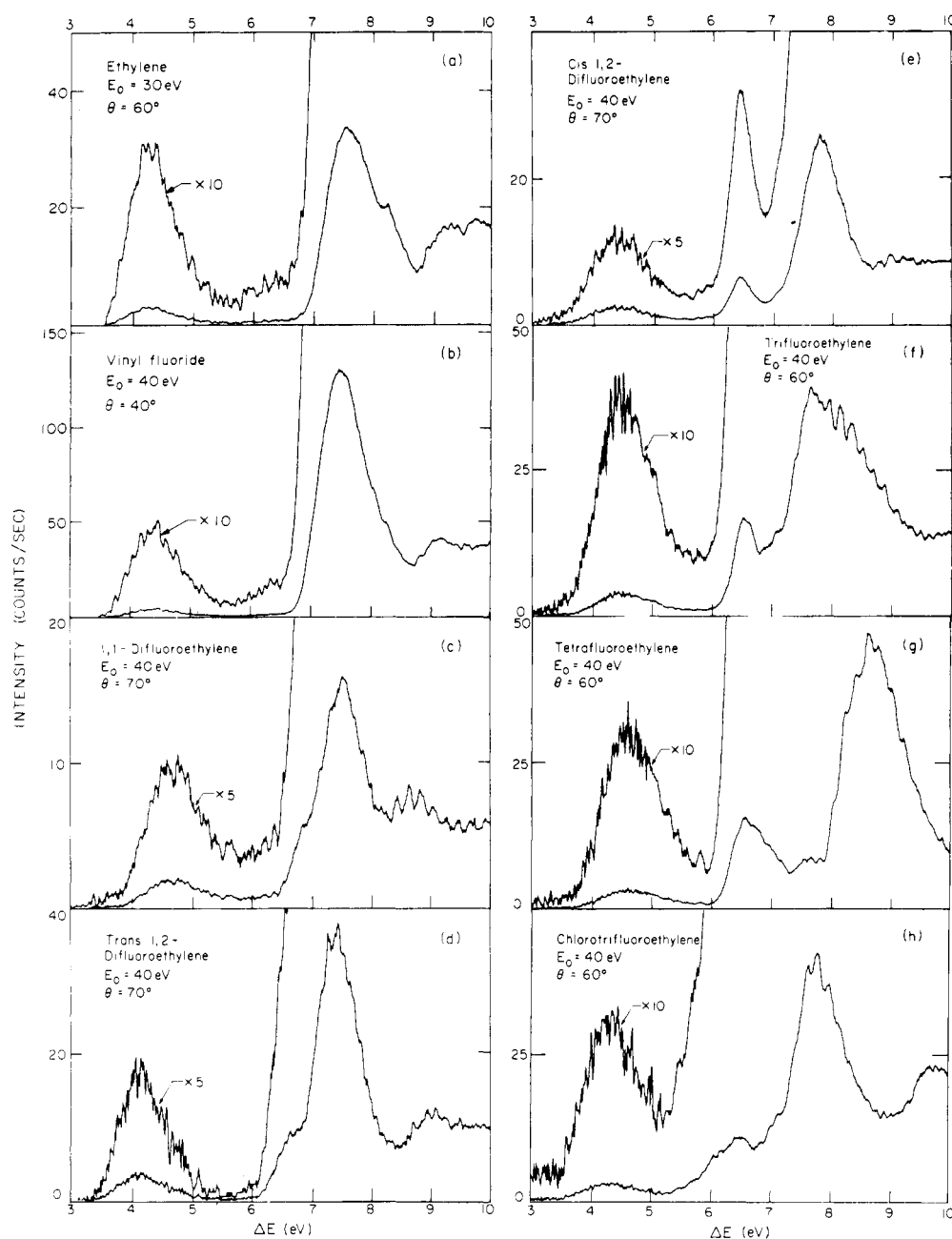
Figure 5. Low-energy-loss part of energy-loss spectra of ethylene, the fluoroethylenes and chlorotrifluoroethylene at large scattering angle. Symbols have same meaning as in Figure 3.

to two weak features in acetylene at about 5.2 and 6.0 eV energy loss (Figure 7) were first detected by variable-angle electron-impact spectroscopy,[48] and the corresponding excited states were identified as triplet states. In both propyne and 1-butyne,[114] two singlet–triplet transitions, analogous to those in acetylene, are observed (Figure 8). No transitions with maxima below 5 eV energy loss are detected in either of these molecules or in acetylene. This contradicts earlier reports[49,50] which had postulated a low-lying triplet in this region. However, these negative results are in agreement with ab initio theoretical calculations[51] on acetylene, which identify the lowest vertical excitations as $\tilde{X}\,^1\Sigma_g^+ \to 1\,^3\Sigma_u^+$ (5.02 eV) and $\tilde{X}\,^1\Sigma_g^+ \to 1\,^3\Delta_u$ (5.87 eV), and ascribe them to $\pi \to \pi^*$ valence excitations. This assignment is supported both by the experimental peak locations in acetylene, and their relative insensitivity to substitution in the σ bond framework of the molecule.

E. Polyenes

The electronic excitation spectra of a number of conjugated polyenes have been studied by variable-angle electron-impact

spectroscopy. These include the prototype of this group, 1,3-butadiene, as well as 1-trans-3-pentadiene, isomerically mixed 1,3-hexadiene, and cis-2-trans-4-hexadiene. The spectra of three of these molecules are displayed in Figure 9.

The lowest energy-loss feature (N $\to$ T_1) in these molecules is a singlet $\to$ triplet transition, which peaks between 3.11 and 3.22 eV (Figure 9). For 1,3-butadiene the excited state of this feature has been assigned as 1 ^3B_u.[52,53] One of the most accurate ab initio calculations[52a] on this molecule places the $\tilde{X}\,^1A_g$ $\to$ 1 ^3B_u vertical transition energy at 3.24 eV, in excellent agreement with the experimental value, 3.22 eV.[54] Another feature (N $\to$ T_2) in the spectra of Figure 9 has a peak between 4.85 and 4.93 eV. In 1,3-butadiene, this transition has been identified as the $\tilde{X}\,^1A_g$ $\to$ 1 ^3A_g excitation,[52,53] and, again, its calculated transition energy of 4.95 eV[52a] agrees very well with the measured value, 4.91 eV.[54] The strongest feature in these molecules is the transition which peaks between 5.69 eV (cis-2-trans-4-hexadiene) and 5.92 eV (1,3-butadiene). This transition is well known from ultraviolet absorption spectra of 1,3-butadiene[55] and is usually assigned as the optically allowed $\tilde{X}\,^1A_g$ $\to$
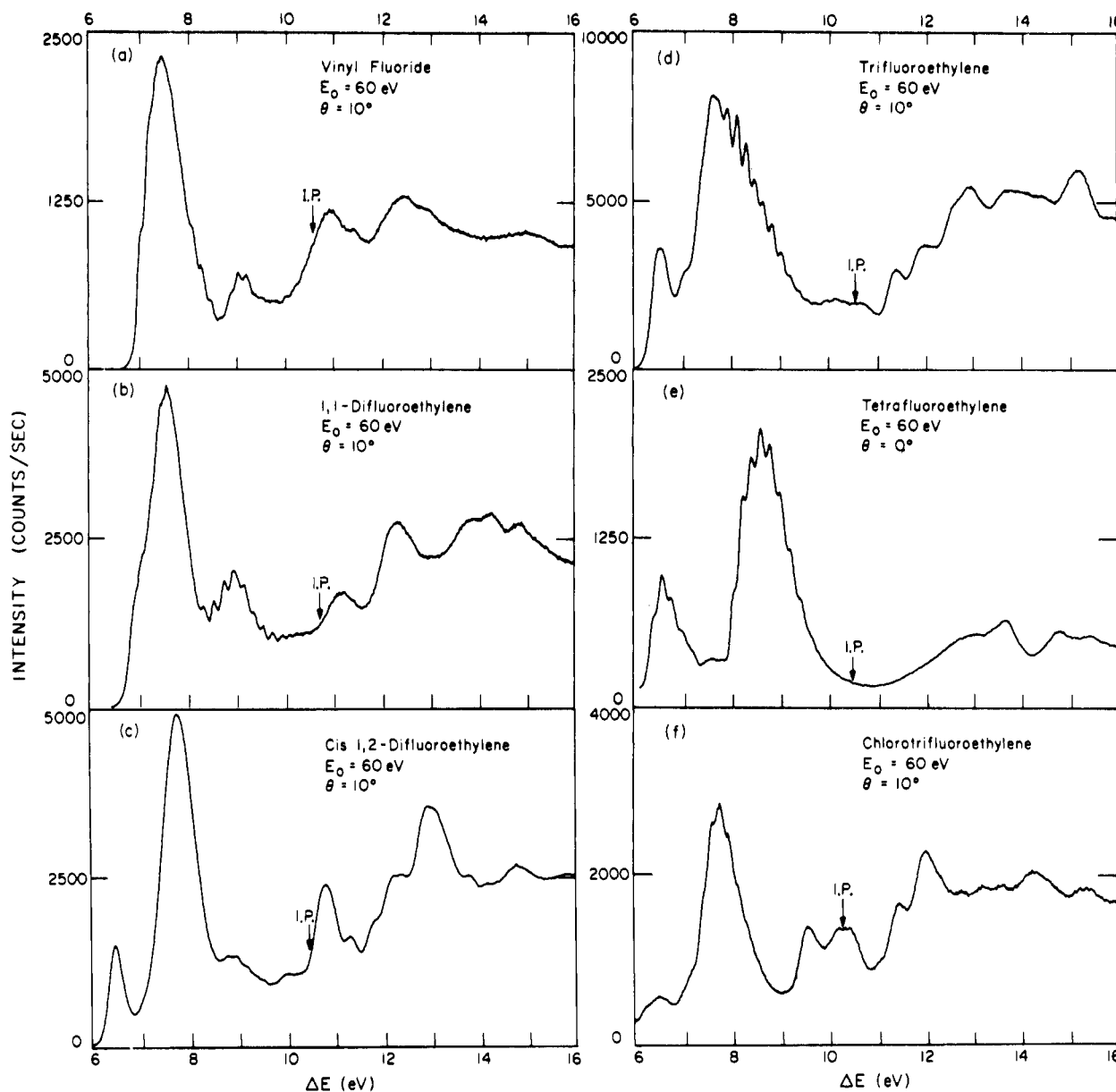
Figure 6. High-energy-loss part of energy-loss spectra of several fluoroethylenes at small scattering angle. Symbols have same meaning as in Figure 3.
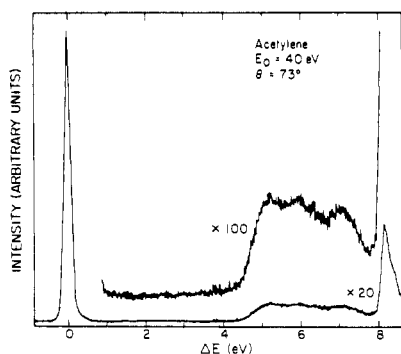

Figure 7. Electron energy-loss spectrum of acetylene. Symbols have same meaning as in Figure 3.

1 ^1B_u (N → V_1) transition.[52,53,56]

It can be seen that the transition energies of the three lowest features observed in these noncylic conjugated dienes are nearly invariant with respect to limited alkyl substitution. Since the first ionization potential of a methyl-substituted butadiene[55] is considerably lower than that of the unsubstituted molecule, we would expect the Rydberg transitions to be red-shifted. The relative constancy of the N → T_1, N → T_2, and N → V_1 transition ener-

gies suggests that all three transitions are valence $\pi \rightarrow \pi^*$ excitations. This description is consistent with the ab initio calculations[52,53] of the two triplet states, but differs from the corresponding characterization of the 1 ^1B_u state as a diffuse state. This difference in descriptions, together with the fact that the calculated $\tilde{X}$ $^1Ag \rightarrow$ 1 ^1B_u transition energy[52,53] is at least 0.7 eV greater than the observed value, indicates that the theoretical characterization of the V_1 state must be further improved. Recent progress toward this goal has been made by Nascimento and Goddard,[57] who find that the N → V_1 transition represents a "nonvertical" excitation to a relatively diffuse or "non-valence" state.

A feature of particular interest in the conjugated polyenes occurs between 7.0 and 7.8 eV in 1,3-butadiene (Figures 9 and 10). The nature of the spin-allowed transitions producing this feature remains uncertain, despite considerable experimental[54,55,58-60,115] and theoretical[52,53,56b,61] discussion. Suggested assignments for the excited states in the 7.0-7.8 eV transition energy range of 1,3-butadiene include one or more parity-forbidden ^1A_g states (V_2, V_3),[60,61] a diffuse optically allowed ^1B_u state,[52a,53] one or more n = 3 Rydberg states,[58,59] a $\sigma \rightarrow \pi^*$ transition,[60] or absorption due to s-cis-butadiene.[56b] It seems likely that, in fact, there are several overlapping transitions in this region, with the band structure representing vibronic
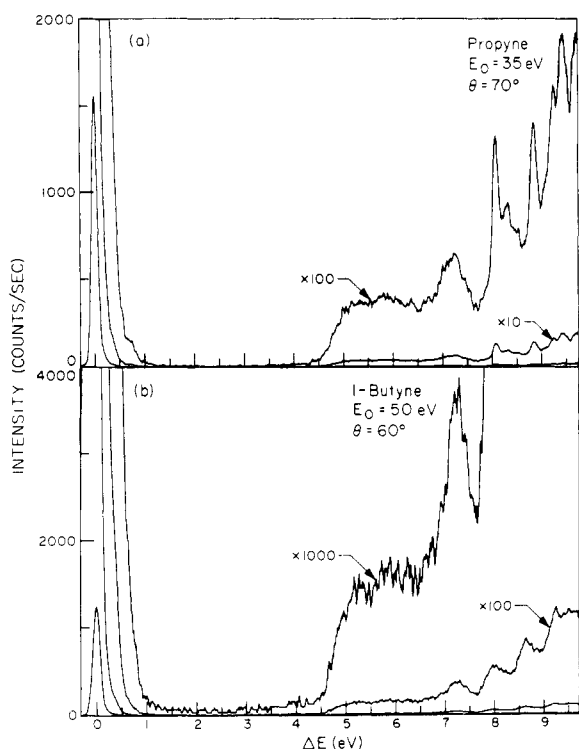
Figure 8. Energy-loss spectra of propyne and 1-butyne at large scattering angles. Symbols have same meaning as in Figure 3.

members of at least two Rydberg transitions,[58,59] which are superimposed upon the continuous absorption of underlying valence transitions (N → V_2, V_3).[60]

Figure 11 shows the electron-impact spectra of two other polyenes, 1,3,5-hexatriene and 1,3-cyclohexadiene, which are photochemically interconvertible.[62,63] This system has been extensively studied because of its relationship to the vitamin D_2-steroid system.[62,64] The low-energy-loss hexatriene spectrum[67,68,116] is similar to those of the 1,3-dienes discussed earlier, although the corresponding hexatriene transition energies are 0.6–0.8 eV lower. Theoretically, a double excitation $\tilde{X}^1A_g$ → 2 ^1A_g transition is predicted[65,66] to occur in the immediate vicinity of the $\tilde{X}$ ^1A_g → 1 ^1B_u excitation, whose first band has a peak at 4.95 eV (Figure 11a). Post, Hetherington, and Hudson[67] found slight indications of the presence of such a state in the neighborhood of 4.4-eV energy loss. However, a more extensive high-sensitivity investigation[68] at higher resolution and over a range of impact energies failed to confirm that such a state exists in the 4.2–4.6 eV transition energy range. This negative result is also supported by optical[69] and threshold electron-impact[70] studies of hexatriene as well as by recent ab initio calculations.[73] In contrast, optical studies of diphenylhexatriene[117] and larger polyenes[71,72] indicate the presence of the $\tilde{X}$ ^1A_g → 2 ^1A_g transition below the $\tilde{X}$ ^1A_g → 1 ^1B_u transition. The 2 ^1A_g state may be an intermediate in the visual process,[74] which involves the photoisomerization of 11-cis-retinal, a large polyene.

The spectrum of 1,3-cyclohexadiene (Figure 11b) is also of interest because it is a polyene which is locked into an s-cis conformation. It is interesting to note that the lowest energy transition in 1,3-cyclohexadiene, $\tilde{X}$ $^1A_1$ → 1 $^3B_2$, produces a peak at 2.94 eV, in excellent agreement with the calculated value[52a] (2.95 eV) for the analogous transition in a molecule with a similar geometric arrangement of the double bonds, s-cis-1,3-butadiene.

Several spectra of nonconjugated polyenes are displayed in Figure 12. The transition energies for the low-lying features in 1,4-hexadiene (Figure 12a) and 1,5-hexadiene (Figure 12b) are quite similar to those of ethylenic molecules such as propene, and cis- and trans-2-butene. In 1,4-cyclohexadiene (Figure 12c), the singlet → triplet transition also occurs at roughly the same
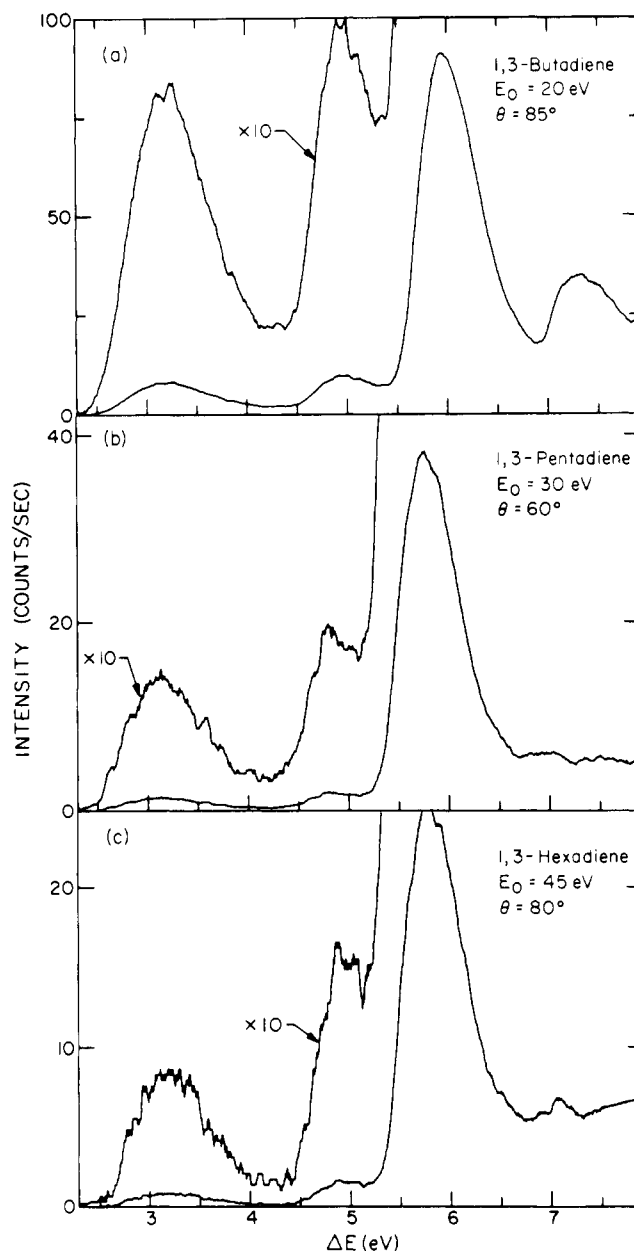

Figure 9. Energy-loss spectra of several 1,3-dienes at large scattering angle. Symbols have same meaning as in Figure 3.
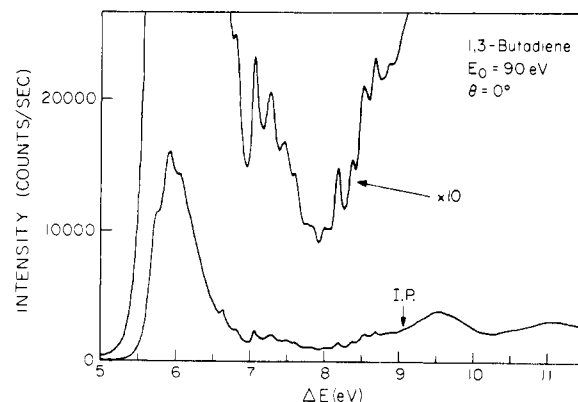

Figure 10. High-energy-loss part of energy-loss spectrum of 1,3-butadiene at high incident energy and in the forward direction. Symbols have same meaning as in Figure 3.

energy (4.29 eV) as in the ethylenic molecules and the nonconjugated dienes. However, in contrast to the monoolefin cyclohexene, in which the N → V transition energy is 6.97 eV, the strongest feature in 1,4-cyclohexadiene peaks at 7.95 eV. This
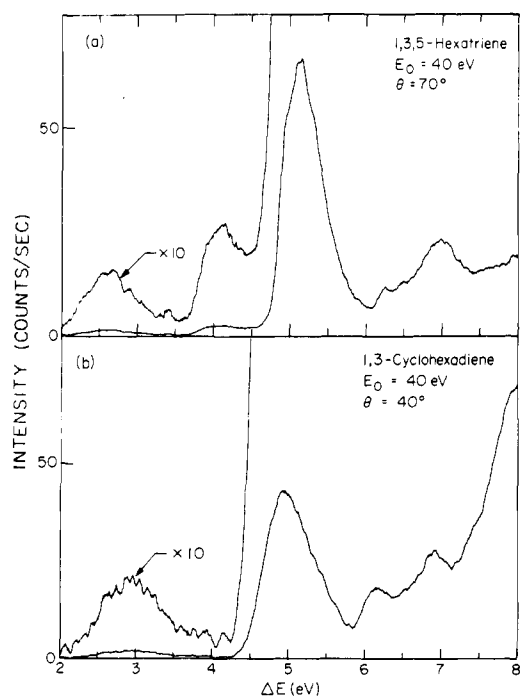
Figure 11. Energy-loss spectra of 1,3,5-hexatriene and 1,3-cyclohexadiene. The peak near 6.9 eV in the 1,3-cyclohexadiene spectrum is probably due to a benzene impurity. Symbols have same meaning as in Figure 3.

hypsochromic shift may be due to interaction of the two π orbitals by hyperconjugation with the σ_{CH} orbitals.[75] Such a "through-bond" interaction would be expected because the geometry of 1,4-cyclohexadiene is favorable to spatial overlap of the π_{CC} and σ_{CH} orbitals.[76] Theoretical models[77,78] of this interaction predict that the lowest $\pi \rightarrow \pi^*$ transition (N $\rightarrow$ V_1) is forbidden, whereas higher ones (N $\rightarrow$ V_2, V_3) are allowed. It seems likely, therefore, that the strong 7.95-eV feature corresponds to the N $\rightarrow$ V_2 and/or N $\rightarrow$ V_3 transition and is not analogous to the strong transitions in 1,4-hexadiene and 1,5-hexadiene. Since the interaction between ethylenic units in 1,4-cyclohexadiene is most probably of the "through-bond" type, the σ,π separability approximation, so useful in modeling the electronic structure of polyenes, does not appear to be valid for this system.

As a final example of a polyene, we show the energy-loss spectrum (Figure 13) of the simplest cumulene, propadiene (allene). The two low-lying features with maxima at 4.28 and 4.89 eV are identified as singlet $\rightarrow$ triplet transitions.[11] The magnitude (0.61 eV) of the splitting between these transitions is a measure of the interaction between the two adjacent, but perpendicular, π molecular orbitals. It is substantially less than than 1.69-eV separation in 1,3-butadiene,[54] even though the orbitals in allene are not physically separated by a C–C single bond, as in 1,3-butadiene. This implies that the interaction of the π MO's in allene is small, despite their physical proximity.

F. Benzene and Fluorobenzenes

Benzene has been the subject of many theoretical[79-81] and experimental[82-96,118,119] studies, but considerably controversy still surrounds the nature of certain transitions in this molecule. The three lowest triplet states have their maximum intensities at about 3.9, 4.85, and 5.7 eV.[87b] These states have been detected by investigators using oxygen-induced optical absorption,[82,83] threshold electron impact,[85] and variable-angle electron-impact[87,96] techniques. The first and third singlet $\rightarrow$ triplet transitions can be seen in Figure 14, but the second spin-forbidden excitation[83,85,87] is obscured by the lowest singlet $\rightarrow$ singlet feature, which has a maximum intensity at 4.90 eV.[84,86] The spectra in Figure 14 and the transition energies listed in
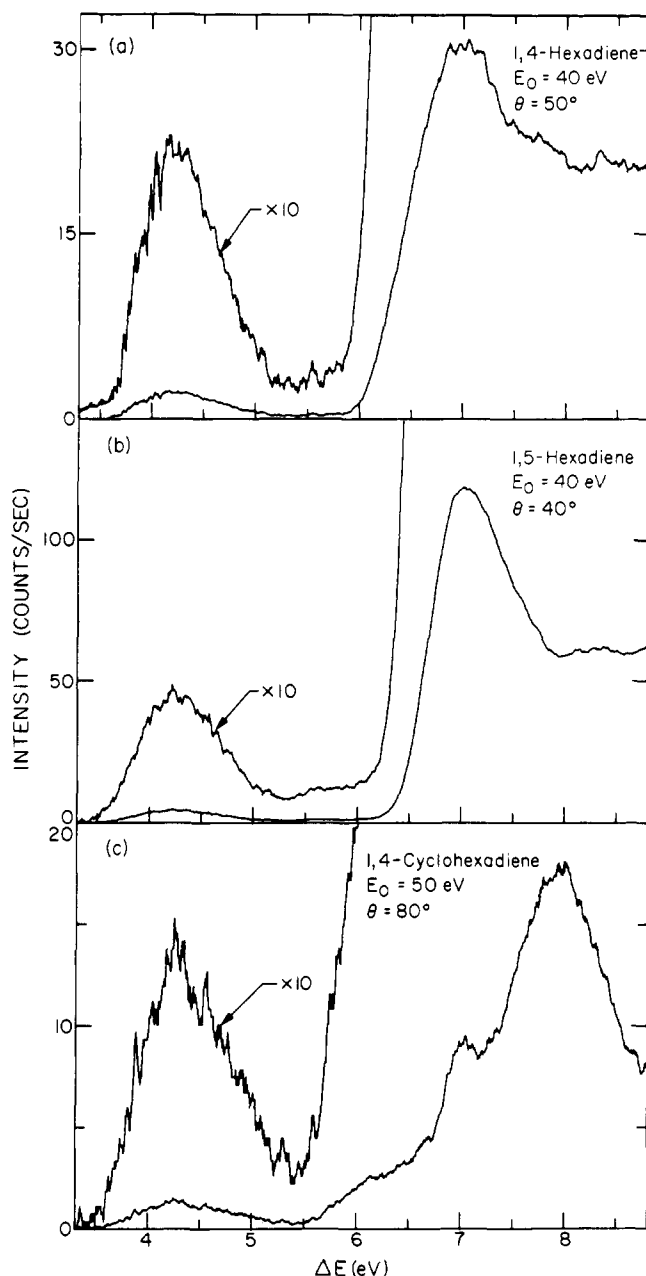

Figure 12. Energy-loss spectra of nonconjugated dienes. The peak at 6.93 eV in Figure 12c is not due to a transition in 1,4-cyclohexadiene, but rather a benzene impurity in the sample. Symbols have same meaning as in Figure 3.
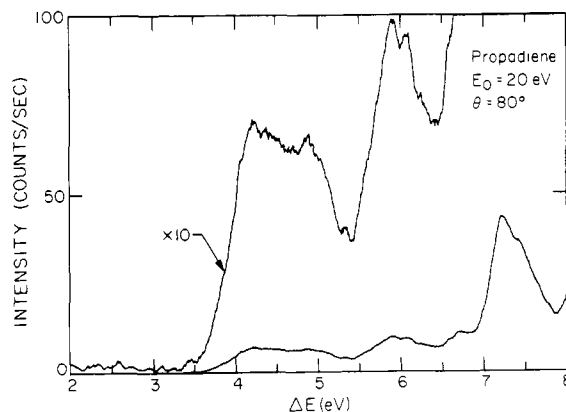

Figure 13. Energy-loss spectrum of propadiene (allene) at low incident energy and large scattering angle. Symbols have same meaning as in Figure 3.
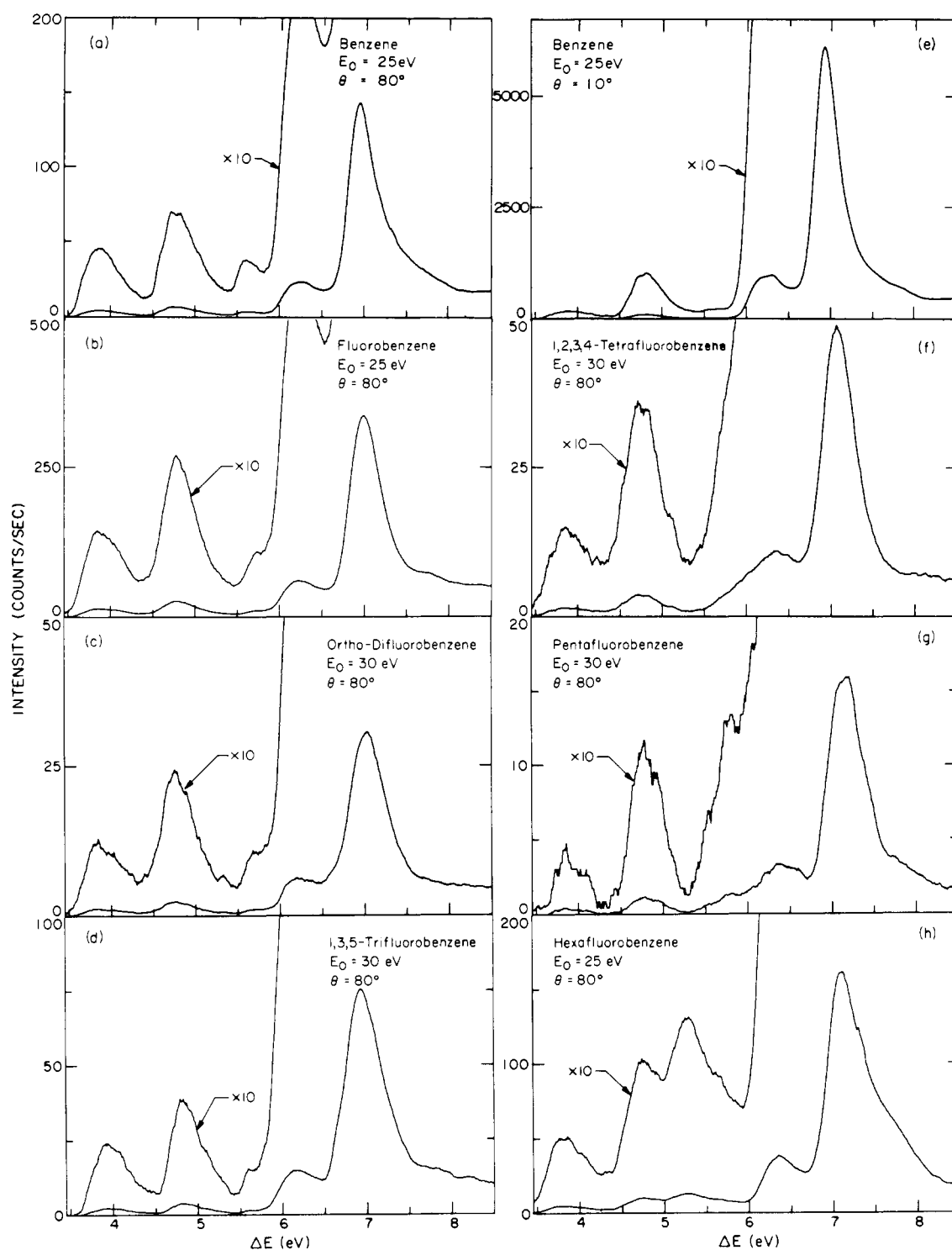
Figure 14. Energy-loss spectra of benzene and several fluorobenzenes at low incident energy and large scattering angle. Symbols have same meaning as in Figure 3.

Table I show that the positions of the first and third triplet states are relatively independent of the number of fluorine substituents. This behavior is consistent with the theoretical description[81] of the low-lying triplet states in benzene as valence-type $\pi \rightarrow \pi^*$ excitations. The lowest energy π-electron promotion ($1e_{1g} \rightarrow 1e_{2u}$) produces $^3B_{1u}$, $^3E_{1u}$, and $^3B_{2u}$ triplet states. Extensive ab initio calculations[80,81] indicate that the energy ordering of these states, from lowest to highest, is that just given.

In contrast to the triplet excited states, the assignments of most of the singlet excited states are less certain. The lowest singlet $\rightarrow$ singlet transition in benzene, at 4.90 eV, has been identified by vibronic and rotational analysis[84] as the $\tilde{X}\ ^1A_g \rightarrow$

1 $^1B_{2u}$ excitation, while the intense transition at 6.96 eV is undoubtedly the optically allowed $\tilde{X}\ ^1A_g \rightarrow$ 1 $^1E_{1u}$ transition.[79-81] Both transitions, as well as the one at 6.25 eV, are observed at approximately the same energy loss in all the fluorobenzenes that have been studied. Since complete fluorine substitution causes a modest 0.88 eV increase in the lowest ionization potential of benzene,[94] the comparative constancy of these three singlet $\rightarrow$ singlet transition energies suggests that the excited states are valence states. This agrees with the theoretical description[81] of the $^1B_{2u}$ state; however, the $^1E_{1u}$ state is predicted[81] to be considerably more diffuse, or Rydberg-like. In fact, the $\tilde{X}\ ^1A_g \rightarrow\ ^1E_{1u}$ transition energy does show somewhat greater,
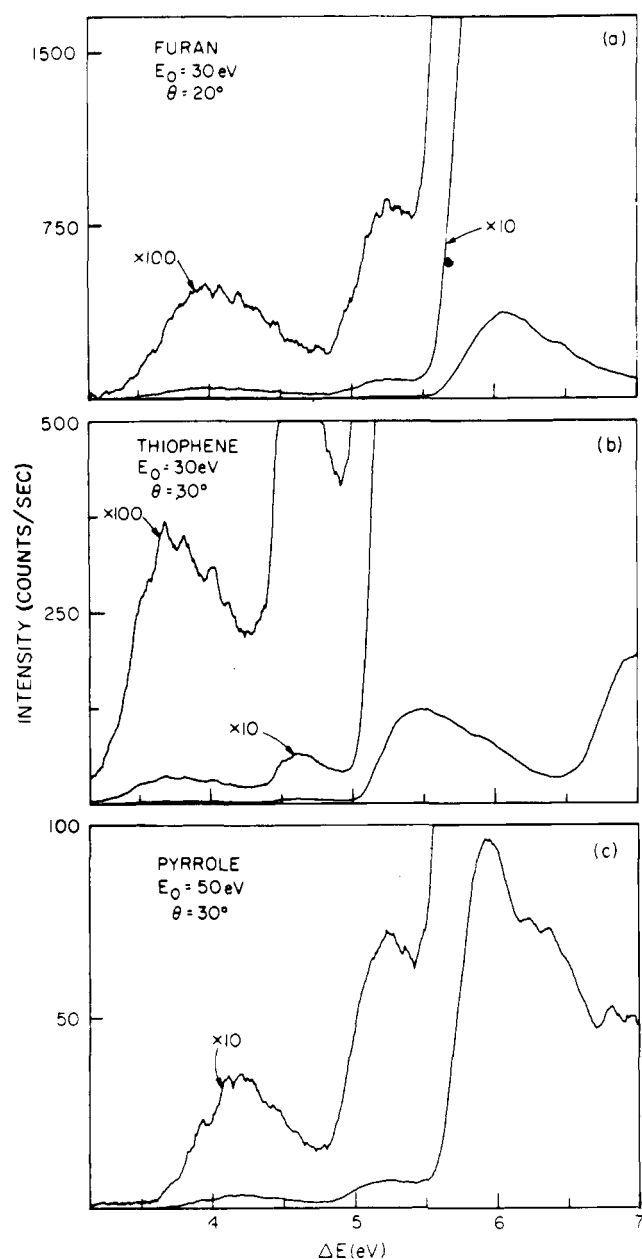
Figure 15. Energy-loss spectra of furan, thiophene, and pyrrole. Symbols have same meaning as in Figure 3.

nonmonotonic fluctuation with increasing substitution than does the $\tilde{X}$ $^1A_g \rightarrow 1$ $^1B_{2u}$ transition energy, but the overall behavior is clearly more like that of a valence transition than a Rydberg one. The assignment of the excitation at 6.25 eV in benzene is not completely certain, but on the basis of a vibronic analysis of the optical bands,[88,89] it is most likely the $\tilde{X}$ $^1A_g \rightarrow 1$ $^1B_{1u}$ ($\pi \rightarrow \pi^*$) transition. However, alternative assignments of this feature as the $\tilde{X}$ $^1A_g \rightarrow 1$ $^1E_{2g}^-$ [90] or as even a $\sigma \rightarrow \pi^*$ excitation[90] cannot yet be eliminated.

One of the most interesting results of recent studies of benzene is the presence of an additional singlet $\rightarrow$ singlet transition at an energy of about 5.8 eV in high-resolution, low-temperature optical investigations.[91,92] It has been suggested that the upper state of this transition is $^1E_{2g}$[91] or $^1E_{2g}^-$,[92] in the "alternant" symmetry notation. This assignment disagrees with the interpretation by Karwowski[79] of flash photolysis studies of benzene.[95] In addition, several theoretical calculations[79,81] place this state above the $^1E_{1u}$ state. The electron-impact spectra in Figure 14 provide no evidence for this transition in benzene or in those fluorobenzenes with fewer than four substitutents.[96] However, in the tetrafluorobenzenes, there is a distinct broad-

ening of the 6.5-eV transition on the low-energy-loss tail. In pentafluorobenzene, a definite shoulder is observed at about 5.85 eV. In hexafluorobenzene, a completely separated, fourth singlet $\rightarrow$ singlet transition is observed with a maximum intensity at 5.32 eV.[96] Nevertheless, because of the magnitude of the hypsochromic shift with increasing fluorine substitution, it seems unlikely that this new feature is analogous to the 5.8-eV transition in benzene. For a similar reason, it is doubtful that the 5.32-eV transition represents excitation of a low-lying Rydberg state.[96] An alternative assignment is that the new feature is related to the transition detected in benzene in higher resolution electron-impact studies[87b] of the 6.0-6.5 eV energy loss region. A new feature has also been observed in benzene between 6.23 and 6.68 eV with the technique of multiphoton ionization spectroscopy.[93] It seems possible that both techniques have detected the same transition, and that it may be the elusive $\tilde{X}$ $^1A_g \rightarrow$ $^1E_{2g}$ excitation or, more likely, the $\tilde{X}$ $^1A_g \rightarrow 1$ $^1E_{1g}$ Rydberg transition.[119] Other possibilities are that the new transition in the fluorobenzenes may involve either a charge-transfer $F_{p_\pi} \rightarrow C_{p_\pi}$ excitation or an $F_{p_\pi} \rightarrow C-F_{\sigma^*}$ transition, in a manner similar to that which has been postulated[97] for a low-lying transition in hexachlorobenzene. Clearly, there is need for further study of this transition by experimental and theoretical techniques.

G. Five-Membered Heterocycles

Electron-impact investigation[98,99] of the five-membered heterocycles furan (C_4H_4O), thiophene (C_4H_4S), and pyrrole (C_4H_4NH) has clarified greatly the transition energy region below 6 eV. Singlet $\rightarrow$ triplet transitions are observed in all three molecules (Figure 15). The locations of these transitions support the inferences[100] that these molecules have considerable aromatic character, and that their low-energy-loss spectra cannot be satisfactorily interpreted as being due to the s-cis diene chromophore formally contained in the canonical electronic structure diagrams.

The lowest singlet $\rightarrow$ triplet $\pi \rightarrow \pi^*$ transition occurs at 3.75 eV energy loss in thiophene, 3.99 eV in furan, and 4.20 eV in pyrrole. For comparison, the lowest singlet $\rightarrow$ triplet transition in benzene occurs at 3.9 eV. The second singlet $\rightarrow$ triplet excitation peaks at 4.62 eV in thiophene,[98] 5.1 eV in pyrrole,[99] and 5.21 eV in furan.[98] Although the 5.1-eV feature in pyrrole was originally assigned to a $\pi \rightarrow \pi^*$ transition, Butscher and Thunemann[101] recently suggested this is actually a Rydberg singlet $\rightarrow$ triplet transition. Nevertheless, it seems possible that this transition energy region may contain two singlet $\rightarrow$ triplet transitions, one Rydberg and one $\pi \rightarrow \pi^*$. In benzene, the second singlet $\rightarrow$ triplet transition occurs in the same energy-loss region, at 4.85 eV.[87b] If these singlet $\rightarrow$ triplet transitions in the heterocycles only involved the two conjugated double bonds, as in s-cis-1,3-butadiene, the lowest state would be predicted to occur at a much lower excitation energy (2.9 eV)[52] than is observed in the heterocycles. In addition, the energy splitting expected between the first two triplet states in an s-cis diene (~2 eV)[52] is considerably greater than that which is observed in furan, thiophene, and pyrrole.

These results provide spectroscopic evidence that two formally nonbonding electrons on the heteroatom in these three molecules are delocalized into the π-electron ring system. In confirmation of this interpretation, the lowest singlet $\rightarrow$ triplet excitation in 1,3-cyclopentadiene, which has no heteroatoms, is observed with a maximum at 3.1 eV.[98] The energy splitting between the two lowest triplet states could not be determined, presumably because the lowest singlet $\rightarrow$ singlet transition overlaps the second singlet $\rightarrow$ triplet feature. However, we can conclude that the splitting between the first two triplet states in 1,3-cyclopentadiene is no less than 1.7 eV. These data indicate that, unlike the heteroatomic cyclic dienes, the triplet states of this system are dienic, rather than aromatic in nature.

Despite the presence of a second pair of formally nonbonding electrons in both furan and thiophene, no evidence has been found for singlet $\rightarrow$ singlet n $\rightarrow$ π^* transitions, in agreement with earlier UV absorption studies.[100] High-quality ab initio calculations on the n $\rightarrow$ π^* transitions in these molecules would be most useful in indicating the appropriate excitation energy ranges in which to search most intensively for these features.

H. Azo Compounds

The electron energy-loss spectra[102] of both azomethane and azo-*tert*-butane are quite similar at energy losses below 5.5 eV (Figure 16). Both contain three transitions, two spin-forbidden and one spin-allowed in this region. The lowest lying triplet state in each molecule, occurring near 2.7-eV energy loss, is presumably the $1\,^3B_g$ state. It is produced by excitation of an electron from a nonbonding orbital (n_+), formed from the lone pair orbitals on the two nitrogens, to a π^* orbital.[102] The transition to the corresponding singlet state $(1\,^1B_g)$, peaks at 3.50 eV in azomethane and 3.37 eV in azo-*tert*-butane. A weak feature peaking between 4.8 and 4.9 eV in these molecules is identified as a $\pi \rightarrow \pi^*$ singlet $\rightarrow$ triplet transition.

It has recently been suggested[103] on the basis of self-consistent nonempirical calculations that the 2.7-eV transition may, in fact, be the second singlet $\rightarrow$ triplet transition, and that the $X\,^1A_g \rightarrow 1\,^3B_g$ excitation was not detected in electron-impact studies, either because it is weak or because such studies did not extend to low enough excitation energies. However, unpublished variable-angle electron-impact spectra[102b] which extend to 0-eV energy loss gave no evidence of lower transitions, which, if they do exist, must be at least a factor of 5 weaker than the 2.7-eV transition.

The energies of the three lowest-lying transitions are relatively insensitive to alkyl substitution. This suggests that these transitions involve only electrons on the diimide diradical group $(-N{=}N-)$ and should be observed at approximately the same transition energy in other nonaromatic acyclic azo compounds. The transitions in azomethane and azo-*tert*-butane above 5.5 eV, however, are not similar in transition energy or intensity, and therefore presumably involve the alkyl group, or Rydberg orbitals.

I. Additional Molecules

A number of other interesting molecules and series of compounds have been investigated by variable-angle, electron-impact spectroscopy, and discussions of these systems have been published recently or will be published in forthcoming articles. Among these molecules are nitric oxide,[104] ammonia,[120] water,[123] nitromethane,[121] ketene,[12] thiophosgene,[105] sulfur hexafluoride,[124] norbornene,[106] norbornadiene,[106] acetonitrile,[122] and uranium hexafluoride.[107] Transition energies for some of these systems are listed in Table I.

V. Conclusion

The examination of the energies of singlet $\rightarrow$ triplet and of singlet $\rightarrow$ singlet transitions permitted by variable-angle, low-energy electron-impact spectroscopy has helped elucidate the electronic structure of many π-electron systems. Variation of these transition energies with chemical substitution has helped clarify their valence or Rydberg character; for polyenes, the magnitude of the separation between the triplet states has given information about π-electron interactions. The knowledge obtained has been useful in checking the accuracy of ab initio calculations of the electronically excited states of interesting molecules and has provided useful guidance and suggestions for future calculations. The positions and shapes of singlet $\rightarrow$ triplet band systems are useful for the prediction and interpretation of the magnitude of phosphorescence yields and life-
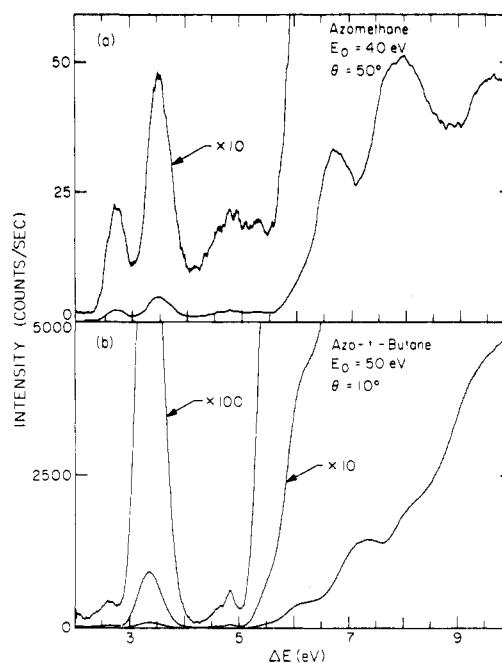

Figure 16. Energy-loss spectra of azomethane and azo-*tert*-butane. Symbols have same meaning as in Figure 3.

times[108] and for the interpretation of photosensitization experiments.[109]

The wide range of transition energies which can easily be detected (1 to >20 eV), corresponding to an optical wavelength of 1236 nm to below 62 nm, permits easy extension of the investigation of many molecules into the far-vacuum ultraviolet region of their spectra. This capability has permitted the detection of many previously unobserved transitions to superexcited states which lie in the ionization continuum and which undoubtedly play an important role in radiation chemistry and physics.[110] The relatively low sample pressures required by this technique, of the order of 1–10 mTorr, and its wide dynamic range, allowing detection of transitions differing by as much as four orders of magnitude in intensity, contribute to make this method useful for the investigation of a wide variety of substances and of quite weak transitions. The use of molecular beam targets and heated sample inlet systems should permit the study of free radicals and of relatively high molecular weight substances in the near future. The main shortcoming of the electron-impact technique is its energy resolution, typically of the order of 0.05–0.15 eV. This is very low resolution when compared with that common in many optical spectra $(10^{-4}$ eV). However, the other advantages of variable-angle, low-energy, electron-impact spectroscopy outlined above, and especially its ability to detect and assign low-lying triplet states, make it a very useful spectroscopic tool, which nicely complements optical spectroscopy.

VI. References and Notes

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