

Supporting Information

for

The Structure of the Hydrogen Ion (H_{aq}^+) in Water

Evgenii S. Stoyanov, Irina V. Stoyanova, Christopher A. Reed

(9 pages)

Experimental

H(CHB₁₁Cl₁₁) acid and Cs(CHB₁₁I₁₁) salt were prepared as previously described (*1*). The aqueous form of the H(CHB₁₁I₁₁) acid was prepared by dichloroethane (DCE) extraction from an aqueous Cs(CHB₁₁I₁₁) solution containing 2 M H₂SO₄. The organic phase was separated and the solvent removed by distillation under reduced pressure. Chlorinated cobalt(III) dicarbollide ion, Co(C₂B₉H₈Cl₃)₂⁻ (abbreviated {CCD⁻}), 90% in H-form and 10% in Na-form with an analysis of 9.35% Co and 29.05% Cl, was received from KatChem (Czech Republic) and converted into 100% H-form by shaking a DCE solution with 3 M aqueous H₂SO₄ for 5 min and retaining the DCE layer. Solid aquated H{CCD} was isolated by removing the solvent at reduced pressure. Water solutions of H(CHB₁₁Cl₁₁), H(CHB₁₁I₁₁) and H{CCD} were prepared by dissolution of weighed portions of solid. Acid concentrations were determined by titration with standardized NaOH solutions.

IR spectra were recorded in ATR mode by placing a drop of solution on a diamond crystal using a Perkin Elmer Spectrum-100 spectrometer in the 4000–400 cm⁻¹ frequency range. IR data were manipulated using GRAMMS software.

Spectral subtraction to determine the IR spectrum of H_{aq}⁺ in water.

To isolate the spectrum of the H_{aq}⁺ cation, the spectrum of the anion, water perturbed by the anion and bulk water must be sequentially subtracted from the spectrum of an ionized acid. The spectrum of water perturbed by the anion is obtained from the spectrum of its alkali metal salt because the spectrum of a hydrated alkali metal cation, M(H₂O)_n⁺, happens to coincide with that of bulk water.² Thus, when the spectrum of bulk water is subtracted from the spectra of aqueous Na⁺ or Cs⁺ salts and normalized to unit concentration, they coincide. This is illustrated in Fig. S1 for 0.5 M chloride salts (rather than perchlorate or carborane because of low solubility their Cs⁺ salts). A best-fit difference spectrum between the two salts was obtained by using a scaling factor $f = 1.0077$. The variance from 1.0000 corrects for molarity differences arising from experimental errors in preparing the 0.5000 M standard solutions. The difference spectrum produces a flat baseline (red) except for small negative (–S) and positive (+S) peaks at the frequency maxima of the most intense solvent absorptions (see expanded scale). This is typical^{3,4} and is ascribed to the otherwise imperceptible perturbation of water molecules associated with the cations. The criterion for optimal subtraction is to equalize the areas of the positive (+S) and negative (–S) peaks.³⁻⁵

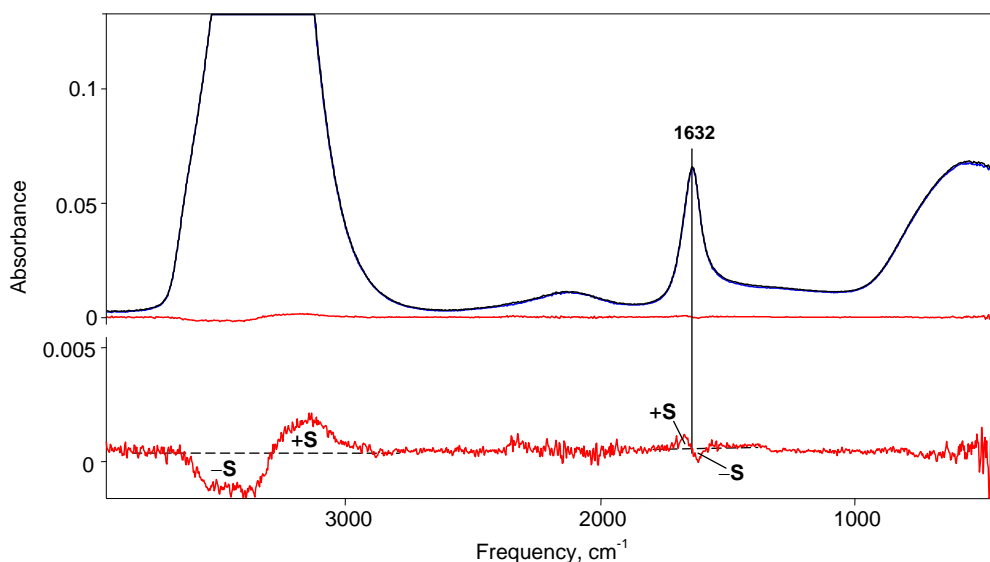


Fig. S1. Overlapping IR spectra of 0.5 M aqueous NaCl (black) and CsCl (blue) solutions and their difference spectrum (red) with equalized $-S$ and $+S$ areas. The red spectrum is reproduced with expanded scale ($\times 10$) (lower).

Thus, the first step in isolating the spectrum of the $\text{H}(\text{H}_2\text{O})_n^+$ cation from aqueous solutions of strong acids is subtraction of the spectrum of its corresponding Na^+ salt using the same molar concentrations and a scaling factor $f = 1$. This is illustrated for HClO_4 in Fig. S2. The resulting spectrum no longer contains the absorptions of the anion and water molecules perturbed by the anion. The spectrum of bulk water is also removed in this process except that it will be over-subtracted by an amount equal to the number of water molecules included in the $\text{H}(\text{H}_2\text{O})_n^+$ cation, giving rise to the spectrum of $\text{H}(\text{H}_2\text{O})_n^+$ distorted by negative peaks from bulk water at ~ 3400 and at $\sim 1630 \text{ cm}^{-1}$ (Fig. S2 blue).

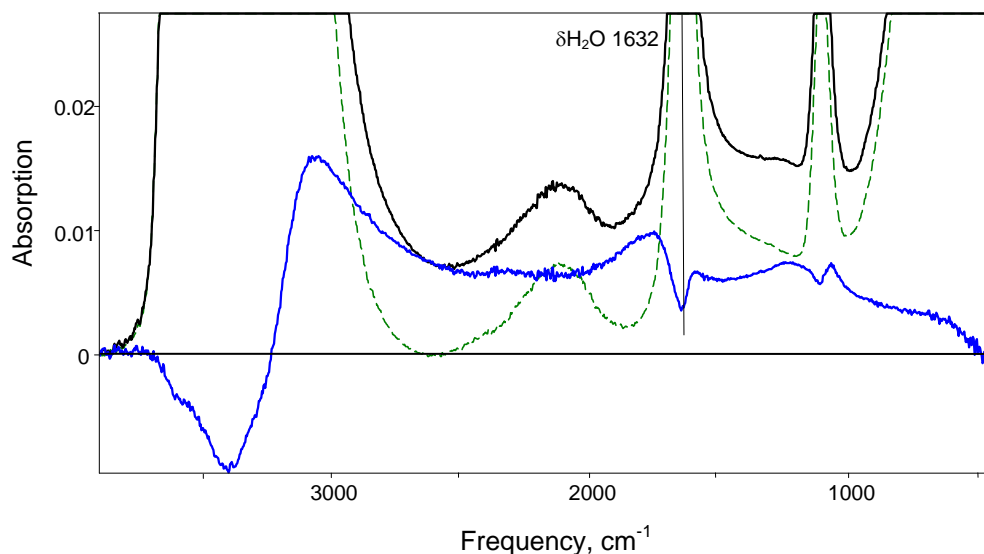


Fig. S2. Step 1 in the procedure for isolating the IR spectrum of the $\text{H}^+(\text{H}_2\text{O})_n$ cation. From the spectrum of 0.750 M HClO_4 (black) was subtracted the spectrum of 0.750 M NaClO_4 with $f = 1$ (green dashed). The resulting difference spectrum (blue) is distorted by overcompensation with the spectrum of bulk water.

In a second step, the spectrum of bulk water is added with a scaling factor that provides optimal removal of the distortions using the $-S/+S$ equalization criterion. Fig. S3 shows a series of spectra with gradually changing f . In order to obtain the most accurate equalization, the narrowest band of bulk water is chosen. This is the $\delta\text{H}_2\text{O}$ band at 1632 cm^{-1} which happens to occur on the slope of a broad H_{aq}^+ band at 1750 cm^{-1} so the $-S/+S$ criterion must be applied to a Gaussian fit of the underlying absorption rather than to a flat baseline. As shown in the Fig S3 insert, essential equality of $+S$ and $-S$ is obtained with $f = 0.0767$ (red). Precise equality can be obtained from the crossing point of plots of $-S$ and $+S$ as a function of f and leads to $f = 0.0775$ (Fig. S4).

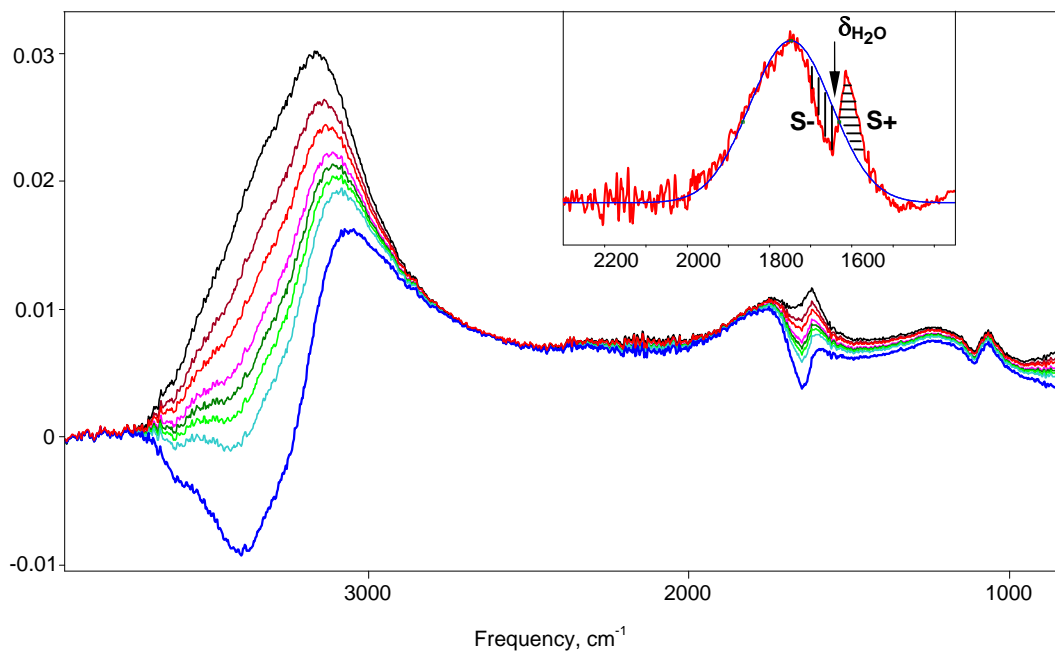


Fig. S3. Step 2 in the procedure to isolate the spectrum of the $\text{H}^+(\text{H}_2\text{O})_n$ cation. Sequential additions of the spectrum of bulk water have been made to the difference spectrum from Fig. S2 (blue) with scaling factors $f = 0.0357; 0.0463; 0.0542; 0.0621; 0.0767; 0.0900; 0.1123$. The optimal f has areas $-S = +S$ (see inset) giving rise to the red spectrum, which is the true spectrum of H_{aq}^+ .

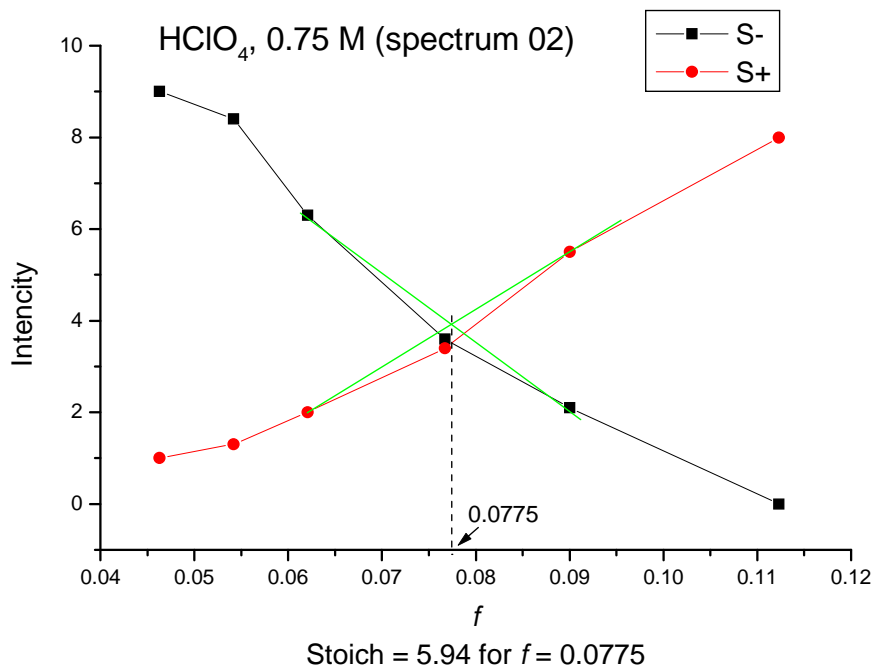


Figure S4. The plots of $-S$ and $+S$ as a function of f for spectrum of 0.750 M HClO_4 solution.

The resulting spectrum is the true spectrum of the $\text{H}^+(\text{H}_2\text{O})_n$ cation (Fig. S3 red) and is reproduced with band deconvolution in Fig. S5.

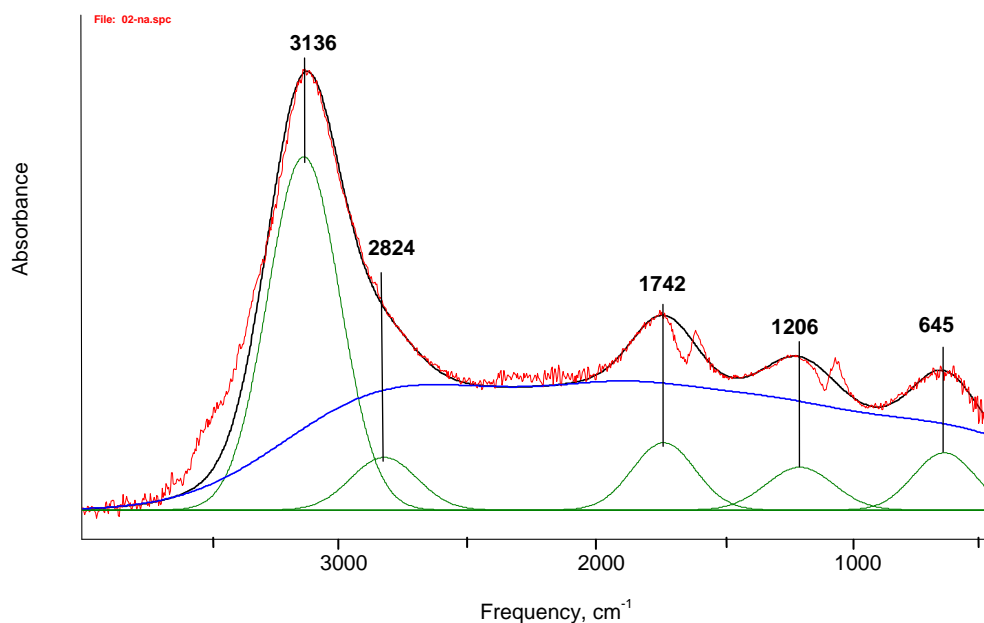


Figure S5. Isolated IR spectrum of $\text{H}(\text{H}_2\text{O})_n^+$ for 0.750 M aqueous HClO_4 showing deconvolution into 5 bands (green), continuous broad absorption (blue) and their summation (black).

The same spectrum was obtained from aqueous solutions of three carborane acids: $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$, $\text{H}(\text{CHB}_{11}\text{I}_{11})$ and the acid form of the chlorinated cobalt(III) dicarbollide anion (CCD^-) (Figures S6-S8).

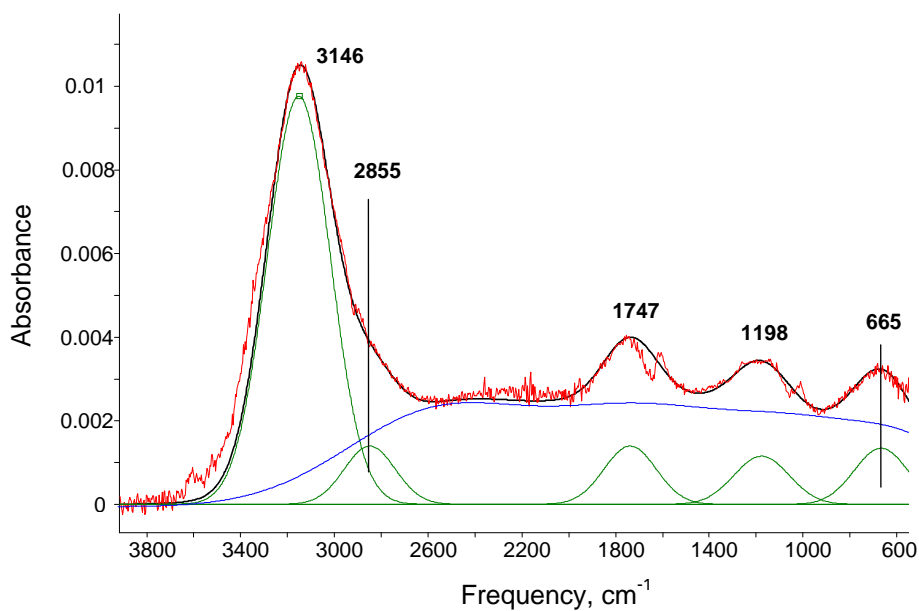


Fig. S6. Isolated IR spectrum of $\text{H}(\text{H}_2\text{O})_n^+$ from 0.330 M aqueous $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$ (red) showing deconvolution into 5 bands (green), continuous broad absorption (blue) and their summation (black).

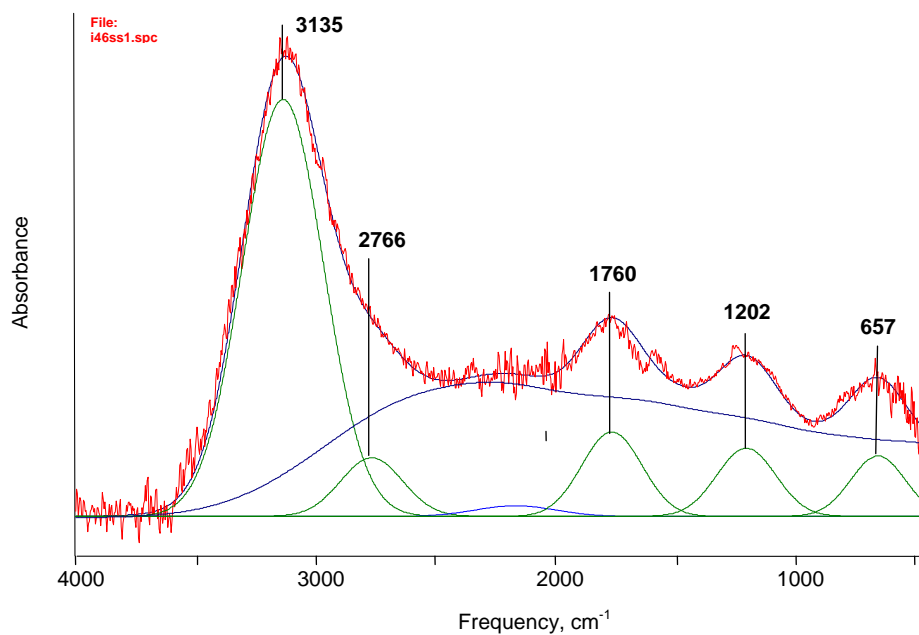


Figure S7. Isolated IR spectrum of $\text{H}(\text{H}_2\text{O})_n^+$ for 0.176 M aqueous $\text{H}(\text{CHB}_{11}\text{I}_{11})$ showing deconvolution into 5 bands (green), continuous broad absorption (blue) and their summation (black).

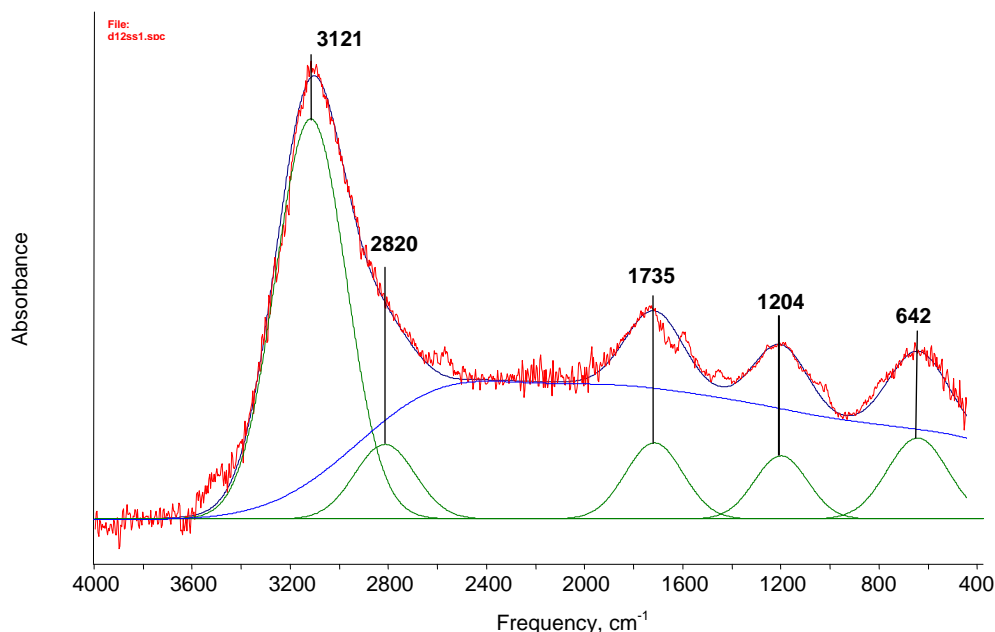


Figure S8. Isolated IR spectrum of $\text{H}(\text{H}_2\text{O})_n^+$ for 0.427 M aqueous $\text{H}(\text{CCD})$ showing deconvolution into 5 bands (green), continuous broad absorption (blue) and their summation (black).

Determination of n in $\text{H}(\text{H}_2\text{O})_n^+$.

Using the f value of 0.0775 used to obtain the true IR spectrum of H_{aq}^+ for perchloric acid, the molarity of water involved in $\text{H}(\text{H}_2\text{O})_n^+$ ions is calculated to be $0.0775 \times 55.455 = 4.30$ (where 55.455 is the molarity of pure water whose spectrum was used for the subtraction). This calculation would be valid if the molarity of water in the HClO_4 and NaClO_4 solutions was identical. However, these solutions are known to have slightly different molarities due to slightly different molar volumes of the solutes. They contain 53.700 M and 53.546 M H_2O respectively.⁶ The difference between these molarities ($53.700 - 53.546 = 0.154$ M) must be added to the value calculated above. Thus, the molarity of water in $\text{H}(\text{H}_2\text{O})_n^+$ ions in perchloric acid solution is $4.30 + 0.154 = 4.46$ M, leading to an average value of n of $4.46/0.750 = 5.95$. If the same calculation is done using the red spectrum of Fig. 3 with $f = 0.0767$, having the visually closest equality of $-S \approx +S$ areas, the n value is 5.88. This gives an indication of the error limits in the stoichiometry of $\text{H}(\text{H}_2\text{O})_n^+$ when estimating the equality of S^+ and S^- visually, as is typically performed. Table 1 in the main text lists the n

values derived from measurements with the four different acids at different concentrations. As expected, deviations from $n = 6.0$ increase with decreasing concentration and these errors are comparable to those associated with the standard volumetric methods of analytical chemistry.

References

1. Juhasz, M.; Hoffmann, S.; Stoyanov, E.; Kim, K.-C.; Reed, C A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5352–5355.
2. Stangret, J. *J. Phys. Chem. A* **2002**, *106*, 5393.
3. Stoyanov, L. V.; Lastovka, E. S. *Zr. Neorg. Khimii (Russ)*, **1981**, *26*, 1613.
4. Stoyanov, E. S. *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 2803.
5. Stoyanov, E. S. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2961.
6. *Handbook of Chemist (Spravochnik Himika)*, Ed.: B. P. Nikol'skii, Moscow-Leningrad, 1964, Vol. 3, 2nd edition (Russian). For English version, see http://molbiol.ru/eng/protocol/01_23.html.