

Singlet→triplet transitions in C≡N containing molecules by electron impact^{a)}

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The electron-impact excitation spectra of hydrogen cyanide (HCN), acetonitrile (CH₃CN), malononitrile [CH₂(CN)₂], propionitrile (C₂H₅CN), and butyronitrile (C₃H₇CN) have been studied experimentally at impact energies of 25, 50, and 75 eV and at scattering angles from 5° to 80°. Results for hydrogen cyanide are in excellent agreement with previous work. Previously unobserved singlet→triplet transitions of acetonitrile, propionitrile, and butyronitrile are reported. Also, the first study of the electronic spectrum of malononitrile is reported. Tentative assignments for transitions observed are reported.

INTRODUCTION

Although much has been published on the electronic spectroscopy of C≡N containing molecular systems, especially hydrogen cyanide, the assignments of transitions observed are still very much in question.¹⁻¹⁶ In order to resolve some of these questions, we have applied the technique of low-energy, variable-angle, electron-impact spectroscopy to hydrogen cyanide, acetonitrile, malononitrile, propionitrile, and butyronitrile.

Electron impact spectroscopy has proven to be a very powerful technique for studying the electronic structure of molecules.¹⁷⁻²⁰ The shape of the differential cross-section (DCS) vs scattering angle curve is a great aid in the identification of the nature of a transition. Excitations which are fully allowed with respect to dipole selection rules exhibit very strongly forward peaked DCS's. The DCS's of such transitions are most intense at 0° scattering angle and decrease by about two orders of magnitude as the scattering angle (θ) is increased from 10° to 80°. Spin-forbidden transitions exhibit DCS's which are nearly constant, to within a factor of 2 or 3, over a similar angular range. Spin-allowed but symmetry-forbidden transitions display an intermediate behavior. The DCS is forward peaked but not so much as that of a fully allowed transition. Thus, measuring the DCS of a transition may add valuable information as to the type of transition observed. The lower energy region of the spectra of CN containing molecules is expected to be dominated by $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions within the C≡N group. Therefore, hydrogen cyanide, the simplest and most thoroughly studied member of this group, will serve as a model to assist in assigning transitions in the remainder of the group. Hydrogen cyanide is linear in its ground state and thus belongs to the C_{∞v} point group. The electronic configuration in the ground state is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4$ yielding the ground state symmetry of $^1\Sigma^+$.^{5,6} The higher energy regions of the spectra are expected to be dominated by Rydberg transitions.

Hydrogen cyanide is bent in many of its excited states and in these cases possesses C_s symmetry.³ This results in a splitting of the π orbitals into a' and a'' components. In C_s symmetry, the ground state is $1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 1a''^2$ ($^1A'$).^{5,6} Assignments for transitions of the alkyl cyanides will be listed in accordance with the C_{∞v} symmetry of the C≡N group only.

EXPERIMENTAL

The electron spectrometer used in this study was that described by Kuppermann *et al.*¹⁷ Spectra of hydrogen cyanide, acetonitrile, propionitrile, butyronitrile, and malononitrile in the energy loss range 0→17 eV were obtained at impact energies of 25, 50, and 75 eV and scattering angles from 5° to 80°. Sample pressures in the scattering chamber were typically 2–4 mTorr, as indicated by an uncalibrated Schulz–Phelps ionization gauge while the incident electron beam current varied from 10 to 100 nA. The samples of hydrogen cyanide (99.5%), acetonitrile (99 + %), propionitrile (98 + %), butyronitrile, and malononitrile (99 + %) were obtained from Fumico Inc., Aldrich Chemical Co., Inc., Eastman Kodak Co., Matheson, Coleman and Bell, and Aldrich Chemical Co., Inc., respectively. The minimum stated purity, when available, is given in parentheses. All samples were subjected to several trap-to-trap distillations (HCN) or freeze–pump–thaw cycles before use. No indication of impurity was observed in any spectrum.

RESULTS AND DISCUSSION

Figure 1 shows the electron impact spectra of hydrogen cyanide (HCN), acetonitrile (CH₃CN), malononitrile [CH₂(CN)₂], propionitrile (C₂H₅CN), and butyronitrile (C₃H₇CN) from 4.6 to 11.6 eV energy loss at an impact energy of 25 eV and scattering angles of 10° and 80° (70° for HCN). The spectra of hydrogen cyanide at 10° and 70° scattering angles are repeated in Fig. 2 so that the vibrational structure we report may be more readily observed. Differential cross-section vs scattering angle curves for several of the features appearing in this energy loss region in hydrogen cyanide, acetonitrile, and malononitrile are shown in Figs. 3, 4, and 5, respectively. The features in the spectra of propionitrile and butyronitrile are so heavily overlapped that differential cross sections could not be obtained. Figure 6 shows

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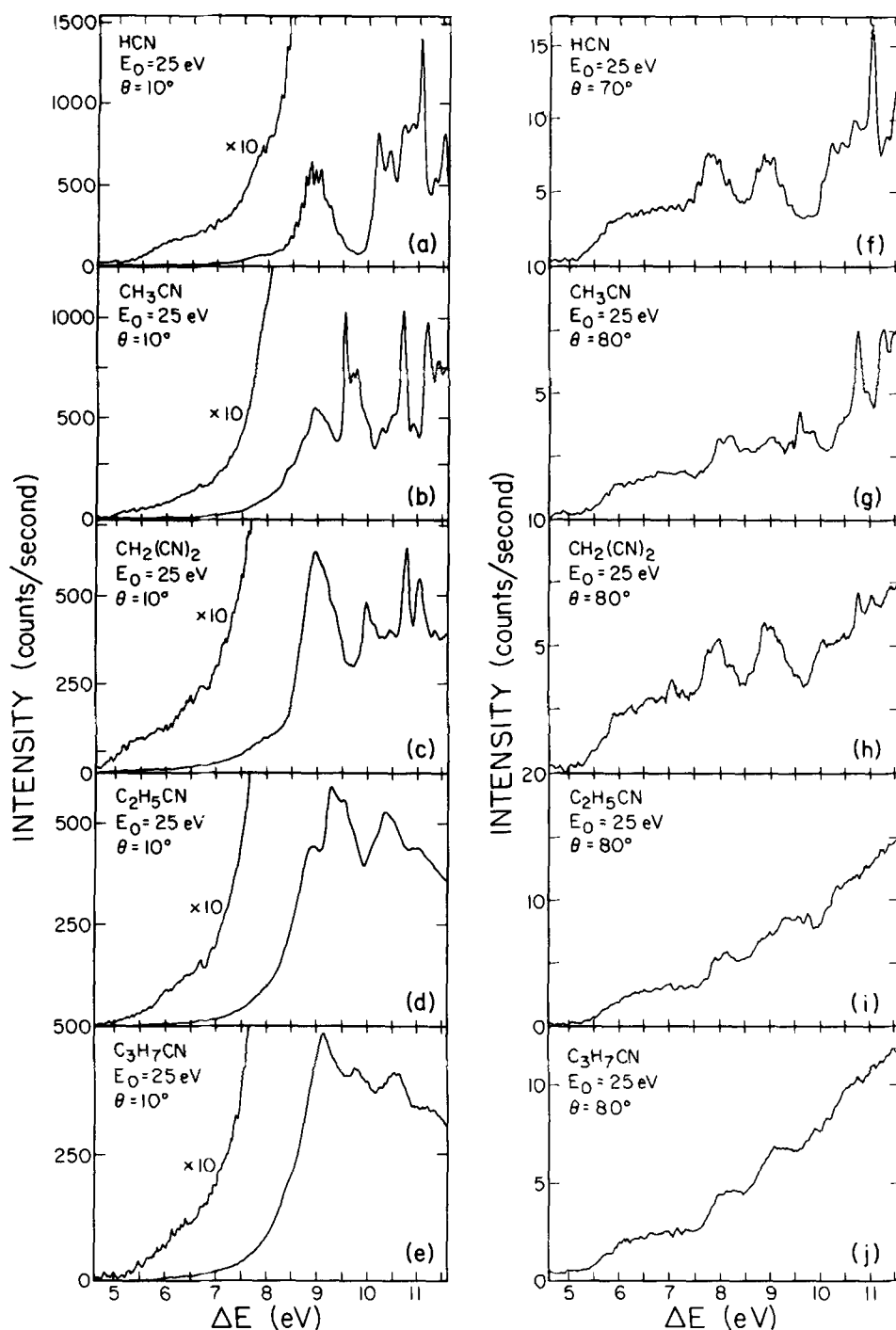


FIG. 1. Electron-impact energy-loss spectra of hydrogen cyanide at scattering angles (a) 10° and (f) 70° , acetonitrile at (b) 10° and (g) 80° , malononitrile at (c) 10° and (h) 80° , propionitrile at (d) 10° and (i) 80° , and butyronitrile at (e) 10° and (j) 80° . The impact energy was 25 eV. Typical experimental parameters for these spectra and those presented in later figures are: sample pressure ranging from 3.0 and 7.0 mTorr as measured with an uncalibrated Schulz Phelps ionization gauge, incident electron beam currents ranging from 10 to 50 nA, and resolution in the range 60 to 90 meV.

the spectra of hydrogen cyanide, acetonitrile, malononitrile, propionitrile, and butyronitrile from 10 to 17 eV energy loss at an impact energy of 75 eV and a scattering angle of 5° .

HYDROGEN CYANIDE

Intense features are observed with intensity maxima at 8.75, 10.17, 10.41, 10.70, 10.86, 11.03, 11.30, and 11.50 eV in the 10° spectrum of hydrogen cyanide. A considerable amount of vibrational structure is evident on the 8.75 eV feature. In addition to these intense features much weaker features with apparent intensity maxima at about 6.4 and 7.8 eV are observed. The feature at 6.4 eV has been previously observed in both electron impact¹⁰ and optical spectra³ and

has been attributed to the $\tilde{X}^1\Sigma^+ \rightarrow \tilde{A}^1A''$ ($\pi \rightarrow \pi^*$) excitation. The theoretical calculations of Schwenzler *et al.*⁶ indicate that this transition is the lowest lying singlet-singlet excitation. They have adjusted their calculated transition energies to match the observed value of 6.48 eV. The $\tilde{X}^1\Sigma^+ \rightarrow \tilde{A}^1A''$ transition is forbidden in the linear configuration (the excited state bond angle is 125.0°) so the intensity is expected to be low. The second feature in the low angle spectrum of hydrogen cyanide occurs between 7.5 and 8.0 eV. This transition has also been previously observed at 7.5 eV in the electron impact spectra of Chutjian *et al.*¹⁰ Schwenzler *et al.*⁶ predict the $\tilde{X}^1\Sigma^+ \rightarrow \tilde{B}^1A''$ transition, which is also forbidden in the linear configuration, to occur at 7.52 eV. However, Asbrink *et al.*,¹¹ on the basis of HAM/3 calculations, have suggested

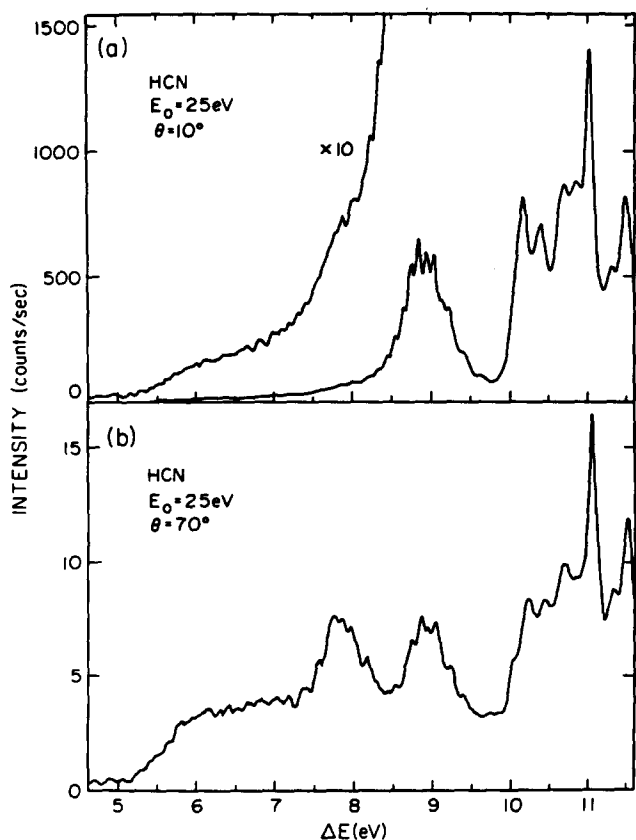


FIG. 2. Electron energy-loss spectrum of hydrogen cyanide at 25 eV impact energy and scattering angles of (a) 10° and (b) 70° . Experimental conditions as described in Fig. 1. Resolution approximately 65 meV. Spectra are repeated here to better display vibrational structure observed.

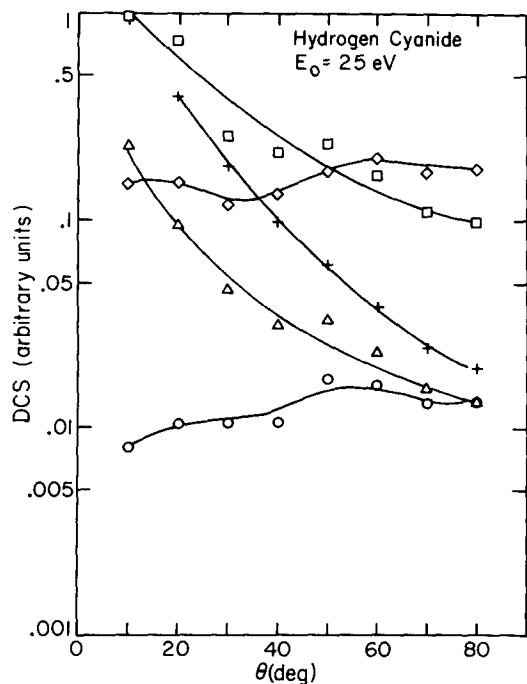


FIG. 3. Differential cross sections of HCN as a function of scattering angle at an incident electron energy of 25 eV; for elastic scattering (+) and for excited states: $T_{5.7}$ (O), $T_{7.86}$ (\diamond), $S_{8.84}$ (\triangle), and $S_{11.03}$ (\square). The elastic peak DCS was multiplied by 0.1 before plotting. The DCS's for $T_{7.86}$ and $S_{11.03}$ were multiplied by 10 before plotting. The letters S and T indicate singlet and triplet upper states, and the index represents the corresponding transition energy.

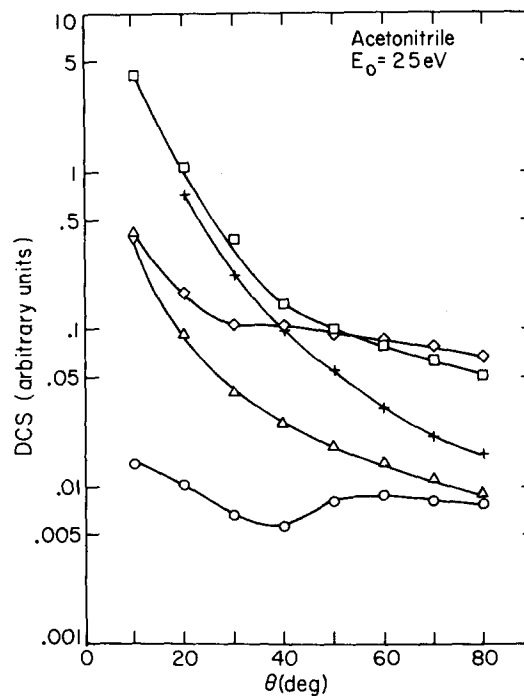


FIG. 4. Differential cross sections of acetonitrile as a function of scattering angle at an incident electron energy of 25 eV; for elastic scattering (+) and for excited states $T_{5.2-7.5}$ (O), $T_{8.1}$ (\diamond), $S_{8.96}$ (\square), and $S_{10.75}$ (\triangle). Letter designations and indices as described for Fig. 3. The elastic peak DCS were multiplied by 0.1 before plotting. The DCS's for $T_{8.1}$ and $S_{8.96}$ were multiplied by 10 before plotting.

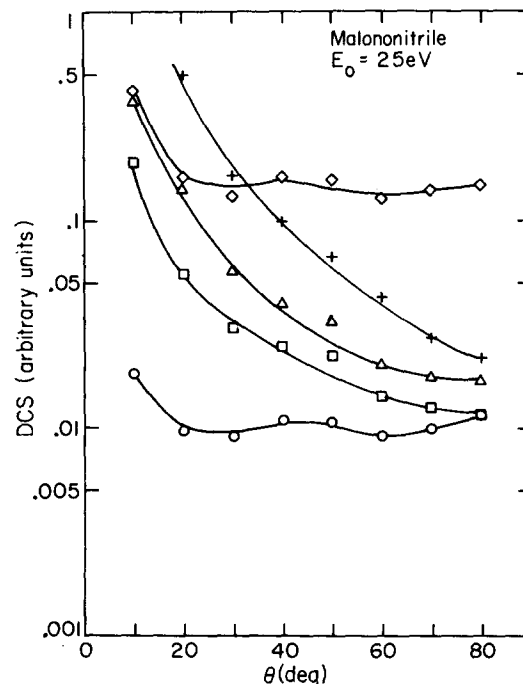


FIG. 5. Differential cross section of malononitrile as a function of scattering angle at an impact energy of 25 eV; for elastic scattering (+) and for excited states $T_{3.2-7.1}$ (O), $T_{7.95}$ (\diamond), $S_{8.94}$ (\triangle) and $S_{10.74}$ (\square). Letter designations and indices as in Fig. 3. The elastic peak DCS was multiplied by 0.1 before plotting.

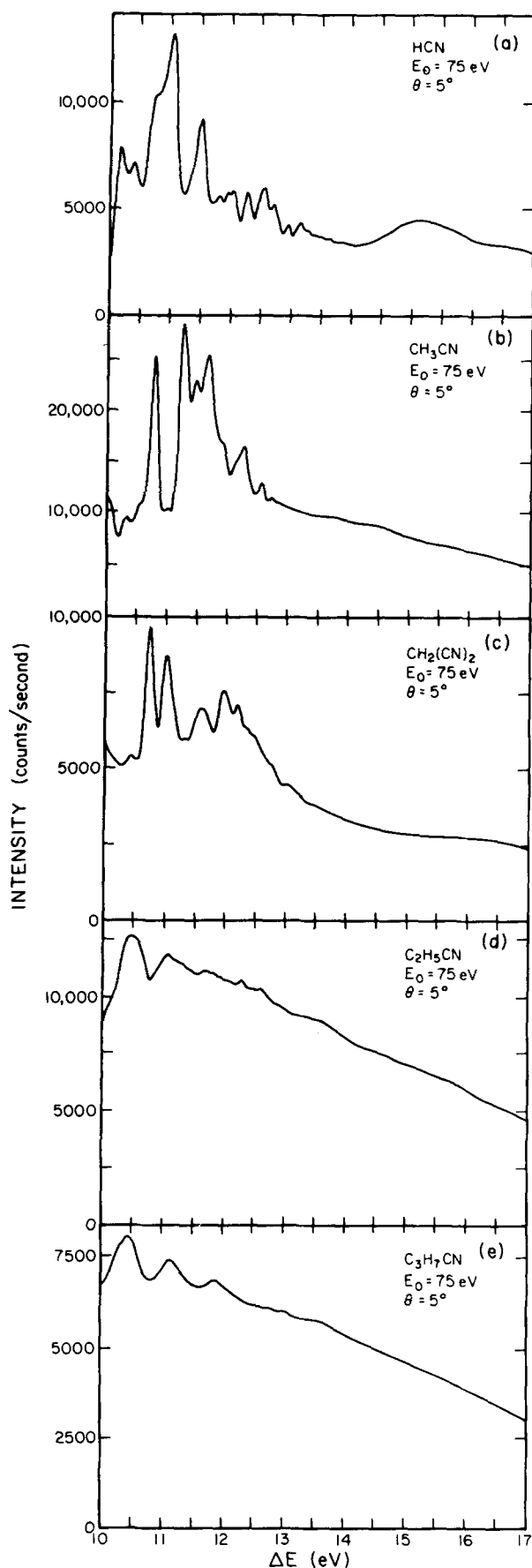


FIG. 6. Energy loss spectra of (a) hydrogen cyanide, (b) acetonitrile, (c) malonitrile, (d) propionitrile, and (e) butyronitrile at an incident electron energy of 75 eV and a scattering angle of 50°. Experimental conditions as described in Fig. 1.

that the transitions observed at 6.48 and 7.5 eV in both the optical and electron impact spectra result from transitions to triplet excited states and that due to low intensities the $\tilde{X}^1\Sigma^+ \rightarrow 1^1A''$ and $\tilde{X}^1\Sigma^+ \rightarrow 2^1A''$ transitions are not observed. In our 25 eV, 70° spectrum [Fig. 2(b)], we observe a broad feature between 5.5 and 7.25 eV and another feature at 7.86 eV which on the basis of the DCS's measured (shown in Fig. 3) may be assigned as singlet \rightarrow triplet transitions. Vibrational structure is evident on both features. Chutjian *et al.*¹⁰ also observed transitions at 6.0, 6.8, 7.1–7.9, and 7.9 eV which they have assigned on the basis of the calculations of Schwenzer *et al.*⁶ to the transitions $\tilde{X}^1\Sigma^+ \rightarrow 1^3A'$, $1^3A''$, $2^3A'$, $X^1\Sigma^+ \rightarrow 2^3A''$, $\tilde{X}^1\Sigma^+ \rightarrow 3^3A'$, and $\tilde{X}^1\Sigma^+ \rightarrow 3^3A''$, respectively. No vibrational structure was observed in their spectra at their stated resolution of 80 to 100 meV. Close examination of our 25 eV, 10° spectrum reveals the presence of vibrational structure which also appears with much greater intensity in the 25 eV, 80° spectrum and may definitely be assigned to singlet \rightarrow triplet transitions. Unfortunately, it is only possible at this time to state that our results are consistent with assignment of the transitions observed between 5.5 and 7.25 and between 7.5 and 8.0 eV in both optical and low-angle electron impact spectra to singlet \rightarrow triplet excitations.

The first intense feature in the 10° spectrum of hydrogen cyanide appears between 8.0 and 9.63 eV. Previous investigations have identified two transitions in this region, the $\tilde{X}^1\Sigma^+ \rightarrow \tilde{C}^1A'$ and the $\tilde{X}^1\Sigma^+ \rightarrow \tilde{D}^1A'$.^{3,11} The 0–0 bands of these transitions have been reported to be at 8.139 and 8.881 eV, respectively. We observe a progression in the bending mode ν_2 of about 0.10 eV beginning at 8.03 eV. This is in excellent agreement with the ν_2 frequency for the \tilde{C} state of 869 cm^{-1} (0.108 eV) obtained by Herzberg.³ No vibrational structure was resolved in this energy region in the previous electron impact studies of Chutjian *et al.*¹⁰ and Tam and Brion.⁷ Fridh and Asbrink⁸ have observed and assigned the vibronic peaks of the $\tilde{X}^1\Sigma^+ \rightarrow \tilde{C}^1A'$ and $\tilde{X}^1\Sigma^+ \rightarrow \tilde{D}^1A'$ transitions but did not obtain an absolute energy scale calibration and have therefore based their reported transition energies on the values obtained by Herzberg.³ We therefore suggest that the true 0–0 transition for the $\tilde{X}^1\Sigma^+ \rightarrow \tilde{C}^1A'$ excitation occurs at 8.03 eV and that the previously reported value of 8.139 actually includes one quantum of the bending mode. Additional members of this progression are listed in Table I. The long progression in the bending mode is due to the decrease in the bond angle of the \tilde{C}^1A' state ($\alpha = 141^\circ$) relative to that of the ground state (180). A significant enhancement of the intensities of peaks at 8.84 and 9.03 eV is due to overlap with elements of the $\tilde{X}^1\Sigma^+ \rightarrow \tilde{D}^1A''$ transition. In our spectra, the 0–0 band of the $\tilde{X} \rightarrow \tilde{D}^1A'$ transition (8.881 eV) is not resolved from the $\tilde{X}^1\Sigma^+ \rightarrow \tilde{C}^1A'$ ($\nu_2 = 8$) transition which occurs at 8.84 eV. A progression in the $C\equiv N$ stretching mode (ν_3) is evident with additional members of the progression occurring at 9.03, 9.22, 9.42, and 9.63 eV. The peak at 9.03 also overlaps with the $\tilde{X}^1\Sigma^+ \rightarrow \tilde{C}^1A'$ ($\nu_2 = 10$) transition. The spacing of elements of this progression of about 0.2 eV compares well with the frequencies of the ν_3 mode of the \tilde{A} and \tilde{C} states, 1495 (0.185 eV) and 1530 cm^{-1} (0.190 eV), respectively.

TABLE I. Excitation energies of hydrogen cyanide (in eV).

State	Excitation ^a	Valence excitations			
		Theoretical ^a	Previous experimental	This work	
$x^1\Sigma^+(1A'')$	Ground state	0	0	0	
$1^3A'$	$6a' \rightarrow 7a' (\pi \rightarrow \pi^*)$	4.42		5.46, 5.60, 5.83 ^c	
$1^3A''$	$1a'' \rightarrow 7a' (\pi \rightarrow \pi^*)$	5.46	6.0 ^b	5.99, 6.08, 6.18	
$2^3A'$	$1a'' \rightarrow 2a'' (\pi \rightarrow \pi^*)$	5.91		6.31, 6.42, 6.53	
$1^1A''(\bar{A})$	$6a' \rightarrow 7a' (\pi \rightarrow \pi^*)$	6.48	6.8-7.5, ^b 6.48 ^d	6.45	
$2^1A'$	$6a' \rightarrow 7a' (\pi \rightarrow \pi^*)$	6.78	7.1 ^b		
$2^3A''$	$5a' \rightarrow 7a' (\sigma \rightarrow \pi^*)$	6.85	6.8 ^b	6.83, 7.00, 7.10 ^e	
$3^3A'$	$1a'' \rightarrow 2a'' (\pi \rightarrow \pi^*)$	6.98	7.1-7.9 ^b	7.18, 7.36, 7.55	
$3^3A''$	$5a' \rightarrow 7a' (\sigma \rightarrow \pi^*)$	7.41	7.9 ^b	7.75, 7.86, 7.97	
$2^1A''(\bar{B})$	$1a'' \rightarrow 2a'' (\pi \rightarrow \pi^*)$	7.52	7.5 ^b	8.08, 8.19, 8.41	
$3^1A''(\bar{C})$ 000	$5a' \rightarrow 7a' (\sigma \rightarrow \pi^*)$	7.85		8.03	
010	$1a'' \rightarrow 2a'' (\pi \rightarrow \pi^*)$		8.139, ^c	8.139 ^f 8.13	
020	$6a' \rightarrow 7a' (\pi \rightarrow \pi^*)$			8.245 ^f 8.23	
030				8.350 ^f 8.33	
040				8.460 ^f 8.44	
050				8.565 ^f 8.54	
060				8.670 ^f 8.64	
070				8.770 ^f 8.75	
080				8.87 ^f 8.84	
090				8.965 ^f 8.94	
010				9.145 ^f 9.03	
011				9.12	
012				9.320 ^f	
$3^1A''(\bar{D})$ 000	$5a' \rightarrow 2a'' (\sigma \rightarrow \pi^*)$	8.97	8.93, ^b 8.881, ^c	8.881 ^f 8.84	
001				9.065 ^f 9.03	
100				9.175 ^f	
002				9.250 ^f 9.22	
200				9.360 ^f	
003				9.445 ^f 9.42	
300				9.515 ^f	
004				9.64 ^f 9.63	
	$4\sigma \rightarrow \pi^*$			15.2 ^f 15.7	
		Rydberg excitations			
Excitation	Previous experimental	This work	Calculated ^h	Quantum defect	
$1\pi \rightarrow 3s$ 000	10.18, ^f 10.20 ^g	10.17	10.17	1.01	
001	10.40, ^f 10.43 ^g	10.41			
$5\sigma \rightarrow 3s$ 000	10.70, ^f 10.73 ^g	10.70	10.68	0.98	
020	10.82, ^f 10.82 ^g	10.86			
001	10.90, ^f 10.88 ^g				
				10.93 ^g	
$1\pi \rightarrow 3p_x$					
$1\pi \rightarrow 3p_y$	11.036, ^f 11.06 ^g	11.03	11.04	0.70	
$5\sigma \rightarrow 3p_x$	11.345, ^f 11.32 ^g	11.30	11.30	0.76	
$5\sigma \rightarrow 3p_y$	11.482, ^f 11.54 ^g	11.50	11.44		
$1\pi \rightarrow 3d_x$		11.77	11.79	0.26	
$1\pi \rightarrow 3d_y$		11.91	11.92	0.16	
$1\pi \rightarrow 4s$ 000	12.060, ^f 12.07 ^g	12.03	12.08		
001	12.288, ^f 12.30 ^g	12.25			
$5\sigma \rightarrow 4s$	12.543, ^f 12.48 ^g	12.45	12.52		
$1\pi \rightarrow 4d_x$	12.543, ^f 12.57 ^g	12.54	12.63		
$5\sigma \rightarrow 4p\sigma$		12.74	12.71		
$5\sigma \rightarrow 4p\pi$			12.76		
$1\pi \rightarrow 5s$ 000			12.75		
$1\pi \rightarrow 5s$ 001	12.99 ^g	12.92			
$5\sigma \rightarrow 4d\sigma$			13.03		
$1\pi \rightarrow 6s$	13.09 ^g	13.06	13.06		
$5\sigma \rightarrow 4d\pi$			13.09		
$5\sigma \rightarrow 5s$	13.18 ^g	13.13	13.17		
$1\pi \rightarrow 7s$		13.25	13.23		
$5\sigma \rightarrow 6s$		13.45	13.47		
$5\sigma \rightarrow 7s$		13.61	13.64		
$4\sigma \rightarrow 3s$	16.6 ^f	16.9			

^a Reference 16.

^b Reference 10.

^c Excitation energies listed correspond to unassigned vibronic peaks of one or more electronic transitions.

^d Reference 3.

^e Reference 4.

^f Reference 8.

^g Reference 7.

^h Calculated according to $E = \text{I.P.} - [R/(n - \delta)^2]$.

Numerous features are observed in our spectra with excitation energies above 10 eV. All these transitions with the exceptions of those at 10.70, 10.86, 15.17, and 16.9 eV have been assigned to Rydberg series converging to the first and second ionization potentials of 13.607 and 14.011 eV, respectively.⁸ Excitation energies obtained are in excellent agreement with previous results. The transitions at 10.70 and 10.86 eV which have been assigned by Tam and Brion⁷ as vibronic components of excitations from the 5σ orbital to the $3s$ orbital have also been assigned by Asbrink *et al.*¹¹ as components of the $\tilde{X}^1\Sigma^+ \rightarrow ^1\Sigma^+ (\pi \rightarrow \pi^*)$ transition who suggest that the $5\sigma \rightarrow 3s$ transition has negligible intensity. The suggestion that the $5\sigma \rightarrow ns$ series has negligible intensity prohibits the assignment of transitions occurring at 12.48, 13.13, 13.45, and 13.61 eV to this series. However, these transitions are fitted quite well to a Rydberg series with a quantum defect of 0.98. In addition, Tam and Brion⁷ observed vibrational structure in the 10.64 to 10.88 eV region with spacings which correlate well with those obtained in photoelectron spectra. We, therefore, assign the peaks in this region to the

$5\sigma \rightarrow 3s$ transition. The two very broad structureless features observed at 15.17 and 16.9 eV have been assigned by Fridh and Asbrink⁸ to the $4\sigma \rightarrow \pi^*$ and the $4\sigma \rightarrow 3s$ transitions, respectively. A summary of the energies of features observed in hydrogen cyanide as well as assignments of those features is given in Table I.

ACETONITRILE

The spectrum of acetonitrile in the 4.6 to 9.3 eV energy loss region closely resembles that of hydrogen cyanide. In the 25 eV, 10° spectrum three weak, highly overlapped features are observed with apparent maxima at about 5.5, 6.7, and 7.7 eV. In addition, an intense feature is observed at 8.96 eV with shoulders at 8.45, 8.64, 8.72, 9.11, and 9.21 eV. The 25 eV, 80° shows a broad unresolved feature between 5.2 and 7.5 eV as well as another feature at 8.1 eV which were not observed in the 10° spectrum. The DCS's of these transitions, shown in Fig. 4, indicate that these features are due primarily to singlet \rightarrow triplet excitations. Numerous other features are observed in the spectrum of acetonitrile above 9.3 eV

TABLE II. Excitation energies (in eV) of acetonitrile.

Valence excitations						
Excitation	Excited state spin		Previous experimental		This work	
$\pi \rightarrow \pi^*$	Triplet		6.1 ^{a,c}		5.2–7.5	
	Singlet ?				5.5	
	Singlet ?				6.7	
	Singlet ?		7.5, ^a	7.32 ^b	7.7	
$\pi \rightarrow \pi^*$	Triplet				8.1	
	Singlet		8.45 ^c		8.45	
$\pi \rightarrow \pi^*$	Singlet				8.64	
	Singlet				8.72	
$n \rightarrow \pi^*$	Singlet		9.04, ^a	8.95, ^d	9.00 ^c	8.96
	Singlet			9.11 ^d		9.11
	Singlet			9.22 ^d		9.21
Rydberg excitations						
Excitation	Previous experimental		This work	Calculated ^f	Quantum defect	
$\pi \rightarrow 3p_\sigma$	9.63, ^a	9.59, ^c	9.59 ^c	9.58	9.57	0.73
$\pi \rightarrow 3p_\sigma + v_4$	9.70, ^c	9.71 ^c		9.71		
$\pi \rightarrow 3p_\sigma + v_2$	9.82, ^a	9.84, ^c	9.83 ^c	9.80		
$\pi \rightarrow 3p_\sigma + v_2 + v_4$		9.94, ^c	9.93 ^c	9.95		
$\pi \rightarrow 3p_\sigma + 2v_2$	10.04, ^a	10.07, ^c	10.06 ^c	10.03		
$\pi \rightarrow 3d_\sigma$		10.29 ^c		10.29	10.29	0.34
$\sigma \rightarrow 3p_\sigma$	10.52 ^a			10.54	10.54	0.72
$\sigma \rightarrow 3p_\pi$	10.76, ^a	10.78, ^c	10.78 ^c	10.75	10.76	0.62
$\pi \rightarrow 4p_\sigma$	10.95, ^a	10.92, ^c	10.92 ^c	10.94	10.94	
$\pi \rightarrow 4d_\sigma$	11.34, ^a	11.26, ^c	11.22 ^c	11.25	11.19	
$\sigma \rightarrow 3d_\sigma$					11.24	
$\pi \rightarrow 5p_\sigma$					11.46	
$\sigma \rightarrow 3d_\pi$				11.46	11.46	0.17
$\sigma \rightarrow 3d_\sigma + v_2$					11.68	
$\sigma \rightarrow 3d_\sigma + 2v_2$	11.67 ^a			11.68		
$\sigma \rightarrow 4p_\sigma$		11.95 ^c		11.94	11.90	
$\sigma \rightarrow 4p_\pi$					11.97	
$\sigma \rightarrow 4d_\sigma$		12.18 ^c		12.14	12.14	
$\sigma \rightarrow 4d_\pi$					12.24	
$\sigma \rightarrow 5d_\pi$		12.53 ^c		12.57	12.58	
$\sigma \rightarrow 6d_\pi$		12.76 ^c		12.75	12.76	
$\sigma \rightarrow 7d_\pi$		12.85 ^c		12.85	12.87	
				13.84	13.84	
				14.51	14.51	

^a Reference 15.

^b Reference 12.

^c Reference 16.

^d Reference 14.

^e Reference 13.

^f $E = \text{I.P.} - [R/(n - \delta)^2]$.

which may not be readily correlated to features appearing in the hydrogen cyanide spectrum. The excitation energies for all features observed in the acetonitrile spectra are listed in Table II.

The weak features observed in our spectra at 5.5 and 6.7 eV have not been previously observed. Intense features due predominantly to singlet→triplet transitions are observed in this energy region in our higher angle spectra. It is not possible to determine whether the weak features appearing at 5.5 and 6.7 eV are also due to these same transitions or are due to the very weak singlet→singlet excitations.

In the 70 eV electron impact studies of Stradling and Loudon a fairly strong feature was observed at 6.1 eV in spectra taken at scattering angles of both 0° and 90°, which they assigned tentatively as a singlet→triplet excitation. An attempt by Fridh¹⁶ to observe this same feature was unsuccessful in spite of the use of an identical impact energy (70 eV) and scattering angle (0°). Fridh has suggested that the feature observed by Stradling and Loudon is due to an impurity. In our high angle spectra, a broad feature is observed between 5.2 and 7.5 eV which bears no resemblance to the feature Stradling and Loudon observed. The feature we observe is probably due to the overlap of several singlet→triplet, $\pi \rightarrow \pi^*$ transitions.

Herzberg and Scheibe¹² observed a broad continuum with a maximum at 7.32 eV. Stradling and Loudon also observed a weak feature in this region, at 7.5 eV. In our spectra, a weak feature is observed with an apparent maximum at 7.7 eV. Agreement between our results and those of previous workers is poor due to our inability to resolve this feature from the intense 8.96 eV feature. This 7.7 eV feature has been suggested to correspond to an $n \rightarrow \pi^*$ transition or a forbidden component of a $\pi \rightarrow \pi^*$ transition.

An intense feature is observed in our spectra taken at both low and high scattering angles at 8.96 eV. Shoulders appear on this feature at 8.45, 8.64, 8.72, 9.11, and 9.21 eV. Stradling and Loudon¹⁵ have also observed a transition in this region, at 9.04 eV. Okabe and Dibeler¹⁴ measured the fluorescence yield from CN produced by photolysis of acetonitrile as a function of wavelength and observed a quasicontinuum with features at about 8.95, 9.01, 9.11, 9.22, and 9.33 eV. Fridh¹⁶ observed diffuse bands at 8.45 and 9.0 eV. Our results are in excellent agreement with this previous work. Fridh has suggested assignment of the features at 8.45 and 9.0 eV to a $\pi \rightarrow \pi^*$ transition and an $n \rightarrow \pi^*$ transition, respectively. The similarity of the acetonitrile spectrum in this region to that of hydrogen cyanide which has been assigned to overlapping $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions supports this assignment.

Nearly all features with excitation energies greater than 9.3 eV have been previously observed and may be assigned to Rydberg series converging to the first and second I.P.'s of 12.20 and 13.14 eV, respectively.²¹ Stradling and Loudon have suggested assignment of the peak which they observe at 9.04 eV to the $\pi \rightarrow 3s$ excitation. The similarity between our acetonitrile and hydrogen cyanide spectra below 9.3 eV suggests that the predominant contribution to this feature results from the valence $n \rightarrow \pi^*$ transition. The absence of sharp structure for the spectrum of acetonitrile at about 9 eV

comparable to that observed for the $\pi \rightarrow 3s$ transition in hydrogen cyanide suggests that the intensity of the $\pi \rightarrow ns$ series is significantly less for acetonitrile than for hydrogen cyanide. We have assigned all the peaks in the 9.3 to 13 eV region to Rydberg excitations to np_σ , np_π , nd_σ , and nd_π orbitals. Quantum defects obtained are comparable to those obtained for similar orbitals of hydrogen cyanide. Table II lists transition energies and assignments for the acetonitrile spectrum.

MALONONITRILE

The electronic spectrum of malononitrile has not been reported previously. The spectrum of malononitrile in the energy loss region less than 9.5 eV is very similar to the spectra of hydrogen cyanide and acetonitrile. Weak highly overlapped features are observed at about 5.6, 6.5, and 7.9 eV in the 25 eV, 10° spectrum. Features possessing DCS's (Fig. 5) typical of singlet→triplet transitions are observed from 5.2 to 7.1 eV and at 7.95 eV. The rapid decrease in the DCS's for those features between 10° and 20° suggests that the singlet triplet transitions overlay weak spin allowed transitions. Two weak shoulders occurring at 9.14 and 9.33 eV are observed on the intense feature at 8.94 eV. In accordance with our assignments for the corresponding transitions in hydrogen cyanide and acetonitrile we assign both singlet→triplet transitions to $\pi \rightarrow \pi^*$ excitations. The features observed at 5.6, 6.5, and 7.9 eV probably result from singlet→singlet

TABLE III. Excitation energies (in eV) of malononitrile.

Valence excitations			
Excitation	Excited state spin		Observed
$\pi \rightarrow \pi^*$	Triplet		5.2–7.1
	Singlet ?		5.6
	Singlet ?		6.5
	Singlet ?		7.9
$n \rightarrow \pi^*$	Triplet		7.95
	Singlet		8.94
$n \rightarrow \pi^*$	Singlet		9.14
	Singlet		9.33
	Singlet		9.33
Rydberg excitations			
Excitation	Observed	Calculated	Quantum defect
$\pi_1 \rightarrow 3R$	9.96	9.96	0.76
$\pi_1 \rightarrow 3R + v$	10.13		
$\pi_1 \rightarrow 3R + 2v$	10.26		
$\pi_1 \rightarrow 3R'$	10.43	10.43	0.54
$\sigma_1 \rightarrow 3R$	10.74	10.69	0.74
$\pi_2 \rightarrow 3R''$	11.01	11.01	0.45
$\sigma_1 \rightarrow 3R''$	11.32	11.32	0.45
$\pi_1 \rightarrow 4R$	11.58	11.54	
$\pi_1 \rightarrow 5R$	11.98	11.92	
$\pi_1 \rightarrow 5R$		12.00	
$\pi_2 \rightarrow 4R''$		12.02	
$\pi_1 \rightarrow 6R$	12.20	12.18	
$\pi_1 \rightarrow 6R'$		12.22	
$\sigma_1 \rightarrow 4R''$	12.36	12.33	
$\pi_1 \rightarrow 7R$		12.36	
$\pi_1 \rightarrow 7R'$		12.36	
$\pi_2 \rightarrow 5R''$	12.47	12.44	
$\sigma_1 \rightarrow 5R''$	12.77	12.75	
$\sigma_1 \rightarrow 6R''$	13.03	12.97	
	13.47		
	16.34		

$\pi \rightarrow \pi$ excitations. The feature at 8.94 is tentatively assigned to an $n \rightarrow \pi^*$ transition.

The feature observed having excitation energies greater than 9.5 eV may be assigned to Rydberg series converging to the first four I.P.'s of 12.68, 13.10, 13.41, and 13.59 eV.²² The interaction of the two CN groups splits the CN π and n orbitals into two sets of two orbitals. Table III lists the transitions observed and our tentative assignments. As with acetonitrile, no evidence of excitations to ns Rydberg orbitals is found. The quantum defect we obtain for the np_σ series (about 0.75) agrees quite well with the values previously obtained for hydrogen cyanide and acetonitrile. Three additional series may be fitted using quantum defects of 0.55, 0.45, and 0.45. Such quantum defects seem low for transitions to p_π orbitals and high for transitions to d_σ orbitals. Therefore, the correct excited orbital designation is not clear.

PROPIONITRILE

The electron impact spectrum of propionitrile resembles those of hydrogen cyanide, acetonitrile, and malononitrile in the 4.6 to about 9 eV energy loss region. In the low angle spectrum, highly overlapped features are observed with apparent maxima at about 6.5 and 7.8 eV and an intense feature is observed at 8.95 eV. At high scattering angle, additional features are observed between 5.4 and 7.5 eV and at 8.14 eV. The similarity to the spectrum of hydrogen cyanide in this region again suggests assignment of these features to valence transitions. We therefore assign the 5.4 to 7.5 eV feature as overlapping singlet \rightarrow triplet $\pi \rightarrow \pi^*$ transitions. A feature was observed by Stradling and Loudon¹⁵ at about 6.4 eV in spectra taken at scattering angles of 0° and 90° and an impact energy of 70 eV. This feature was tentatively assigned as a singlet \rightarrow triplet excitation and corresponds to the feature they observed in the spectrum of acetonitrile at 6.1 eV which Fridh¹⁶ has suggested was due to an impurity. The broad structureless transition we observe at high angle bears no resemblance to that feature observed by Stradling and Loudon.

The features observed in our spectra at about 6.5 and 7.8 eV have not been previously reported although the feature Stradling and Loudon report at 6.4 eV may correspond to the 6.5 eV feature we observe. Both of these transitions are probably due to spin-allowed, symmetry-forbidden components of a $\pi \rightarrow \pi^*$ transition.

The feature observed in our spectra at 8.14 eV is not observed in our low angle spectra. Due to the similarity of this feature to the corresponding features of hydrogen cyanide, acetonitrile, and malononitrile for which DCS curves could be obtained, we assign this feature as a singlet \rightarrow triplet excitation.

The intense feature observed at 8.95 eV may be assigned as an $n \rightarrow \pi^*$ transition. The 8.95 eV feature is overlapped with another feature at 9.35 eV which corresponds to the first element of a Rydberg series converging to the first vertical I.P. of 12.11 eV.²¹ The quantum defect of 0.67 indicates that the upper state is probably a $3p$ orbital. The additional transitions observed at higher excitation energies may also be tentatively assigned as Rydberg excitations converging to

TABLE IV. Excitation energies (in eV) of propionitrile.

Valence excitations				
Excitation	Excited state spin	Previous experimental ^a	This work	
$\pi \rightarrow \pi^*$	Triplet	6.4	5.4–7.5	
	?		6.5	
	?		7.8	
$n \rightarrow \pi^*$	Triplet	8.74	8.14	
$\pi \rightarrow \pi^*$	Singlet		8.95	
Rydberg excitations				
Excitation	Previous experimental	This work	Calculated	δ
$\pi \rightarrow 3R$	9.39	9.35	9.34	0.67
	9.52	9.56		
	9.86	9.74		
$\pi \rightarrow 3R'$	10.09	10.12	10.12	0.20
	10.34			
$\sigma \rightarrow 3R$	10.50	10.44	10.45	0.65
$\pi \rightarrow 4R$	10.65		10.62	
$\pi \rightarrow 5R$	10.87	11.01		0.23
		11.09	11.12	
$\sigma \rightarrow 3R'$			11.14	
	11.19			
$\pi \rightarrow 6R$	11.30	11.32	11.37	
$\pi \rightarrow 5R + \nu$			11.38	
$\pi \rightarrow 6R'$		11.47	11.45	
$\sigma \rightarrow 4R$		11.7	11.7	
		11.8		
$\sigma \rightarrow 4R'$		11.96	11.95	
$\sigma \rightarrow 5R$		12.28	12.2	
$\sigma \rightarrow 5R'$			12.31	
$\sigma \rightarrow 6R$		12.46	12.44	
$\sigma \rightarrow 6R'$			12.50	
		12.63	12.61	
		12.94		
		13.63		

^a Reference 15.

the first and second I.P.'s of 12.11 and 12.91, respectively.²¹ The quantum defects calculated, 0.67, 0.65, 0.20, and 0.23, suggest that only transitions to two series of upper states, probably np and nd orbitals are involved. Excitation energies we observe are in good agreement with those obtained by Stradling and Loudon¹⁵ in this energy region. Excitation energies and assignments for these transitions are listed in Table IV.

BUTYRONITRILE

The electron impact spectrum of butyronitrile taken at an impact energy of 25 eV and a scattering angle of 10° in the energy loss region 4.6 to 11.6 eV displays a weak highly overlapped feature at about 6.4 eV and intense features at 9.12, 9.77, 10.60, and 11.30 eV. The 6.4 eV feature may correspond to a weak $\pi \rightarrow \pi^*$ transition similar to those observed in the previously discussed alkyl cyanides. The spectrum taken at 75 eV, 5° (not shown) displays two peaks at 9.18 and 9.42 eV having intensities roughly 75% of that of the 10.60 eV peak. Spectra of propionitrile at similar impact energies and scattering angles indicate that the intensity of the valence transition occurring at 8.95 is reduced by about a factor of 2 relative to that of the higher lying Rydberg transi-

TABLE VI. Excitation energies (in eV) of butyronitrile.

Valence excitations			
Excitation	Excited state spin	Previous experimental ^a	This work
$\pi \rightarrow \pi^*$	Triplet	5.9	5.4–7.6
	?		6.4
	?	7	
$n \rightarrow \pi^*$	Triplet		8.2
$n \rightarrow \pi^*$	Singlet		9.12
Rydberg excitations			
Excitation	Previous experimental	This work	
$\pi \rightarrow 3R$	9.3	9.18	
$\pi \rightarrow 3R + V$		9.42	
	9.85	9.80	
	10.5	10.6	
		11.27	
		12.03	
		13.65	

^aReference 15.

tions (9.35 and 10.44 eV) when the impact energy is increased from 25 to 75 eV and the scattering angle is decreased from 10° to 5°. This suggests that the feature observed at 25 eV, 10° is due to the overlap of the $n \rightarrow \pi^*$ observed in the previously discussed alkyl cyanides at about 9 eV and the first member of a Rydberg series occurring at 9.18 and 9.42 eV (the 9.42 eV peak probably includes one quantum of the C≡N stretching frequency).

The spectrum taken at 25 eV, 80° shows additional features between 5.4 and 7.6 eV and at 8.2 eV which are virtually identical to the features observed in the other alkyl cyanides and which we have assigned to singlet→triplet transitions. We therefore assign the 5.4 to > 6 eV feature to the overlap of several $\pi \rightarrow \pi^*$ singlet→triplet transitions. The feature appearing in butyronitrile is also assigned to a singlet→triplet, possibly $n \rightarrow \pi^*$, transition.

Stradling and Loudon¹⁵ have again observed a feature at about 6 eV which appears in both 0° and 90° spectra taken at an impact energy of 70 eV, which they have tentatively assigned as a singlet→triplet transition. As was the case for acetonitrile and propionitrile, the feature we observe in our high angle spectra of butyronitrile bears no resemblance to the feature which they observe.

Peaks which probably correspond to Rydberg excitations converging to the first (11.65 eV)²³ and second (not reported) I.P.'s are observed at 9.18, 9.42, 9.80, 10.60, 11.27, and 12.03 eV. The 9.18 eV feature may be assigned to a $\pi \rightarrow 3p$ excitation with a quantum defect of 0.65, which is very close to the quantum defect observed for the corresponding transition of propionitrile. We are presently unable to assign the higher lying features. Transition energies and

assignments (if any) for the features we observe in butyronitrile are listed in Table V.

CONCLUSIONS

We have obtained electron impact spectra of hydrogen cyanide, acetonitrile, malononitrile, propionitrile, and butyronitrile at several different impact energies and scattering angles from 5° to 80°. Our results for hydrogen cyanide are in excellent agreement with previous ones. We have reported previously unobserved singlet→triplet transitions in acetonitrile, propionitrile, and butyronitrile. In addition, we report the first study of the electronic spectrum of malononitrile. We have assigned both valence and Rydberg transitions observed in acetonitrile, malononitrile, propionitrile, and butyronitrile relying heavily on the similarities of the spectra to those of hydrogen cyanide.

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