The Intensities of the VibrationRotation Bands of HCl

Edwin C. Kemble

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Isotope Ratio in Petroleum

The natural separation of isotopes of hydrogen in benzene and kerosene found by M. Dole[1] was called in question by the author himself because of later experiments with benzene (under modified conditions).[2] The results of his initial experiments were explained by him as a consequence of fractional condensation of water vapors from the products of combustion.

I burned the motor-petroleum from Machach-Kala in a calorimetric bomb, so that the possibility of fractional condensation was excluded. All the water obtained was subjected to an elaborate purification. The interferometric analysis gave 1.5 parts deuterium per 5000 parts of hydrogen for the concentration of deuterium in petroleum if, as usually, the mole fraction of the former in ordinary distilled water is taken as 1 : 5000. If the tank oxygen used for the combustion has an increased concentration of heavy oxygen isotopes (as it was found by Smith[3]), then according to Luten[4] this would decrease the value of Δn, i.e., the ratio 1.5 : 5000 for concentration of deuterium in investigated motor-petroleum is decreased.

I wish to express my sincere gratitude to Professor Dr. A. E. Brodski for suggesting this work and for his valuable advice.

N. S. FILIPPOVA

Institute of Chemical Technology,
Dniepropetrovsk, U.S.S.R.,
February 25, 1935.

[1] M. Dole, J. Chem. Phys. 2, 337 (1934).
[2] M. Dole, J. Chem. Phys. 2, 548 (1934).
[3] E. R. Smith, J. Chem. Phys. 2, 298 (1934).
[4] D. B. Luten, Phys. Rev. 45, 161 (1934).

The Intensities of the Vibration-Rotation Bands of HCl

The writer's attention has recently been called to Professor Mulliken's *Note on Electric Moments and Infrared Spectra* and to the subsequent note of correction.[1] In his second communication Mulliken takes cognizance of the recent intensity measurements of Bartholomé on the $0{\rightarrow}1$ bands of HCl, HBr and HI, and of the serious discrepancy between the results obtained by Bartholomé and those previously obtained by Bourgin.[2] Mulliken accepts at its face value Bartholomé's argument in favor of the superiority of his method and combines the Bartholomé result for the $0{\rightarrow}1$ band of HCl with that of Dunham[3] for the $0{\rightarrow}2$ band to derive a pair of alternative values for the coefficient of the quadratic term of the expansion of the electric moment ρ in powers of the vibrational displacement.

Since the measurements of Bourgin and Dunham were both carried out by the same method under the general supervision of the writer, some comment on the validity of their conclusions is, perhaps, in order. The method consists in the observation of the areas A under the absorption curves (measured in percent) of the individual band lines for a variety of tube-lengths x. The initial slope of this curve $(dA/dx)_0$ is the integrated absorption coefficient α for the corresponding line. The criticism's of the method made by Bartholomé are (a) that there may be some surface absorption due to adsorbed vapor on the end plates of the absorption tube, and (b) that there must be a very large probable error in the determination of the initial slope of the A, x curve in view of the marked curvature in the neighborhood of the origin. In the writer's opinion these criticisms are wholly inadequate to account for the discrepancy between Bourgin's result and Bartholomé's.

According to Bartholomé the true intensity of the $0{\rightarrow}1$ band should be only one-fourth of that observed by Bourgin. This discrepancy factor is subject to a correction even if we grant for the moment the validity of Bartholomé's method and results. In his second paper Bourgin re-estimated the initial slope of the A, x curve by several methods and corrected numerical errors in the previously published computations of the transition probabilities and effective electric moment of the molecule. The most probable value of the absolute integrated absorption coefficient obtained by averaging the results of four methods given in the second paper is 41×10^{10} instead of the value 49×10^{10} given in his first paper. The corresponding value of the Einstein transition probability for the first line of the R branch is[4] 8.6×10^{15}. This transition probability, which we denote by $B_{01}{}^{+1}$, is to be distinguished from the average transition probability for the entire band $(\overline{B_{01}})$ observed by Bartholomé. These two quantities would be the same according to the summation rules if the frequency differences between the different band lines were negligible. Assuming the theoretical formula for the relative intensities of the band lines derived by the writer and confirmed within the limits of experimental error by Bourgin, calculation indicates that at 20°C $B_{01}{}^{+1} = 0.96\overline{B_{01}}$. From Bartholomé's value of $\overline{B_{01}}$ we obtain $(B_{01}{}^{+})_{\text{Barth.}} = 1.83 \times 10^{15}$, or approximately 21 percent of Bourgin's

value. Thus the use of Bourgin's revised figures together with the application of the above correction factor slightly increases the discrepancy previously noted.

Let us now return to the criticisms of Bourgin's method. As regards adsorbed vapor, one may note that the vapor pressure of HCl at room temperature is about 45 atmospheres. Since the pressure of the gas actually used was one atmosphere, one may reasonably assume that the adsorbed layer would not be much more than one molecule deep. Taking the cross section of the molecule standing on end to be 10^{-16} sq. cm, one readily calculates that the number of adsorbed molecules per square centimeter on the front and back quartz surfaces is equal to the number per sq. cm in a layer of gas less than a hundredth of a millimeter thick. Even if the adsorbed molecules were free to rotate normally and contribute as much to the absorption as free molecules, their contribution would have been too small to detect experimentally. Moreover, the base-line readings were taken without removing the adsorbed gas by heating, so that most of its contribution to the absorption must have been eliminated by subtraction.

Finally an examination of the A, x curves (cf. Fig. 4 in the first paper and Fig. 1 of the second paper) should make it evident that Bourgin's estimate that the extrapolated value of the initial slope is reliable within 20 percent, is a fair one. These estimates were made with the aid of two-parameter semitheoretical curves which were fitted to the complete absorption curve and gave due weight to the observations made with long tubes. In fact we can derive from the A, x curves a lower bound to the value of $B_{01}{}^{+1}$ which is several times as large as that given by Bartholomé. From the fundamental formula for the area, $viz.$, $A(x) = \int (1 - e^{-\mu x}) d\nu$, it follows that $dA/dx = \int \mu(\nu) e^{-\mu x} d\nu$. Hence dA/dx and all the higher derivatives of $A(x)$ are monotonically decreasing functions of x. It follows that *the initial slope must be greater than the slope of any chord connecting two points on the curve.* Joining the origin with the points for the two shortest tubes and using the data for the third line of the R branch (the strongest in the band) one obtains the lower bounds 7.05×10^{15} and 5.84×10^{15} for $B_{01}{}^{+1}$. The other lines yield similar bounds. Thus it is quite impossible to reconcile Bourgin's data with Bartholomé's low value of the transition probability.

Let us next consider the possibility of error in Bartholomé's experiment. The observations consisted in measuring the absorption with a relatively wide spectrometer slit and an absorption tube containing one atmosphere of HCl mixed with air at total pressures up to 60 atmospheres. The theory of the experiment is that at sufficiently high pressures the lines will be broadened enough to destroy the rotational structure of the band and give a smooth curve for the absorption coefficient plotted against frequency. Under these circumstances with a slit-width small enough to cover one line at a time, but not necessarily small enough to resolve rotational structure, the radiation reaching the radiometer should be sensibly homogeneous as regards its absorption coefficient. By means of the exponential absorption law it should then be

possible to determine the smeared-out absorption coefficient curve from observations made with a single tube-length. It is assumed that the transition probability is sensibly independent of the pressure and on that point the evidence is reasonably conclusive.

It is rather difficult and dangerous to criticize an experiment from as meager an account of the experimental details and data as that given by Bartholomé, but one weak point is apparent. He gives his slit width as equivalent to 800A. If we assume that the entrance and exit slits of the spectrometer were of equal width, as is customary in such work, the extreme range of wavelengths reaching the thermopile would be 1600A. As the distance between the points of maximum intensity for the R and P branches is about 1400A, it is quite clear that even when the lines were broadened so as to eliminate the rotational fine structure, the radiation reaching the microradiometer must have been very inhomogeneous as regards its absorption coefficient. In the R branch for example, the 4th line has an intensity five times as great as the 8th line which differs in wavelength by only 750A. Thus it is not permissible to extrapolate to zero tube-length by means of the exponential absorption law and an attempt to determine the transition probability by means of such an extrapolation is sure to underestimate seriously its true value. With higher resolving power Bartholomé's method should be good.

EDWIN C. KEMBLE

Harvard University,
   Research Laboratory of Physics,
   March 27, 1935.

[1] R. S. Mulliken, J. Chem. Phys. **2**, 400, 712 (1934).
[2] D. G. Bourgin, Phys. Rev. **29**, 794 (1927); **32**, 237 (1928).
[3] J. L. Dunham, Phys. Rev. **34**, 438 (1929).
[4] The value given in Bourgin's first paper was wrong by a factor of two.

Active Hydrogen

Four years ago I expressed my doubts in what at that time was considered to be proofs for the existence of triatomic hydrogen.[1] It appeared that a final decision had been reached when Conrad in his mass-spectrographical work[2] found an uncharged molecule corresponding to the mass (3). Unfortunately the significance of his investigation was greatly reduced[3] after deuterium was discovered. A strict distinction should be made between HD and H^3 even in mass-spectrograph analysis. This has not been done in every case.[4] Hence positive ray analysis as applied to this problem must take account of the two facts, (1) that the presence of HD may obliterate an unequivocal decision, (2) that only such particles[5] can be considered as a proof of H^3 which were uncharged for some definite length of time and received their charge later on by electron transfer.

The H^3 molecule may have properties identical with those of the H-atom. One would have to assume this, reading the publications of Grubb and co-workers[6] if their argumentations were conclusive in every respect. Only their most weighty argument of their most recent publica-