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## The Absorption Spectrum of Ethylene Oxide in the Vacuum Ultraviolet

TA-KONG LIU\* AND A. B. F. DUNCAN

*Department of Chemistry, University of Rochester, Rochester, New York*

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The spectrum of ethylene oxide was investigated from the visible down to about 600A, with high resolution in the vacuum region. No discontinuous absorption was found above 1713A. Two Rydberg series, beginning at 1435 and 1382A were found, which converge to the same ionization potential at about 10.81 ev. Two non-Rydberg transitions were found, with origins apparently at 1713.4 and 1572.4A. An analysis and discussion is made of the spectrum. It is concluded that the Rydberg transitions arise by excitation from a molecular bonding orbital, very similar to one responsible for Rydberg series in ethylene and related compounds.

### INTRODUCTION

THE electronic spectra of ethylene oxide vapor have not been reported, in spite of the fact that the structure and chemical properties of this compound are interesting and important. It appears from the present work that these spectra lie entirely in the vacuum ultraviolet region. Some recent discussion of the electronic structure of this molecule has been published.<sup>1-9</sup> The infra-red and Raman spectra of the molecule are fairly well understood, and are consistent with a symmetry group  $C_{2v}$ .<sup>10</sup> Electron diffraction measurements<sup>11,12</sup> show that the two carbons and oxygen are on the corners of an isosceles triangle which is almost equilateral. We have investigated the absorption spectrum with high resolving power and dispersion in the vacuum region. The results are presented here, with some interpretation and discussion.

### EXPERIMENTAL DETAILS AND RESULTS

The best samples of ethylene oxide usually contain enough acetaldehyde, even after several vacuum fractionations, to show the strong bands of the latter. A specially purified sample\*\* was used and found satisfactory. After repeatedly outgassing the sample, it was fractionated twice in vacuum and only the middle fraction was used.

\* Part of a dissertation presented to the Faculty of the Graduate School of the University of Rochester in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>1</sup> A. D. Walsh, *Nature* **159**, 165 (1947).

<sup>2</sup> See reference 1, p. 712.

<sup>3</sup> A. D. Walsh, *Nature* **160**, 903 (1947).

<sup>4</sup> R. Robinson, *Nature* **159**, 400 (1947).

<sup>5</sup> R. Robinson, *Nature* **160**, 162 (1947).

<sup>6</sup> R. Robinson, *Nature* **161**, 176 (1948).

<sup>7</sup> J. W. Linnett, *Nature* **160**, 162 (1947).

<sup>8</sup> T. M. Sugden, *Nature* **160**, 367 (1947).

<sup>9</sup> H. A. Skinner, *Nature* **160**, 902 (1947).

<sup>10</sup> Gerhard Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand and Company, New York, 1945), p. 340.

<sup>11</sup> P. G. Ackermann and J. E. Mayer, *J. Chem. Phys.* **4**, 377 (1936).

<sup>12</sup> R. Wierl, *Ann. d. Physik* **13**, 453 (1932).

\*\* Obtained by Dr. W. D. Walters from Dr. D. R. Stull of Dow Chemical Company.

Exploratory measurements were made with a Cario and Schmidt-Ott vacuum fluorite spectrograph, which covered the visible and ultraviolet regions down to about 1400A with low dispersion. The ethylene oxide was in a cell 40 cm long with lithium fluoride windows, waxed between a conventional hydrogen discharge tube and the spectrograph. The pressure range covered was from 730 down to 0.05 mm. Exposures were usually for three minutes on Eastman III-0 u.v. sensitized plates. Long exposures led to the appearance of a group of bands at 1815A, identified as strong bands of acetaldehyde formed in a photochemical reaction. Under these conditions no discontinuous absorption was observed above about 1713A. At high pressures continuous absorption extended up to about 2120A, possibly due to the broadening of the 1713.4A transition.

The structure below 1713A was examined in a vacuum grating spectrograph, with a four inch, 120000 line, two-meter radius of curvature grating, used at about normal incidence. This gave a dispersion of about 4.1A/mm in the first order. The vapor was admitted into the spectrograph, which served as the absorbing column, and the pressure was read with a calibrated thermocouple gauge. The Lyman continuum, used as a source, was produced in a tube described by Worley.<sup>13</sup> About 500 flashes, made once or twice a second, from the discharge of an 8-microfarad capacitor charged to about 3000 volts, was sufficient to give good blackening on Eastman III-0 u.v. sensitized plates. Helium (Ohio Chemical Company, 96 percent purity) at 0.5-2-mm pressure was used in the discharge. The slit width was 0.08 mm. The pressure range investigated under these conditions was from 0.5 to 0.005 mm. The whole system of bands was well developed within this range.

The spectral regions from 2200-1200 and 1600-600A were covered in two settings of the grating. A number of plates were measured, with a precision

<sup>13</sup> R. E. Worley, *Rev. Sci. Inst.* **13**, 67 (1942).

TABLE I. Absorption spectrum of ethylene oxide.\*

Wave number	Relative intensity	Assignment
58362(1713.4A)	58	$V_I$
59157	39	$V_I + \nu_5$
63597(1572.4A)	36	$V_{II}$
64722	31(U)	$V_{II} + \nu_3$
69684(1435.0A)	9	$R_I(2)$
70462	8	$R_I(2) + \nu_5$
70811	19	$R_I(2) + \nu_3$
70986	0	$R_I(2) + \nu_2$ (or $2\nu_5$ )
71988	0	substructure of $R_{II}(3)$
72123	0	ditto
72347(VE)(1382.2A)	100	$R_{II}(3)$
72656	6	$R_{II}(3) + \nu_3 - \nu_5$ (or $R_I(2) + \nu_1$ )
73026(VE)	14(U)	$R_{II}(3) + \nu_5$
73486(VE)	27	$R_{II}(3) + \nu_3$
73554	1	$R_{II}(3) + 2\nu_5$ (or $\nu_2$ )
73750	5	$R_{II}(3) + \nu_3?$
74170(VE)	0	$R_{II}(3) + \nu_3 + \nu_5$
74609(VE)	2	$R_{II}(3) + 2\nu_3$
75005	3	$R_{II}(3) + 2\nu_7$ (or $2\nu_{10}$ or $\nu_1$ )
75209	3	—
75427	1	—
75670	0	$R_{II}(3) + 3\nu_3$
77108	1	—
78211	12	$R_I(3)$
78712	2	$R_I(3) + \nu_5$
79318	6	$R_I(3) + \nu_3$
79510	6	$R_I(3) + \nu_2$
80730	38(U)	$R_{II}(4)$
81896	8	$R_I(4)$
82138	7	$R_I(4) + \nu_5$
82476	1	$R_I(4) + \nu_3$
82967	23	$R_{II}(5)$
83492	3	$R_I(5)$
84101	19	$R_{II}(6)$
84621	2	$R_I(6)$
84976	7	$R_{II}(7)$
85230	1	$R_I(7)$
85474	3	$R_{II}(8)$
85732	1	$R_I(8)$
86000(1162.8A)	1	$R_I(9)$

\* Explanation of Table I.  $R_I(n)$  and  $R_{II}(n)$  indicate members of Rydberg series I and II.  $V_I$  and  $V_{II}$  are non-Rydberg transitions, possibly of type  $N \rightarrow V$ .  $\nu_i$  are vibrations, in the notation of Herzberg (reference 10). (VE) indicates that the violet edge is sharper. (U) indicates uncertainty because of overlapping source line.

comparator, employing the following standards:<sup>14</sup> O IV 1338.603, 1343.507; O V 1371.287; C IV 1548.214, 1550.790 with other secondary standards identified from Boyce and Moore's Tables. The error in measurement of comparatively sharp bands does not exceed 5  $\text{cm}^{-1}$ , but may be 10  $\text{cm}^{-1}$  or a little more for some diffuse bands. A few very weak diffuse bands were measured from microphotometer tracings, with about the same accuracy as could be obtained from comparator measurements.

Wave numbers of the absorption bands are found in Table I, with relative intensity estimates, obtained from microphotometer tracings. We did not attempt any absolute intensity measurements. The strongest band at 72347  $\text{cm}^{-1}$  was assigned an intensity of 100. Some representative micropho-

tometer tracings are shown in Fig. 1. Some weak absorption bands may have been missed because of the presence of the usual emission and absorption lines in the source used. None of the bands in Table I can be ascribed to any impurities which might conceivably be present.

## DISCUSSION

A qualitative examination of the spectrum as a whole shows these essential features. The two longest wave-length regions are diffuse, with origins apparently at 58362 and 63597  $\text{cm}^{-1}$ . These are without doubt two separate electronic transitions. There is only one vibrational transition accompanying each of these electronic transitions. The two transitions as a whole are narrow, but broaden symmetrically with increase in pressure.

The remainder of the spectrum from 69684 up is stronger and the structure is sharper. Some of the bands are shaded definitely to the red. Most of this spectrum appears at 0.025 mm, and the strongest bands at 0.005 mm. There is apparently little continuous absorption in this pressure range below 83000  $\text{cm}^{-1}$ . Above this it is possible that some very weak bands may be obscured by the weak continuum. Strong continuous absorption begins at about 87200 and nothing more can be seen at higher wave numbers, even at the lowest pressures. It will be convenient to discuss the spectrum above and below 69684  $\text{cm}^{-1}$  separately.

The spectrum at wave numbers greater than 69684 is thought to arise mainly from two series of Rydberg transitions accompanied by few vibrational transitions, as is usual. An exception is the transition at 72374 which shows a moderately elaborate vibrational pattern. This transition, assigned as the first member of Rydberg Series II, also departs notably from the series formula. This shows probably that an equilibrium distance is changed from its normal state value more in this transition than in the others.

The two series appear to converge to essentially the same ionization potential (about 10.81 ev), and fit the following formulas:

$$\begin{aligned} \nu_0^n - 87236 &= R/(n+0.45)^2 = R_I(n) & n=2, 3 \dots \\ \nu_0^n - 87175 &= R/(n+0.05)^2 = R_{II}(n) & n=3, 4 \dots \end{aligned}$$

The agreement of observed and calculated terms, based on these ionization potentials is shown in Table II. This table shows also experimental terms in acetylene and ethylene taken from the data of Price.<sup>15</sup> A comparison of terms in acetylene series I with terms in ethylene oxide I is very striking, indicating, of course, about the same Rydberg denominator in the two cases. Agreement of ethylene oxide II with acetylene II and with

<sup>14</sup> J. C. Boyce and J. T. Moore, "Provisional Wavelength Identification Tables for the Vacuum Ultraviolet." (Mimeographed for private distribution, 1941.)

<sup>15</sup> W. C. Price, Phys. Rev. **47**, 444 (1935).

ethylene is less good, particularly with more recent results on ethylene.<sup>16</sup> We believe that these comparisons are significant.

Further comparison of terms in other molecules<sup>17</sup> containing carbon-carbon double and triple bonds with terms of molecules containing  $C=O$  shows that generally the former have Rydberg series formulas with denominators approximately  $(n+0.45)^2$  and  $(n+0.05)^2$  while carbonyl compounds have  $(n+0.3)^2$  and  $(n+0.6)^2$ . This leads us to conclude that the Rydberg spectra of ethylene oxide have little resemblance to comparable spectra of carbonyl compounds, where a  $2p(0)$  non-bonding electron is excited. A similar comparison with water,<sup>18</sup> shows that its Rydberg spectrum is not like that of ethylene oxide. It also appears probable, although not certain, that  $2p(0)$  in ethylene oxide might have a higher ionization potential (as in water) than in carbonyl compounds, and higher than that of an unsaturation orbital in ethylene.

The electron structure and molecular orbitals of ethylene oxide have been discussed recently.<sup>1-3, 8</sup> We do not propose to enter this discussion, espe-

TABLE II. Experimental terms (in  $\text{cm}^{-1}$ ).

<i>n</i>	Ethylene Oxide I		Acetylene I
	(Observed)	(Calculated)	(Price) (Observed)
2	17552	18282	17560
3	9025	9220	8936
4	5340	5542	5411
5	3744	3695	3645
6	2615	2638	2612
7	2006	1977	—
8	1504	1537	1516
9	1236	1229	1216

<i>n</i>	Ethylene Oxide II		Acetylene II	Ethylene
	(Observed)	(Calculated)	(Price) (Observed)	(Price, 1935) (Observed)
2	—	26112	26160	27040
3	14828	11797	11834	12230
4	6445	6690	6724	6820
5	4208	4304	4314	4340
6	3074	2998	3004	3020
7	2199	2208	2207	2220
8	1701	1693	1690	—
9	—	1340	1340	—

cially not in its relation to the chemical properties and reactivity of the compound. We believe, how-

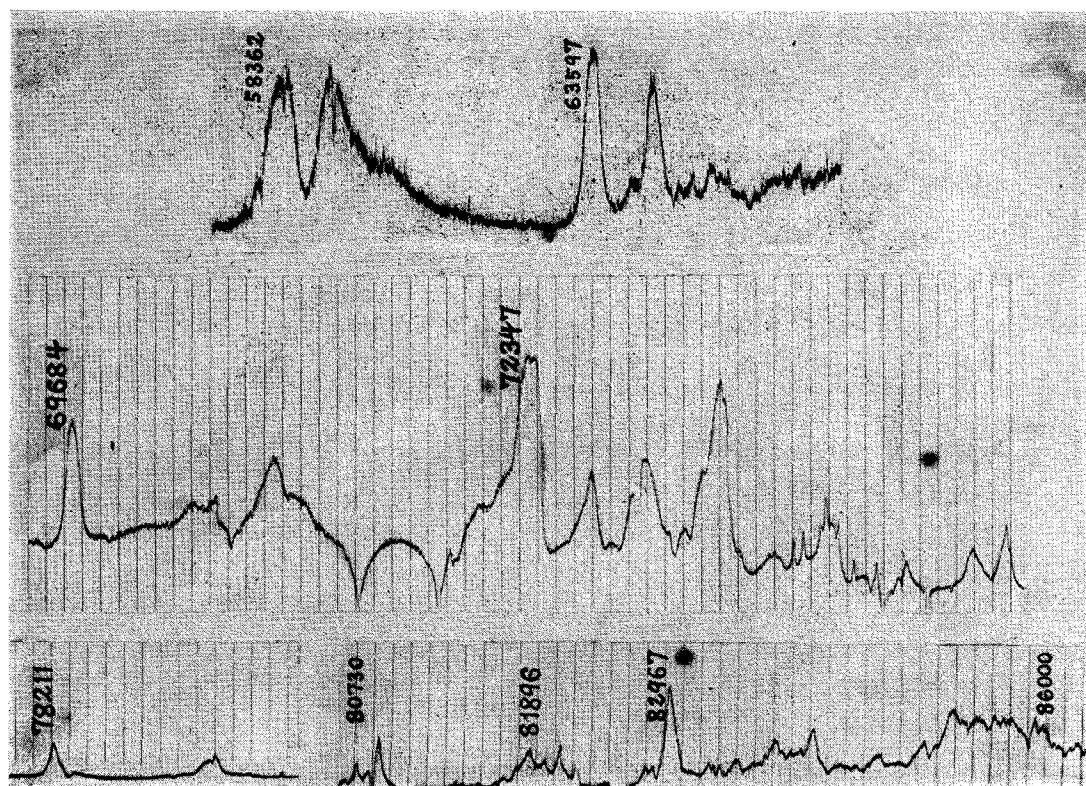


FIG. 1. Microphotometer tracings of the spectrum of ethylene oxide.

<sup>16</sup> W. C. Price and W. T. Tutte, Proc. Roy. Soc. (London) A174, 207 (1940).

<sup>17</sup> W. C. Price and A. D. Walsh, Trans. Faraday Soc. 41, 381 (1945), methyl acetylene; W. C. Price and A. D. Walsh, Proc. Roy. Soc. (London) A174, 220 (1940), conjugated dienes; W. C. Price, J. Chem. Phys. 3, 256 (1935), formaldehyde; A. D. Walsh, Proc. Roy. Soc. (London) A185, 176 (1946), acetaldehyde; A. D. Walsh, Trans. Faraday Soc. 41, 498 (1945), acrolein.

<sup>18</sup> W. C. Price, J. Chem. Phys. 4, 147 (1936).

ever, that the ideas of Walsh can very well be used to account for most of the features of the electronic spectra, especially the similarity of these to ethylene and acetylene.

For ethylene oxide with symmetry  $C_{2v}$ , it is appropriate to take the  $z$  axis along the symmetry axis and  $y$  in the plane of CCO perpendicular to  $z$ . With this choice, the unsaturation orbitals of ethylene are called  $(z_1+z_2)$  rather than  $(x_1+x_2)$  in the following discussion. From  $(z_1+z_2)$  of ethylene and  $2p(0)$  we can construct a semilocalized bonding molecular orbital of ethylene oxide, written in LCAO form, coefficients omitted, as

$$\chi_{cco} = (z_1 + z_2 + 2p(0)).$$

The two non-bonding 0 electrons are in a  $2p_x$  orbital; the other two 0 electrons are not distinguished in direction in a plane perpendicular to  $x$ , and are written  $2p(0)$ , as are their orbitals. The two carbons in ethylene are held together by a  $\sigma$ -bonding orbital also, which may be approximated in a localized treatment as  $(t_y(1) + t_y(2))$ , where  $t_y(1)$  is the trigonal orbital of carbon (1) in the CC bond direction. (In the same localized treatment the other trigonal orbitals would be used in CH bonds.) In ethylene oxide with  $C_{2v}$  symmetry,  $(t_y(1) + t_y(2))$  transforms like  $A_1$  and so can mix with  $\chi_{cco}$ . This suggests that for a discussion of the bonding properties of ethylene oxide a non-localized treatment should be used. But since it is not intended to discuss this aspect of the problem, attention can be confined to  $\chi_{cco}$  as written.

The stronger Rydberg Series II of ethylene oxide ( $R_{II}(n)$  in Table I) can be correlated with Price's series in ethylene, which has been identified by Mulliken<sup>19</sup> and Price and Tuttle<sup>16</sup> as due to  $(x_1+x_2) \rightarrow ns$ , with upper states  $B_{3u}$ . In ethylene oxide, with the axes above, the transitions are  $(z_1+z_2+2p(0)) \rightarrow ns$ , with upper states  $A_1$ . Price and Tuttle mention a weaker series in ethylene with Rydberg denominator  $(n+0.4)^2$  with which we may correlate ethylene oxide Series I. The upper states of this second series are possibly  $B_2$ , resulting from a configuration  $(z_1+z_2+2p(0))np$  (or  $nd$ ). The relative intensities of series members may be found roughly by adding the intensities given in Table I of the vibrational transitions belonging to appropriate electronic transitions. The decrease in in-

tensity from low to high members of a series appears normal.

The transitions at smaller wave numbers than 69684 are believed to arise by excitation of an electron from  $(z_1+z_2+2p(0))^2$  to one of the anti-bonding forms of this orbital. There will be a number of these, formulated  $(z_1+z_2-2p(0))$ ,  $(z_1-z_2+2p(0))$ ,  $(z_1-z_2-2p(0))$ , of which the first transforms like  $A_1$  and the others like  $B_2$ . The  $N \rightarrow V$  transition in ethylene (Mulliken's notation)<sup>19</sup> is between states  $A_{1g}$  and  $(B_{3u})(B_{2g}) = B_{1u}$ . In ethylene oxide this is equivalent to a transition  $A_1$  to  $B_2$ . The orbitals  $(z_1-z_2 \pm 2p(0))$  fulfill this requirement.

The experimental term value of  $N \rightarrow V$  lies at about 28800  $\text{cm}^{-1}$  below the ionization potential of  $(x_1+x_2)$  in ethylene. If it is assumed that  $N \rightarrow V$  in ethylene oxide will lie about as far below the ionization potential of  $(z_1+z_2+2p(0))$ , the transition should occur at about 58400  $\text{cm}^{-1}$ . The transition observed at 58362 may very probably arise from  $(z_1+z_2+2p(0))^2 \rightarrow (z_1+z_2+2p(0))(z_1-z_2+2p(0))$ ;  $N \rightarrow V$ . It is possible that the other non-Rydberg transition at 63597 is another  $N \rightarrow V$  transition, possibly to  $(z_1+z_2-2p(0))$ .

The assignment of vibrational transitions is given in Table I and needs not be discussed in detail. These have been identified mostly as modifications of the normal state frequencies  $\nu_3$ ,  $\nu_5$ ,  $\nu_2$ ,  $\nu_1$ . It appears reasonable that  $\nu_3$  and  $\nu_5$  should appear more prominently than the others. It may be expected that  $\nu_7$ ,  $\nu_{10}$ , and  $\nu_{12}$ , which are not totally symmetrical, will appear with even number of quanta only, if at all. The decrease of  $\nu_3$  with increase of  $n$  in the Rydberg members is quite large so that in  $R_I(4)$  it has only about one-third its normal state value. The decrease of  $\nu_5$  is less marked but drops to one-half its normal state value in the same term.

In conclusion, we wish to thank Dr. W. D. Walters for the purified sample of ethylene oxide used. One of us (TKL) expresses his appreciation for a Research Fellowship from Academia Sinica, China.

*Note added in proof:* Dr. A. Langer of the Research Laboratories of the Westinghouse Electric Corporation has informed us recently that he has obtained a value of  $11.2 \pm 0.5$  eV for the lowest ionization potential of ethylene oxide. We thank Dr. Langer and his associates for communicating this information.

<sup>19</sup> R. S. Mulliken, J. Chem. Phys. **3**, 518 (1935).