

## Polarization of Raman Lines of sDichloroethane

John T. Neu, Abraham Ottenberg, and Wm. D. Gwinn

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should thus expect 6 or 7 fundamental modes polarized  $A_1$ , depending on the configuration, but only if 7 are accounted for can the results be interpreted with any certainty.

Samples of oriented urea crystals were prepared by evaporation of urea from a methanol solution onto a AgCl plate. The evaporation was controlled by placing at one edge of the plate a heated transite rod; the crystals grew with the tetragonal axis parallel to the changing thermal gradient thus produced.

Assuming for the moment that urea is planar, representation  $A_1$  will contain three groups of modes: two symmetrical H stretches; modes principally C—O stretch, symmetrical N—C—N bent and stretch; and two symmetrical H bends. The H stretch modes occur in a region (about 3200  $\text{cm}^{-1}$ ) where the resolving power of our instrument is inadequate, so that polarization data is poor. In the non-planar model only one of these modes should be active. We found two bands polarized  $A_1$  at 1680 and 546  $\text{cm}^{-1}$ , assignable to the C—O stretch and N—C—N bend, respectively. The N—C—N stretch has been found at 1010  $\text{cm}^{-1}$  but is too weak to give good polarization data. Raman work,<sup>5</sup> however, provides ample evidence for this assignment. These three modes would be polarized similarly in the non-planar structure. The most crucial data concerns the H bends, only one of which would be expected to be active in the non-planar model. We found two bands at 1160 and 1590  $\text{cm}^{-1}$  polarized along the tetragonal axis and attributable to these modes. It is true that all first overtones, as well as certain combinations, will be polarized  $A_1$ , but none of the frequencies observed by us or by other investigators would be expected to contribute to the spectrum at the frequencies listed above.

Our ability to account satisfactorily for 7 fundamental frequencies polarized  $A_1$  leads us to choose the entirely planar structure for the urea molecule in the crystal.

The author wishes to acknowledge gratefully the suggestions given him during the course of the work by Professor E. B. Wilson, Jr. and Mr. W. L. Hyde.

<sup>1</sup> R. W. G. Wyckoff, *Zeits. f. Krist.* **81**, 102 (1932); R. W. G. Wyckoff and R. B. Corey, *ibid.* **89**, 462 (1934).

<sup>2</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1939), p. 212*f*.

<sup>3</sup> L. Kellner, *Proc. Roy. Soc.* **177A**, 546 (1941).

<sup>4</sup> R. S. Halford, *J. Chem. Phys.* **14**, 8 (1946).

<sup>5</sup> For example, J. W. Otvos and J. T. Edsall, *J. Chem. Phys.* **7**, 632 (1939).

## Polarization of Raman Lines of *s*-Dichloroethane

JOHN T. NEU, ABRAHAM OTTENBERG, AND WM. D. GWINN  
Department of Chemistry, University of California,  
Berkeley, California

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IN a recent paper Gwinn and Pitzer<sup>1</sup> use the *s*-dichloroethane frequency assignments of Wu<sup>2</sup> with the exception that a  $C_2$  (staggered configuration) rather than a  $C_{2v}$  (eclipsed configuration) model is taken as one of the two forms. Ananthakrishnan's<sup>3</sup> evaluations of the 123- $\text{cm}^{-1}$  and 1206- $\text{cm}^{-1}$  lines as depolarized are not consistent with this  $C_2$  assignment, however. Other investigators<sup>4</sup> have reported polarization on dichloroethane but only Anantha-

krishnan has evaluated the 123- $\text{cm}^{-1}$  line and his work was qualitative. The  $C_2$  configuration, in which the 123- $\text{cm}^{-1}$  line is polarized, is similar to the  $C_{2v}$  configuration, in which the 123- $\text{cm}^{-1}$  line would be depolarized, differing only in an internal rotation of 60°. It would not be expected, therefore, that the 123- $\text{cm}^{-1}$  line, corresponding to the torsional vibration, would be strongly polarized. Since the 123- $\text{cm}^{-1}$  line is somewhat obscured by the background from the exciting line, it is not surprising that the other investigators did not obtain polarization data, nor is it unlikely that a qualitative estimate of polarization, where the background intensity is high, might be in error if the polarization is not pronounced. The 1206 line is reported as depolarized by Ananthakrishnan and as polarized ( $\rho=0.36$ ) by Cheng.<sup>3</sup> In order to assign the polarization of these lines definitely, the writers have made a quantitative determination of the polarization.

The sample of dichloroethane obtained from Eastman Kodak Company was purified by washing with sulfuric acid, steam distilling, drying over  $\text{MgSO}_4$ , and finally distilling into the Raman tube through a thirty-theoretical-plate fractionating column. A Steinheil GH type spectrograph with  $f:10$  collimator and  $f:3$  camera was used with a slit of 0.017 mm. The method used to obtain polarization was a combination of schemes either cited or described by Glockler and Baker.<sup>4</sup> Illumination was furnished by two G.E. AH11 mercury arcs lying in a plane inclined 45 deg. to the vertical. Wratten 2A gelatin filters and baffles to eliminate light not perpendicular to the Raman tube were interposed between the arcs and the Raman tube. A quartz Wollaston prism with its axis inclined 45 deg. was placed between the collimator lens and the first prism of the spectrograph. Thus a single exposure produced two representations of the spectrum, one above the other and shifted slightly, in which the polarized lines appeared less intense in one representation than in the other. Differential reflection at the prism surfaces was eliminated by the device of inclining the plane of illumination and the Wollaston prism at an angle of 45 deg. Spectra were recorded on Eastman 103 H spectroscopic plates with exposure time varying from 6 to 24 hours. Intensity calibrations were placed on each plate by means of a rotating stepped sector disk, and intensity traces of plates were made with a microphotometer of our own design. Wave number assignments were taken from the work of Ananthakrishnan.<sup>3</sup> A graph was obtained by plotting the photometer reading of the intensity calibration at the frequency of the particular line against the intensity of the light that produced the calibration. Line intensities were

TABLE I.

$\text{cm}^{-1}$	$\rho$	$\text{cm}^{-1}$	$\rho$	$\text{cm}^{-1}$	$\rho$
123	0.63	880	0.88	1302	0.45
263	0.31	940	0.26	1429	0.82
302	0.40	989	$P^*$	1440	$D^*$
411	0.81	1052	0.47	2844	$P^*$
654	0.18	1144	$D^*$	2872	$P^*$
675	$D^*$	1206	0.65	2956	0.23
754	0.23	1262	$D^*$	3002	$D^*$

\* This line was too weak for quantitative evaluation of  $\rho$ .  $P$  (polarized) or  $D$  (depolarized) represents a qualitative estimate.

evaluated in the usual manner by subtracting the background intensity from the line intensity as evaluated from the graph. In the special case of the  $123\text{-cm}^{-1}$  line, the apparent background was sketched in and the intensities of the Raman line at small increments of frequency were plotted against a uniform scale. This served to show that the background had been sketched in so that the line had the correct shape and was symmetric.

Indeed, a visual estimate of the polarization seemed to indicate that the  $123\text{-cm}^{-1}$  line was depolarized, but careful determination of the value of  $\rho$  indicated that the line was polarized. The average value from five plates was 0.63, the average deviation from this value being 0.06. The  $1206\text{-cm}^{-1}$  line was also found to be weakly polarized. Table I below lists the values of  $\rho$  for all the lines.

These data indicate that the high energy form of *s*-dichloroethane is  $C_2$  and not  $C_{2v}$ .

<sup>1</sup> W. D. Gwinn and K. S. Pitzer, *J. Chem. Phys.* **16**, 303 (1948).

<sup>2</sup> Ta-You Wu, *Vibration Spectra and Structure of Polyatomic Molecules* (Edwards Brothers, Inc., Ann Arbor, Michigan, 1946), second edition, pp. 306-312.

<sup>3</sup> R. Ananthakrishnan, *Proc. Ind. Acad. Sci.* **5A**, 285 (1937).

<sup>4</sup> G. Glockler and H. T. Baker, *J. Chem. Phys.* **11**, 446 (1943).

### Note on the Theory of Ethylene

RODOLFO H. BUSCH

*Facultad de Ciencias Exactas, Físicas y Naturales, Perú 222,  
Buenos Aires, Argentina  
August 6, 1948*

IN a recent paper, Mulliken and Roothaan<sup>1</sup> use the semi-empirical linear combination of atomic orbitals, the molecular orbital method for some computations on the ethylene molecule. The purpose of this note is to direct the attention to another starting point in the double-bond problem, which is suggested by the following.

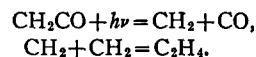
In its ground state, the carbon atom is divalent. To account for the fact that it is normally quadrivalent it must be postulated that in carbon compounds the atom is in an excited state with one *s* and three *p* electrons, all with unpaired spins.

There is no doubt of the correctness of this assumption in a great number of cases, but in the treatment of the double-bond problem there seems to exist another possibility, consisting in emphasizing the fact that the carbon atom does have the alternative of being two- or quadrivalent, and seek for the explanation of its chemical particularities by the systematic application of this argument.

The starting point may be the consideration of the problem of methylene, which is known to exist in two forms (Pearson, Purcell, and Saigh;<sup>2</sup> Burton, Davis, Gordon, and Taylor<sup>3</sup>), as the "molecule"  $CH_2$  and as the short lived "radical"  $>CH_2$ . The energy required to raise the  $CH_2$  molecule to the radical structure is about 15 kcal. (Long and Norrish<sup>4</sup>).

In the photolysis of ketene, investigated by Norrish, Crone, and Saltmarsh,<sup>5</sup> the products obtained were

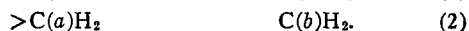
quantitatively carbon monoxide and ethylene. Ross and Kistiakowsky<sup>6</sup> suggested the following mechanism:



This reaction may be the key for the theory of ethylene. We assume that the formation of ethylene is due to the interaction of the two forms of methylene:



If we label the two carbon atoms as  $C(a)$  and  $C(b)$ , it follows that the system consisting of a "molecule"  $CH_2$  and a "radical"  $>CH_2$  at great distances is doubly degenerate:



The symmetry of this problem is in some respects similar to that of the hydrogen molecule ion; at shorter distances the interaction between the two forms may give rise to two solutions, one of which may correspond to the ethylene molecule.

The double bond might be thus interpreted as a kind of "excitation resonance." Using the data of the paper of Long and Norrish,<sup>4</sup> the interaction energy results in the order of 130 kcal.

In view of the preceding discussion, we think it would be interesting to compute the interaction energy by the methods of quantum mechanics.

<sup>1</sup> R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.* **41**, 201 (1947).

<sup>2</sup> Pearson, Purcell, and Saigh, *J. Chem. Soc.* **1**, 459 (1938).

<sup>3</sup> Burton, Davis, Gordon, and Taylor, *J. Am. Chem. Soc.* **63**, 1956 (1941).

<sup>4</sup> Long and Norrish, *Proc. Roy. Soc. A* **187**, 337 (1946).

<sup>5</sup> Norrish, Crone, and Saltmarsh, *J. Chem. Soc.* 1533 (1933).

<sup>6</sup> Ross and G. B. Kistiakowsky, *J. Am. Chem. Soc.* **56**, 1112 (1934).

### Addendum: Continuous Spectra and OH Absorption in Carbon Monoxide-Oxygen Explosions

G. A. HORNBECK

*Applied Physics Laboratory, The Johns Hopkins University,  
Silver Spring, Maryland  
August 3, 1948*

THE structural part of the CO-oxygen spectrum referred to as flame bands in a recent note<sup>1</sup> have been identified as belonging to the  $^3\Sigma \rightarrow ^3\Sigma$  transition of the neutral oxygen molecule. The agreement of our measurements with those of Lochte-Holtgreven and Dieke<sup>2</sup> of the oxygen bands observed in a high tension arc by Runge are generally better than  $0.2\text{ cm}^{-1}$ . Current measurements confirmed the existence of several bands of the  $^3\Sigma \rightarrow ^3\Sigma$  transition in the spectra obtained from the CO-oxygen explosion. The bands found thus far are the (0-12), (0-13), (0-14), (0-15), and the (2-15). A detailed discussion of this spectrum as observed in CO-oxygen combustion will be reported in the near future.

<sup>1</sup> G. A. Hornbeck, *J. Chem. Phys.* **16**, 845 (1948).

<sup>2</sup> W. Lochte-Holtgreven and G. H. Dieke, *Ann. d. Physik* **3**, 937 (1929).