

# Electron-impact spectroscopy of the fluoroethylenes\*

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The electron-impact excitation spectra of the six fluoroethylenes and chlorotrifluoroethylene have been investigated at impact energies of 60, 40, and either 20 or 25 eV, and at scattering angles from 0° to 80°. The energy and angular dependence of the relative differential cross sections was determined for several features in the energy-loss range 0–16 eV. This information was used to identify transitions as either spin-forbidden or spin-allowed. In each molecule, the lowest observed inelastic transition is a spin-forbidden excitation with maximum intensity between 4.18 and 4.68 eV. The locations of these transitions, which are analogous to the  $N \rightarrow T$  transition in ethylene, can be used to interpret the results of some photochemical electronic energy transfer experiments. A second weak singlet–triplet transition occurs in vinyl fluoride with a maximum intensity at 6.4 eV. The other features observed in the 6–10 eV energy-loss region of these molecules agree well with optical spectra. In particular, the large positive shift in the  $N \rightarrow V$  transition energy of tetrafluoroethylene is confirmed. However, no such shift occurs in the  $N \rightarrow V$  maximum intensity transition energy of chlorotrifluoroethylene (7.80 eV), indicating that the steric resistance to torsion is probably not the cause of the observed shift in tetrafluoroethylene. Transitions to many superexcited states lying above the first ionization potential are observed in each molecule. Using the term value method, many of these transitions, as well as lower-lying ones, are assigned to Rydberg series. The average term values obtained in this study agree well with those determined from other series of molecules.

## I. INTRODUCTION

Measurements of the electronic spectra of the six fluoroethylene molecules provide an opportunity to assess the effects of fluorine atom substitution on the electronic structure and spectrum of ethylene.<sup>1–3</sup> Recent optical studies<sup>4</sup> of the fluoroethylenes have shown that the  $N \rightarrow V$  transition energies in five of these molecules are close to that in ethylene, but that there is a large hypsochromic (positive) shift in this energy for tetrafluoroethylene. These experiments have been limited both by the optical selection rules and by the relatively narrow range of transition energies studied (6.2–10.8 eV). As a result, no information has been obtained concerning transitions outside of this energy range, nor have any spin-forbidden singlet–triplet transitions been observed optically. While both ion impact<sup>5</sup> and threshold electron-impact<sup>6</sup> investigations have recently produced evidence for spin-forbidden transitions in several of the fluoroethylenes, no complete study of these excitations is available.

In an effort to overcome these deficiencies, a systematic study of the electronic transitions in the six fluoroethylenes as well as chlorotrifluoroethylene was undertaken using the low energy, variable-angle electron-impact technique.<sup>3</sup> This method provides information on electronic transition energies over a broad energy-loss range (0–16 eV in these studies), and permits reliable identification of each electronic transition as spin-allowed or spin-forbidden. The suitability of the electron-impact technique for obtaining this type of information is well documented.<sup>3</sup> In the present study, excitation spectra were obtained at 60, 40, and either 20 or 25 eV impact energy ( $E_0$ ), and scattering angles ( $\theta$ ) from 0° to 80°.

In the following sections, previous experimental and theoretical work is summarized, the pertinent experimental details of the present work are given, and the

results are presented and discussed. The assignments of various transitions are made with reference to the known states of ethylene, in the case of valence excitations, and by using the term value approach<sup>7</sup> for Rydberg transitions. A brief discussion of the implications of this work for the photochemistry of some of the fluoroethylenes is also given.

## II. PREVIOUS EXPERIMENTAL AND THEORETICAL STUDIES OF THE ELECTRONIC STRUCTURE OF THE FLUOROETHYLENES

### A. Optical spectroscopy

The only complete optical investigation of the fluoroethylenes is that due to Bélanger and Sandorfy.<sup>4</sup> Their study, extending from 2000 Å (6.2 eV) to 1150 Å (10.8 eV), revealed a strong  $\pi \rightarrow \pi^*$ , singlet–singlet transition in each molecule. Most of the maxima were at an energy near that of the strong  $N \rightarrow V$  absorption of ethylene,<sup>1</sup> except for tetrafluoroethylene, for which a large (1.2 eV) blue shift was observed. In addition, for each molecule several Rydberg series converging to the first ionization potential (I.P.) were identified. The results of this optical study are listed in Table I.

The vacuum ultraviolet absorption spectrum of chlorotrifluoroethylene has been studied in the region from 2100 Å (5.9 eV) to 1200 Å (10.3 eV) by Scott and Russell.<sup>8</sup> They assigned bands belonging to the  $N \rightarrow V$  transition and three separate Rydberg series, and also determined an adiabatic ionization energy.

### B. Ion-impact and threshold electron-impact spectroscopy

Several members of the fluoroethylene series have been studied by ion-impact<sup>5</sup> and threshold electron-impact<sup>6</sup> techniques. In each case, these methods have revealed low-lying absorptions which were attributed to spin-forbidden singlet–triplet transitions.

TABLE I. Vertical transition energies for the fluoroethylenes (eV).

Molecule	Transition							
	$N \rightarrow T$			$N \rightarrow V$			$N \rightarrow$ Superexcited states	
	Expt.		Calc. <sup>d</sup>	Expt.		Calc. <sup>d</sup>		
	Present work	Other work		Present work	Other work	Present work <sup>e</sup>	Other work <sup>b</sup>	
C <sub>2</sub> H <sub>3</sub> F	4.40 (3.4–5.4) <sup>a</sup>	4.4 <sup>b</sup>	5.30	7.50	7.44 <sup>a</sup> , 7.2 <sup>b</sup>	8.17	11.1, 12.5 <sub>5</sub> , 15.2	11.0, 11.35, 12.55, 14.95, 16.55
1,1-C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	4.63 (3.8–5.5) <sup>a</sup>	4.6 <sup>c</sup>	5.43	7.50	7.50 <sup>e</sup> , 7.6 <sup>c</sup>	8.19	11.0 <sub>5</sub> , 12.2, 13.8; 14.2, 14.7	11.3, 12.3, 13.9, 14.3, 14.9, 18.4, 20.25
<i>cis</i> -1,2-C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	4.43 (3.7–5.4) <sup>a</sup>	...	4.58	7.82	7.81 <sup>a</sup>	7.41	10.9, 11.4, 11.9, 12.3, 13.0, 13.8, 14.8	...
<i>trans</i> -1,2-C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	4.18 (3.5–5.2) <sup>a</sup>	...	4.58	7.39	7.28 <sup>a</sup>	7.40	10.9, 12.0, 12.4 <sub>5</sub> , 12.9, 13.2, 13.7, 15.2, 16.9	...
C <sub>2</sub> HF <sub>3</sub>	4.43 (3.5–5.4) <sup>a</sup>	...	5.27	7.65	7.61 <sup>a</sup>	8.17	11.4, 12.0, 12.9, 13.8, 15.2	...
C <sub>2</sub> F <sub>4</sub>	4.68 (3.6–5.6) <sup>a</sup>	...	6.00	8.84	8.88 <sup>a</sup>	9.16	13.3, 13.9, 15.0, 15.7	...
C <sub>2</sub> ClF <sub>3</sub>	4.43 (3.6–5.2) <sup>a</sup>	...	...	7.80	7.79 <sup>f</sup>	...	11.4, 12.0, 12.7, 13.2, 14.3, 15.4	...

<sup>a</sup>Estimated Franck-Condon region.<sup>b</sup>Reference 6.<sup>c</sup>Reference 5.<sup>d</sup>Reference 17.<sup>e</sup>Reference 4.<sup>f</sup>Reference 8.<sup>g</sup>A preliminary list of these transition energies was published in Ref. 20. Some of the present values differ from the earlier ones, and represent the results of a more comprehensive, computerized analysis of the data.<sup>h</sup>Reference 29.

Using 3 keV He<sup>+</sup> ions, Moore<sup>5</sup> observed a transition at 4.6 eV in 1,1-difluoroethylene. The absence of this feature in the corresponding H<sup>+</sup> impact spectra suggests that it is excited by an electron exchange process, giving rise to a singlet-triplet transition. The peak was assigned to the  $N \rightarrow T$  ( $\pi \rightarrow \pi^*$ ) transition in analogy with the  $N \rightarrow T$  singlet-triplet absorption seen at 4.32 eV in ethylene.<sup>9</sup> An additional peak was observed in 1,1-difluoroethylene at 7.6 eV in the energy-loss spectra of both ions, and was therefore assigned as the  $N \rightarrow V$  singlet-singlet transition.

O'Malley and Jennings<sup>6</sup> have observed a transition, presumably the  $N \rightarrow T$ , at 4.4 eV in monofluoroethylene in a threshold electron impact study using SF<sub>6</sub> as a scavenger for thermal energy electrons in an ion cyclotron resonance mass spectrometer. The spectrum, obtained at 0.5 eV resolution, shows additional transitions at 7.2 and 9.6 eV. The former is presumably the  $N \rightarrow V$  singlet-singlet transition, while the latter was not identified. The transition energies obtained by the threshold electron-impact method,<sup>6</sup> as well as those from the ion-impact study,<sup>5</sup> are listed in Table I.

### C. Ionization potentials

The effects of fluorine substitution on the energies of the neutral ground state and the various ionic states of ethylene can be seen in the ionization potentials of the fluoroethylenes. Measurements of the first I.P., corresponding to the removal of an electron from the highest occupied  $\pi$  orbital of each of the fluoroethylenes, have been made both by photoionization<sup>10–12</sup> and electron impact methods.<sup>13</sup> The results show only a  $\pm 0.2$  eV variation over the entire series with respect to the 10.51 eV first I.P. of ethylene.<sup>10</sup> The second I.P. values, which correspond to  $\sigma$  electron removal, have been

measured by several investigators.<sup>10,12</sup> In contrast with the first I.P. values, they increase by 3 eV in going from ethylene to tetrafluoroethylene.

The photoelectron spectrum of chlorotrifluoroethylene was obtained by Lake and Thompson.<sup>12</sup> Their results, as well as the corresponding values for the other fluoroethylenes, are listed in Table II.

### D. Theoretical calculations

Several theoretical studies<sup>14–17</sup> have made predictions of the effect of fluorine substitution on both the electronic excitation and photoelectron spectra of the parent ethylene molecule. Simple Hückel-type molecular orbital calculations by Landau *et al.*<sup>14</sup> have shown that the energy of the electron in the highest occupied  $\pi$  orbital of the fluoroethylenes is close to that of the electron in the ethylene  $\pi$  orbital. This finding has been confirmed in the case of monofluoroethylene by Meza and Wahlgren<sup>15</sup> using a simple Gaussian basis set in an SCF calculation.

However, these calculations<sup>14,15</sup> do not provide any information on the  $N \rightarrow T$  or  $N \rightarrow V$  transition energies of the fluoroethylenes. Recently, semiempirical MO-CI calculations for the singlet-triplet and singlet-singlet transition energies of the fluoroethylenes have been performed by Salahub.<sup>17</sup> Energies were obtained for both the  $N \rightarrow T$  and  $N \rightarrow V$  transitions, and are discussed below.

### III. EXPERIMENTAL METHODS

Both the electron-impact spectrometer and the data accumulation and reduction methods have been described previously.<sup>18,19</sup> An electron beam, energy-selected by a hemispherical electrostatic energy analyzer, is scattered off the target gas contained in a flexible

TABLE II. Vertical transition energies, term values, and assignments of Rydberg series in fluoroethylenes.<sup>a</sup>

Molecule	Ionization potential (eV)	Vertical transition energy (eV)	Term value (eV)	Assignment
C <sub>2</sub> H <sub>3</sub> F	10.58 <sup>b</sup>	7.02	3.56	3s
		8.08	2.50	3p
		8.67	1.91	4s
		8.87	1.71	3d
		9.37	1.21	4p
		9.72	0.86	5s
		9.84	0.74	5p
		10.03	0.55	6s
		10.2 <sub>2</sub>	3.57	3s
		11.1	2.69	3p
1,1-C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	13.79 <sup>b</sup>	12.5 <sub>5</sub>	1.24	4p
		6.95	3.77	3s
		8.23	2.49	3p
		9.08	1.64	4s
		9.26	1.46	3d
		9.44	1.28	4p
		9.81	0.91	5s
		10.01	0.71	5p
		11.0 <sub>5</sub>	3.74	3s
		12.2	2.59	3p
<i>cis</i> -1,2-C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	10.72 <sup>b</sup>	13.8	0.99	5s
		14.2	0.59	6s
		14.7	3.52	3s
		14.79 <sup>b</sup>		
		18.22		
		6.52	3.91	3s
		8.38	2.05	3p
		8.81	1.62	4s
		9.01	1.42	3d
		9.20	1.23	4p
<i>trans</i> -1,2-C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	10.43 <sup>c</sup>	9.55	0.88	5s
		10.2 <sub>5</sub>	3.72	3s
		11.4	2.57	3p
		11.9	2.07	4s
		12.3	1.67	3d
		13.0	0.97	5s
		13.97 <sup>c</sup>		
		6.44	3.94	3s
		7.88	2.50	3p
		8.68	1.70	4s
C <sub>2</sub> HF <sub>3</sub>	10.38 <sup>c</sup>	8.80	1.58	3d
		8.97	1.41	4p
		9.53	0.58	5s
		10.2	3.70	3s
		10.9	3.00	3p
		12.0	1.90	4s
		12.4 <sub>5</sub>	1.45	3d
		12.9	1.0	5s
		13.90 <sup>c</sup>		
		C <sub>2</sub> HF <sub>3</sub>	10.53 <sup>c</sup>	6.56
7.98	2.55			3p
8.74	1.79			4s
8.91	1.62			3d
9.31	1.22			4p
9.53	1.00			5s
C <sub>2</sub> HF <sub>3</sub>	10.53 <sup>c</sup>	11.4	3.24	3s
		12.0	2.64	3p

TABLE II (Continued)

Molecule	Ionization potential (eV)	Vertical transition energy (eV)	Term value (eV)	Assignment
C <sub>2</sub> F <sub>4</sub>	14.64 <sup>c</sup>	12.9	1.74	3d or 4s
		13.8	0.84	5s
	10.52 <sup>c</sup>	6.62	3.90	3s
		8.01	2.51	3p
		8.84	1.68	4s
		9.04	1.48	3d
		9.44	1.08	4p
		9.65	0.87	5s
	15.95 <sup>c</sup>	13.3	2.65	3p
		13.9	2.05	4s
		15.0	0.95	5s
	C <sub>2</sub> ClF <sub>3</sub>	10.24 <sup>b</sup>	6.51	3.74
7.79			2.45	3p
8.26			1.98	4s
8.50			1.74	3d
8.94			1.30	4p
13.01 <sup>b</sup>		9.60	0.64	5s
		11.4	1.61	3d or 4s
			12.0	1.01

<sup>a</sup>Except for the ionization potentials, the values listed in this table are the results of the present study.

<sup>b</sup>Reference 11.

<sup>c</sup>Reference 9.

collision chamber. The electrons scattered at a variable, preselected angle have their energy determined by a second electrostatic energy analyzer, and are detected with an electron multiplier and pulse counting system.

Spectra were obtained with an instrumental resolution chosen between 0.06 and 0.15 eV, as measured by the full width at half-maximum (FWHM) of the elastic peak. The gas sample pressure in the scattering chamber was maintained at approximately  $5 \times 10^{-3}$  torr, as measured by an uncalibrated Schulz-Phelps ionization gauge.

The monofluoroethylene (vinyl fluoride), the 1,1-difluoroethylene and the chlorotrifluoroethylene were obtained from Matheson Gas Products with stated purities of 99.9%, 99.0%, and 99.0%, respectively. All other gas samples were from PCR Incorporated, and had 97.0% minimum purity. Each sample was subjected to a liquid nitrogen freeze-pump-thaw cycle before use, and no evidence for impurity absorption was observed in any of the spectra.

The areas under the elastic peak and each of several inelastic features are obtained by numerical integration<sup>18</sup> as described previously. The relative differential cross section (DCS) values for each molecule were also determined by a previously described method.<sup>19</sup> These cross sections are normalized by setting the elastic DCS at a given impact energy to 1.0 at  $\theta = 40^\circ$ . The arbitrary units thus determined are therefore different for each molecule and for each impact energy.

## IV. RESULTS AND DISCUSSION

A preliminary report on these studies has been published elsewhere.<sup>20</sup> Tables I and II summarize the excitation energies obtained in the present experiments. Peak locations below the first I.P. determined from the electron impact spectra have an uncertainty of  $\pm 0.05$  eV, peak locations of transitions to superexcited states above the first I.P. have an uncertainty of  $\pm 0.1$  eV, while the Franck-Condon limits of each transition are estimated to  $\pm 0.1$  eV.

### A. Vinyl Fluoride

Figure 1 shows two energy-loss spectra of vinyl fluoride at scattering angles of  $10^\circ$  and  $40^\circ$  at an impact energy of 40 eV. The first observed inelastic feature has an onset at about 3.4 eV and extends to about 5.4 eV, with a peak at 4.40 eV. This value agrees with the peak position obtained by the threshold electron-impact study,<sup>6</sup> as given in Table I. The ratio of the area under this inelastic feature to that under the singlet-singlet absorption at 7.5 eV is shown in Fig. 2(a), as a function of the scattering angle for an impact energy of 40 eV. An increase in this ratio by a factor of about 50 over the angular range from  $10^\circ$  to  $80^\circ$  is apparent. In addition, the ratio at  $E_0 = 25$  eV is larger than at  $E_0 = 40$  eV for all scattering angles studied. This behavior is indicative of a spin-forbidden transition.<sup>2,3,18-20</sup> The nearly isotropic nature of the DCS curves in Fig. 3 also supports this conclusion. In analogy with the 4.32 eV

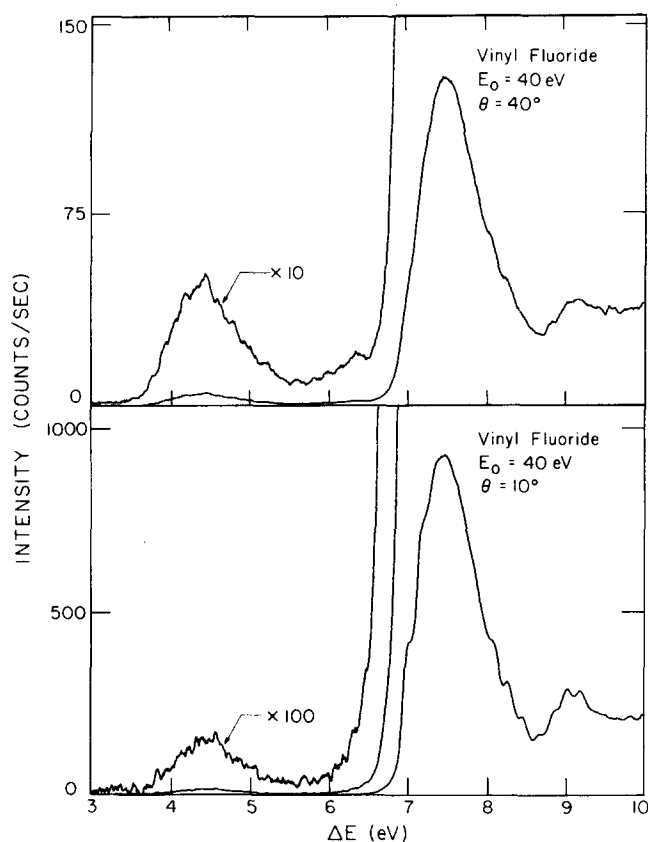


FIG. 1. Electron energy-loss spectrum of vinyl fluoride at an impact energy ( $E_0$ ) of 40 eV. (a)  $\theta = 10^\circ$ ; 0.10 eV FWHM (full width at half-maximum of elastic peak); 2.0 mtorr sample pressure reading from an uncalibrated Schulz-Phelps ionization gauge; (b)  $\theta = 40^\circ$ ; 0.12 eV FWHM; 2.6 mtorr sample pressure reading.

singlet-triplet ( $\pi-\pi^*$ ) transition in ethylene, this feature is designated as the  $N-T$  transition.

At scattering angles of  $30^\circ$  and above, a weak transition appears as a shoulder on the low energy-loss side of the 7.50 eV excitation. This feature was more prominent at an impact energy of 25 eV than at 40 eV. Using a  $\theta = 0^\circ$  spectrum of vinyl fluoride as a reference, this peak was more accurately located by deconvoluting<sup>18</sup> a  $\theta = 60^\circ$  spectrum. The resulting peak, located at 6.4 eV, is shown in Fig. 4. While a quantitative evaluation of the energy and angular dependences of this feature was not possible due to its weakness, a qualitative examination of its behavior indicates that it is a singlet-triplet transition corresponding to the sharp singlet-singlet excitation observed at 7.0 eV. The latter has been identified as the first member of a  $\pi-\sigma^*(3s)$  Rydberg series.<sup>1</sup> Alternately, it could be associated with one of the optically forbidden Rydberg singlet-singlet transitions which have been predicted to lie in this region,<sup>1</sup> but which have never been detected. A third possibility is that the 6.4 eV singlet-triplet feature may be associated with one of the other singlet-singlet transitions above 7.1 eV, but this is not very likely since it would require that the triplet-singlet energy splitting be larger than is normally found for such Rydberg states.<sup>1</sup> Careful examination of all spectra re-

vealed no evidence for this transition in any of the other fluoroethylenes. However, observation of a second triplet excited state in the other molecules would be more difficult because of the downward energy shift of the singlet-singlet Rydberg transition (see below) in the excitation energy range from 6 to 7 eV.

The most intense absorption feature in the vinyl fluoride energy-loss spectrum is the transition at 7.50 eV. The DCS curve shown in Fig. 3 is strongly forward peaked, and this confirms its assignment as a fully allowed singlet-singlet transition. The 7.50 eV peak is designated as the  $N-V$  transition in analogy with the corresponding absorption in ethylene at 7.6 eV.<sup>1</sup> The values of the  $N-V$  transition energy in vinyl fluoride obtained in the optical<sup>4</sup> study (7.44 eV) and the threshold electron-impact<sup>9</sup> study (7.2 eV) are in fair agreement with the 7.50 eV peak value.

The features observed in the 6-10 eV region of the energy-loss spectra of vinyl fluoride (Fig. 1) have also been observed in the optical absorption spectrum,<sup>4</sup> and have been identified as members of various Rydberg series. A more complete analysis of these features will be given in Sec. IV.D. Several broad absorption fea-

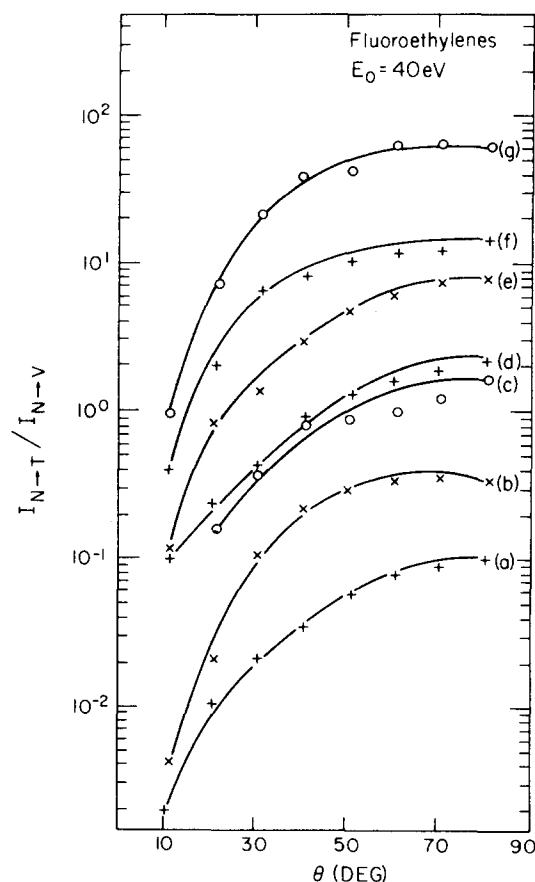


FIG. 2. Ratio of the intensity of the  $N-T$  transition ( $I_{N-T}$ ) to that of the  $N-V$  transition ( $I_{N-V}$ ) as a function of scattering angle ( $\theta$ ) at an incident electron energy of 40 eV for each of the fluoroethylenes and chlorotrifluoroethylene. The curves are identified as follows: (a) vinyl fluoride, (b) 1, 1-difluoroethylene, (c) *cis*-1,2-difluoroethylene, (d) *trans*-1,2-difluoroethylene, (e) trifluoroethylene, (f) tetrafluoroethylene, (g) chlorotrifluoroethylene. Curves (b)-(g) have been shifted vertically from the (a) curve by successive factors of 5.

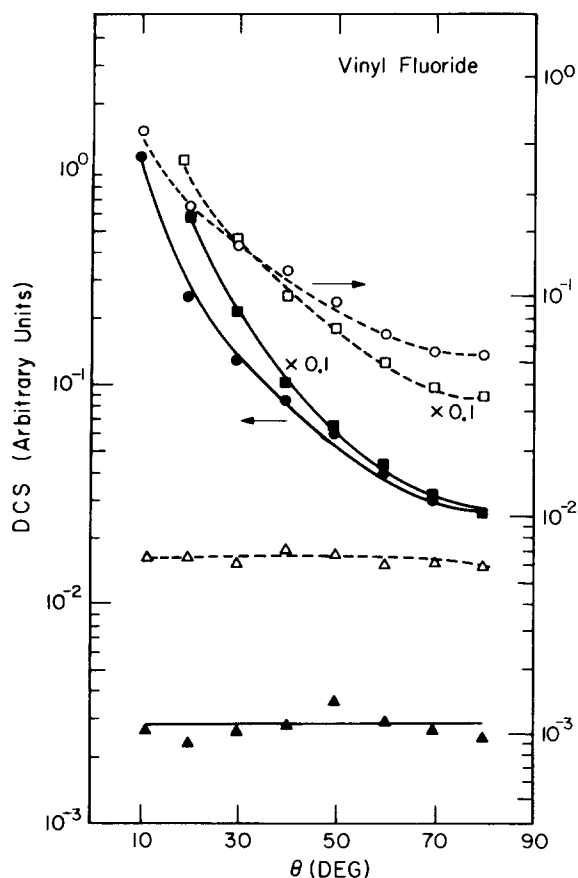


FIG. 3. Differential cross sections for vinyl fluoride as a function of scattering angle ( $\theta$ ) at an incident energy ( $E_0$ ) of 25 eV (dashed curves, right scale) and 40 eV (solid curves, left scale). The scattering processes shown are as follows: elastic scattering  $\times 0.1$  ( $\square$ );  $N \rightarrow V$  excitation ( $\circ$ ); and  $N \rightarrow T$  excitation ( $\Delta$ ).

tures occur at energies above the first ionization potential at 10.58 eV (see Sec. IV. D). The exact nature of the superexcited states<sup>7,18-24</sup> involved in these transitions is not well understood, although it is clear that they do not consist of temporary negative ions, since the

transitions are still observed at impact energies 25 eV above threshold. These superexcited states may be either valence-like states or members of Rydberg series converging to the second or higher ionization potential, as in the fluoromethanes.<sup>7(a)</sup> In either case, they may lead to autoionization, predissociation, or fluorescence of the molecule.<sup>22-24</sup> Recently, superexcited states have been observed in a number of molecules<sup>7,18-21</sup> and their importance in both radiation chemistry<sup>22-24</sup> and chemical reactions<sup>25</sup> has been discussed.

The peak locations of transitions to the superexcited states are listed in Table I, and discussed further in Sec. IV. D.

### B. Difluoro- and Trifluoroethylenes

A spectrum of 1,1-difluoroethylene obtained for a scattering angle of  $70^\circ$  and an impact energy of 40 eV is shown in Fig. 5(a). As with vinyl fluoride, the first inelastic transition is the  $N \rightarrow T$  transition, peaking at 4.63 eV, with a Franck-Condon region from 3.8 to 5.5 eV. The ion-impact spectrum of Moore<sup>5</sup> is in good agreement with these results, having a peak value at 4.6 eV. The  $N \rightarrow V$  maximum in 1,1-difluoroethylene occurs at 7.50 eV, which agrees with the optical value. Both the ion-impact<sup>5</sup> value and the theoretical result<sup>17</sup> are somewhat higher.

Spectra of *trans*- and *cis*-1,2-difluoroethylene are shown in Figs. 5(b) and 5(c). Both the  $N \rightarrow T$  and  $N \rightarrow V$  transition energies in the *cis* isomer (4.43 and 7.82 eV, respectively) are somewhat higher than the corresponding energies (4.18 and 7.39 eV, respectively) for the *trans* isomer.

Figure 5(d) shows the  $\theta = 60^\circ$  energy-loss spectra for trifluoroethylene taken at 40 eV impact energy. For this molecule, the  $N \rightarrow T$  transition has a maximum intensity at 4.43 eV and a Franck-Condon region from 3.5 to 5.4 eV. The corresponding  $N \rightarrow V$  transition has a peak value of 7.65 eV.

The variation of the ratio of the areas under the tran-

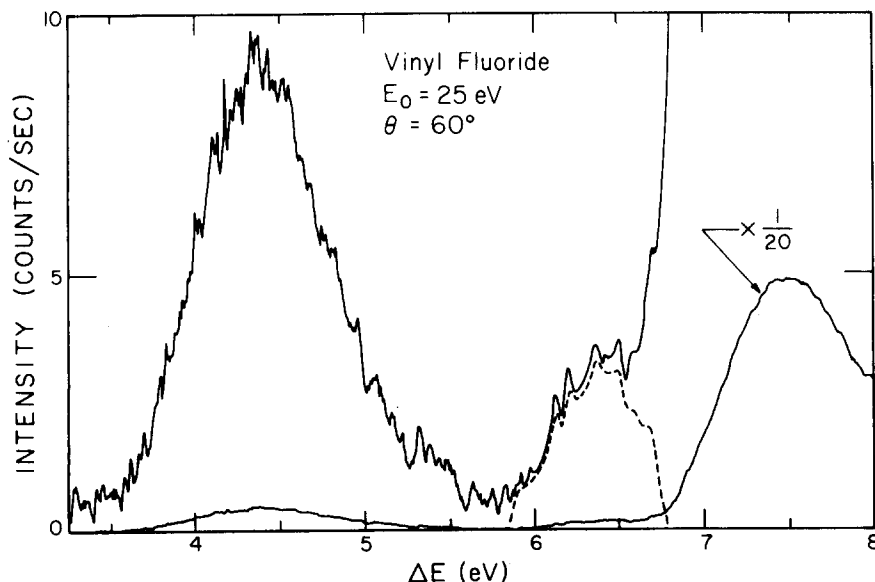


FIG. 4. Deconvolution of the singlet  $\rightarrow$  triplet transition in the 6-7 eV energy-loss region of a vinyl fluoride spectrum obtained at an impact energy ( $E_0$ ) of 25 eV and a scattering angle ( $\theta$ ) of  $60^\circ$ . The band-shape of the  $N \rightarrow V$  transition used in the deconvolution procedure was determined from an  $E_0 = 40$  eV,  $\theta = 0^\circ$  spectrum. The apparent structure in the deconvoluted transition is not reproducible.

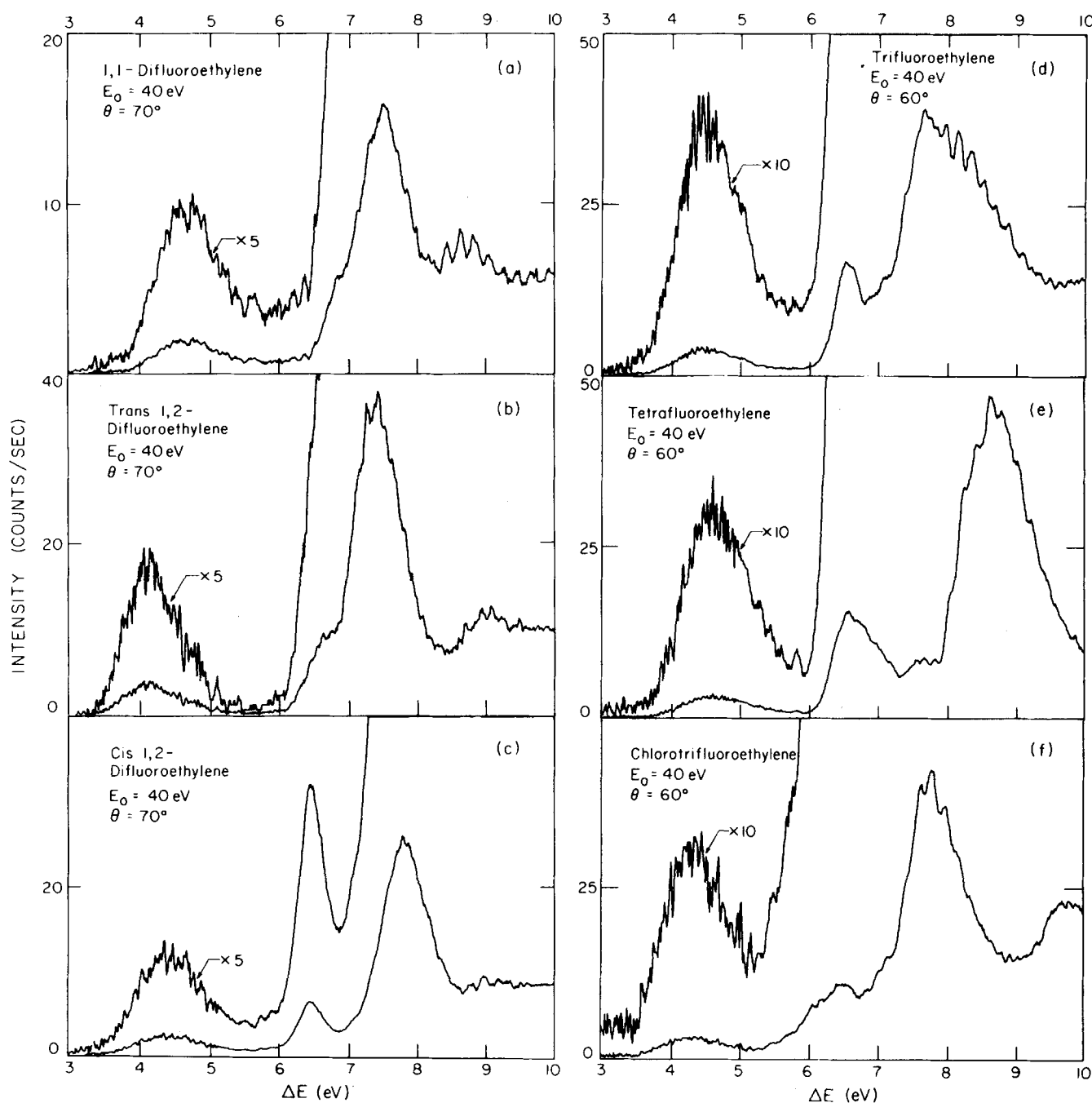


FIG. 5. Electron energy-loss spectra at an impact energy ( $E_0$ ) of 40 eV for the following molecules: (a) 1,1-difluoroethylene, 0.12 eV FWHM; (b) *trans*-1,2-difluoroethylene, 0.13 eV FWHM; (c) *cis*-1,2-difluoroethylene, 0.12 eV FWHM; (d) trifluoroethylene, 0.13 eV FWHM; (e) tetrafluoroethylene, 0.11 eV FWHM; (f) chlorotrifluoroethylene, 0.14 eV FWHM.

sitions with scattering angle at an impact energy of 40 eV are shown for 1,1-difluoroethylene, *cis*- and *trans*-1,2-difluoroethylene, and trifluoroethylene in Fig. 2(b)–(e). The elastic peak,  $N \rightarrow T$ , and  $N \rightarrow V$  DCS curves for these molecules are given in Figs. 6–9. The well-resolved Rydberg features as well as the superexcited states of these molecules are discussed in Sec. IV.D.

### C. Tetrafluoroethylene and chlorotrifluoroethylene

The electron-impact excitation spectra of tetrafluoroethylene measured at a scattering angle of 60° and at

40 eV impact energy is shown in Fig. 5(e). The peak location of the  $N \rightarrow T$  singlet-triplet transition occurs at 4.68 eV, with a Franck-Condon region from 3.6 to 5.6 eV. The ratio of the area under this feature to that under the 8.84 eV transition, as a function of scattering angle, is plotted in Fig. 2(f). Based on its Franck-Condon bandwidth and intensity, the 8.84 eV transition apparently corresponds to the  $N \rightarrow V$  transition in ethylene. However, it is conceivable that the weak singlet-singlet transition at 7.7 eV [see Fig. 5(e)] could correspond to the  $N \rightarrow V$  transition, but if this were so, it would entail a radical change in transition intensity in comparison with the other fluoroethylenes. More likely, this

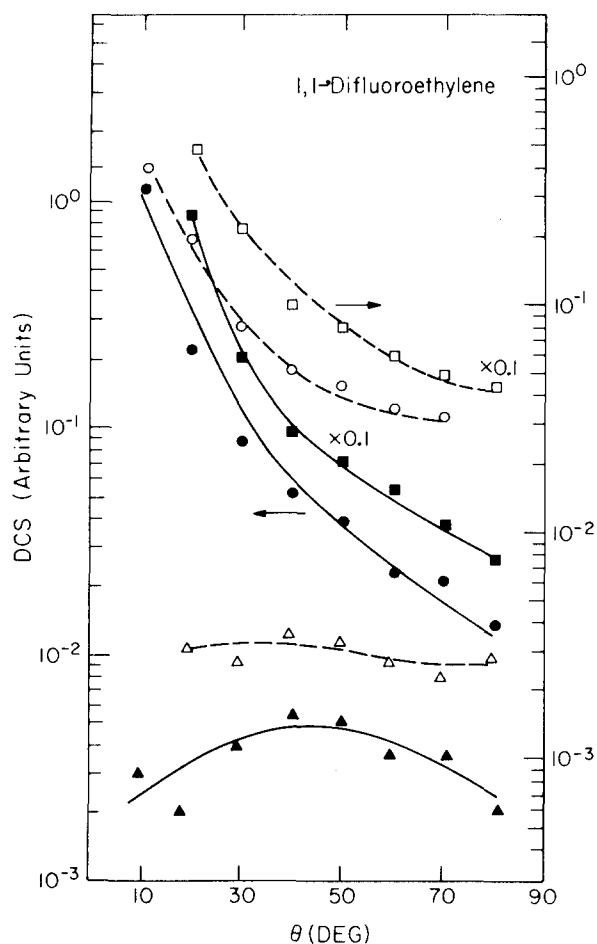


FIG. 6. Differential cross sections for 1,1-difluoroethylene as a function of scattering angle ( $\theta$ ) at an incident energy ( $E_0$ ) of 20 eV (dashed curves, right scale) and 40 eV (solid curves, left scale). The symbols are the same as in Fig. 3.

transition, as well as the one at 7.1 eV in trifluoroethylene [see Fig. 5(d)], correspond to  $\pi \rightarrow \sigma^*$  valence shell excitations, as suggested by Robin.<sup>26</sup> The DCS curves for tetrafluoroethylene are displayed in Fig. 10.

While the  $N \rightarrow T$  transition in tetrafluoroethylene shows a slight shift to higher energy loss compared to the other fluoroethylenes, the corresponding  $N \rightarrow V$  transition exhibits a much larger hypsochromic shift, in excess of 1 eV. The optical value<sup>4</sup> of 8.88 eV for the maximum of this  $N \rightarrow V$  transition agrees with the value of 8.84 eV of the present study. Resistance to torsional motion in the excited state caused by substitution of the final hydrogen was previously invoked to explain the large energy shift.<sup>4</sup> To test this idea, we measured the electron-impact excitation spectra of chlorotrifluoroethylene. In this molecule the fourth hydrogen is replaced by another halogen, chlorine, which should constitute an even greater hindrance for torsional motion of the molecule.

Figure 5(f) displays a spectrum of chlorotrifluoroethylene at a scattering angle of  $60^\circ$ . The inelastic feature extends from 3.6 to 5.2 eV with a peak at 4.43 eV. This absorption is assigned to the singlet  $\rightarrow$  triplet,  $N \rightarrow T$  transition. The strongest feature is the fully al-

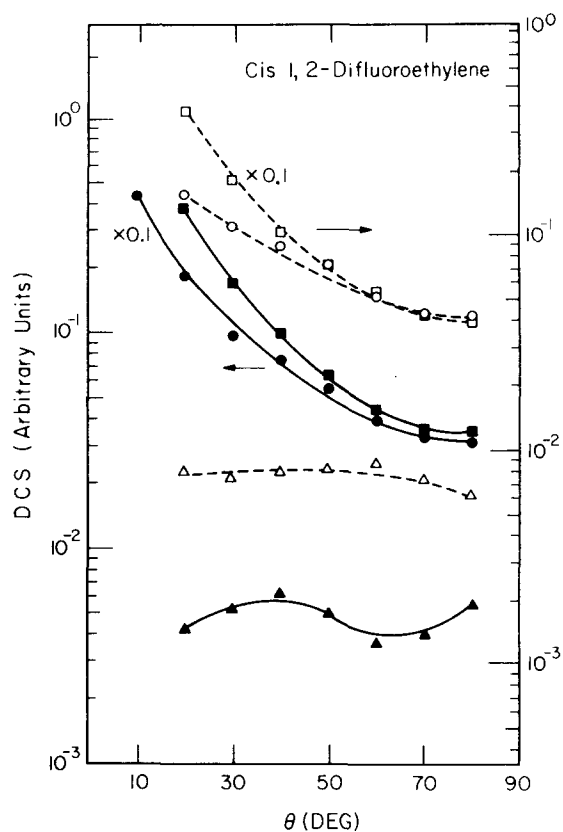


FIG. 7. Same as Fig. 3 for *cis*-1,2-difluoroethylene.

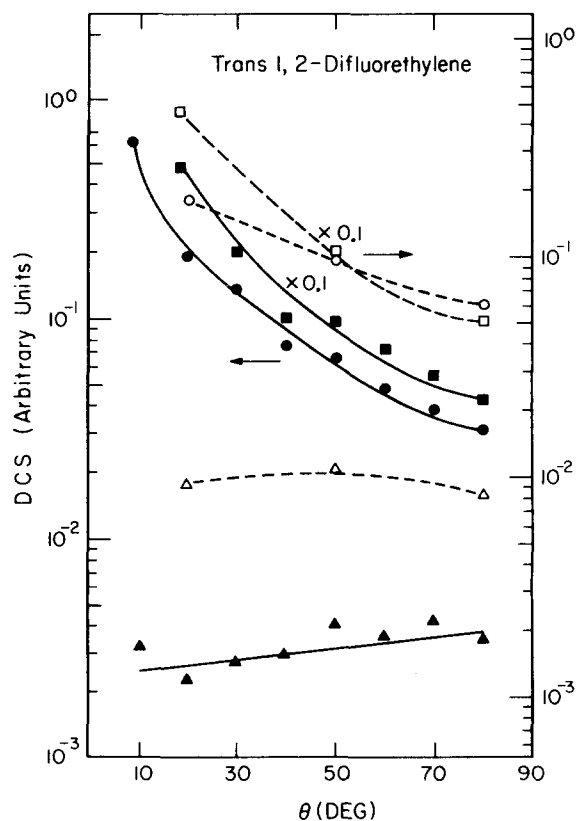


FIG. 8. Same as Fig. 3 for *trans*-1,2-difluoroethylene.



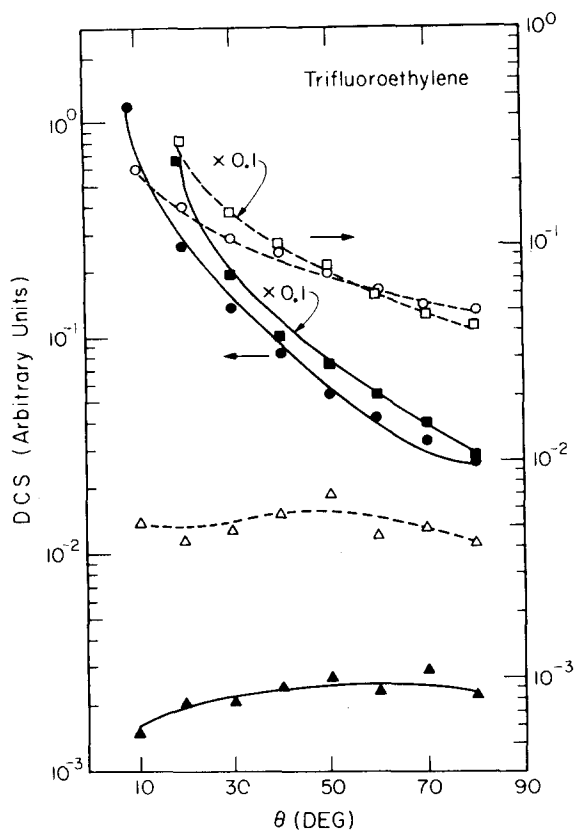


FIG. 9. Same as Fig. 3 for trifluoroethylene.

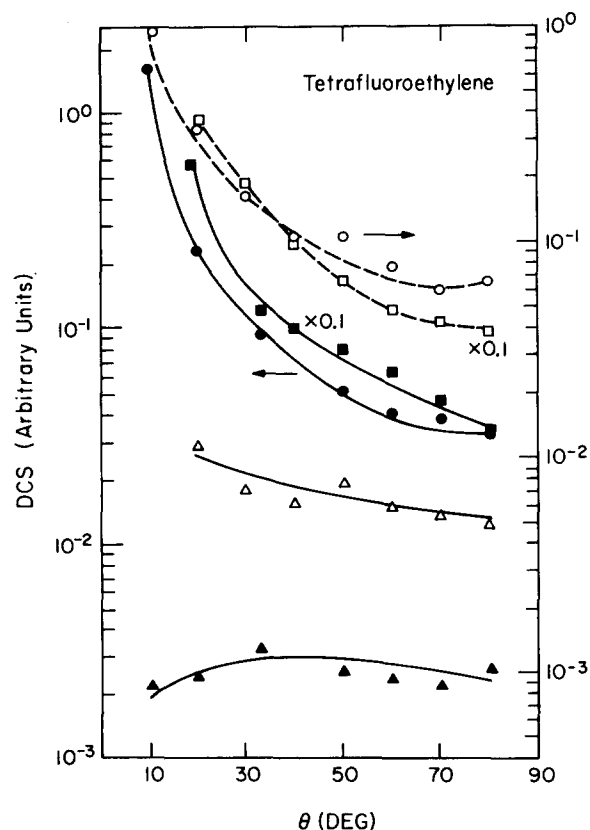


FIG. 10. Same as Fig. 3 for tetrafluoroethylene.

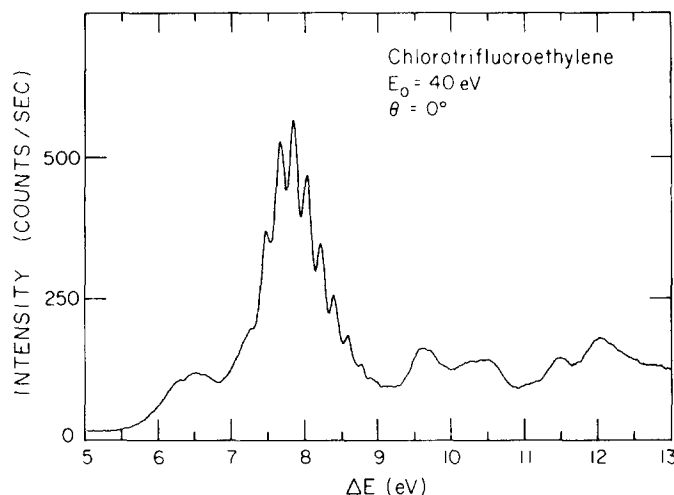


FIG. 11. High resolution electron energy-loss spectrum of chlorotrifluoroethylene at an impact energy ( $E_0$ ) of 40 eV and a scattering angle ( $\theta$ ) of  $0^\circ$ ; 5.8 mtorr sample pressure reading from an uncalibrated Schulz-Phelps ionization gauge; 0.058 eV FWHM.

lowed  $N \rightarrow V$  transition. It has a peak at 7.80 eV, which agrees with the optically determined value<sup>8</sup> of 7.79 eV, and is within the range of values for the  $N \rightarrow V$  transitions in all of the other fluoroethylenes, with the exception of tetrafluoroethylene. A high resolution spectrum of chlorotrifluoroethylene is displayed in Fig. 11.

A plot of the ratio of the area under the  $N \rightarrow T$  transition in chlorotrifluoroethylene to that under the  $N \rightarrow V$  transition, as a function of scattering angle, is displayed in Fig. 2(g). The curve is similar to those shown for the other fluoroethylenes, and confirms the spin-forbidden nature of the  $N \rightarrow T$  transition. Further confirmation of the assignments given is found in Fig. 12, which shows the corresponding DCS curves for chlorotrifluoroethylene, and in Fig. 13, which displays the DCS for the  $N \rightarrow T$  transition in all the molecules studied.

The results given above show that no appreciable shift in the  $N \rightarrow V$  transition energy was produced by the replacement of the last hydrogen in trifluoroethylene by chlorine. Therefore, the large shift in the  $N \rightarrow V$  transition of perfluoroethylene is presumably not due to a steric effect. Optical studies<sup>26</sup> of the chlorine-substituted ethylenes lend some support to this conclusion, since no major shift is observed in the  $N \rightarrow V$  transition energy between tetrachloroethylene and chloroethylene. In addition, the  $N \rightarrow V$  transition energies in the chloroethylenes are similar to that found in ethylene.

An alternate explanation of this energy shift has been made by Salahub.<sup>17</sup> Without configuration interaction (CI), his calculations predict an upward shift of the  $N \rightarrow V$  transition energy of tetrafluoroethylene of between 0.31 and 1.14 eV relative to the  $N \rightarrow V$  transition energies of the other fluoroethylenes. When CI, including  $\sigma \rightarrow \sigma^*$  excitations, is included in the calculation, the corresponding shifts increase to between 1.28 and 2.08 eV. These results reflect the fact that the CI is

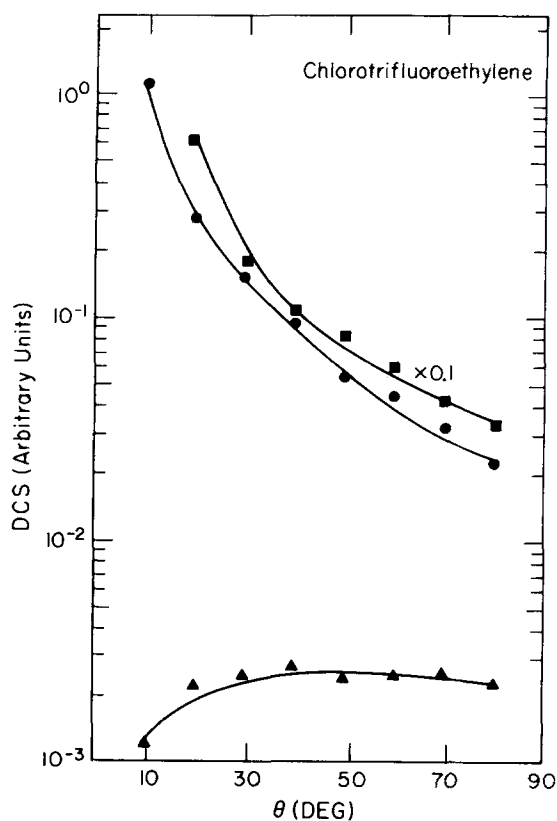


FIG. 12. Same as Fig. 3 for chlorotrifluoroethylene.

more effective in lowering the  $N-V$  transition energy of the hydrogen-containing fluoroethylenes than that of tetrafluoroethylene. Salahub<sup>17</sup> suggests that this is due to the much higher energy of configurations involving  $\sigma-\sigma^*$  excitations from C-C-F  $\sigma$  orbitals when compared with the energy of configurations involving C-C-H  $\sigma$  orbitals. Of course, C-C-H orbitals are not present in either tetrafluoroethylene or chlorotrifluoroethylenes. Presumably, configurations arising from  $\sigma-\sigma^*$  excitations from a C-C-Cl  $\sigma$  orbital, such as in chlorotrifluoroethylene, are also of lower energy than configurations arising from  $\sigma-\sigma^*$  excitations in tetrafluoroethylene. The effect of Cl appears to account for 30% to 70% of the calculated shift in tetrafluoroethylene. Mulliken<sup>27</sup> has recently stressed the importance of such  $\sigma-\pi$  mixing for the accurate description of the  $V$  state of ethylene.

#### D. Rydberg and superexcited states

From their optical data for the fluoroethylenes in the 6 to 10 eV region, Bélanger and Sandorfy<sup>4</sup> have fit a large number of peaks to three Rydberg series, all converging to the first ionization potential of these molecules. In the present study, we have used the transition energies measured by electron impact, in conjunction with photoionization values of the first and second I.P., to determine term values associated with each transition. The term value is defined as the difference between the vertical I.P. and the vertical Rydberg transition energy. This method was described in detail by Harshbarger *et al.*<sup>7</sup> It has been shown<sup>28</sup> that for a given

$N-R_n$  Rydberg transition, where  $n$  indexes the respective transitions, the term values for a series of molecules lie within a narrow band, and converge to a limit with increasing substitution. This characteristic also appears to be valid for Rydberg series converging to the second and higher ionization potentials, provided, of course, that the I.P. in question is used to find the term value. Furthermore, empirical correlations exist between the values of the quantum numbers  $n$  and  $l$  of a given Rydberg state and the corresponding term values.<sup>7,28</sup> Using this procedure, it is possible to assign all Rydberg transitions in the 6 to 10 eV region of each of our spectra. Where possible, superexcited states (Figs. 14 and 15) are fit, based upon their term values, into a Rydberg series leading to higher ionization potentials. The locations of the  $N-R_n$  peaks, their corresponding terms values, and designations are listed in Table II, along with the superexcited states that could be assigned as Rydberg states by this method. The resulting assignments in the 6 to 10 eV region are all in agreement with those found in the optical study<sup>4</sup> of the states below the first I.P. The limiting  $3s$ ,  $3p$ , and  $3d$  term values of 3.9, 2.5, and 1.5 eV are found to be similar to the corresponding term values (3.9, 2.7, and

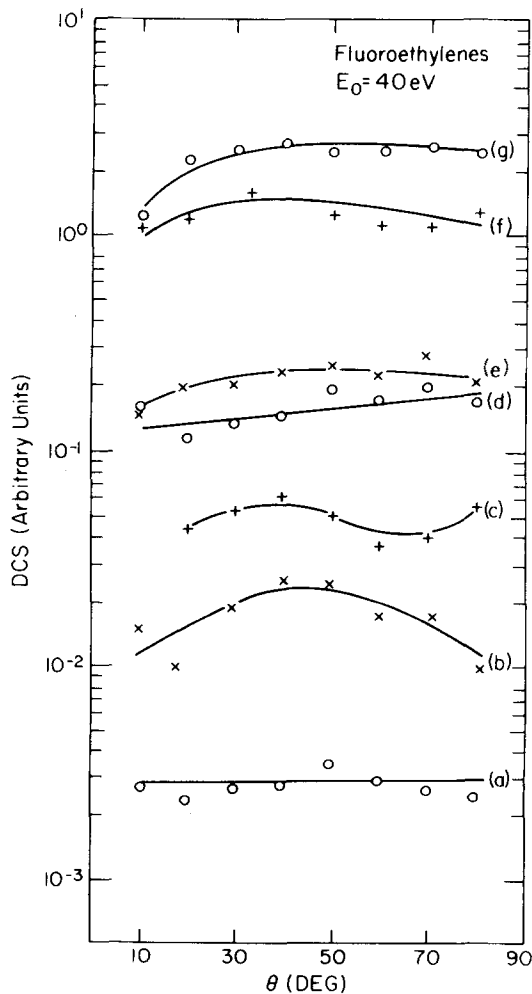


FIG. 13. Differential cross sections for the  $N-T$  transition in the fluoroethylenes at an impact energy ( $E_0$ ) of 40 eV. The curves are labeled as in Fig. 2.

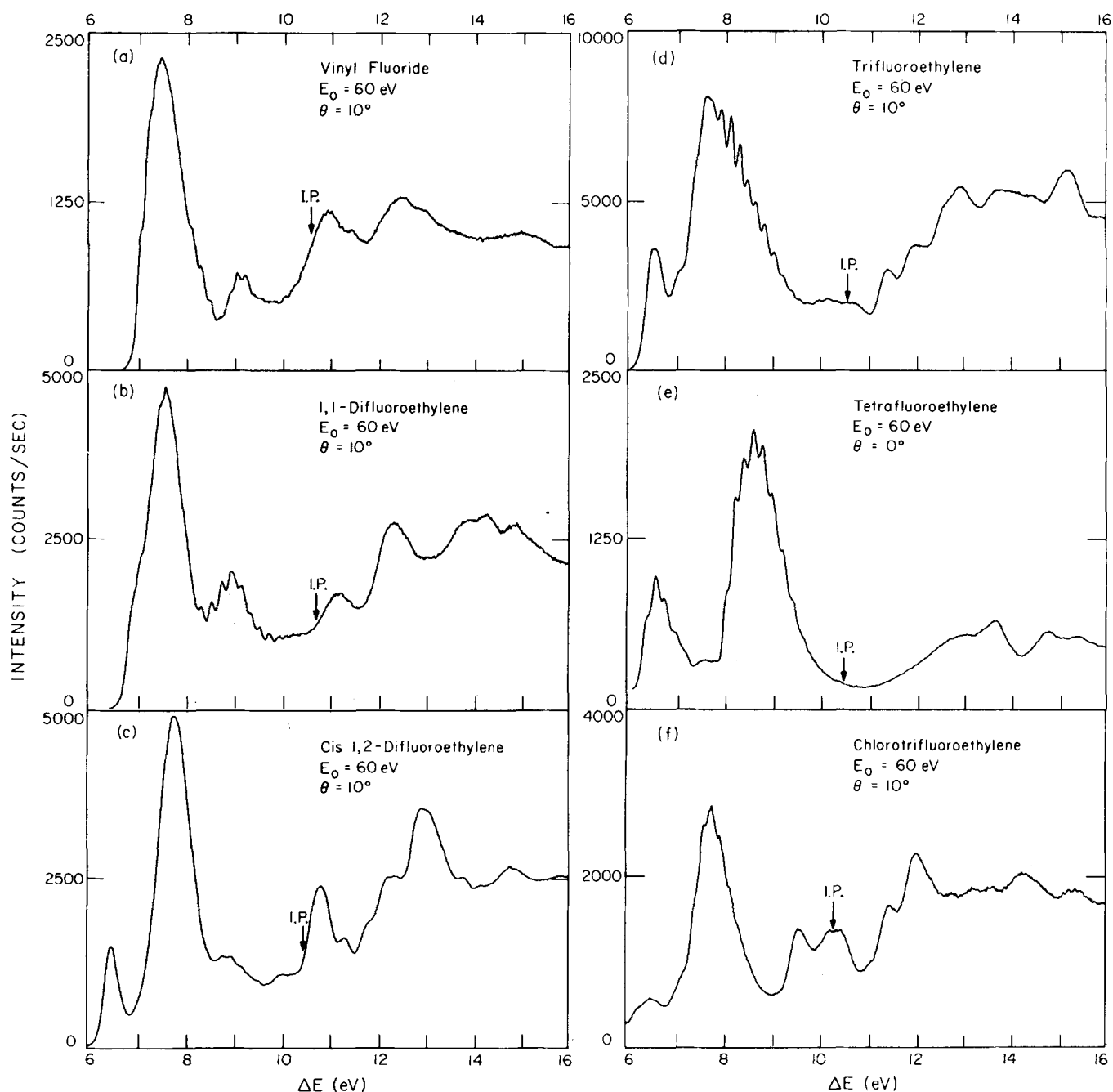


FIG. 14. Electron energy-loss spectra in the range 6–16 eV energy loss for the following molecules: (a) vinyl fluoride; (b) 1,1-difluoroethylene; (c) *cis*-1,2-difluoroethylene; (d) trifluoroethylene; (e) tetrafluoroethylene; (f) chlorotrifluoroethylene. The spectra were obtained at an impact energy ( $E_0$ ) of 60 eV, and a 3 mtorr sample pressure reading from an uncalibrated Schulz-Phelps ionization gauge.

1.6 eV, respectively) in the fluoromethanes.<sup>7(a)</sup>

It has been suggested<sup>4</sup> that valence  $\sigma \rightarrow \sigma^*$  transitions may occur above 10 eV in the fluoroethylenes. Since a number of superexcited states listed in Table II do not seem to be members of higher Rydberg series, it is possible that some of them correspond to such valence transitions.

Recently, Reinke<sup>20</sup> has measured the total absorption cross sections of vinyl fluoride and 1,1-difluoroethylene from 10 to 22 eV using synchrotron radiation. In both

cases, he observed a number of features beyond the first I.P. corresponding to excitations to superexcited states. These peak locations agree well with the results of the present investigation (see Table I).

## V. PHOTOCHEMISTRY

The quenching of the  $1^3B_{1u}$  excited state of benzene by vinyl fluoride and 1,1-difluoroethylene has been studied by Das Gupta and Phillips.<sup>30</sup> Vinyl fluoride was found to be almost 20 times more effective than 1,1-di-

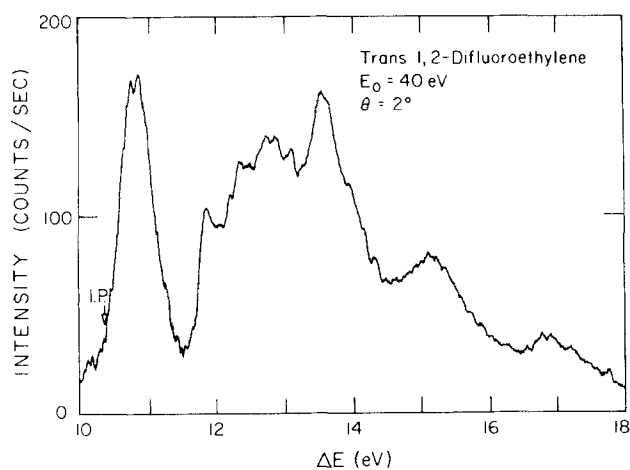


FIG. 15. Electron energy-loss spectrum of *trans*-1,2-difluoroethylene at a scattering angle ( $\theta$ ) of  $2^\circ$  in the 10–18 eV energy-loss region; 40 eV incident electron energy ( $E_0$ ); 52 nA incident electron current; 4.3 mtorr sample pressure reading from an uncalibrated Schulz–Phelps ionization gauge; 0.095 eV FWHM.

fluoroethylene in quenching the  $1^3B_{1u}$  state. Our interpretation of these results is based upon the triplet–triplet energy transfer mechanism postulated<sup>30</sup> for this process. The rate of such energy transfer in solids is governed by the overlap of the singlet–triplet absorption spectrum of the acceptor with the phosphorescence spectrum of the donor,<sup>31</sup> and it has been suggested that a similar spectral overlap criterion applies in the gas phase as well.<sup>18,19(a),32</sup> The phosphorescence curve for the  $1^3B_{1u}$  state of benzene is known to extend from about 2.68 to 3.66 eV.<sup>33</sup> Comparison of this upper limit of the donor phosphorescence with the lower absorption limits of the Franck–Condon regions of the acceptors vinyl fluoride (3.4 eV) and 1,1-difluoroethylene (3.8 eV) (see Table I) shows that the origin of the wide disparity in the quenching cross sections is probably due to the differing amounts of spectral overlap.

A number of experimental measurements<sup>34–37</sup> have been made of the quenching cross section for mercury in the  $6^3P_1$  state at 4.89 eV by the fluoroethylenes. All the cross sections fall within the range from 10 to 30  $\text{\AA}^2$ , as compared with 31  $\text{\AA}^2$  for ethylene. While the peaks of the singlet–triplet transitions of the fluoroethylenes are somewhat below the Hg  $6^3P_1$  state, the broad Franck–Condon regions (Table I) result in sufficient spectral overlap with the Hg  $6^3P_1 - 1^1S_0$  emission line at 4.89 eV to yield large quenching cross sections for all the fluoroethylenes. It is therefore consistent with the arguments of the previous paragraph that the cross sections for the fluoroethylenes and ethylene are comparable, since the postulated quenching mechanism is the formation of the lowest excited triplet state of the olefin.

## VI. CONCLUSIONS

In each of the six fluoroethylenes, as well as in chlorotrifluoroethylene, a spin-forbidden, singlet–triplet ( $N-T$ ) transition has been observed with maximum intensity in the range from 4.18 to 4.68 eV. In addition,

in vinyl fluoride a second singlet–triplet transition has been observed at 6.4 eV.

With the exception of the large blue shift in the  $N-V$  transition energy in tetrafluoroethylene, the singlet–singlet,  $\pi-\pi^*$  electronic transition energies of the fluoroethylenes are all relatively similar. This behavior is also consistent with conclusions drawn from earlier ionization potential studies. The hypsochromic shift in tetrafluoroethylene appears not to be due to any torsional barrier effects, but may be caused in part by the removal from a configuration interaction description of this transition configurations due to  $\sigma-\sigma^*$  excitations from C–C–H  $\sigma$  orbitals.

The term value method has proved to be very useful in assigning several of the superexcited states in the fluoroethylenes to members of Rydberg series converging to higher ionization potentials. In general, the term values found for the fluoroethylenes are comparable to those determined from other molecules. Additional superexcited states, which apparently do not fit into Rydberg series, have been observed. These may be due to  $\sigma-\sigma^*$  valence-type transitions.

The Franck–Condon band system profiles obtained in these electron-impact studies have been used in conjunction with the spectral overlap criterion to explain differing observed gas phase electronic energy quenching cross sections. This result lends further support to the use of the spectral overlap criterion in the gas phase.

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<sup>1</sup>A. J. Merer and R. S. Mulliken, *Chem. Rev.* **69**, 639 (1969).

<sup>2</sup>A. Kuppermann and L. M. Raff, *Disc. Faraday Soc.* **35**, 30 (1963).

<sup>3</sup>(a) A. Kuppermann, J. K. Rice, and S. Trajmar, *J. Phys. Chem.* **72**, 3894 (1968); (b) S. Trajmar, J. K. Rice, and A. Kuppermann, *Advan. Chem. Phys.* **18**, 15 (1970).

<sup>4</sup>G. Bélanger and C. Sandorfy, *J. Chem. Phys.* **55**, 2055 (1971).

<sup>5</sup>J. H. Moore, Jr., *J. Phys. Chem.* **76**, 1130 (1972).

<sup>6</sup>R. M. O'Malley and K. R. Jennings, *Int. J. Mass Spectrom. Ion Phys.* **2**, Appendixes 1–3 (1969).

<sup>7</sup>(a) W. R. Harshbarger, M. B. Robin, and E. N. Lassetre, *J. Electron Spectrosc.* **1**, 319 (1972/73); (b) W. R. Harshbarger, N. A. Kuebler, and M. B. Robin, *J. Chem. Phys.* **60**, 345 (1974).

<sup>8</sup>J. D. Scott and B. R. Russell, *J. Am. Chem. Soc.* **94**, 2634 (1972).

<sup>9</sup>W. M. Flicker, O. A. Mosher, and A. Kuppermann, *Chem. Phys. Lett.* **36**, 56 (1975).

<sup>10</sup>C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Bosch, *J. Am. Chem. Soc.* **94**, 1451 (1972).

<sup>11</sup>R. Bralsford, P. V. Harris, and W. C. Price, *Proc. R. Soc. London Ser. A* **258**, 459 (1960).

<sup>12</sup>R. F. Lake and H. Thompson, *Proc. R. Soc. London Ser. A* **315**, 323 (1970).

<sup>13</sup>C. Lifshitz and F. A. Long, *J. Phys. Chem.* **67**, 2463 (1963).

<sup>14</sup>M. A. Landau, S. S. Dubov, and A. N. Medvedev, *Russ. J. Phys. Chem.* **42**, 827 (1968).

- <sup>15</sup>S. Meza and U. Wahlgren, *Theor. Chim. Acta* **21**, 323 (1971).
- <sup>16</sup>D. T. Clark, J. N. Murrell, and J. M. Tedder, *J. Chem. Soc.* 1250 (1963).
- <sup>17</sup>(a) D. R. Salahub, *Theor. Chim. Acta* **22**, 330 (1971); (b) D. R. Salahub, Ph.D. thesis, Université de Montreal, Montreal, Canada (1970).
- <sup>18</sup>O. A. Mosher, W. M. Flicker, and A. Kuppermann, *J. Chem. Phys.* **59**, 6502 (1973).
- <sup>19</sup>(a) O. A. Mosher, W. M. Flicker, and A. Kuppermann, *J. Chem. Phys.* **62**, 2600 (1975); (b) O. A. Mosher, M. S. Foster, W. M. Flicker, A. Kuppermann, and J. L. Beauchamp, *J. Chem. Phys.* **62**, 3424 (1975).
- <sup>20</sup>M. J. Coggiola, O. A. Mosher, W. M. Flicker, and A. Kuppermann, *Chem. Phys. Lett.* **27**, 14 (1974).
- <sup>21</sup>R. H. Huebner, R. J. Celotte, S. R. Mielczarek, and C. E. Kuyatt, *J. Chem. Phys.* **59**, 5434 (1973).
- <sup>22</sup>V. I. Makarov and L. S. Polak, *High Energy Chem. USSR* **4**, 1 (1970).
- <sup>23</sup>(a) R. L. Platzman, *Radiat. Res.* **17**, 419 (1962); (b) R. L. Platzman, *Vortex* **23**, 372 (1962).
- <sup>24</sup>J. Person, *Radiat. Res.* **52**, 1 (1972).
- <sup>25</sup>(a) Y. Hatano, S. Shida, and S. Sato, *Bull. Chem. Soc. Japan* **41**, 1120 (1968); (b) Y. Hatano, *ibid.* **41**, 1126 (1968).
- <sup>26</sup>M. B. Robin, *Higher Excited States of Polyatomic Molecules* (Academic, New York, 1975), Vol. II.
- <sup>27</sup>R. S. Mulliken, *Chem. Phys. Lett.* **25**, 305 (1974).
- <sup>28</sup>M. B. Robin, *Int. J. Quantum Chem., Symp. No.* **6**, 257 (1972).
- <sup>29</sup>(a) D. Reinke, Report No. F41-73/6, Deutsches Elektronen-Synchrotron DESY, Hamburg, 1973; (b) D. Reinke, R. Kraessig, and H. Baumgartel, *Ber. Bunsenges. Phys. Chem.* **78**, 205 (1974).
- <sup>30</sup>G. Das Gupta and D. Phillips, *J. Chem. Phys.* **76**, 3688 (1972).
- <sup>31</sup>D. L. Dexter, *J. Chem. Phys.* **21**, 836 (1953).
- <sup>32</sup>(a) M. W. Schmidt and E. K. C. Lee, *J. Am. Chem. Soc.* **90**, 5919 (1968); (b) M. W. Schmidt and E. K. C. Lee, *J. Am. Chem. Soc.* **92**, 3579 (1970).
- <sup>33</sup>T. V. Ivanova and B. Ya. Sveshnikov, *Optics and Spectrosc.* **11**, 322 (1961).
- <sup>34</sup>B. Atkinson, *J. Chem. Soc.* 1952, 2684.
- <sup>35</sup>(a) A. R. Trobridge and K. R. Jennings, *Trans. Faraday Soc.* **61**, 2168 (1965); (b) A. R. Trobridge and K. R. Jennings, *Proc. Chem. Soc. London* 1964, 335.
- <sup>36</sup>M. G. Bellas, Y. Rousseau, O. P. Strausz, and H. E. Gunning, *J. Chem. Phys.* **41**, 768 (1964).
- <sup>37</sup>O. P. Strausz, R. J. Norstrom, D. Salahub, R. K. Gosavi, H. E. Gunning, and I. G. Csizmadia, *J. Am. Chem. Soc.* **92**, 6395 (1970).