# Electronic Spectra of the Free Allyl Radical and some of its Simple Derivatives

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Received 21st August, 1967

Electronic spectra in the 2100-2500 Å region, were reported for the allyl radical, the  $\beta$ -methallyl radical, the  $\alpha$ -methallyl radical, the  $\beta$ -ethallyl radical and the cyclopentenyl radical. The vibrational structures of the allyl and  $\beta$  substituted radicals indicate that in the main regions of absorption, the  $\alpha$ (C—H) stretching frequency is excited. A single band progression observed in flashed allyl cyanide, was tentatively assigned to a free radical derived from pyrrole.

The free allyl radical is the simplest example of a conjugated system, and its electronic structure has been investigated in several theoretical approximations.<sup>1-4</sup> The radical should be planar in the ground electronic state, and the electron spin resonance spectrum <sup>5</sup> is consistent with a molecule of  $C_{2v}$  symmetry:



In the Hückel approximation, the ground state  $\pi$ -system is composed of two  $b_1$  bonding orbitals and a single  $a_2$  non-bonding orbital  $(b_1)^2(a_2)$ ,  ${}^2A_2$ , corresponding to an equality of electron density on each of the C atoms. The two lowest doublet-excited-states have  ${}^2B_1$  symmetry, and result either from excitation of the  $a_2$  electron to an antibonding  $b_1$  orbital, or from excitation of a  $b_1$  orbital to fill the non-bonding  $a_2$  orbital. In this approximation both electric dipole transitions would be strong and the excitation energies would be equal. More sophisticated theories predict excitation is predicted to be weak, and the other to be strong.<sup>3</sup> The excitation energy of the  ${}^4A_2$  state, with one electron in each of the three orbitals, has been predicted to be about 5-6 eV.<sup>3,4</sup> There should not be any other state of the radical which can cause a strong electronic transition in the quartz ultra-violet.

There have been several reports of the production of transient absorption bands in irradiated polyethylene at low temperature, which have been assigned to the short wavelength transition of the allyl radical incorporated in a hydrocarbon chain. Bodily and Dole<sup>6</sup> recorded an absorption maximum at 2580 Å, and considered that the  $\alpha, \alpha'$  substitution causes a "bathochromic shift" from the theoretically predicted shorter wavelength for the unsubstituted radical. In the gas phase, Currie and Ramsay <sup>7</sup> have detected a weak and diffuse band system in absorption (40 m path), with an "apparent" O—O band at 4083 Å, in the flash photolysis of each of nine compounds containing the allyl group. Full deuteration caused a shift to shorter wavelength. They have provisionally assigned the spectrum to the long wavelength transition of the allyl radical. Considering the predicted energy and intensity of the transition, together with established photochemical mechanisms, the evidence seems to be compelling notwithstanding the impossibility of a rotational analysis. The vibrational structure was discussed only in outline, pending the availability of deuterated isomers.

We report here the detection of new band systems, produced by the flash photolysis of a wide variety of olefinic compounds in the gas phase. On the basis of photochemical and structural evidence, spectra have been assigned to the allyl radical, the  $\beta$ -methallyl radical, the  $\alpha$ -methallyl radical, the  $\beta$ -ethallyl radical and the cyclopentenyl radical. They all exhibit intense band systems in the far ultra-violet, and the character of the electronic change is very probably similar in each case, corresponding to the transition from the  ${}^{2}A_{2}$  to the higher of the  ${}^{2}B_{2}$  states. The allyl spectrum has been detected in the flash photolysis of 8 compounds containing the allyl group, and the original assignment <sup>8</sup> has been strengthened by the observation of derivatives of the allyl radical produced in analogous photochemical processes. All the spectra described here are transient, with half lifetimes of about 50  $\mu$ sec. All experiments comprise " isothermal " conditions.

## EXPERIMENTAL

The flash photolysis apparatus was of standard design. All quartz components were spectrosil grade, and the volume containing the flash lamp and reaction vessel (75 cm long) was flushed out with  $N_2$ . A single optical pass resulted in sufficient absorption to record the band systems, with flash energies from 100-2000 J. Most of the spectra were recorded with either Hilger small or medium quartz-prism instruments. Ilford H.P.3 plates were sensitized with sodium salicylate, except when the highest definition was required.

## MATERIALS

All parent compounds were repeatedly degassed and roughly fractioned by bulb distillation, retaining the middle fractions. The sources and purity are listed as follows:

(PRG = Phi)	llips Research	Grade,	PPG =	• Phillip	ps	Pure	Grade,	KL =	Koch	Light.)
	propylene			PRG	99	•99 mo	ole %			
	butene-1			PRG	99	·8 wt	%			
	isobutene			PRG	99	∙8 wt	%			
	trans-butene-2	2		PPG	99	mole	%			
	cis-butene-2			PPG	99	mole	%			
	allyl cyanide			KL				(pure)		
	crotonitrile			KL				(pure)		
	crotylalcohol			KL				(pract)		
	3-choro-buter	ie-1		KL				(pract)		
	2-methyl bute	ne-1		KL				(pract)		
	2-methyl bute	ne-2		KL				(95 %)		
	$\beta$ -methallyl al	cohol		KL				(pure)		
	$\beta$ -methallyl ch	nloride		KL				(pure)		
	2,5-dimethyl l	nexa-1,5-c	liene	KL				(pract)		
	cis-pentene-2			KL				(pure)		
	allyl amine			BDH						
	allyl alcohol			BDH						
	allyl bromide			BDH						
	allyl ether			BDH						
	pyrrole			BDH						
	cyclopentadie	ne		Fluka				(99.9 %	)	
	2-ethyl butene	<del>&gt;</del> -1		Fluka				(95 %)		
	1,5-hexadiene			Kodal	ĸ					

#### RESULTS

# ALLYL RADICAL

Fig. 1a shows the main region of absorption of what we believe to be the  ${}^{2}B_{2} \leftarrow {}^{2}A_{2}$ short wavelength transition of the free allyl radical. Diallyl (1,5-hexadiene) and allyl bromide are the best sources of the radical with these particular experimental conditions, though it can be detected strongly in flashed butene-1, and also in flashed propylene. The radical has also been observed in the flash photolysis of allyl alcohol, allyl amine, diallyl ether and allyl cyanide. Except for allyl cyanide and butene-1, the only spectra recorded in the flash photolysis were those of allyl and methyl radicals. The hydrocarbons diallyl, propylene and butene-1 are the best sources of the spectrum, because they do not absorb strongly in the 2200-2300 Å region. Even with these parent molecules, the selection of optimum conditions requires care because of the production of other species which absorb continuously;

wavelength Å	intensity	$\nu  \mathrm{cm}^{-1}$
2483.1	vw	40262
2457.0	w	40688
2419.4	vw	41326
2411.4	vw	41463
2404.8	w	41583
2383.0	vw	41951
2372.8	w	42144
2324.2	vw	43016
2308-3	m	43314
2295.5	m	43559
2287.3	s	43711
2281.6	m	43826
2277.1	m	43904
2270.0	s	44039
2258.5	m	44272
2248.8	vs	44469
2243.0	m	44569
2237.6	s	44687
2226-7	m	44908
2223.0	m	44970
2215.7	m	45131

allene itself absorbs strongly in the same wavelength region as the allyl radical. The allyl spectrum could be detected only faintly, in the flash photolysis of allyl cyanide. The radical was detected weakly in the flash photolysis of trans-butene-2 (as well as the  $\alpha$ -methallyl radical), this being the only compound which yielded the spectrum and does not specifically contain the allyl group (H<sub>2</sub>C=CH-CH<sub>2</sub>-).

In fig. 1b are shown comparatively weak bands of the allyl radical, to the long wavelength of the main system. These bands were detected only in the flash photolysis of diallyl, allyl bromide and butene-1, though undoubtedly they belong to the same carrier, because of the independence of the intensity ratio to the main region of absorption, with changing experimental conditions. We have not detected any absorption to the short wavelength of the main bands, from 2150-1900 Å. Continuous absorption tends to make ineffective attempts to investigate this region, under conditions of high radical concentration. There are no strong features at short wavelength as in the  $\beta$ -methallyl system.

A large number of weak bands, almost line-like features at this dispersion, occur in the 2300 Å region. An underlying continuum, due to the free radical, appears to set in at 2270 Å, though strong bands are still evident down to 2200 Å, with the strongest at 2249 Å (band centre). The first recorded " band " or " head " at 2324 Å in the main system, almost certainly is not the first member of this group. There is no obvious regularity in the spacing of the bands, nor a repeated pattern in the two wavelength regions. The general impression is of a transition which involves complex changes in the geometry of the molecule. The positions of the band centres are listed in table 1. Some of the measurements are uncertain because of interference by emission lines.

#### $\beta$ -METHALLYL RADICAL

The main region of absorption of the  $\beta$ -methallyl radical occurs in the 2300-2430 Å region (fig. 2). The best source of the radical is  $\beta$ -methallyl chloride, though it can easily be detected in flashed isobutene, 2-methyl butene-1,  $\beta$ -methallyl alcohol and 2,5-dimethyl hexa-1,5-diene. The spectrum can be recorded with less difficulty than that of the allyl radical itself, because of comparatively little complication due to continuous absorption. The  $\beta$ -methallyl spectrum was also observed weakly in flashed 2-methyl butene-2, which does not contain the  $\beta$ -methallyl group (H<sub>2</sub>C = C(CH<sub>3</sub>)-CH<sub>2</sub>-).

#### TABLE 2.— $\beta$ -METHALLYL SPECTRUM

wavelength Å	intensity	r cm <sup>−1</sup>
2578·0	w	38778
2568·0	w	38929
2554·0	w	39143
2551·0	w	39189
2547.2	w	39250
2423.5	w	41258
2406.5	S	41488
2402.2	S	41616
2384.5	vs	41925
2369.5	m	42190
2363.0	S	42306
2343.0	m	42667
2322.0	w	43053
2251.0	S	44411
2231.0	S	44809

The general feature of fig. 2 is a progression of bands which become successively broader and possibly more complex at shorter wavelength. The band at 2423 Å appears to be the first of this group; at the highest radical concentrations no additional member could be detected to the immediate long wavelength. Each of the bands appear to exhibit long wavelength "heads" which are listed in table 2.

In fig. 3b are shown a number of weaker bands, due to the  $\beta$ -methallyl radical, in the 2540-2600 Å region. The bands, and those to short wavelength shown in fig. 2, are comparatively narrow and sharp. The positions of the "centres" are included in table 2. On none of the plates was there any suggestion of a band lying to the immediate long wavelength of the 2251 Å band, and it appears to be the first member of this group.

#### α-METHALLYL RADICAL

In fig. 3*a* is shown the spectrum of the  $\alpha$ -methallyl radical; it consists of about 8 fairly broad and diffuse bands in the region 2260-2380 Å. The spectrum appears to constitute a double progression. The best sources of the radical were 3-chlorobutene-1 and 3-methylbutene-1. The spectrum was also detected in flashed crotyl alcohol (CH<sub>3</sub>CH=CHCH<sub>2</sub>OH), cis-pentene-2, trans-butene-2, butene-1 (weak)

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wavelength Å	intensity	v cm⁻1
2378	vs	42039
2360	S	42360
2349	S	42558
2332	S	42869
2320	m	43090
2304	w	43389
2292	w	43617
2277	w	43904

and cis-butene-2 (weak). No other regions of absorption were detected and the 0-0 band appears to occur at 2380 Å. Difficulty was at first experienced in obtaining this spectrum because of competition by continuous absorption. It is particularly difficult to study the region below 2250 Å. The band centres are listed in table 3. Trans-butene-2 is a better source than cis-butene-2, and all spectra were apparently identical with respect to relative band intensities. If the radical has a planar skeleton, it should have cis- and trans- forms.

# $\beta$ -ethallyl radical

The spectrum of fig. 4 was detected in flashed 2-ethylbutene-1, and is probably due to the  $\beta$ -ethallyl radical. It is remarkably similar to the spectrum of the  $\beta$ -methallyl radical and exhibits a main region of absorption in the 2300-2420 Å

wavelength Å	intensity	v cm <sup>−1</sup>
2597·0	w	38494
2570-2	w	38898
2433.2	vw	41089
2416.9	w	41377
2406.2	m	41550
2402.0	m	41619
2396.5	S	41723
2385.7	VS	41915
2380.1	vs	42004
2361.5	m	42341
2338·0	w	42758

Table 4.—Spectrum of  $\beta$ -ethallyl radical

range with the intensity distributed in a similar manner, though the spacing of the bands shows less regularity. Like the  $\beta$ -methallyl radical, the transient derived from 2-ethyl butene-1 exhibits absorption in comparatively narrow bands to the long wavelength of the main progressions. Two such bands were detected with



FIG. 1.—Spectrum of the allyl radical (wavelength in Å); 0.5 mm diallyl +100 mm Ar. (a) Main system, 100 J; (b) long wavelength bands, 1000 J.

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Fig. 2.—Spectrum of the  $\beta$ -methallyl radical (wavelength in Å); 0.05, 0.25, 1, 5 mm isobutene + 100 Ar; 1620 J.





FIG. 3.—(a) Spectrum of the α-methallyl radical. 0.5 mm 3-chlorobutene-1+200 mm Ar; 1620 J.
(b) Long wavelength bands of β-methallyl radical; 5 mm β-methallyl chloride+100 mm Ar; 800 J.
(c) Spectrum of the cyclopentenyl radical; 0.25 mm cyclopentene+100 mm Ar; 1620 J.



FIG. 4.—Spectrum of the  $\beta$ -ethallyl radical; 0.25, 1, 5 mm 2-ethyl butene-1+100 mm Ar; 1620 J.



FIG. 5.—(a) Spectrum tentatively assigned to a pyrrolyl radical; 2.5 mm allyl cyanide+100 Ar; 2000 J. (b) Long wavelength bands of the  $\beta$ -ethallyl radical; 1 mm 2-ethylbutene-1+100 mm Ar; 1620 J.

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certainty and are shown in fig. 5b. In the  $\beta$ -ethallyl radical, the features below 2300 Å degrade to an indistinct progression of broad, "red-shaded" bands (fig. 4) which are not listed in the table. A further absorption region was observed at 2160 Å and largely overlapped the Herzberg methyl band at that wavelength. In table 4 are listed the centres of the long wavelength bands and long wavelength "heads" in the intense region.

#### CYCLOPENTENYL RADICAL

Fig. 3c shows a single, diffuse band at 2480 Å, which was detected in the flash photolysis of cyclopentene. The transient was observed with difficulty due to the production of stable species with continuous absorption in this wavelength region (e.g. cyclopentadiene).

## TRANSIENT SPECTRUM IN FLASHED PYRROLE

In fig. 5a is shown the formation and decay of a single progression of red-shaded bands which was first observed in flashed allyl cyanide  $(CH_2=CHCH_2CN)$ . The spectrum was later detected with about equal intensity in flashed crotyl nitrile  $(CH_3-CH=CH-CN)$ , and also in flashed pyrrole. The bands become progressively broader with decreasing wavelength. They were not detected in flashed

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wavelength Å	intensity	$\nu  \mathrm{cm}^{-1}$
3045-1	S	32831
2953.9	S	33853
2869.3	m	34854
2791.8	m	35818
2717.0	m	36794
2580 (broad	) m	38750

methyl and ethyl cyanides. The radical  $CH_2CHCHCN$  may undergo ring closure, which could account for the simple vibrational structure. Since several possible structures can undergo sub-Rydberg transitions, no specific assignment or discussion will be attempted here. The same spectrum was observed in flashed allyl cyanide by Currie and Ramsay.<sup>9</sup> The band at 2580 Å may be the first member of a second system.

## DISCUSSION

#### ASSIGNMENT OF SPECTRA FROM PHOTOCHEMICAL EVIDENCE

The evidence for the suggested assignments of the allyl and  $\alpha$ - and  $\beta$ -methallyl radicals arises not only from the detection of particular spectra from a variety of related parent molecules, but also in consideration of the different free radicals which may be prepared according to prediction from the initial structure. The flash photolysis of about 50 compounds has been required for the present study, and, except for two where a minor degree of H atom rearrangement occurs in the excited state or derived radicals, there is the most direct relationship between the parent

and the derived radical. The type of initial structure is preserved following photodecomposition, which usually yields the radical by scission of the weakest bond; e.g., the  $\alpha$ -methallyl radical may equally well be produced from initial structures having either the  $\alpha$ -methallyl or the  $\gamma$ -methallyl group via either of the classical structures,

# CH2=CH--CH3 and CH3-CH=CH--CH2.

The individual photochemical reactions which are required to interpret the assignments, receive qualitative support from established photochemical mechanisms.<sup>10-15</sup> The production of both allyl and  $\alpha$ -methallyl free radicals in the direct photolysis of butene-2 has been postulated by Chesick.<sup>16</sup> Of itself, our work appears to constitute a significant body of self-consistent photochemical data. Notwithstanding the absence of rotational and vibrational analysis, we consider that the assignments of these three spectra are conclusive.

There is concordance between the present results and those of Currie and Ramsay.<sup>7</sup> We did not detect their long wavelength system because of lower flash energy, lower path-length, and inadequate dispersion in that region. However, three of the parent molecules are common to the two investigations and Currie and Ramsay did not report detection of the allyl radical from flashed allyl cyanide, which we found to be a poor source of the radical.

Each of the spectra of fig. 4 and 3c have been detected only from a single parent molecule, and consequently no definite assignment can be attempted. However, the provisional headings are evident. The replacement of the  $\beta$ -methyl for an  $\beta$ -ethyl group would be expected to have only a minor effect on the conjugated system, and should leave essentially unchanged that part of the transition which is Franck-Condon allowed. Comparing figures 2 and 4, this seems to be the case. An electronic transition of the allylic group confined in a ring structure, is likely to incur little change in geometry and result in absorption in a restricted wavelength region. The position of the band is considerably displaced from the absorption detected by Bodily and Dole.<sup>6</sup> The free allyl spectrum is widely different from that observed in pulsed radiolysis experiments.<sup>17</sup>

# VIBRATIONAL STRUCTURE

The longest wavelength members of the  $\beta$ -methallyl "satellite" bands are each separated by  $\sim 2830 \text{ cm}^{-1}$  from the first strong head in the main progression. A similar relationship exists in the  $\beta$ -ethallyl spectrum where the separation between the longest wavelength band at 2597 Å and the first strong "head" at 2396 Å is  $3230 \text{ cm}^{-1}$ . In the allyl spectrum, the "centres of gravity" of the main bands and those at longer wavelength, are displaced by about  $3000 \text{ cm}^{-1}$ . These features, probably common to three spectra, suggest that the main regions of absorption correspond to a single member of a progression in a CH vibration. Certainly there are many details that would require examination, e.g., the comparatively narrow appearance of the  $\beta$ -methallyl "satellite" bands. However, for the unsubstituted allyl radical there seems to be no alternative to CH excitation, because although the long wavelength bands are weak compared to those in the 2250 Å region, they represent a strong transition and cannot correspond to a  ${}^{4}A_{2}$ -- ${}^{2}A_{2}$ system. If the strongest region of absorption does not populate the zero point of the CH co-ordinates, it follows that the electronic transition changes the CH equilibrium configurations (see ref. (18)).

The  $\beta$ -methallyl spectrum exhibits a regular progression in the main bands, with a spacing of 350 cm<sup>-1</sup>. However, the two short wavelength members have a separation of 400 cm<sup>-1</sup>, which is also found between the strongest two bands in the long

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wavelength region (2578 Å and 2554 Å). It was considered desirable to investigate the three normal frequencies and co-ordinates of the carbon skeleton, which are totally symmetric in the  $C_{2v}$  point group. The order of magnitude of the force constants is uncertain, but the calculation should give a true indication of the type of motion associated with bending the C-C-C conjugated system. We have assumed that the  $\beta$ (C—C) bond (co-ordinate 1) has about one half of the normal strength, corresponding to a force constant of about  $2.7 \times 10^5$  dynes/cm. The conjugated C—C bonds (co-ordinate 2) were each assigned force constants of  $6.3 \times 10^5$ dynes/cm, and the bending mode  $0.5 \times 10^5 r_{\rm CC}^2$  dynes/cm. The third co-ordinate is the product of co-ordinate 2 with one half of the angle of the C-C-C conjugated system, which was assumed to be  $60^{\circ}$  in the equilibrium configuration. The derived normal frequencies are 410, 600 and 1000 cm<sup>-1</sup>, and the amplitude factors are listed in table 6. The lowest frequency essentially corresponds to a bending mode, though there is an appreciable shift of the  $\beta(C-C)$  distance, and the amplitude of vibration of the CH<sub>3</sub> group is comparatively even larger with respect to the centre of gravity because of the signs of the amplitude factors. We suppose that the  $\sim$  350 cm<sup>-1</sup> spacing in the strong region of the spectrum, could correspond to the bending frequency. The short wavelength doublet could be interpreted to be a result of excitation of the  $\beta$ (C—H) stretching co-ordinate; a third member to short wavelength would be  $\sim 3000 \text{ cm}^{-1}$  from the Franck-Condon maximum in the main bands, and its absence could be understood from the Franck-Condon principle.

Table 6.—Amplitude factors for totally symmetric vibrations of the  $\beta$ -methallyl carbon skeleton.

	amplitud	le factors	
co-ordinate	410 cm <sup>-1</sup>	600 cm <sup>-1</sup>	1000 cm <sup>-1</sup>
1	·4	.8	·74
2	—·15	·6	·43
3	·91	•06	·52

The occurrence of strong bands about 3000 cm<sup>-1</sup> to the long wavelength of the main region of the allyl and  $\beta$ -methallyl transitions, and the absence of this feature in the  $\alpha$ -substituted radicals, indicates that it is the  $\alpha$ (C-H) equilibrium distance which is directly involved in the electronic transition. This would be unexpected if the radicals are planar in the excited state, because a change of the  $\pi$  structure would be expected to cause only a minor perturbation of the trigonal hybridization if the molecule does remain planar. It is not possible to deduce any specific evidence concerning the symmetry of the upper states from the detailed vibrational structure, and there are no closely analogous systems for comparison. However, if the  $\alpha$ -H atoms lie slightly out of the plane of the C atoms in the excited state, and if the  $\alpha$ (C—H) distance is extended, the geometrical change indicated by the allyl spectrum could be best accounted for. This scheme does indicate that the  $\beta$ -methally long wavelength and short wavelength satellites have a different origin; indeed in the  $\beta$ -ethallyl spectrum, the long wavelength bands are only slightly perturbed whereas the short wavelength satellites become very broad. These interpretations are open to direct test by isotopic substitution.

We acknowledge discussions with Dr. R. J. Cvetanović, and thank the Asia Foundation and Lee Foundation, Singapore, for financial support.

- <sup>1</sup> J. W. Linnett and O. Sovers, Disc. Faraday Soc., 1963, 35, 58.
- <sup>2</sup> D. M. Hirst and J. W. Linnett, J. Chem. Soc., 1962, 1935.
- <sup>3</sup> H. C. Longuet-Higgins and J. A. Pople, Proc. Physic. Soc. A, 68, 1955, 591.
- <sup>4</sup> W. Moffit, Proc. Roy. Soc. A, 1953, 218, 486.
- <sup>5</sup> R. W. Fessenden and R. H. Schuler, J. Chem. Physics, 1963, 39, 2147.
- <sup>6</sup> D. M. Bodily and M. Dole, J. Chem. Physics, 1966, 44, 2821.
- <sup>7</sup> C. L. Currie and D. A. Ramsay, J. Chem. Physics, 1966, 45, 488.
- <sup>8</sup> A. B. Callear and H. K. Lee, *Nature*, 1967, 213, 693.
- <sup>9</sup> C. L. Currie and D. A. Ramsay, private communication, 1967.
- <sup>10</sup> F. P. Lossing, K. U. Ingold and I. H. S. Henderson, J. Chem. Physics, 1954, 22, 621.
- <sup>11</sup> C. A. Heller and A. S. Gordon, J. Chem. Physics, 1965, 42, 1262.
- <sup>12</sup> R. J. Cvetanović, Prog. Reaction Kinetics, vol. 2, ed. Porter (Pergamon, 1964).
- <sup>13</sup> J. R. McNesby and H. Okabe, Advances in Photochemistry, vol. 3, ed. Noyes et al. (Interscience).
- <sup>14</sup> K. A. Maas and D. H. Volman, Trans. Faraday Soc., 1964, 60, 1202.
- <sup>15</sup> J. G. Calvert and J. N. Pitts, *Photochemistry* (Wiley, 1966).
- <sup>16</sup> J. P. Chesick, J. Chem. Physics., 1966, 45, 3934.
- <sup>17</sup> E. J. Burrell and P. K. Bhattacharyya, J. Physic. Chem., 1967, 71, 774.
- <sup>18</sup> G. Herzberg, Electronic Spectra of Polyatomic Molecules (Van Nostrand, 1966).