

Solutions Containing Zwitterions: Erratum

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$r=0$, most rapidly for HI, least rapidly for HCl, causing the HI curve to have its maximum at smaller r than HBr or HCl, does not, however, seem convincing. As Bartholomé points out, quantitative intensity data on the various $0 \rightarrow 2$ bands, together with good frequency data on HI, might help greatly in determining the true form of the $\mu(r)$ curves.

ROBERT S. MULLIKEN

Ryerson Physical Laboratory,
University of Chicago,
August 20, 1934.

¹ R. S. Mulliken, J. Chem. Phys. **2**, 400 (1934). In Eq. (1) and the text, the possible values of the coefficient of ξ^2 in Eq. (1) should have been given as 0.035, 2.28 instead of 0.07, 4.56; the change is, however, unessential. In Figs. 1a and 1b, the μ scale should read 1.0 instead of 0.8, and other values in proportion; this, however, has no effect on the forms of the curves or on the discussion.

² E. Bartholomé, Zeits. f. physik. Chemie **B23**, 131 (1933).

³ J. L. Dunham, Phys. Rev. **35**, 1347 (1930), Eq. (19). This paper seems to have been overlooked by Bartholomé.

Solutions Containing Zwitterions: Erratum

(J. Chem. Phys. **2**, 351, 1934).

Eq. (18) on page 355 should read

$$Q_n = \int \int \{ \rho_0(r, \vartheta, \varphi) \rho_0(r', \vartheta', \varphi') r^n r'^n P_n(\cos \gamma) \} dv' dv$$

$$\cos \gamma = \cos \vartheta \cos \vartheta' + \sin \vartheta \sin \vartheta' \cos(\varphi - \varphi').$$

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August 24, 1934.

On a Test for Free Radicals of Short Life

In the chemical investigation of free radicals of short life two major difficulties are encountered, first, their high rate of reaction, excluding all methods in which a gas is pumped out of the reaction vessel and analyzed afterwards, and secondly, closely connected with it, their small concentration. Actually, no characteristic chemical tests are known for free radicals as OH, NH, CH.

In the experiments to be described, the concentration of OH radicals present in the electric discharge through water vapor was observed by the intensity of their absorption spectrum. After interrupting the discharge, their gradual disappearance was traced by snapshots indicating the decay of their absorption spectrum with time.

The absorption spectrum of OH radicals has been observed in *thermally dissociated water vapor* at temperatures up to 1600°C by Bonhoeffer and Reichardt.¹ Various failures, however, to observe the same spectrum in *electric discharges* or *chemical reactions* have been reported in particular by Bonhoeffer and Pearson,² investigating the electric discharge through water vapor, and by Geib and Harteck³ investigating various chemical reactions. It seems probable that the failures have in common the application of medium sized spectrographs. Actually, extremely high resolving power is required to observe a

faint and sharp *absorption* line—contrary to the corresponding problem in *emission*. Hence in the present experiment the absorption spectrum was investigated in the second order of a 21-foot grating. This method is so sensitive that any carbon arc in air, without an absorption tube, shows the absorption spectrum of OH. Therefore the carbon arc has to be operated in dry nitrogen in order to provide the continuous background for the absorption experiment.

The electric discharge through water vapor was operated in series with a mechanical switch, turned by a synchronous motor, letting through one-half period of 60 cycle a.c. and interrupting through the following three halves, or, in other experiments, letting through one full period and interrupting the following 9 periods. A sector disk fixed on the same axis with the switch, rotating immediately in front of the slit of the spectrograph, screened off the inevitable emission spectrum of the discharge through water vapor and let through the continuous light from the carbon arc with the absorption spectrum for a brief snapshot after interrupting the discharge. The time interval between the breaking of the discharge and the snapshot could be varied by adjusting the phase of the sector disk on the axis with respect to the switch. This process of discharge and following snapshot went on periodically until an adequate total time of exposure was secured.

With the 21-foot grating the absorption spectrum of OH in the uninterrupted electric discharge through water vapor can be observed, provided that the continuous background is strong as compared with the emission of the discharge. It can be observed without this restriction after interrupting the discharge. These absorption bands of OH radicals show an intensity far above the minimum intensity observable with the present apparatus.

Their aspect, based on their intensity distribution, is different from the well-known OH emission bands. The strong heads, characteristic in emission, disappear in absorption. The reason is that in absorption the rotation of the OH molecules is low, determined by the temperature, whereas in emission much higher rotational quanta come out with great intensity. This difference has been interpreted in a recent paper.⁴

After interrupting the discharge a marked decay of the intensity of absorption was observed. The rate of reaction is such that after 1/8 sec. some absorption is left. This time limit was given by the present construction of the switch; it does not indicate the limit of the absorption spectrum observable.

The persistence of the absorption spectrum of OH radicals does not necessarily indicate a correspondingly long life of *OH radicals* after the interruption of the discharge. Instead, it might be that the average life of OH radicals is much shorter and that a new supply of OH is permanently reproduced by combination of O and H atoms so that actually the lifetime of *these atoms* is being observed.⁵ It is hoped to decide this alternative by other experiments.

In order to study the kinetics of the OH radicals⁶ a quantitative determination of their concentration will be attempted by photographic photometry.

The experiments discussed originated from H. N. Russell's⁷ discussion of the absorption spectra of stellar atmospheres in which he mentioned the fact that the astronomer, restricted to the glass and part of the quartz region, is observing absorption spectra mainly of *unstable* molecules, whereas most *stable* molecules have their absorption spectra in the extreme ultraviolet. This property of unstable molecules suggested the application of the spectrograph to such reactions in gases.

O. OLDENBERG

Research Laboratory of Physics,
Harvard University,
Cambridge, Massachusetts,
September 12, 1934.

¹ K. F. Bonhoeffer and H. Reichardt, *Zeits. f. physik. Chemie* **139**, 75 (1928).

² K. F. Bonhoeffer and T. G. Pearson, *Zeits. f. physik. Chemie* **14**, 1 (1931).

³ P. Harteck, *Trans. Faraday Soc.* **30**, 139 (1934). Cf. W. Frankenburg and H. Klinkhardt, *Zeits. f. physik. Chemie* **15**, 440 (1931).

⁴ O. Oldenberg, *Phys. Rev.* **46**, 210 (1934).

⁵ This has been pointed out by Bonhoeffer and Pearson² discussing the afterglow of water vapor discovered by G. I. Lavin and F. B. Stewart (*Proc. Nat. Acad. Sci.* **15**, 829 (1929)).

⁶ W. H. Rodebush and M. H. Wahl (*J. Chem. Phys.* **1**, 696 (1933)) obtained H₂O₂ as the principal product of the electric discharge through water vapor. Their hypothesis of a bimolecular association OH + OH → H₂O₂ is based on the assumption of a very short life of OH.

⁷ Russell, Lecture at the Harvard Observatory, 1931; *Astrophys. J.* **79**, 317 (1934).

The Raman Spectrum of Deuterio-Benzene (C₆D₆)

In order to facilitate the interpretation of the Raman spectrum of benzene, we have investigated the Raman spectrum of deuterio-benzene. Efforts were made to synthesize this material in our laboratory. An experiment with an exchange reaction between heavy water and benzene showed that no exchange took place in the vapor state at 450° in the presence of platinum black or between the two liquid phases which were in contact for ten days. An attempt to prepare deuterio-benzene by the polymerization of acetylene made from heavy water and calcium carbide yielded only about one cubic millimeter of liquid hydrocarbon from 3 cc of heavy water although the by-products were recovered and reprocessed several times. This indicates that the reaction with deuterio-acetylene gives a very small yield of benzene compared to the reaction with ordinary acetylene as judged by preliminary trial experiments and by the work of Zelinsky¹ on this reaction.

The material used in this investigation was loaned to us by Professor Zanetti of Columbia University who prepared it from heavy water of better than 99 percent purity by the polymerization of acetylene, working on a much larger scale. Due to the very small yield, the product could not be purified very thoroughly but a small amount of a liquid which smelled like benzene was obtained. The preparation of this material will be described elsewhere by Professor Zanetti. The liquid was distilled once in air over a water bath and then distilled into the Raman tube in vacuum, passing the vapors over P₂O₅ to remove traces of water.

The technique used for obtaining the Raman spectrum was that described by Murray and Andrews.² The Raman tube was made of Pyrex capillary of 1.2 mm bore fused to a Pyrex window. The length of the illuminated portion of the tube was 15 mm. Two spectra were obtained using the 4358 mercury line as the exciting light and one using the 4046 mercury line.

The two plates taken with the 4358 excitation showed a Raman line of 943 cm⁻¹ displacement. Due to the very small size of the tube required, satisfactory elimination of parasitic light was impossible and the spectra were superimposed upon a rather strong continuous background which masked the other lines. Two other lines appeared to be present but are so weak as to be doubtful. These lines were at about 2290 excited by the 4046 line and 1600 excited by the 4358 line.

The selection rules for Raman spectra indicate that the 992 cm⁻¹ line in benzene originates in a very symmetrical type of vibration. This suggests that it is due to the motion in which the six carbon atoms and the six carbon atoms attached to them move in and out along the lines drawn through the atoms to the center of the ring, all of the atoms vibrating in phase with each other. Other assignments have been suggested by various authors. The correctness of this assumption has been confirmed by studies with vibrating mechanical models of the two series of compounds: C₆H₆, C₆H₅CH₃, C₆H₅Cl, C₆H₅Br, C₆H₅I; and C₆H₆, C₆H₅Cl, *o*, *m*, and *p* C₆H₄Cl₂, (1, 2, 3), (1, 2, 4), and (1, 3, 5) C₆H₃Cl₃, and C₆Cl₆. The first of these series was studied by D. Teets, and the second by J. W. Murray and V. Deitz, the results being in process of publication in *The Journal of Chemical Physics*. In passing from compound to compound, the shifts of the mechanical frequency associated with the symmetrical expansion correspond exactly in sign and magnitude with the shifts observed in this strong line in the Raman spectra. Similar evidence indicates that the 3065 cm⁻¹ line in benzene compounds corresponds to symmetrical expansion with the hydrogen atoms in a phase opposite to that of the carbon atoms.

On the basis of these correlations, a calculation may be made of the shift to be expected from the substitution of six deuterium atoms for the six hydrogen atoms in benzene. Let us assume that in this type of motion, the effect of the C—C bonds attached to one carbon atom is the same as if that carbon were attached by a bond to a fixed point in the center of the ring. Let *S*_I be the stretching force constant for this fictitious bond and *S*_{II} for the C—H bond. We may then define the motions of the atoms by the equations:

$$m_1 4\pi^2 \nu \alpha^2 x_{\alpha 1} = S_I x_{\alpha 1} + S_{II} (x_{\alpha 1} - x_{\alpha 2}),$$

$$m_2 4\pi^2 \nu \alpha^2 x_{\alpha 2} = S_{II} (x_{\alpha 2} - x_{\alpha 1}),$$

where $\alpha = 1$ or 2 , $\nu_1 = 992.5$ cm⁻¹, $\nu_2 = 3065$ cm⁻¹, $m_1 = 12$ and $m_2 = 1.008$. Since the amplitude of the vibration is arbitrary, we may let $x_{\alpha 1} = 1$. Solving these equations simultaneously, we obtain $S_I = 7.55$ dynes cm⁻¹, and $S_{II} = 6.12$ dynes cm⁻¹. Using these values, we may let $m_2 = 2.016$ and solve for ν_1 , obtaining a value of 945 cm⁻¹. The close agreement of this with the observed value indicates several things. First, it supports the assumed identity of the