

**162.** *The Absorption Spectrum of Allene in the Vacuum Ultra-violet.*

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The absorption spectrum of allene has been photographed in the vacuum ultra-violet. Most of the bands to short wave-lengths of 1800 Å can be classified as separate electronic transitions belonging to numerous Rydberg series. Some of these series are only fragmentary, but all appear to converge to the same ionization limit,  $10.19 \pm 0.01$  v. Some discussion of the nature of the series is given. Continuous absorption to long wave-lengths of 1800 Å probably represents several different non-Rydberg transitions.

PRICE, TEEGAN, and WALSH (*J.*, 1951, 920) reported a study of the absorption spectrum of keten  $\text{CH}_2\text{:C:O}$ , in the far ultra-violet. The present paper describes the spectrum of the isoelectronic molecule allene,  $\text{CH}_2\text{:C:CH}_2$ .

*Experimental.*—Allene (b. p.  $-35^\circ$ ) was prepared by heating Eastman Kodak 2 : 3-dibromopropene with zinc dust and alcohol (Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Amer. Chem. Soc.*, 1936, **58**, 146). The crude allene was condensed in a liquid-nitrogen trap and was purified by re-distilling it three times in a high-vacuum system. Absorption bands of methylacetylene or propylene were absent from the spectrum.

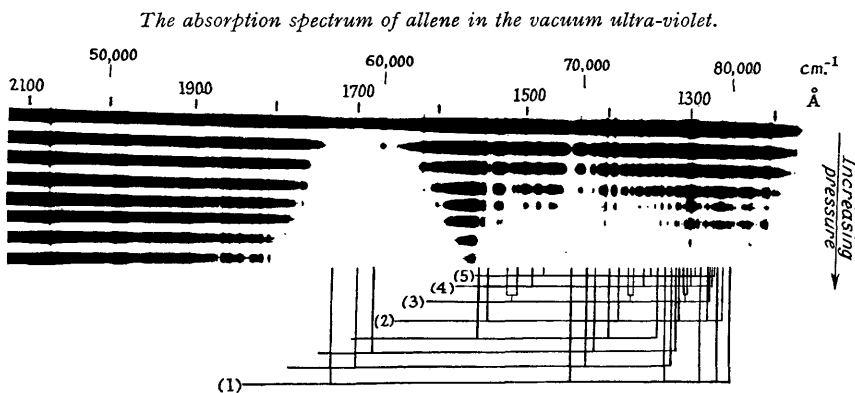
The spectrum was photographed with a normal-incidence spectrograph, with the Lyman continuum as background. The grating, kindly lent by Dr. W. C. Price, was of glass and gave a dispersion of about 8 Å/mm.

*Description and Analysis of the Spectrum.*—The spectrum is shown in the figure. To long wave-lengths of 1200 Å, the most intense absorption occurs between 1800 and 1600 Å ( $\lambda_{\text{max}}$ , ca. 1710 Å). A number of bands is present in this region. Precise measurement is impossible, partly because of the diffuseness of the bands and partly because of the presence of emission lines in the Lyman continuum; but the order of magnitude of the positions and separations of some of the bands given in Table 1.

TABLE 1. Separations of the bands in the 1800—1600-Å region (all as  $\text{cm}^{-1}$ ).

57 800	58 310	58 500	58 820	59 560	60 240	60 700	61 300	61 960	62 500	63 100
	190									
510	510		740	680	460	600	660	540	600	

If it is assumed for the moment that the bands represent vibrational parts of a single electronic transition, a main frequency of  $610 \pm 100 \text{ cm}^{-1}$  is involved. One or two bands representing a smaller frequency ( $\sim 200 \text{ cm}^{-1}$ ) also appear. Because of its intensity, the electronic transition in this region is certainly an allowed one and occurs from the vibrationless ground state. By the selection rules, therefore, the two frequencies must correspond



to totally symmetrical ( $a_1$ ) vibrations of the upper state. By analogy with ethylene and other derivatives of ethylene and because the excitation is probably that of an electron in the C—C—C bonds, the main frequency probably represents the  $a_1$  C=C—C valency vibration reduced by the excitation from its value of  $1071 \text{ cm}^{-1}$  in the ground state (Herzberg, "Infra-red and Raman Spectra," van Nostrand, 1945). The proportionate reduction in ethylene ( $1623$  to  $\sim 1370 \text{ cm}^{-1}$ ; ratio 0.8) and in keten ( $1120$  to  $\sim 860 \text{ cm}^{-1}$ ; ratio 0.8) is rather smaller than in allene ( $1071$  to  $610 \pm 100 \text{ cm}^{-1}$ ; ratio 0.5—0.7), but the only other ground state  $a_1$  frequencies of allene are considerably higher ( $1432$  and  $2993 \text{ cm}^{-1}$ ) and represent essentially C—H stretching and bending. It does not seem likely that the low subsidiary frequency can represent one of these  $a_1$  vibrations. Possibly it represents two quanta of a non-totally symmetrical vibration; this would be equivalent, so far as symmetry is concerned, to an  $a_1$  vibration. Suitable vibrations to choose would be either the twisting vibration ( $b_1$ , probably  $820 \text{ cm}^{-1}$  in the ground state) of the two  $\text{CH}_2$  groups about the C=C—C axis or the degenerate bending vibration ( $e$ , perhaps  $852 \text{ cm}^{-1}$  in the ground state) of the chain  $\text{H}_2 > \text{C}=\text{C} < \text{H}_2$ . It has been concluded (Price, Teegan, and Walsh, *loc. cit.*) that the corresponding excited-state frequency of keten probably represents a  $\text{H}_2 > \text{C}=\text{C}=\text{O}$  bending vibration. In this connection it should be remembered that keten and allene are *isoelectronic* with carbon dioxide. Now there is a strong theoretical expectation (see Mulliken, *Rev. Mod. Physics*, 1942, **14**, 204; Walsh, in the press) and some experimental evidence (Gaydon, "Spectroscopy and Combustion Theory," Chapman and Hall, 2nd Edn., 1948) that in certain low-lying excited states the carbon dioxide molecule, in its equilibrium form, is bent. It may well be therefore that, in the equilibrium form of

the excited state of allene (or keten) referred to above, the C·C·C (or C·C:O) chain is not linear; and therefore that the excitation tends to arouse bending vibrations of the chain. On the other hand, the short spacing in the corresponding absorption region of ethylene (*ca.* 400 cm.<sup>-1</sup>) probably represents a twisting vibration of the two CH<sub>2</sub> groups about the C—C axis, since the excited state involved probably has a considerably reduced resistance to twisting (Mulliken, *Rev. Mod. Physics*, 1942, **14**, 265). The CH<sub>2</sub> planes in certain excited states of allene may tend to twist relative to each other; and excitation to these states may arouse the twisting vibration.

It is quite possible, however, that more than one electronic transition is involved in the 1800—1600 Å region, so that some of the separations recorded in Table 1 may be of electronic rather than of vibrational origin. This possibility is referred to again below.

To the long wave-length side of the 1800—1600 Å region, continuous absorption stretches from *ca.* 2030 to 1800 Å; it appears at a pressure several times greater than that required to bring out the 1710 Å absorption peak. At wave-lengths short of 1600 Å a pair of strong bands occurs at *ca.* 1540 Å with weaker bands to either side. Moderately strong bands lie at *ca.* 1520, *ca.* 1490, and *ca.* 1477 Å. A particularly strong band lies at 1446 Å and is followed by a considerable number of bands gradually decreasing in intensity until they disappear between 1250 and 1200 Å. At wave-lengths short of 1225 Å, except for a single stronger band at *ca.* 1204 Å and certain bands due to residual traces of oxygen in the spectrograph, only strong continuous absorption is observed.

All the bands in the spectrum are diffuse. Analysis is therefore difficult, but certainly the bands from 1446 to 1250 Å have the look of Rydberg bands, gradually getting weaker and closer together until they reach an ionization limit between 1250 and 1200 Å. By taking the 1446-Å band as one member of a Rydberg series proceeding to such a limit, it is possible to pick out four other bands which approximately conform to the expression,

$$\nu_0^n = 82\,210 - R/(n - 1.06)^2 \quad \dots \quad (1)$$

Table 2 shows the observed and calculated frequencies (cm.<sup>-1</sup>). The agreement is about as good as could be expected in view of the diffuseness of the bands. Apart from this agreement, there is little doubt of the reality of series (1), partly because it yields an ionization limit (1216 Å) in the expected region and especially because the term values of its members agree closely with those of the members of the strongest Rydberg series found with many other molecules containing C=C groups. Thus the quantum defect of the best-developed series in the ethylene spectrum is 1.09 (see Price and Tutte, *Proc. Roy. Soc., A*, 1940, **174**, 207) and that of the keten Rydberg series (known to be due to excitation of an electron largely, if not entirely, localized originally in the C=C group) is 1.07 (Price, Tegan, and Walsh, *loc. cit.*).

TABLE 2. *Observed and calculated frequencies (cm.<sup>-1</sup>) of the bands of series (1).*

<i>n</i>	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	$\nu_{\text{C}_2\text{H}_4}$	$\nu_{\text{C}_2\text{H}_4} - \nu_{\text{allene}}$
3	<i>ca.</i> 57 800	53 053	<i>ca.</i> +4750	57 340	<i>ca.</i> -460
4	69 163	69 514	- 351	71 790	2627
5	75 153	75 141	+ 12	77 600	2547
6	77 702	77 713	- 11	80 215	2513
7	79 100	79 100	0	81 625	2525
8	79 856	79 932	- 76	—	—
∞	82 210	—	—	84 750	2540

Since series (1) represents excitation of an electron from an orbital compounded from *L*-shell atomic orbitals, one expects it to begin with a *n* = 3 member. The calculated position for this member lies between 1800 and 1900 Å, but one expects a considerable deviation of  $\nu_{\text{obs.}}$  from  $\nu_{\text{calc.}}$  because the comparatively low excitation implies that the size of the excited orbital cannot be vast compared to the nuclear framework of the molecule. On grounds of intensity, the 1800—1600-Å transition seems the only reasonable choice.

This leaves the 1540 Å doublet unassigned. It is very likely that it represents the first member of a second Rydberg series. Indeed it is possible to pick out bands lying between the successive members of series (1) which approximately fit the formula,

$$\nu_0^n = 82\,190 - R/(n - 0.70)^2 \quad \dots \quad (2)$$

The agreement between observed and calculated frequencies is given in Table 3. The 1540-Å doublet is a poor fit in this series but (a) this is not unreasonable for a first member

TABLE 3. *Observed and calculated frequencies (cm.<sup>-1</sup>) of the bands of series (2).*

<i>n</i>	<i>v</i> <sub>obs.</sub>	<i>v</i> <sub>calc.</sub>	<i>v</i> <sub>obs.</sub> - <i>v</i> <sub>calc.</sub>	<i>n</i>	<i>v</i> <sub>obs.</sub>	<i>v</i> <sub>calc.</sub>	<i>v</i> <sub>obs.</sub> - <i>v</i> <sub>calc.</sub>
3	64 705	61 446	+ 3259	6	78 278	78 283	-5
4	72 081	72 113	- 32	7	79 426	79 425	+1
5	76 258	76 255	+ 3				

and (b) on grounds of intensity and position it seems the most reasonable choice as first member. The reality of series (2) is supported by the facts that it gives practically the same limit as series (1), that in the spectrum of ethylene a Rydberg series of nearly the same term values (quantum defect 0.6) occurs (see Price and Tutte, *loc. cit.*), and that it begins, as expected, with an *n* = 3 member.

The separations of the bands at *ca.* 1520, *ca.* 1490, and *ca.* 1477 Å from each other and from the 1540-Å electronic transition, considered in relation to the magnitude of the ground state C=C totally symmetrical frequency, make it unlikely that the bands are vibrational in nature. More probably, they each represent electronic transitions inaugurating other Rydberg series proceeding to the same limit as series (1) and (2). One can pick out a recurring pattern of at least three fairly strong bands between the successive *n* and (*n* + 1) members of series (2) and (1), respectively. The recurring, but rapidly converging, pattern strengthens belief in the 1520-, 1490-, and 1477-Å bands' representing separate electronic transitions. The series beginning with the *ca.* 1520-Å band has the approximate formula,

$$v_0^n = 82\,190 - R/(n - 0.55)^2 \quad \dots \quad (3)$$

Its higher members, because of their diffuseness, become indistinguishable from the bands of what appears to be a second series of closely similar formula. The latter series begins with a very diffuse band which is partially obscured by emission lines and lies at *ca.* 1511 Å. Table 4 gives the observed and the calculated frequencies for the means of corresponding members of these two series.

TABLE 4. *Observed and calculated frequencies (cm.<sup>-1</sup>) for the bands of series (3).*

<i>n</i>	<i>v</i> <sub>obs.</sub>	<i>v</i> <sub>calc.</sub>	<i>v</i> <sub>obs.</sub> - <i>v</i> <sub>calc.</sub>	<i>n</i>	<i>v</i> <sub>obs.</sub>	<i>v</i> <sub>calc.</sub>	<i>v</i> <sub>obs.</sub> - <i>v</i> <sub>calc.</sub>
3	65 808 66 188 mean = 65 998	63 918	+2080	5	76 460 76 772 mean = 76 616	76 648	-32
4	72 724 73 092 mean = 72 908	72 970	-62	6	78 529	78 495	+34
				7	79 566	79 552	+14

The series beginning with the *ca.* 1490-Å band has the approximate formula (4) and

$$v_0^n = 82\,200 - R/(n - 0.40)^2 \quad \dots \quad (4)$$

Table 5 shows the agreement between observed and calculated frequencies.

TABLE 5. *Observed and calculated frequencies (cm.<sup>-1</sup>) for the bands of series (4).*

<i>n</i>	<i>v</i> <sub>obs.</sub>	<i>v</i> <sub>calc.</sub>	<i>v</i> <sub>obs.</sub> - <i>v</i> <sub>calc.</sub>	<i>n</i>	<i>v</i> <sub>obs.</sub>	<i>v</i> <sub>calc.</sub>	<i>v</i> <sub>obs.</sub> - <i>v</i> <sub>calc.</sub>
3	67 108	65 967	+1141	6	Obscured	78 701	—
4	73 721	73 733	- 12	7	79 635	79 681	-46
5	77 057	77 014	+ 43				

The series beginning with the *ca.* 1477-Å band has the approximate formula (5) and

$$v_0^n = 82\,210 - R/(n - 0.30)^2 \quad \dots \quad (5)$$

Table 6 shows the agreement between observed and calculated frequencies.

TABLE 6. *Observed and calculated frequencies (cm.<sup>-1</sup>) for the bands of series (5).*

<i>n</i>	<i>v</i> <sub>obs.</sub>	<i>v</i> <sub>calc.</sub>	<i>v</i> <sub>obs.</sub> - <i>v</i> <sub>calc.</sub>	<i>n</i>	<i>v</i> <sub>obs.</sub>	<i>v</i> <sub>calc.</sub>	<i>v</i> <sub>obs.</sub> - <i>v</i> <sub>calc.</sub>
3	67 726	67 157	+569	5	77 280	77 242	+38
4	74 240	74 194	+ 46	6	78 828	78 832	- 4

The  $n = 3$  member deviates considerably from the calculated position in each of these series, but it is satisfactory to note that the deviation decreases as the height of the excitation increases, *i.e.*, in the order series (1), (2), (3), (4), (5).

The existence of series (5) completes the parallel with ethylene; for in the ethylene spectrum a third and weak Rydberg series is observed, of quantum defect 0.3 (see Price and Tutte, *loc. cit.*).

At wave-lengths just longer than the 1540-Å doublet (at 64 362  $\text{cm}^{-1}$ ), a weaker band occurs. The intensity is too high for it to be plausibly interpreted as a transition from a vibrational level of the ground state to the upper state of the 1540-Å transition. It appears to represent another electronic transition that inaugurates still another Rydberg series. Bands that appear to represent  $n = 4$  and  $n = 5$  members occur at 71 506 and 76 084  $\text{cm}^{-1}$ . Judged from the latter bands, the quantum defect lies between 0.75 and 0.80.

Two fairly strong bands (at *ca.* 1426 and *ca.* 1415 Å) lying between the  $n = 4$  members of series (1) and (2) remain to be considered. They again probably represent separate electronic transitions. Their term values with respect to the ionization potential are too low for them to be interpreted as  $n = 3$  members of further series. They must be  $n = 4$  members of such series; and the only bands that can plausibly be interpreted as  $n = 3$  members are two of those in the 1700-Å region. One or two higher members of each can be picked out, from which it appears that the quantum defect for both series is about 0.90.

The above classification covers practically all the bands in the spectrum.

*Discussion.*—The conclusion from the above analysis is that a large number of separate electronic transitions is present in the spectrum and that these can practically all be arranged into numerous Rydberg series all converging to the same limit. None of the series can be followed very far, but the cumulative evidence is very strong in favour of an ionization limit close to 82 200  $\text{cm}^{-1}$ . This corresponds to 10.19 v. An electron impact determination of the first ionization potential of allene has yielded the value  $9.9 \pm 0.2$  v (Delfosse and Bleakney, *Phys. Review*, 1939, **56**, 256). A theoretical calculation of the ionization potential by Parr and Taylor (*J. Chem. Physics*, 1951, **19**, 497) gave the value 10.4 v. The ionization potential of 10.19 v for allene is to be compared with the values 10.50 and 9.60(5) v which are the corresponding limits for ethylene and keten, respectively.

Although the first ionization potential of allene is considerably less than that of ethylene, the first Rydberg bands are hardly shifted in passing from ethylene to allene. This is brought out in Table 2. The members of series (1) from  $n = 4$  upwards suffer an almost constant shift relative to the corresponding bands in ethylene; but the  $n = 3$  band is hardly shifted at all. A very similar phenomenon was observed in the spectrum of keten (Table 6 of Price, Teegan, and Walsh, *loc. cit.*). It implies that the lowering of the ionization potential in allene and keten is primarily due to a stabilization of the  $\text{C}_3\text{H}_4^+$  or  $\text{C}_2\text{H}_2\text{O}^+$  ions, respectively, relatively to the  $\text{C}_2\text{H}_4^+$  ion. Only when the upper state is so highly excited that it resembles the ion does the stabilization show itself. The stabilization is presumably caused by the tendency of the electrons in the  $\text{CH}_2$  "p" group-orbital or in the O  $2p$  lone-pair orbital to occupy the place vacated in the C=C bond by the ionized electron. One can understand therefore why the lowering in allene should be less than that in keten, for one would expect the  $\text{CH}_2$  electrons (if only because of their positions in space) to be less available than the O lone-pair electrons.

The following is a list of the Rydberg series which appear to be present in the spectrum :

(a)	{	one series of quantum defect	1.06
		two series    "            "	<i>ca.</i> 0.90
(b)	{	one series of quantum defect	0.75 to 0.80
		one series    "            "	0.70
		two series    "            "	<i>ca.</i> 0.55
(c)	{	one series of quantum defect	0.40
		one series    "            "	0.30

It is not unlikely that more series even than this are present, represented by weaker bands. Weak bands at wave-lengths just short of the *ca.* 1477 Å band seem particularly

likely to represent  $n = 3$  members of other series with small quantum defects ( $\sim 0.2$ ). The types of Rydberg series likely to be found can be divided into series of allowed transitions to upper states built from  $ns$ ,  $np$ , or  $nd$  orbitals on the carbon atoms. The magnitudes of the quantum defects make it probable that the series grouped as (a) are all to upper states built from  $ns$  orbitals; that those grouped as (b) are all ( $np$ ) series; and that those grouped as (c) or which have even smaller quantum defects are ( $nd$ ) series. A full discussion of the magnitudes of quantum defects in molecular Rydberg series will be given elsewhere. Suffice it to say for the moment that the defects of the allene (or ethylene) series are expected to be similar to those of Rydberg series observed or expected in the spectrum of free carbon atoms. It is for this reason that the series in (a), (b), and (c) have term values close to those of the three similar series found in the spectrum of ethylene.

The existence of so many different Rydberg series in the allene spectrum is in full accord with what one might expect. The most weakly bound electrons of the allene ground state lie in an ( $e$ ) orbital which involves out-of-phase overlap of a " $p$ "  $\text{CH}_2$  group-orbital and a " $\pi$ " C-C orbital. If  $V_d$  symmetry is assumed for the upper states of allene, there are several possible states to which transition from the ground state is allowed and which can be built from each of the types of orbital  $ns$ ,  $np$ , and  $nd$ . For example, three non-degenerate orbitals can be built from  $s$  atomic orbitals on the carbon atoms, the resulting transitions being all  ${}^1E \leftarrow {}^1A_1$  (*i.e.*, two-fold degenerate) and all allowed. Similarly, numerous upper states to which transition from the ground state is allowed can be built from  $p$  atomic orbitals on the carbon atoms, especially since the  $p$  orbitals may be oriented in different ways with respect to the nuclear symmetry. These transitions include both  ${}^1E \leftarrow {}^1A_1$  and  ${}^1B_2 \leftarrow {}^1A_1$  symmetry types. If, further, one takes into account the possibility, referred to above, that in some of the upper states the C-C-C chain may not be linear or that the  $\text{CH}_2$  planes may be twisted relatively to each other in the equilibrium form, the degeneracy of  ${}^1E \leftarrow {}^1A_1$  transitions may be split and still further series of transitions may occur. It becomes clear that the existence of so many Rydberg series is not surprising but to be expected.

The probability that several ( $ns$ ) series exist, all having their  $n = 3$  members in the 1800—1600-Å region, makes it clear that, even apart from the diffuseness of the bands, a full analysis of the region is likely to be complicated.

All the bands from 1800 Å onwards seem best interpreted as Rydberg transitions. The weaker continuous absorption to wave-lengths longer than 1800 Å is best interpreted as due to intra-valency-shell transitions. In certain other molecules (*e.g.*, acetylene) where a clear distinction between Rydberg and non-Rydberg transitions is possible, the non-Rydberg transitions also require a considerably higher appearance pressure than the Rydberg ones. It is expected that the absorption regions observed in the spectrum of allene shall correspond to (though they lie at shorter wave-lengths than) those observed in the spectrum of ethylallene. An absorption curve for the long-wave-length end of the ethylallene spectrum has been published by Carr and Stücklen (Seventh Summer Conference on Spectroscopy, Wiley, New York, 1940, p. 128). Judged from this, the continuous absorption to wave-lengths longer than 1800 Å in allene represents at least three and perhaps five separate transitions. In ethylallene the first of these transitions is represented by a "step-out" at *ca.* 2560 Å with  $\log \epsilon \sim 0$ . The second is represented by a steep rise (between *ca.* 2500 and 2380 Å) to a maximum (of  $\log \epsilon \sim 2.8$ ) between *ca.* 2330 and 2270 Å. A rough absorption curve that we have plotted from data obtained by Lind and Livingston (*J. Amer. Chem. Soc.*, 1933, 55, 1036) indicates that the corresponding steep rise in the allene spectrum occurs around 2330—2230 Å. Lind and Livingston write of appreciable absorption occurring some 40—80 Å to long wave-lengths of this steep rise: such absorption may be due to the allene analogue of the ethylallene 2560 Å "step out." The third region of the ethylallene spectrum is represented by a smaller rise in the absorption curve to a fairly flat absorption region between *ca.* 2050 and 1950 Å ( $\log \epsilon \sim 3.1$  or 3.2). (Further, rather stronger, absorption stretching to 1600 Å may belong to the same transition or, more probably, to further transitions.) Judged from our photographs, the corresponding transition in allene appears to cause a rise in the absorption curve around 2030 Å. The allene maximum at *ca.* 1710 Å appears to correspond to a maximum ( $\log \epsilon \sim$

3·8) at *ca.* 1800 Å for ethylallene. These values are very approximate, but are of some interest since Parr and Taylor (*loc. cit.*) have recently attempted to calculate the position of certain intra-valency-shell transitions of allene; they give 5·1 v (2430 Å) for the mean height of the first singlet and triplet excited states.

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