

INTENSITY MEASUREMENTS IN INFRARED SPECTRA

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AT the present time one of the most important problems in infrared molecular spectroscopy is the development of accurate and simple methods of measuring intensities in absorption spectra.

In the present paper we describe the present state of the art and describe various applications of these measurements.

The basic intensity characteristic in an absorption spectrum is the spectral distribution of the absorption coefficient. This coefficient k_ν , the incident flux $I_{0\nu}$, the flux transmitted through the absorbing layer I_ν and the thickness of the layer d , are related by the Bouguer-Beer equation

$$I_\nu = I_{0\nu} e^{-k_\nu d} \quad (1)$$

It is assumed that $I_{0\nu}$ and I_ν are corrected for reflection at the boundaries of the absorbing medium.

The physical nature of the absorption coefficient is complicated. It is easy to show that

$$k_\nu = \frac{1}{c} N h \nu g(\nu), \quad (2)$$

where N is the number of molecules capable of absorbing a radiation quantum $h\nu$ and $g(\nu)$ is the absorption probability.¹

The definition of the quantity N for the components of a mixture under conditions in which $g(\nu)$ is constant or when its variation is taken into account is basic for quantitative molecular spectral analysis.

The change in $g(\nu)$ is a very sensitive indication of changes in an absorbing atomic group in a molecule, for example, effects due to nearby atoms or molecules. Measurements of this quantity allow us to get information as to the magnitude and nature of these effects.

The characteristics of vibrational spectra as obtained by intensity and wavelength measurements are still semi-empirical. In spite of the abundance and variety of the available data and the many attempts at classification and interpretation, there is still no general theory to explain the dependence of absorption on external factors.

Absorption spectroscopy (in particular, in the infrared region) has one great advantage over emission spectroscopy (for example, Raman spectroscopy) in that the former allows us to obtain

absolute data regardless of the magnitude of the interaction energy; hence standards are not required.

This means that absorption can be studied under various conditions, for example, in matter in various states in which, generally, the use of a standard would be impossible. Systematic measurements of the absolute absorption strengths by a substance in various states, in particular, in different solutions, make it possible to set up a table of the absorption coefficients that characterize the absorbing molecule and its state; these data are independent of the apparatus which is used for the measurements.

Unfortunately the determination of absolute intensities entails a number of difficulties, some of which will be described in greater detail below; these derive from the properties of the apparatus as well as the nature of absorption spectra. Although these problems have not been solved completely in presently available spectroscopic apparatus, it is reasonable to assume that they will be in the near future.

In analytic work the measurement procedure used in intensity measurements can be simplified. For example one can use standard solutions of the same composition with known concentrations of the absorbing component (close to that being determined).

The analytic procedure becomes much more reliable if the mixture being analyzed is dissolved in as neutral a solution as possible and at small concentrations. One of the components of the mixture can be the solvent. Generally the environment of the absorbing molecules is kept the same while the relative amounts of the individual components are varied. In terms of the Bouguer-Beer equation

$$I_\nu = I_{0\nu} e^{-\sum k_{\nu i} c_i d} \quad (3)$$

this means that in the limits of the concentrations (c_i) of the individual components used, their absorption coefficients $k_{\nu i}$ are independent of these concentrations.

It is obvious that these coefficients, which must be known for analysis, should be determined with the absorbing molecule in the same environment as in the analyzed mixture.

For analytic purposes one usually measures the

optical density

$$D_\nu = \ln \frac{I_{0\nu}}{I_\nu}; \quad (4)$$

so that in practice the uncorrected values $I_{0\nu}$ and I_ν can be used only if the apparatus parameters remain fixed (the cells, monochromator slit width, and so on), since distortions in the spectrum are generally proportional to the light flux. These distortions frequently arise from technical limitations of the apparatus or improper use of the apparatus, but are also frequently of more fundamental nature. The first type of distortion and the measures that can be taken to avoid it are described in handbooks.^{2,3} Here we describe the less familiar distortions that arise in automatic recording of spectra as a result of time delays in the recording apparatus. In practice, rotation of the prism generally means a reduction in the practical resolving power, a reduction of the intensity peaks, loss of detail in the distributions, and sometimes spurious asymmetries in the band. These can be avoided by a point-by-point method using automatic recording, as shown in Fig. 1.

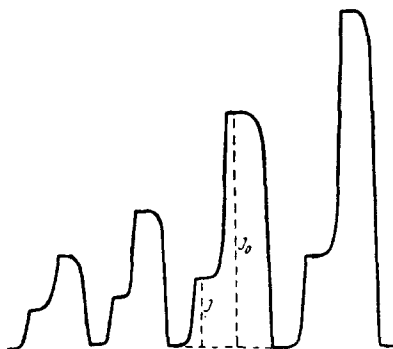


FIG. 1. Recording of a spectrum by point-by-point measurements.

The cell is moved when the meter reading has become stable. This procedure avoids the distortions in recording indicated above and also provides a partial check on the zero reading. Obviously this method of recording requires a long time (depending on the density of points); however, it must be used in cases in which reliable and precise values of the intensity are needed. Measurements of the spectrogram, required for computing the optical density, are much simpler in this case than for a spectrogram in the form of a curve.

A basic difficulty in measuring absorption in the infrared region lies in the proper corrections for the distortion due to the finite width of the monochromator slits. Because of detector-sensitivity considerations, there is a certain minimum value for the slit widths; this value depends on the radiation intensity.

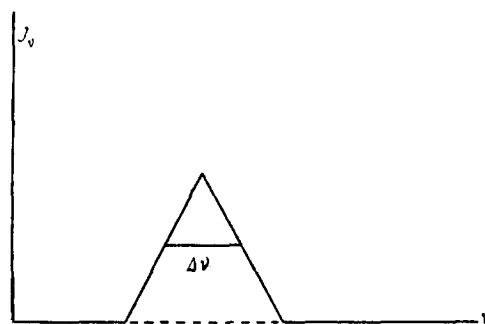


FIG. 2. Determination of the spectral width of the slit $\Delta\nu$.

The finite slit width means that if the monochromator is set at a definite wave number ν_0 and its input slit illuminated by monochromatic radiation, the spectrum will exhibit an intensity distribution of approximately the form shown in Fig. 2 (isosceles triangle). In this case $\Delta\nu$ the width of the triangle at half-height characterizes the spectral width of the slit. The intensity distribution shown in the figure is only approximately correct. It is somewhat distorted because of the finite resolving power of the monochromator, optical aberrations, and inadequate compensation for the distortion of the monochromatic line by the input slit. For this reason, we introduce an effective slit width $\Delta\nu_e$ in which all these factors are taken into account.

The averaging effect due to the finite width of the slit leads to a reduction and broadening of the band peaks. In measuring the intensity of an isolated infrared band it is necessary to take account of the effect of $\Delta\nu_e$ on the true maximum absorption coefficient $k_{\max}^{(\text{true})}$, the true half-width of the band* $\Delta\nu_{1/2}^{(\text{true})}$, and the true value of the integrated absorption coefficient $K^{(\text{true})} = \int k_\nu^{(\text{true})} d\nu$. This correction must be made for the observed values $k_{\max}^{(o)}$, $\Delta\nu_{1/2}^{(o)}$, and $K^{(o)}$. The integrated absorption coefficient is the best characteristic for the probability of a transition from one vibrational state to another. The quantity k_{\max} is frequently used for analytic purposes. A comparison of k_{\max} with $\Delta\nu_{1/2}$ and K allows us to judge (in simple bands) the absorption probability and its distribution within the band.

The determination of the true values of k_{\max} , $\Delta\nu_{1/2}$, and K for more or less isolated bands or groups of bands in spectra of different organic compounds is one of the most important problems of contemporary infrared spectroscopy.⁴

This problem is most difficult for gases, the spectra of which consist of large numbers of lines which are usually not resolved by conventional infrared equipment. In considering gases we shall

*The band width at half-height.

limit ourselves to a description of integrated-intensity measurements, which are of greatest interest for the purposes of the present paper.

The relation between the integrated flux as measured by conventional apparatus and its true value is very complicated and depends on the widths of the monochromator slits and on the line width,³ which itself changes with vapor pressure. Hence, in order to determine the integrated intensity one introduces a neutral gas which has little effect on the absorption coefficient being determined; the introduction of the gas smears out the rotational structure of the absorption band, so that the intensity measurement is carried out in two steps. In the first step one determines the pressure of the added gas (for a given pressure of the absorbing gas) at the point at which the absorption parameter being measured becomes independent of further increases in pressure. In Fig. 3 is given a curve of this type for nitrous oxide N_2O (the 2224 cm^{-1} band) with excess nitrogen; this curve was obtained by Thompson.⁵ In the case of N_2O and certain other gases which have been investigated in the laboratory, a pressure of 1 to 3 atmos is required for the added gas. The work may become extremely complicated if the Q-branch is narrow as compared with $\Delta\nu_e$.⁶

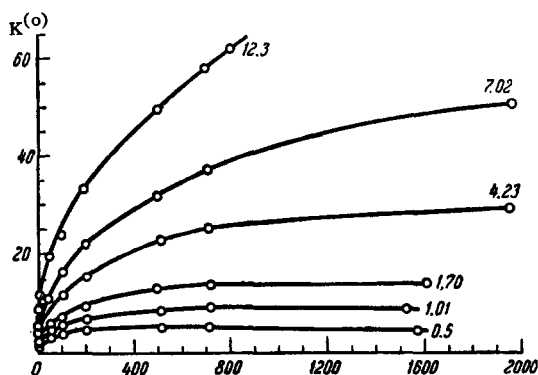


FIG. 3. The observed integrated absorption coefficient for nitrous oxide in a mixture with nitrogen as a function of total pressure (in mm Hg) for different partial pressures of N_2O (indicated in mm Hg on each curve).

The second stage of the work can be carried out, for example, using the method of Wilson and Wells,⁷ who showed that the observed integrated absorption reduced to unit pressure p and thickness d of the absorbing layer (divided by pd) approaches the true value as the absorption is reduced ($pd \rightarrow 0$).

Thus, in this stage the experimental procedure becomes essentially the determination of a number of values

$$K^{(0)} = \int \ln \frac{I_{0\nu}^{(0)}}{I_{\nu}^{(0)}} d\nu$$

and the extrapolation of the curve plotted from the observed values of $K^{(0)}$ as a function of pd to the limit $pd = 0$, where obviously $K^{(0)} = 0$.

The true value of K , referred to $pd = 1$, is determined by the tangent of the slope angle of this curve at $pd = 0$.

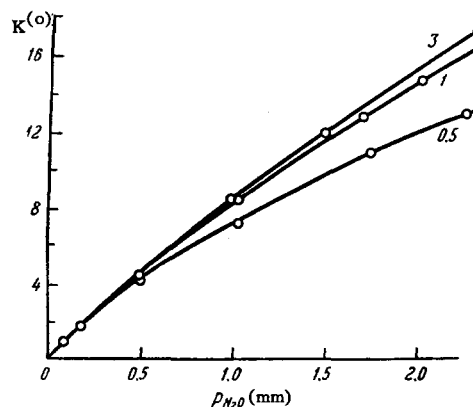


FIG. 4. The integrated absorption coefficient for N_2O in a mixture with N_2 as a function of N_2O partial pressure (in mm Hg). The total pressure is indicated in atmospheres for each curve.

In Fig. 4 is shown a series of such curves obtained by these authors⁵ for the same nitrous oxide band as a function of the nitrous oxide partial pressure (in mm Hg) for three values of the nitrogen pressure in atmospheres. It is apparent from the figure that the position of the tangent approaches a limit at reasonable values of p_{N_2O} .

The determination of the absolute intensity of an absorption band in liquids is of much greater practical value. In the case of simple bands it is possible to determine all three parameters which characterize the band: k_{\max} , $\Delta\nu_{1/2}$, and K . In spite of the apparent simplicity of the shape of the band in liquids and the large number of investigations which have been carried out, up to the present time there are no exact and reliable values of the true magnitudes of these parameters and no checks between the theoretical and experimental values.

The difficulties in these determinations in the infrared region are due to the following causes:

1. The effective monochromator slit width which can be achieved with conventional apparatus is comparable with the half-width of the band; this means that there are considerable distortions in k_{\max} and $\Delta\nu_{1/2}$. The determination of K from the area under the curve is made difficult by the very slow drop in band intensity. Even if the measurement is limited to a region which is five times greater* than $\Delta\nu_{1/2}$

*Measurements over broader regions become inaccurate because of the small absorption at points remote from the band.

the uncertainty in the area is approximately 5%.⁸

2. A theoretical estimate of the distortions in the parameters being determined requires a knowledge of the true distribution of intensity. Such a relation, valid for all bands, does not exist.

3. For purposes of calculation, as well as for extrapolation of the observed values of the parameters to true values, it is necessary to have a knowledge of the effective width of the slit as a function of the geometric width and other pertinent factors. These factors have never been calculated. For this reason the data obtained in most work is not as accurate as one would desire.

As a result of many investigations it has been shown that the shape of simple absorption bands is approximately Lorentzian and can be written in the form

$$k_\nu = \frac{a^2}{(\nu - \nu_0)^2 + \left(\frac{b}{2}\right)^2}, \quad (5)$$

where $k_{\max} = \frac{a^2}{(b/2)^2}$ and $b = \Delta\nu_{1/2}$ is the half-width of the band.

Calculations of the distorting effect of the finite width of the slits on k_{\max} , $\Delta\nu_{1/2}$, and K has been carried out in various ways.^{8,9,10} Here we use the simple and convenient formulas obtained by I. V. Peisakhson¹⁰ under the assumption that the widths of the input and output slits are the same and that there is a Lorentzian intensity distribution in the band:

$$k_{\max}^{(\text{true})} = k_{\max}^{(o)} \left[1 + \frac{2}{3} \left(\frac{\Delta\nu_e}{b^{(o)}} \right)^2 \right], \quad (6)$$

$$b^{(\text{true})^2} = b^{(o)^2} \left[1 - \left(2 - \frac{k_{\max}^{(o)}}{3} \right) \left(\frac{\Delta\nu_e}{b^{(o)}} \right)^2 \right], \quad (7)$$

$$K^{(\text{true})} = K^{(o)} \left[1 + \frac{k_{\max}^{(o)}}{12} \left(\frac{\Delta\nu_e}{b^{(o)}} \right)^2 \right], \quad (8)$$

These approximations are derived for the case $\Delta\nu_e < b/2$ and $k_{\max}^{(o)} \leq 2$. The error should be less than 3% if the line is truly Lorentzian. The error introduced in the integrated absorption for the mean value of $k_{\max}^{(o)}$ is almost an order of magnitude smaller than for $k_{\max}^{(o)}$ itself.

For experimental purposes the first two formulas can be simplified and written in the form

$$b^{(o)^2} = b^{(\text{true})^2} + c_1 \Delta\nu_e^2, \quad (9)$$

$$k_{\max}^{(o)} = k_{\max}^{(\text{true})} - c_2 \Delta\nu_e^2, \quad (10)$$

where c_1 and c_2 may be taken as constant in the first approximation.

Of all the experimental work on the determination of the true parameters, that of the greatest

interest is the work of Russell and Thompson.¹¹ These authors have measured the values of $\Delta\nu_{1/2}^{(o)}$ and $k_{\max}^{(o)}$ for ten bands of different half-width in several materials with different slit widths, as well as the NH band in weak solutions of diphenylamine and indole in CCl_4 at various concentrations.

The work was carried out with a diffraction grating and with a prism. Of the results obtained by these authors we shall consider only those which are of greatest importance.

It was shown that at small slit widths the extrapolated value of $\Delta\nu_{1/2}$ is almost independent of the concentration, whereas the dependence of the extrapolated value of k_{\max} is marked. It follows, then, that the Wilson-Wells technique should not be used to determine integrated absorption for liquids unless its applicability is checked. Much better results are given by the Ramsay expression⁸

$$K^{(o)} = K^{(\text{true})} [1 + c k_{\max}^{(o)}], \quad (11)$$

especially if the constant c is determined experimentally by measurements at several points instead of being computed from the dispersion curve. A comparison of the extrapolated values of $\Delta\nu_{1/2}$ with those obtained by calculation with the Peisakhson formula, where it is possible to do so, indicates satisfactory agreement. A comparison of $k_{\max}^{(o)}$ [$\Delta\nu_e = \frac{1}{2} \Delta\nu_{1/2}^{(\text{true})}$] with $k_{\max}^{(\text{true})}$ computed from Eqs. (6) and (7) gives the relation

$$k_{\max}^{(o)} = 0.82 k_{\max}^{(\text{true})}.$$

Computing the quantity $k_{\max}^{(o)}$ from the dispersion formula gives the value 0.83. In the case in which the band is Gaussian this coefficient is 0.89; that is, in the cases being considered, the Lorentzian distribution leads to a value which, on the average, is close to the true value.

From what has been indicated above it is apparent that even for presently available apparatus we can more or less determine the true characteristics of simple absorption bands. The difficulties described here can be avoided completely when instruments with the highest resolving powers are used, for example high-transmission diffraction gratings. Russell and Thompson¹¹ have shown that with a spectral slit width which does not exceed one fifth of the true half-width of the band, $\Delta\nu_{1/2}^{(o)}$ and $k_{\max}^{(o)}$ practically reach their limiting values; i.e., the observed values can be taken as the true values of these parameters.

The determination of the intensity of infrared bands in solids requires more complicated procedures. Usually, particularly in work with powders, this work is complicated by the scattering inside

the sample which makes it difficult, if not impossible, to measure absolute intensities. It is difficult to draw any definite conclusions as to the future development of work in this field.

Up to this point we have discussed only simple bands. If a complicated band is formed as a result of the superposition of two simple bands, for example the bands of a solvent and solute, the characteristics of the latter may be obtained by using a cell of variable thickness and comparing a monochromatic source which is viewed through the solution with a source which is viewed through the solvent.* In practice this work is carried out with two cells of the same thickness d . In this case

$$\ln \frac{I_{(2)\nu}}{I_{(1)\nu}} = Cd (k_{(1)\nu} - k_{(2)\nu}). \quad (12)$$

This formula makes it possible to determine C or $k_{(1)\nu}$ from the quantity $k_{(2)\nu}$ if the latter is not small[†] compared with $k_{(1)\nu}$. Obviously this procedure is meaningful only for work at concentrations for which $k_{(1)\nu}$ and $k_{(2)\nu}$ are independent of concentration.

In those cases in which the band of interest is superimposed on other bands due to the same material, the determination of the integrated intensity and the half-width of the band may turn out to be impossible and the distribution characteristics for the intensity k_{ν} uncertain if the spectral width of the slit cannot be made small enough. As is well-known, analytic work^{2,3} may be completely reasonable in these cases if certain conditions are satisfied.

We consider two relatively poorly known examples which may turn out to be very useful in practice for the spectroscopist.

In most cases where it is necessary to determine only one of the components of a mixture by its band, which is superimposed on the rather strong absorption slope of the solvent (which may be complicated and of unknown composition), the base-line method¹²⁻¹⁶ is very useful (see Fig. 5).

For purposes of analysis it is sufficient to know that between points λ_1 and λ_2 the solvent curve can be approximated by a straight line segment which, in different samples, may be at different heights and have different slopes. One must be sure that the spectra of the solute and the solvent are additive (this is usually the case for small concentrations of the material being determined). The points λ_1 and λ_2 may be arbitrary (although, naturally they

*It is still necessary to know the concentration C of the solution.

[†]In this case the total absorption of the layer of solvent $dk_{(2)\nu}$ can also be large.

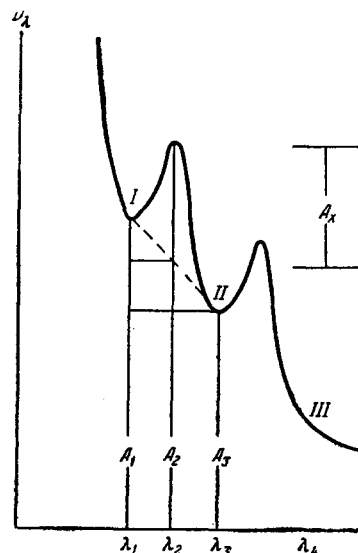


FIG. 5. The base-line method. The band at λ_2 belongs to a definite dissolved material. D_{ν} of the solvent varies linearly with λ between points I and II (dashed line).

should preferably be located at neighboring minima), but kept fixed.* Under these assumptions it has been shown¹⁴ that the height of the segment A_x is proportional to the concentration of the component that is being determined. The coefficient of proportionality can be obtained from experimentally determined quantities.

In the second-derivative method¹⁷ one does not use the optical density curve D but rather its second derivative as a function of scan time or wavelength λ . The second derivative is proportional to the optical density itself and can be used, as was done by these authors, for analytic purposes. In this method all of the factors which vary slowly with λ (instrumental uncertainties, background, etc.) are eliminated in plotting the curve. It is not necessary to determine the zero. However the requirements at the Bouguer-Beer law are still the same as for D . The characteristics of the curves for D_{λ} , $\frac{dD_{\lambda}}{d\lambda}$ and $\frac{d^2D_{\lambda}}{d\lambda^2}$ are shown in Fig. 6.

The maximum for the $\frac{d^2D_{\lambda}}{d\lambda^2}$ curve is much sharper than for the D_{λ} curve; this is especially important. The half-width of the curve is much less dependent on the width of the slit in this case. This feature makes the second-derivative method very valuable for studying superposition of bands when this superposition is discernible only in an asymmetry of the absorption band being observed. Better separation of bands can be achieved by the second-derivative method even in those cases in which the spectral width of the slit is such as to cover both peaks. There is a certain complication in the method (which is easily overcome) due to the existence of two

*The authors of reference 15 dispense with this requirement.

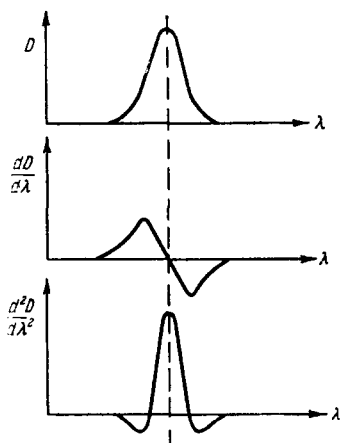


FIG. 6. Dependence of optical density D and its first two derivatives on wavelength λ in a simple band.

minima in the $\frac{d^2D}{d\lambda^2}$ curve.

The absorption strength of a molecule is intimately connected with any electrical asymmetry in the positions of the charges which form it and with changes in these positions. In the simplest case, valence oscillation of a simple group of atoms in the molecule, this asymmetry is characterized by the dipole moment, which depends on the distance $\mu(r)$ between the oscillating charges. This dependence is not the same for different types of bonds, and hence the intensity of the valence oscillations on the main line is proportional to $\left(\frac{d\mu}{dr}\right)^2$ and can serve to characterize it. It turns out to be a very sensitive indicator of changes in the polarizability of the absorbing group which result from the introduction of active atoms and effects due to neighboring molecules,^{2,18} for example, different solvents.

Thus the intensity of a band can be used together with the wavelengths for structural analysis. Intensities are especially important in the determination of the structural elements of complicated organic molecules, or for studying changes which take place in these molecules as the result of external agents (for example, optical and thermal effects in polymers).

A calculation of the change of intensity (absorption coefficient) when a substance goes into solution is necessary in any analytic work. A molecule in solution can never be taken as a free molecule even in the poorest solvent.

Measurements of these changes in intensity, caused by the effect of neighboring molecules in a solution or pure matter, which take account of the change in ν at the band maximum, are effective means of studying these mechanisms and making qualitative and quantitative determinations of the compounds formed in the liquid.

At the present time we know of two important different types of intermolecular bonds in liquids.

In the first type a continuous change of concentration causes a continuous change in the spectral parameters of the band. In this case the molecule is linked with many molecules in its environment. The nature of this interaction can be complicated, but its effect in the spectrum is determined chiefly by the effect of polarization and partial orientation of the surrounding molecules on the dipole moment of the absorbing molecule.

In this case the change in intensity and position of the band in the spectrum is comparatively small and is more or less regular, depending on the dielectric constant or refractive index of the medium surrounding the molecule.

The second type of intermolecular bond exhibits saturation effects and is similar to ordinary covalent chemical bonding. The parameters that characterize the band change discretely when the substance goes into solution or when one solvent is substituted for others. Again we can consider different cases; we shall consider those which have been studied most frequently. Important for all these cases of saturated intermolecular bonds, even if only at one of the molecules being bonded, is the formation of electron configurations which extend beyond the molecule. For example, in the formation of the hydrogen bond between chloroform and benzol or between alkyne molecules it has been shown in our laboratory that the proton of one of the molecules is bonded with the π -electrons of the other. In the case of liquid nitrols apparently the π -electrons of both molecules participate in the intermolecular bond of the $C \equiv N$ group.

The intermolecular bond acquires even more of the distinctive nature of the ordinary chemical bond when the atoms of the molecule contain a donor or acceptor of the proton from an unshared electron pair. It is known that in atoms, such as the halogens, oxygen, nitrogen, etc., only some of the outer electrons participate in the formation of chemical bonds with other atoms. The remaining electrons (unshared pairs) remain near the nucleus. These electrons represent a reserve for additional interactions. When these bonds achieve equal status with the others they are classified as chemical bonds. Quadruply valent carbon is formed in this way. It is obvious that there is a readjustment of the entire external part of the electron cloud (the formation of hybrid electron states). This is also how the stable $(NH_4)^+$ group is formed.

In the formation of the water molecule there is also formed in the oxygen atom a hybrid electron configuration with a tetrahedral distribution of electron density. Two of its wings are bonded with the hydrogen atoms and form the H_2O molecule.

The two others participate in the formation of an intermolecular hydrogen bond which is similar in nature to the coordinating chemical bond.

It is possible that the difference between the natural saturated molecular bond and the ordinary chemical co-valent bond is not as great as is usually thought, and that we are now beginning the development of a new area of knowledge which will concern physical chemistry and organic chemistry and which will be studied by physical methods. Molecular spectroscopy has played an important role in this field. It may be assumed that the development of molecular spectroscopy, especially methods of measuring intensity in the infrared region, will continue to be decisive.

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Translated by H. Lashinsky