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The Electronic Spectrum of Acrylonitrile

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The vapor absorption spectrum of acrylonitrile CH_2CHCN has been measured in the vacuum ultraviolet region. In addition, an all-valence-electron molecular orbital calculation has been used to calculate the electronic structure and spectrum of the molecule. On the basis of the MO calculation, as well as a vibrational analysis of the observed spectrum, several electronic transitions are assigned. The lowest energy absorption band (2107 Å, $\varepsilon = 150$) is assigned as an $n \to \pi^*$ transition. Absorption bands at 2030 Å ($\varepsilon = 1600$), 1725 Å ($\varepsilon = 2100$), and 1570 Å ($\varepsilon = 1920$) are assigned as $0-0$ bands associated with transitions that are, respectively, $\pi \to \pi^*$, $\sigma \to \sigma^*$, and $\pi \to \pi^*$ in character.

Das UV-Absorptionsspektrum von dampfförmigen Acrylnitril wurde gemessen und eine CNDO/2-Rechnung für die Elektronenstruktur durchgeführt. Auf dieser Basis konnten unter Zuhilfenahme der Analyse der Schwingungsstruktur im beobachteten Spektrum mehrere Banden zugeordnet werden: die 2107-Å-Bande ($\varepsilon = 150$) einem $n \to \pi^*$-Übergang, die drei Banden bei 2030 Å ($\varepsilon = 1600$), 1725 Å ($\varepsilon = 2100$) und 1570 Å ($\varepsilon = 1920$) $0-0$-Übergängen von $\pi \to \pi^*$-, $\sigma \to \sigma^*$- bzw. $\pi \to \pi^*$-Banden.

Mesure du spectre d'absorption en phase vapeur de l'acrilonitrile CH_2CHCN dans la région de l'ultraviolet. Par ailleurs, la structure électronique et le spectre de la molécule ont été calculés à l'aide d'une méthode des orbitales moléculaires semi-empirique pour tous les électrons de valence. Sur cette base, ainsi que sur une analyse vibrationnelle du spectre expérimental, on procède à l'attribution de plusieurs transitions électroniques. La bande d'absorption de plus basse énergie (2107 Å, $\varepsilon = 150$) est attribuée à une transition $n \to \pi^*$. Les bandes d'absorption à 2030 Å ($\varepsilon = 1600$), 1275 Å ($\varepsilon = 2100$) et 1570 Å ($\varepsilon = 1920$) sont considérées comme des bandes $0-0$ associées à des transitions $\pi \to \pi^*$, $\sigma \to \sigma^*$ et $\pi \to \pi^*$ respectivement.

Introduction

This paper reports the measurement of the vapor absorption spectrum of acrylonitrile in the vacuum ultraviolet region down to 1250 Å. The electronic transitions are assigned on the basis of a vibrational analysis of the spectrum and a molecular orbital (MO) calculation including all valence electrons in the molecule. Previous work on the ultraviolet absorption of acrylonitrile has not been extended below 1800 Å [1, 2]. In Ref. [2], π-electron molecular orbital calculations were utilized as an aid in assigning two bands as separate electronic transitions, $n \to \pi^*$ and $\pi \to \pi^*$. Our theoretical and experimental results support the relative ordering of the $n \to \pi^*$ and $\pi \to \pi^*$ transitions previously reported [2] but not the band assignments.

Experimental Methods

A commercial sample of acrylonitrile monomer free of divinylacetylene, methylvinylketone, and cyanobutadiene contaminants was purified by three vacuum sublimations. The refractive index of the purified sample was $n_D^{22} = 1.3907 \pm 0.0002$.

The instrument, vapor cell and experimental procedure have been described previously [3, 4]. The concentration of acrylonitrile was calculated from the vapor pressure data of Stull [5]. The error in concentration is estimated to be 2%.

Method of Calculation

The MO calculation of the ground state of acrylonitrile was carried out using the CNDO/2 theory of Pople and co-workers [6]. In this method, the only input necessary to perform the calculation is the positional coordinates of the atoms in the molecule, i.e., the molecular geometry. Accordingly, the MO calculation was performed using the molecular structure data for acrylonitrile as obtained from microwave spectroscopy [7]. The numbering of the atoms in the molecule is shown in Fig. 1 and the resultant electronic charge distributions is given in Table 1.

Del Bene and Jaffé [8] have shown that the CNDO/2 theory of Pople must be modified in order to study excited states and electronic spectra of molecules. We used the method of Del Bene and Jaffé, including configuration interaction due to the 25 lowest singly excited states, to calculate the absorption spectrum

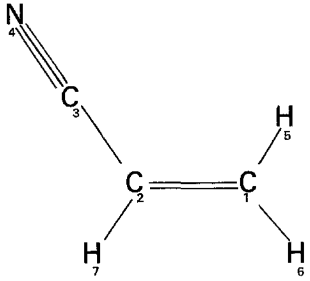

Fig. 1. Numbering of the atoms in acrylonitrile

Table 1. *Calculated electron populations in acrylonitrile*[a]

Atom	Pople calc. $(C \equiv N) = 1.16$ Å	Del Bene and Jaffé calc. $(C \equiv N) = 1.01$ Å
C (1)	6.01	6.02
C (2)	5.99	6.01
C (3)	5.92	5.82
N (4)	7.14	7.25
H (5)	0.97	0.97
H (6)	0.98	0.97
H (7)	0.97	0.97

[a] The numbering of the atoms in acrylonitrile is given in Fig. 1.

of acrylonitrile. Unfortunately, the iterative SCF treatment did not converge for the known molecular geometry of the molecule. In order to obtain convergence, we attempted the calculation with several different values assumed for the $C\equiv N$ bond length. The calculation did converge for bond-length values between 0.95 Å and 1.05 Å (experimental value = 1.16 Å); however, the results are a very sensitive function of the assumed $C\equiv N$ distance. We have chosen to report the results for the molecular orbital calculation performed with a $C\equiv N$ bond length of 1.01 Å because the ground state electronic charge distribution obtained for that calculation best agrees with that obtained with the Pople method using the observed $C\equiv N$ bond length of 1.16 Å (see Table 1). The dipole moment calculated from the Del Bene and Jaffé electronic distribution is 3.38 D (experimental $\mu = 3.89$ D) [9]. The direction of the dipole moment of acrylonitrile is calculated by MO theory to lie essentially along the $C\equiv N$ bond, in agreement with the results of microwave spectroscopy [7, 9].

The calculated orbital energy levels can be equated to the molecular ionization potentials by Koopmans' theorem [10]. As can be seen from Table 2, the agreement between theory and the photoelectron results of Lake and Thompson [11] is good. The assignment of these orbitals will be discussed later in this paper. The calculated and observed electronic transitions for acrylonitrile are given in Table 3.

Table 2. *Calculated and observed ionization potentials* (eV) *of acrylonitrile*

Calc.	Assignment	Obs.[a]	Assignment[a]
10.56	80% $C=C$ π	10.91	$C=C$ π
12.76	60% $C\equiv N$ σ	12.36	$C\equiv N$ π
13.08	50% n	13.04	n
14.76	80% $C\equiv N$ π	13.56	
15.53	σ	14.43	
17.27	σ	16.17	
21.40	σ	17.62	

[a] Lake, R. F., Thompson, H.: Proc. Roy. Soc. (London) A **317**, 187 (1970).

Table 3. *Calculated and observed spectral transitions in acrylonitrile*

Assignment[a]	Calc. (Å)	f	Obs. (Å)	ε
$n\rightarrow\pi^*$	1951	0	2107	150
$\pi\rightarrow\pi^*$	1921	0.20	2030	1600
$n\rightarrow\pi^*$	1886	0		
$\pi\rightarrow\sigma^*$	1880	0		
$\sigma\rightarrow\sigma^*$	1661	0.05	1725	2100
$\pi\rightarrow\sigma^*$	1634	0		
$\sigma\rightarrow\pi^*$	1616	0		
$\pi\rightarrow\pi^*$	1576	0.43	1570	1920
$\pi\rightarrow\sigma^*$	1411	0		
$\sigma\rightarrow\pi^*$	1407	0		

[a] The transitions are generally mixed in character (see text). The entry corresponds to the leading term in the CI wavefunction.

Results and Discussion

The absorption spectrum of acrylonitrile vapor is given in Fig. 2 as a plot of molar extinction coefficient (ε) in units of liters mole^{-1} cm^{-1} versus wavenumber (kK). The spectrum consists of several electronic transitions with associated diffuse vibrational structure. We observed a weak shoulder at ca. 47.4 kK (2107 Å) with $\varepsilon = 150$, a medium intensity series of diffuse bands starting at 49.26 kK (2030 Å) with ε between 1600 and 4600 and a set of relatively sharp bands to the short wavelength side of 69.0 kK.

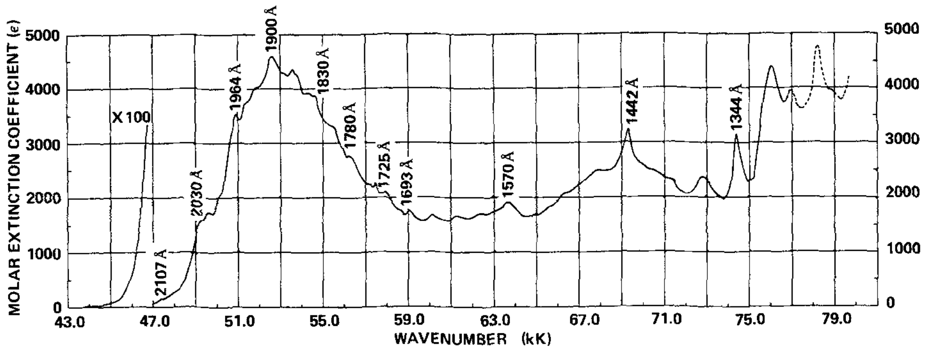

Fig. 2. Vacuum ultraviolet absorption spectrum of acrylonitrile vapor. (The dashed lines between 77 kK and 80 kK indicate that only one measurement was made in this wavenumber interval

On the basis of the MO calculation, shown in Table 3, the long wavelength weak band at 2107 Å has been assigned as a $n \rightarrow \pi^*$ transition. Since the fraction of electrons on the nitrogen atom is only 50%, the calculation indicates considerable delocalization in the σ-orbital from which this electron is promoted. Calculations on diazines have also indicated delocalization of so-called "lone-pair" orbitals [12] and recent experimental evidence [13] has been reported to corroborate this theoretical prediction. The remaining bands were separated into three electronic transitions by the vibrational analysis of the spectrum shown in Table 4. The 0 – 0 bands used in the analysis were 49.26 kK (2030 Å), 57.97 kK (1725 Å) and 63.69 kK (1570 Å) and the resulting correlation with the calculated transitions, characterized by non-zero f values (Table 3), is very satisfactory. According to the molecular orbital calculations the electronic transitions are constituted as follows: the 2030 Å transition is 70% ($\pi \rightarrow \pi^*$) plus 30% ($\sigma \rightarrow \sigma^*$); the 1725 Å transition is 90% ($\sigma \rightarrow \sigma^*$) plus 10% ($\pi \rightarrow \pi^*$) and the 1570 Å transition is 65% ($\pi \rightarrow \pi^*$) plus 35% ($\sigma \rightarrow \sigma^*$).

A possible assignment for all vibrational structure between 49 kK and 69 kK is given in Table 4. The first $\pi \rightarrow \pi^*$ transition shows bands displaced 370 cm^{-1}, 970 cm^{-1}, 1680 cm^{-1}, and 2230 cm^{-1} from the 0 – 0 band at 2030 Å. The bands associated with this $\pi \rightarrow \pi^*$ transition have been represented as combinations of these four frequencies. Infrared and Raman data [14, 15] allow us to assign these

Table 4. *Vibrational analysis of the vapor absorption spectrum of acrylonitrile*

Wave-number (cm^{-1})	Distance from 0–0 Band (cm^{-1})	Assignment					
49260			0–0				
49630	370		370				
50230	970		970				
50940	1680		1680				
51490	2230		2230				
51870	2610	0–0+		970	+1680		=2650
52470	3210	0–0+		970		+2230	=3200
52630	3370	0–0+			2(1680)		=3360
53110	3850	0–0+			1680	+2230	=3910
53620	4360	0–0+		970	+2(1680)		=4330
53760	4500	0–0+				2(2230)	=4460
54330	5070	0–0+			3(1680)		=5040
54640	5380	0–0+	370		+3(1680)		=5410
55330	6070	0–0+		970	+3(1680)		=6010
55870	6610	0–0+				3(2230)	=6690
56180	6920	0–0+		2(970)	+3(1680)		=6980
57140	7880	0–0+			2(1680)	+2(2230)	=7820
57470	8210	0–0+	370		+2(1680)	+2(2230)	=8190
57970			0–0				
58700	9440	0–0+			3(1680)	+2(2230)	=9500
59070	1100		1100				
60130	2160	0–0+	2(1100)				=2200
61240	3270	0–0+	3(1100)				=3300
62400	4430	0–0+	4(1100)				=4400
63690			0–0				
65060	1370		1370				
65750	2060		2060				
66440	2750	0–0+	2(1370)				=2740
67830	4140	0–0+	3(1370)				=4110
69900	6210	0–0+	3(1370)	+2060			=6170
70500	6810	0–0+	2(1370)	+2(2060)			=6860
71900	8210	0–0+	3(1370)	+2(2060)			=8230

frequencies as follows:

370 cm^{-1}	C–C≡N bend	(362 cm^{-1})
970 cm^{-1}	trans CH wag	(970 cm^{-1})
1680 cm^{-1}	C=C stretch	(1630 cm^{-1})
2230 cm^{-1}	C≡N stretch	(2240 cm^{-1}).

The strongest bands of the vibrational structure associated with this $\pi \rightarrow \pi^*$ transition are those containing the C=C stretch vibration. The $\sigma \rightarrow \sigma^*$ transition with the 0–0 band at 57.97 kK shows a progression of diffuse bands separated by ca. 1100 cm^{-1} which may be assigned as representing a symmetrical CH_2 rock vibration [15]. The calculation indicates that the electron promoted in the $\sigma \rightarrow \sigma^*$ transition is associated with the σ structure of the CH bonds. The highest energy

$\pi \rightarrow \pi^*$ transition with $0-0$ band at 63.69 kK possesses diffuse vibrational structure represented by the frequencies 1370 cm^{-1}, 2060 cm^{-1} and combinations of these two frequencies. The 1370 cm^{-1} frequency may be associated with a $C=C$ stretch vibration and the 2060 cm^{-1} frequency with the $C\equiv N$ stretch vibration, both of which are reduced from their ground state values in this highly excited singlet state of the molecule.

The assignment of the individual occupied orbitals has been compared with results from photoelectron spectroscopy [11] in Table 2. The highest filled molecular orbital is calculated to be a π-orbital predominantly ethelynic in character and is thus in agreement with the assignment of Lake and Thompson. Also in agreement with the work of these authors is the assignment of the third molecular orbital which they assign as nitrogen lone pair; actually, the molecular orbital calculation indicates a delocalized σ-orbital nevertheless 50% lone-pair in character. The only source of disagreement between our calculation and the assignments in Ref. [11] lies in the second orbital. This orbital is assigned as a $C\equiv N$ π-orbital by Lake and Thompson, whereas the calculation indicates it to be a σ-orbital largely associated with the nitrile group.

Assignment of Rydberg transitions is difficult inasmuch as the spectrum has been measured only to 80 kK and the ionization potential of acrylonitrile is located at 88 kK. Consequently, we are not able to observe any well-developed Rydberg series. Nevertheless, the relatively sharp bands at 69.32 kK, 74.40 kK, and 76.05 kK appear to be due to Rydberg transitions. Three bands are separated from the 69.32 kK band by ca. 1910 cm^{-1} and multiples of 1910 cm^{-1} whereas the 74.40 kK and 76.05 kK bands show associated bands separated by 1300 cm^{-1} and 1350 cm^{-1} respectively. In addition, the relatively sharp band at 57.14 kK (which is listed alternatively in Table 4 as vibrational structure associated with a valence shell transition) could in fact be the first absorption in a Rydberg series analogous to the lowest energy Rydberg transition (57.34 kK) in ethylene [16]. The experimental techniques of Robin *et al.* [17] would be quite useful in testing these Rydberg assignments.

References

1. Klevens, H. B., Platt, J. R.: Survey of vacuum ultraviolet spectra of organic compounds. Tech. Report ONR Contract N 60 RI-20, Task Order IX, Project NR 019101 (1954).
2. Halper, J., Closson, W. D., Gray, H. B.: Theoret. chim. Acta (Berl.) **4**, 174 (1966).
3. Mullen, P. A., Orloff, M. K.: J. molecular Spectroscopy **30**, 140 (1969).
4. — — J. chem. Physics **51**, 2276 (1969).
5. Stull, D. R.: Ind. Eng. Chem. **39**, 517 (1947).
6. Pople, J. A., Santry, D. P., Segal, G. A.: J. chem. Physics **43**, S 129 (1965). – Pople, J. A., Segal, G. A.: J. chem. Physics **43**, S 136 (1965); **44**, 3289 (1966).
7. Costain, C. C., Stoicheff, B. P.: J. chem. Physics **30**, 777 (1959).
8. Del Bene, J., Jaffé, H. H.: J. chem. Physics **48**, 4050 (1968).
9. Wilcox, W. S., Goldstein, J. H., Simmons, J. W.: J. chem. Physics **22**, 516 (1954).
10. Koopmans, T.: Physica **1**, 104 (1933).
11. Lake, R. F., Thompson, H.: Proc. Roy. Soc. (London) A **317**, 187 (1970).
12. Clementi, E.: J. chem. Physics **46**, 4737 (1967). – Hoffmann, R.: J. chem. Physics **40**, 2745 (1964).
13. Wilson, J. D.: J. chem. Physics **53**, 467 (1970).
14. Colthup, N. B., Daly, L. H., Wiberley, S. E.: Introduction to infrared and raman spectroscopy, p. 211. New York: Academic Press 1964.

15. Halverson, F., Stamm, R. F., Whalen, J. J.: J. chem. Physics **16**, 808 (1948).
16. Herzberg, G.: Molecular spectra and molecular structure, Vol. 3, p. 629. Princeton: D. Van Nostrand Co. Inc. 1967.
17. Robin, M. B., Hart, R. R., Kuebler, N. A.: J. chem. Physics **44**, 1803 (1966).

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