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The Far Ultraviolet Absorption Spectra of Formaldehyde and the Alkyl Derivatives of H₂O and H₂S

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The absorption spectra of formaldehyde and of compounds of the type HOH, ROH, ROR and HSH, RSH, RSR have been observed in the region 2300–1000Å. An analysis of the spectrum of formaldehyde yields a value of 10.83 ± 0.01 volts for the first ionization potential of the C=O bond and about 164 Cal./mole for the strength of this bond. The spectra of the alkyl derivatives of H₂S are all shown to be shifted to the long wavelength region relative to those of H₂O. Rough estimates of their ionization potentials are given and the influence of dipole moment on the ultraviolet absorption spectra and ionization potentials of polyatomic molecules is discussed.

THE author has for some time been investigating the absorption spectra of various organic molecules in the far ultraviolet. Up to the present, work of this nature has been done almost exclusively with fluorite spectrographs by using the H₂ continuum. The instruments used in this work are two vacuum grazing incidence spectrographs which have dispersions of 11–9Å/mm and 2.7–2.0Å/mm, respectively, in the region 2000–1000Å. The source of the continuum was a Lyman discharge tube of the type developed by Collins and Price.¹ The use of this continuum in preference to the H₂ continuum enabled the absorption to be followed down to 1000Å. Both gratings were of glass and each was ruled with 30,000 lines to the inch. The radius of curvature of the smaller was 40 cm and that of the larger was two meters. The path lengths of the absorbing columns in the two spectrographs were about 35 and 150 cm, respectively.

The gas to be investigated is led into the body of the spectrograph through a fine capillary and pumped out through the main evacuating pump. The pressure of the gas used in obtaining these absorption spectra is usually of the order of a tenth of a millimeter. The author has shown that in a large number of cases² the bands obtained under these conditions consist of various electronic series with a superimposed vibrational pattern which go to a limit agreeing fairly well with the ionization potential of the molecule as obtained by electron impact.

A photograph of the absorption spectrum of formaldehyde taken under high dispersion is given in Fig. 1. The gas was obtained by heating paraformaldehyde. The absorption is very strong and most of the bands appear at a pressure of 0.1 mm in a path length of 1.5 meters. On account of the diffuseness of the bands the analysis is rather difficult. It is however plain that the bands converge to a limit around 1150Å.

TABLE I. Comparison between calculated and observed values for the frequency differences between successive series members in formaldehyde.

n	Intensity	Wave number	Difference between successive members (cm ⁻¹)	
			Obs.	Calc.
SERIES (i)				
2	10	71600		
3	10	79420	7820	7766
4	8	82720	3300	3281
5	8	84370	1650	1687
6	7	85350	980	980
7	6	85950	600	619
SERIES (ii)				
2	10 D	64270		
3	10 D	77670	13400	10667
4	9 D	81750	4080	4142
5	8	83810	2060	2028
6	8	84950	1140	1142
7	8	84950	700	705
7	7	85650	700	705
8	5	86120	470	466

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¹ G. B. Collins and W. C. Price, *Rev. Sci. Inst.* **5**, 423 (1934).

² W. C. Price, *Phys. Rev.* **45**, 843 (1934); **46**, 529 (1934); *Phys. Rev.* **47**, 444, 510 (1935).

The strong bands can be classified into two electronic series. The frequencies of their members are given in Table I. As most of the members are a few Angstroms broad, the measurements can only be relied upon to within 50 wave numbers. Also, they all contain a considerable amount of fine structure due to the low moment of inertia of the molecule about the CO axis. Even with the high resolution used here, little could be done with this and the measurements given correspond to the center of the band. The higher members of (i) and (ii) conform fairly well to the following Rydberg series:

- (i) $\nu_0^n = 87,830 - R/(n + 0.60)^2$,
 (ii) $\nu_0^n = 87,710 - R/(n + 0.30)^2$, $n = 2, 3, 4$ etc.

An idea of the accuracy with which these formulas represent the series may be obtained from an inspection of Table I.

The first member of series (ii) is somewhat off the Rydberg formula. This may probably be accounted for by the presence of a dipole in the CH₂ group which means that the electron is escaping in a field given approximately by

$$\nu = e/r_1 + (p \cos \theta)/r_2^2$$

" p " being the moment of the dipole, " r_2 " the distance of the electron from the center of the dipole and θ the angle between r_2 and the dipole. It is obvious that the second term becomes negligible for the higher members of an electronic series, and thus they may be expected to conform to the Rydberg series. Further it can be shown that the values of the dipole moment usually associated with a CH₂ or CH₃ group can produce quite large effects on the ultraviolet absorption spectra and ionization potentials of polyatomic molecules. Thus the method used in getting these electronic series should be to try and fit the higher members into a Rydberg series and then to fit in the lower members by their intensities and the fact that they should fall fairly close to where the band of the Rydberg series would fall. Similarities in vibration pattern also help where these can be observed.

The extremely diffuse band at 1745Å (57,310 cm⁻¹) can possibly be a lower member of Class I though it is very far off the series. If we assume the predissociation of this band to be due to

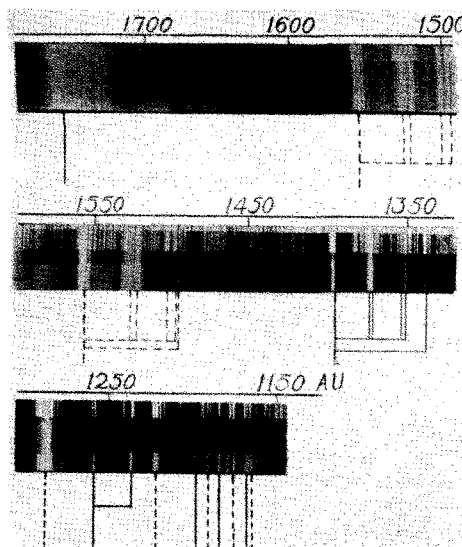


FIG. 1. The far ultraviolet absorption spectrum of formaldehyde.

interaction with the ground state the process being $\text{H}_2\text{CO} \rightarrow \text{CH}_2 + \text{O}$ we find the heat of dissociation of the C=O bond to be about 164 Cal./mole which is in fairly good agreement with the value ~ 172 Cal./mole obtained from thermochemical data. The author has also observed that all the bands in acetaldehyde and acetone which fall in the region below 1745Å are predissociated, the strength of the predissociation depending on how far the bands are removed from this wavelength. The bands at wavelengths longer than this are sharp. It is thus indicated that the C=O bond is roughly of the same strength in all three substances.

The series (i) and (ii) in H_2CO have approximately the same limit which is 10.83 ± 0.01 volts. This compares favorably with the value 11.3 ± 0.5 volts determined by T. N. Jewitt³ for the ionization potential of formaldehyde by the methods of electron impact.

It is fairly certain that the ionization is from the C=O bond. If it were from the CH bond the ionization potential would be expected to be considerably higher and the bands would prob-

³ T. N. Jewitt, Phys. Rev. **46**, 616 (1934).

ably start at about the same wavelength as the corresponding ones in methane⁴ (i.e., around 1300Å). Investigations of the spectra of acetaldehyde and acetone⁵ also indicate that in these molecules the excitation is from the C=O bond.

There are only two electronic transitions for which the vibrational pattern is at all well developed. These are the bands at 1556Å and 1397Å. There are two frequency differences accompanying each. In the case of the first band the differences are 1250 cm⁻¹ and 1470 cm⁻¹ and for the second band they are 1120 cm⁻¹ and 1260 cm⁻¹. These vibration frequencies are presumably types which involve vibration in the C=O bond. Herzberg⁶ has found a frequency of 1187 cm⁻¹ in the near ultraviolet absorption of formaldehyde which he attributes to a vibration in this bond. A few frequency differences of ~2900 cm⁻¹ involving vibrations in the CH bond were observed in the bands reported here but they are very weak.

Although about 150 bands could be observed, the value of giving a complete table of their wavelengths is questionable because the latter, even under high dispersion, cannot be determined very accurately as the bands do not possess sharp edges. A few things however can be said about particular cases: The band at 64,270 cm⁻¹ is really a diffuse doublet with a separation of 80 cm⁻¹, the frequencies of the components being 64,230 cm⁻¹ and 64,310 cm⁻¹. That at 71,600 cm⁻¹ is likewise composed of two bands separated by 50 cm⁻¹. Also all the upper bands of series (ii) have multiple heads which are possibly analogous to the *rR*, etc., branches reported by Dieke and Kistiakowsky⁷ for the near ultraviolet bands.

The spectra of the alkyl derivatives of H₂S and H₂O are given in Fig. 2. They were taken on the smaller spectrograph. It is immediately evident that the spectra of the compounds containing sulphur are all shifted to the long wavelength region relative to those containing oxygen. This is in accord with the fact that the ionization

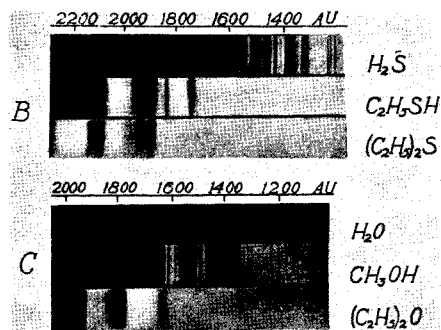


FIG. 2. The far ultraviolet absorption spectra of the alkyl derivatives of H₂S and H₂O.

potential of S(1) is ~10.3 volts and that of O(1) is ~13.6 volts. The spectra of H₂S has been photographed under high dispersion. A complete discussion of it is reserved for publication elsewhere. The bands can be arranged into electronic series which go to several ionization potentials in the neighborhood of 10.5 volts. This agrees very well with the value 10.4 volts⁸ obtained by electron impact.

The bands in H₂O have been followed to a limit around 980Å by Rathenau.⁹ Though no analysis has been made of the bands this limit is about 12.6 volts and it is obvious that they correspond to electronic series going to the ionization potential at 12.7 volts determined by Smyth and Mueller.¹⁰ Thus it is fairly sure that the bands of the other molecules are of the same type, i.e., electronic series going to the first ionization potentials.

There is a very considerable amount of evidence available for spectra of the type reported here, which indicates that the bands of any particular alkyl compound start around the same wavelength and go to about the same ionization potential whatever the nature of the alkyl group, e.g., the spectrum of methyl not ethyl alcohol is given in Fig. 2. However, the spectrum of ethyl alcohol starts at almost the same wavelength. Further, the author has photographed the absorption spectra of ethyl, propyl,

⁴ A. B. F. Duncan, J. Chem. Phys. **2**, 851 (1934).

⁵ G. Scheibe, F. Povenz and C. F. Linström, Zeits. f. physik. Chemie **B20**, 292 (1933); W. A. Noyes, A. B. F. Duncan and W. M. Manning, J. Chem. Phys. **2**, 717 (1934).

⁶ G. Herzberg, Trans. Faraday Soc. **27**, 378 (1931).

⁷ G. H. Dieke and G. B. Kistiakowsky, Phys. Rev. **45**, 4 (1934).

⁸ C. A. MacKay, Phys. Rev. **24**, 319 (1924).

⁹ G. Rathenau, Zeits. f. Physik **87**, 32 (1933).

¹⁰ H. D. Smyth and D. W. Mueller, Phys. Rev. **43**, 116 (1933).

isopropyl and butyl mercaptans and sulphides and found that they all begin around 2100Å and 2300Å, respectively. Also Scheibe, Herzberg¹¹ and others have obtained the spectra of methyl, ethyl and tertiary butyl iodide and found that they all start around 2010Å. This must be related to the fact that the excitation is from the non-alkyl part of the molecule, and also that the dipole moments of the various alkyl groups are not sufficiently different to affect the term value of the excited electron.*

While it is still too early in the development of the spectra of polyatomic molecules to make many definite statements, some tentative remarks on these spectra may however be in order. The excitation in the case of the alcohols and the mercaptans is surely from the CO and the CS bonds, respectively, as the other bonds have higher ionization potentials. That of the sulphides and the ethers is also from the CO and CS bonds but the substitution of an alkyl group for a hydrogen atom has introduced a dipole

which reduces the term values in the adjacent bonds (the negative end of the dipole is towards the excited electron). This diminishes the ionization potential and shifts the absorption bands towards the red. This successive shift towards the red is also found in the spectra of H_2CO , CH_3HCO and $(\text{CH}_3)_2\text{CO}$. Their estimated ionization potentials are 10.83, 10.5 and 10.1 volts, respectively.

It is possible to predict very roughly that for alcohols and ethers the first ionization potentials are around 10.8 and 10 volts, respectively, and for mercaptans and sulphides around 9 and 8.5 volts, respectively.

Preliminary measurements with fluorite spectrographs have been made on methyl and ethyl alcohol by Herzberg and Scheibe¹¹ and on methyl and ethyl ether by Scheibe and Grieneisen.¹² A wavelength table is not given here as it is intended in the near future to photograph the bands with higher dispersion and at a greater variety of pressures.

In conclusion the author wishes to express his gratitude to Dr. G. H. Dieke and Dr. K. F. Herzfeld for many discussions on the material of this article.

¹² Scheibe and Grieneisen, *Zeits. f. physik. Chemie* **B25**, 52 (1934).

* ¹¹ G. Herzberg and G. Scheibe, *Zeits. f. physik. Chemie* **B7**, 390 (1930).

* A dipole of 0.3×10^{-18} e.s.u., such as is usually associated with a methyl group, will change the term value of an electron situated 1 Ångström away by almost one electron volt and can thus change the position of the absorption bands by more than 100Å.

The Calculation of the Free Energy of Polyatomic Molecules from Spectroscopic Data. II

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The methods already developed for computing the free energy from spectroscopic data for diatomic molecules and for triatomic unsymmetrical rotators are extended to handle the case where one or more of the fundamental frequencies is degenerate. New tables, necessary for such calculations, have been computed and the procedure is illustrated by sample calculations for nitrous oxide, hydrogen cyanide and acetylene.

DURING recent years, the calculation of thermodynamic quantities from spectroscopic data has proved to be a most useful method of solving problems of chemical equilibrium. At the moment of writing, with the exception of

steam,¹ carbon dioxide² and nitrous oxide,² precise calculations, taking account of the second and third order terms in the expression for the

¹ Gordon, *J. Chem. Phys.* **2**, 65 (1934).

² Kassel, *J. Am. Chem. Soc.* **56**, 1838 (1934).